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光電工程學系暨研究所
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鈣鈦礦結構對螢光及鐵性材料特性的影響

Influence of perovskite structure on
luminescence and characteristics of ferroics

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中華民國九十八年十月

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鈣鈦礦結構對螢光及鐵性材料特性的影響

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摘要

我們利用拉曼散射實驗研究物質尺寸和介面應力效應對鐵性材料(包含鈣鈦礦和尖石礦結構)物理特性的影響，同時也探討因取代而造成結構變化對摻雜在 ABO_3 鈣鈦礦結構中稀土族元素的發光機制的影響。所有的實驗樣品我們利用簡單的化學溶液合成法加以合成。由於取代效應，利用觀察到螢光和拉曼信號消失的現象，我們發現在鈦酸鋇鉛($Pb_{0.8}La_{0.2}TiO_3$)薄膜中當摻雜的三價鉕離子(Er^{3+})超過 7 mol%時，會對原先微距(short-range)結構中的鈦原子的移位量造成破壞。這個由於鈦原子的移位量造成的擾動(disorder)會破壞寄主(host materials)鈣鈦礦結構之中心對稱，進而激發稀土元素的螢光輻射和鈣鈦礦的拉曼訊號。在另外一個取代效應的研究中，當以 980nm 的半導體雷射激發鉕和鐿雙摻雜的鈦酸鉛、鈦酸鋇、和鈦酸鋇粉末，觀察 upconversion 螢光光譜時，我們發現發紅光的機制由 energy-back-transfer (EBT) 程序所主導。EBT 的效率不僅依賴鐿離子的濃度大小，也和鉕離子($Er: ^4S_{3/2} \rightarrow ^4I_{13/2}$)與鐿離子 ($Yb: ^2F_{7/2} \rightarrow ^2F_{5/2}$) 的殼層躍遷能階大小是否吻合息息相關。而這個殼層能階大小是否吻合，則取決於摻雜取代造成結構變化，所產生的晶格場(crystal field)變化對離子的殼層能階的影響。

響程度。

不同尺寸(size)鈦酸鋇奈米顆粒的晶格動力學研究中，當粉末顆粒由 140 nm 縮減到 30 nm 時，顆粒的四方晶特性(tetragonality)也隨之變弱，同時伴隨著單位晶胞(unit-cell)體積的膨脹，這也是造成光學聲子的縱模和橫模的分裂隨著顆粒尺寸變小而減少的主要機制；另外我們在這部份的研究中，也發現了 $A_1(TO_1)$ 和 $A_1(TO_2)$ 的耦合強度隨著顆粒尺寸變小而減少，進而造成 $A_1(TO_1)$ 原先在拉曼光譜是以下陷(dip)表現的形式變成在奈米尺寸下是以峰型(peak)展示。

最後，在鈦酸鉛-氧化鐵鈷的多重鐵性系統的研究中，發現兩介質介面間的應力造成的磁電效應(magnetoelectric effect)和介質的聲子頻率位移有很強的相關性。受介面影響的聲子能量和多重鐵性系統中的鐵磁物質的鐵電特性都會受到介面間的應力影響；而這個介面間的應力大小，同時受到兩介質晶格不匹配和介質間的化學鍵結程度的影響。在埋有自成層碟型氧化鐵鈷的鈦酸鉛(disk-3 type structure)的樣品，闡明了兩介質間有強的彈性交互作用。而這個較強的作用造成了它的鐵磁特性和晶格特性都有較大的變化，當鐵磁部分有較大的非對稱性磁頑力差和出現不存在飽和的磁化率，伴隨著的是鐵電部分的聲子存在較大的聲子頻率位移。

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Abstract

We investigated on the physical characteristics of ferroics, ABO_3 -type perovskite and AB_2O_4 -type spinel, which depend on size and strain effects by Raman spectroscopy, and the emission mechanism of rare-earth doped / co-doped ABO_3 films on substitution effect. All the samples discussed in this thesis were prepared by chemical solution methods. In one of the cases of substitution effect, we found destruction to a displacement of Ti in the short-range structure by observing the disappearance of emission and Raman signals when the Er^{3+} concentration exceeds 7 mol% in sol-gel-derived $Pb_{0.8}La_{0.2}TiO_3$ (PLT) polycrystalline films. The disorder due to a displacement of Ti breaks the centrosymmetry to activate emission of rare earth ions such as Er^{3+} and Raman modes of perovskites. We found that the symmetry breaking diminishes with introducing more Er^{3+} ions. Furthermore, in another case of substitution effect, we found that quenching of green upconversion (UC) emission accompanied with enhancement of red UC emission under a 980 nm laser pumping was observed dominated by the energy back-transfer (EBT) process in Er^{3+} and Yb^{3+} co-doped $PbTiO_3$ (PTO), $BaTiO_3$ (BTO), and $SrTiO_3$ (STO)

polycrystalline powders. The efficiency of the EBT process depends not only on Yb^{3+} concentration but also on level match of the doped Er^{3+} and Yb^{3+} ions caused by the crystal fields with different symmetries. Results of emission spectra and X-ray diffraction (XRD) confirm that the centrosymmetric crystal field arising from reducing tetragonality causes level match of transition $^4S_{3/2} \rightarrow ^4I_{13/2}$ of Er^{3+} and $^2F_{7/2} \rightarrow ^2F_{5/2}$ of Yb^{3+} that is responsible for enhancing red UC emission.

Moreover, in the case of size-dependent lattice dynamics of BTO nanoparticles, we found, upon decreasing the particle size from 140 nm to 30 nm, the tetragonality of BTO nanocrystallites is reduced accompanied with expanding unit-cell volume, which is the dominant mechanism for reducing giant splitting of longitudinal optical (LO) and transverse optical (TO) phonon modes in BTO system. The weakening coupling of two low-frequency modes among three $A_1(\text{TO})$ phonons leads to change the lowest one from a spectral dip to a peak, whereas the increasing coupling strength between two high-frequency modes, repels them farther so that the less reducing in spectral separation.

Finally, in the part of strain effect, we found the energy of interfacial phonons and ferromagnetic properties depend on stress due to not only the lattice misfit but also the degree of chemical bonding at the interface between CFO and PTO matrices. The disk-3 type structure, the self-assembled CFO disks embedded in PTO matrix, illustrates the strong elastic interactions between these two phases. The largest nonsymmetrical coercivity H_c and the absence of saturation magnetization M_s of CFO matches with the largest Raman shift of $A_1(\text{TO}_2)$ and $A_1(\text{TO}_3)$ modes of PTO found in the disk-3 type as compared with the CFO and PTO multilayered structure and the CFO particles embedded in PTO matrix.

Table of of Contents

Abstract in Chinese.....	I
Abstract in English	III
Contents.....	V
List of Figures.....	IX
List of Tables.....	XIII
 Chapter 1 Introduction.....	 1
1.1 Ferroelectricity, Photorefractive effect, and Perovskite.....	1
1.2 Ferromagnetism and Spinel.....	6
1.3 Multiferroic materials.....	11
1.4 Motive (develop a solution for integrated modifiable devices).....	13
1.4.1 Dependence of crystal structure on substitution, size , and shape.....	13
1.4.2 Dependence of mechanism of luminescence on crystal structure in rare-earth ions doped materials.....	14
1.4.3 Dependence of coupling of electricity and magnetism on lattice mismatch.....	15
1.5 Organization of this dissertation.....	16
References.....	18
 Chapter 2 Theoretical Background.....	 20

2.1	Vibrational spectroscopy.....	20
2.1.1	IR absorption.....	20
2.1.2	Raman scattering.....	22
2.2	Coupled phonon model.....	24
2.3	Born effective charges and LO-TO splitting.....	26
2.4	Optical transitions of rare earth doped materials and upconversion.....	31
2.4.1	Fundamental optical transitions.....	31
2.4.2	Upconversion.....	33
2.5	Multiferroic magnetoelectrics	35
	References.....	39
Chapter 3	Experimental procedures and characterization techniques.....	41
3.1	Synthesis mechanisms and sample preparation.....	41
3.1.1	Barium titanate nanoparticles	41
3.1.2	Barium titanate rods	43
3.1.3	Rare earth doped perovskites.....	45
3.1.3.1	Er ³⁺ -doped PLT poly-crystalline films.....	45
3.1.3.2	Er-Yb codoped ferroelectrics.....	46
3.1.4	Multiferroic films.....	47
3.2	Characterization of structure.....	48
3.2.1	X-ray Diffraction.....	48
3.2.2	Field-Emission Scanning Electron Microscopy (FESEM).....	49

3.2.3 Raman spectroscopy	49
3.3 Characterization of optical properties--Photoluminescence spectroscopy.....	51
3.4 Characterization of magnetic properties--Superconducting quantum interference device magnetometry.....	51
References.....	52
Chapter 4 Destruction of the short-range disorder due to erbium doping in Pb_{0.8}La_{0.2}TiO₃ films.....	53
4.1 Crystal structure (results of XRD).....	53
4.2 Relationship between results of emission spectra and Raman spectra.....	58
4.3 Summary.....	64
References.....	66
Chapter 5 Er-Yb codoped ferroelectrics for controlling visible upconversion emissions.....	67
5.1 Upconversion emission.....	68
5.2 Mechanisms of upconversion emission.....	72
5.2.1 Crystal structure (results of XRD).....	72
5.2.2 Symmetry-dependent upconversion mechanism.....	75
5.2.3 Pump power dependent upconversion.....	76
5.3 Summary.....	78
References.....	80
Chapter 6 Size-dependent lattice dynamics of BaTiO₃ nanoparticles.....	81
6.1 Size-dependent lattice constants of BaTiO ₃ nanoparticles.....	82

6.2 Size-dependent Raman spectra of BaTiO ₃ nanoparticles.....	87
6.3 Born effective charges and LO-TO splitting in BaTiO ₃ nanoparticles system.....	95
6.4 Summary.....	98
References.....	99
Chapter 7 Correlating phonon frequency shift with magnetoelectric effect in the PbTiO₃-CoFe₂O₄ multiferroic system due to interfacial stress.....	101
7.1 Microstructure and morphology.....	102
7.2 Magnetic properties.....	108
7.3 Relationship between interfacial phonon behavior and magnetic properties....	112
7.4 Summary.....	116
References.....	118
Chapter 8 Conclusions and Prospective	119
8.1 Conclusions.....	119
8.2 Prospective.....	123
References.....	127
Vita.....	128
Publication list.....	129

List of Figures

Figure 1.1 Schematic illustrations for A-cell and B-cell types of unit cell for cubic- ABO_3 and possible alternative ways to derive cubic- ABO_3 structure.....	4
Figure 1.2 Properties of paramagnetism, diamagnetism, and ferromagnetism.....	7
Figure 1.3 Arrangement of atoms within the MgAl_2O_4 unit cell.....	10
Figure 1.4 Schematic illustration of multiferroic material.....	12
Figure 2.1 Diagram of dipole moment.....	21
Figure 2.2 Transition from level i to f	22
Figure 2.3 Energy level diagram of PLT:Er^{3+} thin films.....	32
Figure 2.4 Energy level diagram of Er^{3+} and Yb^{3+} ions as well as the proposed mechanisms to produce UC spectra.....	34
Figure 3.1 Flowchart of BaTiO_3 nanocrystals preparation by glycothermal treatment method.....	42
Figure 3.2 Proposed schematic diagram of the synthetic mechanism of BaTiO_3 rods.....	43
Figure 3.3 Flowchart of sol-gel derived Er^{3+} -doped PLT poly-crystalline films.....	45
Figure 3.4 Schematic illustration of three thin films with different connectivity schemes: (a) the 0-3 type with CFO particles embedded in PTO matrix, (b) the 2-2 type with CFO and PTO nanolayers, and (c) the disk-3 type with CFO disc aligned in PTO matrix.....	47
Figure 3.5 BL01C Experimental Station.....	49
Figure 3.6 Setup of typical Raman and PL measurements.....	50
Figure 4.1 XRD patterns of Er^{3+} -doped PLT films with 7 mol% Er^{3+} doping at various sintering temperatures and with different Er^{3+} concentrations at sintering temperature 950°C	55
Figure 4.2 The ratio of lattice constants c/a after Rietveld refinement and the FWHM	

of (100) with different Er^{3+} concentrations at sintering temperature 950°C	57
Figure 4.3 Dependence of the green emission intensities of Er^{3+} -doped PLT films on Er^{3+} concentrations and sintering temperature.....	59
Figure 4.4 Raman spectra of Er^{3+} -doped PLT films with different Er^{3+} concentrations at sintering temperature 950°C and with 7 mol% Er^{3+} dopant at various sintering temperatures.....	61
Figure 4.5 Schematic representation of the position of B atom in ABO_3 structure.....	63
Figure 5.1 UC fluorescence spectra of (a) PbTiO_3 , (b) BaTiO_3 , and (c) SrTiO_3 doped with 6 mol% Er^{3+} ions and various concentrations of Yb^{3+} ions under the same pump power of 980 nm diode laser at 107 mW.....	69
Figure 5.2 XRD patterns of PbTiO_3 and BaTiO_3 doped with 6 mol% Er^{3+} ions and various concentrations of Yb^{3+} ions.....	73
Figure 5.3 Rietveld pattern of PbTiO_3 doped with only 6 mol% Er^{3+} ions and 6 mol% Yb^{3+} ions.	74
Figure 5.4 c/a (a and c are lattice constants) ratio as function of Yb^{3+} - ion concentrations after Rietveld refinement.....	74
Figure 5.5 Pump power dependence of the red upconversion emission of PbTiO_3 and BaTiO_3 doped with 6 mol% Er^{3+} ions and various concentrations of Yb^{3+} ions in a logarithmic scale.....	76
Figure 6.1 Microstructure (FESEM) of BaTiO_3 nanoparticles with average grain size of 140 ± 8 nm, 60 ± 6 nm, and 30 ± 5 nm.....	83
Figure 6.2 Rietveld pattern of BaTiO_3 nanoparticles with average grain size of 60 nm	84
Figure 6.3 The lattice constants a and c of BaTiO_3 nanoparticles after Rietveld	

refinement procedure and the ratio of c/a (b).....	86
Figure 6.4 Size dependence of Raman spectra for BaTiO ₃ bulk ($> 1 \mu\text{m}$) and nanoparticles of diameter 140, 60, and 30nm, respectively.....	88
Figure 6.5 Structural model of the cubic- and tetragonal-phase occurring with bulk BaTiO ₃ crystals.....	89
Figure 6.6 The fitted parameters using the coupled-phonon model as a function of particle size.	93
Figure 6.7 The LO-TO splitting of the $A_1(\text{LO}_3)$ and $A_1(\text{TO}_1)$ modes as function of particle size.....	96
Figure 6.8 Normalized square difference of phonon frequencies of $A_1(\text{LO}_3)$ and $A_1(\text{TO}_1)$ and normalized reciprocal of unit cell volume for nanometer size samples to the micrometer size.....	96
Figure 7.1 Schematic illustration of three thin films with different connectivity schemes: the 0-3 type with CFO particles embedded in PTO matrix, the 2-2 type with CFO and PTO nanolayers, and the disk-3 type with CFO disc aligned in PTO matrix.....	103
Figure 7.2 Top view of FESEM and OM images of the disk-3 type showing the CoFe ₂ O ₄ disks in the PbTiO ₃ matrix.....	103
Figure 7.3 X-ray diffraction patterns of the 2-2, 0-3, and disk-3 multiferroics together with those of, pure CFO powder, pure PTO powder, and PTO on Pt/Si film for comparison.....	104
Figure 7.4 Hysteresis loops of out-of-plane and in-plane magnetization for the pure CFO, 0-3, 2-2, and disk- samples.....	109
Figure 7.5 Micro Raman spectra of disk-3, 2-2, 0-3 multiferroics together with those of PTO on Pt/Si, and PTO powder for comparison.....	113

Figure 7.6 The fitted Raman shift of the $A_1(\text{TO}_3)$, $A_1(\text{TO}_2)$, and $A_1(\text{TO}_1)$ modes as a function of film type.....116

Figure 8.1 SEM images of the three-series products: BT-1, BT-2, and BT-3...125



List of Tables

Table 6-1 Refined crystal parameters and reliability factors of BaTiO ₃ nanoparticles.....	85
Table 7-1 The refined lattice parameters of PTO for the pure PTO powder and the films with different types.....	105
Table 7-2 The refined lattice parameters of CFO for the films with different types.....	105



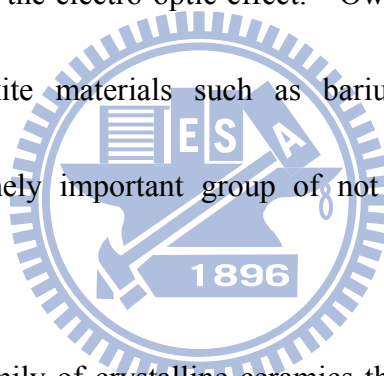
Chapter 1 Introduction

1.1 Ferroelectricity, Photorefractive effect, and Perovskites

Ferroelectricity is a spontaneous electric polarization of a material that can be reversed by the application of an external electric field, upon cooling the material below a certain temperature called the Curie temperature. Ferroelectric ceramics were born in the early 1940s with the discovery of the phenomenon of ferroelectricity with high dielectric constant in barium titanate (BaTiO_3). Ferroelectric materials have long been used in bulk forms in variety of fields such as ceramic capacitors. Furthermore, ferroelectric materials in the forms of thin films are essential for variety of devices such as ferroelectric random access memory (FRAM), infrared pyroelectric sensors, transistors, microwave electronics, electro-optic modulators, and in other integrated devices. Among the many classes of ferroelectric materials, the perovskite compounds such as lead lanthanum titanate (PLT) [1], lead zirconate titanate (PZT) [2], lead titanate (PTO) [3], and barium titanate (BTO) [4] have been the most intensively investigated.

Because of the beneficial properties of light such as wide bandwidth and high speed switching, photonic devices have the trend to replace electronic ones when they are available. Photorefractive materials particularly offer many fascinating

possibilities for applications in the development of communication networks and volume holographic memories [5]. The photorefractive effect is a phenomenon whereby the local refraction index is modified by spatial variations of the light intensity. When two coherent rays interfere with each other in a photorefractive material to form a spatially varying pattern of illumination, charge carriers will be produced in the material and migrate owing to drift or diffusion and space charge separation effects. The resulting electric field from charge separation induces a refractive index change via the electro-optic effect. Owing to the large electro-optic effect present in perovskite materials such as barium titanate, the perovskite compounds are an extremely important group of not only ferroelectric but also photorefractive materials.



Perovskites are a large family of crystalline ceramics that derive their name from a specific mineral known as perovskite. The parent material, perovskite, was first described in the 1830's by a geologist Gustav Rove, who named it after the famous Russian mineralogist Count Lev Aleksevich von Perovski. The general formula of perovskite oxides is ABO_3 (see Fig. 1.1), which is composed of three distinct chemical elements in the ratio of 1:1:3. Ideal oxide perovskite of the aristotype assumes cubic group $Pm\bar{3}m$ with atom positions of cation "A" at $(1/2, 1/2, 1/2)$ of Wyckoff position 1a, cation "B" at $(0, 0, 0)$ of Wyckoff position 1b, and anions "O" at

$(1/2, 1/2, 0)$, $(1/2, 0, 1/2)$ and $(0, 1/2, 1/2)$ of Wyckoff position 3d. The cation “A” is usually larger than cation “B” in the perovskite oxide structure and the “A” and “B” sites are normally occupied by “+2” and “+4” ions, respectively. Conventionally, two types of unit cells with (1) A-cation and (2) B-cation located at center are adopted and often termed the A-cell and B-cell. For type A-cell, the corner-sharing BO_6 octahedra where A-cation is located in the cubo-octahedral interstice of coordination number $\text{CN}=12$ is easily visualized. On the other hand, B-cation of $\text{CN}=6$, forming BO_6 octahedron with six oxygen ions, is situated at the octahedral interstice. The configurations of two types of unit cells are illustrated schematically in Fig. 1.1(a) for A-cell type and Fig. 1.1(b) for B-cell type [Galasso 1970]. B-cell type unit cell has been adopted recently since it clearly represents the BO_6 octahedra from whose distortion the ferroelectricity in t-BaTiO_3 and other ferroic properties, e.g. ferroelasticity, ferromagnetism are derived. Take cubic- ABO_3 ($Pm\bar{3}m$), the 3C-polytype, to exemplify how perovskite structure is constructed is illustrated schematically in Fig. 1.1(c). Its crystal structure designated to E2_1 using Strukturbericht symbols may be derived in the way from either $\alpha\text{-ReO}_3$ (D0_9), $\alpha\text{-Cu}_3\text{Au}$ (L1_2) or CsCl (B2). When A^{2+} is inserted into D0_9 at eight corner sites, the structure becomes perovskite B-cell type. Similarly, removing “A” from B-cell type, the structure becomes ReO_3 with all A-site vacant. Removing “B” from B-site of B-cell type, the crystal

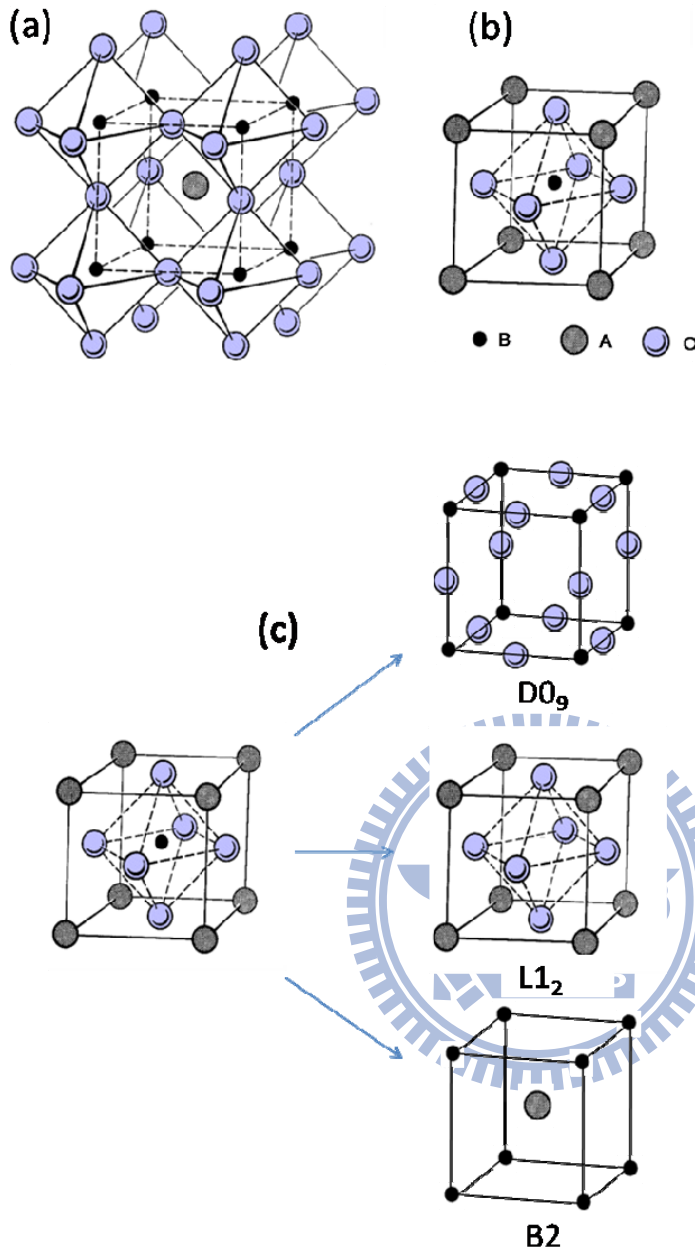


Figure 1.1: Schematic illustrations for A-cell and B-cell types of unit cell for cubic- ABO_3 and possible alternative ways to derive cubic- ABO_3 structure. [Galasso 1970].

structure becomes ordered fcc α - Cu_3Au ($L1_2$). And then, by removing O^{2-} from B-cell type, the structure perovskite is reduced to ordered bcc CsCl (B2). The atomic structure of perovskite is very sensitive to the alteration in the temperature of

the crystal. As the temperature changes, the crystallographic dimensions change and the crystal structures of ABO_3 include cubic, tetragonal, orthorhombic, and rhombohedral due to distortion of the BO_6 octahedra[6]. According to Landau free energy [Putnis 1992], the phase transition is discontinuous first-order in nature. All of the ferroelectric materials have a transition temperature called the Curie temperature (T_c). When the crystal temperature goes above the Curie temperature, $T > T_c$, the elongated crystallographic dimensions allow the B cation to sit at the center of BO_6 skeleton. In this case, the crystal structure is cubic with no spontaneous or permanent electric dipole. Therefore, the crystal doesn't exhibit ferroelectricity. While for $T < T_c$, the shrinkage of the octahedral lets the B cation be more energized to move farther from the center of the original octahedron. Shifting of the B cation causes the structure to alter, thus to induce spontaneous electric dipole. As a result, the distorted octahedral are coupled together, and a very large spontaneous polarization can be achieved. This large spontaneous polarization will lead to a large dielectric constant highly sensitive to temperature. It possesses ferroelectricity in this non-cubic crystal structure and is called ferroelectric phase. A ferroelectric crystal undergoes a phase transition from a non-ferroelectric phase to a ferroelectric phase on decreasing the temperature through the Curie point. The structure of perovskite is also sensitive to A cation substitutions [7-9] and the behavior is similar

to the alteration in the temperature of the crystal.

1.2 Ferromagnetism and Spinel

The spin of an electron combined with its orbital angular momentum results in a magnetic dipole moment and creates a magnetic field. But, the total dipole moment of all the electrons in many materials which have a filled electron shell is zero. Only atoms with partially filled shells can undergo a net magnetic moment in the absence of an external field. Ferromagnetic materials contain many atoms with unpaired spins. When the tiny magnetic dipoles are aligned in the same direction, they create a measurable macroscopic field. These magnetic dipoles tend to align in parallel to an external magnetic field, an effect called **paramagnetism** (see Fig. 1.2(a)). A related but much weaker effect is **diamagnetism** (see Fig. 1.2(b)), due to the orbital motion induced by an external field, resulting in a dipole moment opposite to the applied field. Ferromagnetism involves an additional phenomenon---the dipoles tend to align spontaneously even without any applied field (see Fig. 1.2(c)). This is a purely quantum-mechanical effect. According to the classical electromagnetism, two nearby magnetic dipoles will tend to align in opposite directions. However, they tend to align in the same direction because of the Pauli exclusive principle: two electrons with the same spin cannot sit at the same "position", which effectively

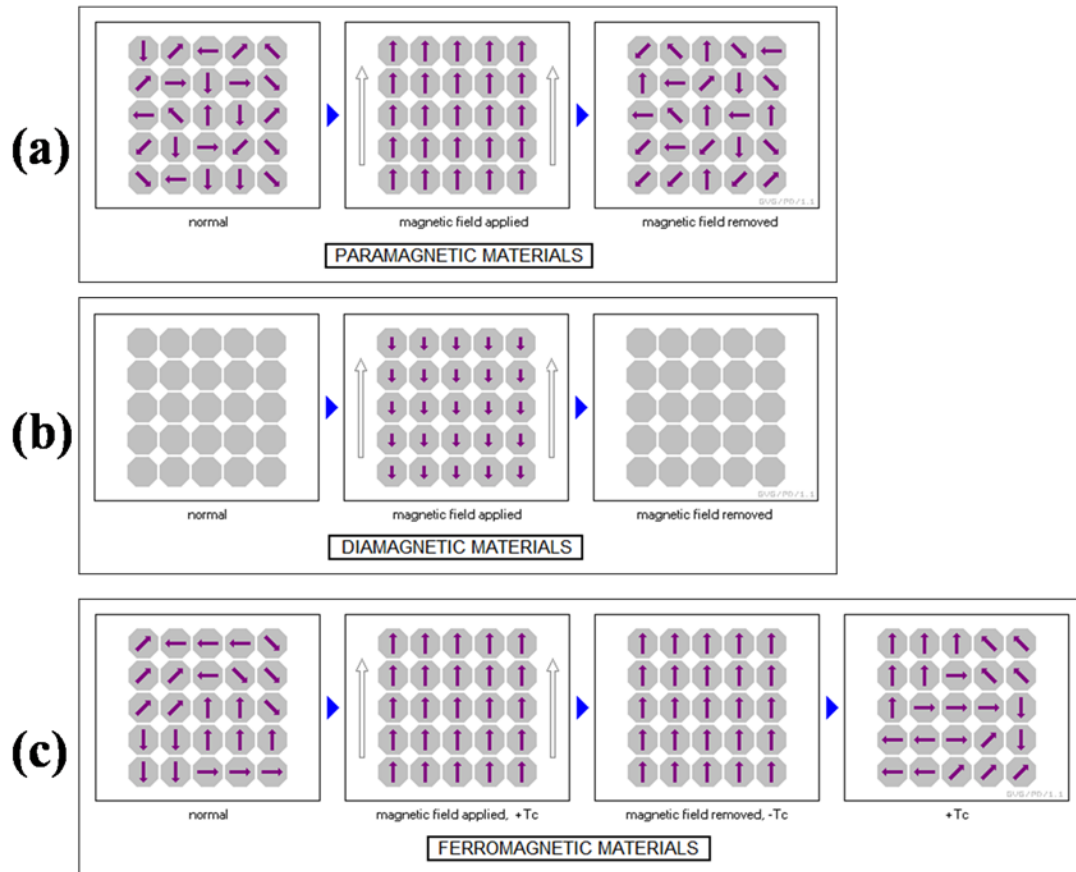


Figure 1.2: Properties of paramagnetism, diamagnetism, and ferromagnetism.

reduces the energy of their electrostatic interaction compared to electrons with opposite spin. This difference in energy is called the exchange energy.

The exchange interaction is primarily responsible for the ordering of atomic moments occurring in magnetic solids and for two other major magnetic ordering types, antiferromagnetism and ferrimagnetism. For instance, in iron (Fe) the exchange interaction between two atoms is about 1000 times stronger than that of classical interaction. There are a small number of "exotic" ferromagnets in which the exchange interactions are exceptionally weak, and then the classical dipole-dipole

interaction may become the dominant ones. However, such systems become ferromagnetic only at very low temperature, usually below 1 K. But if the Curie point in a given material is higher than a few kelvins, then its ferromagnetism is surely produced by exchange interaction. In such systems the classical dipole-dipole interaction may only give rise to secondary effects.

For the long range, the advantage of exchange energy is overtaken by the classical tendency of dipoles to anti-align. This is why, in an equilibrated ferromagnetic material, the dipoles in the whole material are not aligned. Rather, they organize into magnetic domains (also known as Weiss domains) that are aligned at short range, but at long range adjacent domains are anti-aligned. The boundary between two domains, where the magnetization flips, is called a domain wall (i.e., a Bloch/Néel wall, depending upon whether the magnetization rotates parallel/perpendicular to the domain interface) and is a gradual transition on the atomic scale.

Thus, an ordinary piece of iron generally has little or no net magnetic moment. However, if it is placed in a strong enough external magnetic field, the domains will re-orient in parallel with that field, and will remain re-oriented when the field is turned off, thus creating a "permanent" magnet. The domains don't go back to their original minimum energy configuration when the field is turned off because the

domain walls tend to become 'pinned' or 'snagged' on defects in the crystal lattice, preserving their parallel orientation. This is shown by the Barkhausen effect: as the magnetizing field is changed, the magnetization changes in thousands of tiny discontinuous jumps as the domain walls suddenly "snap" past defects. This magnetization as a function of the external field is described by a hysteresis curve. Although this state of aligned domains is not a minimal-energy configuration, it is extremely stable and has been observed to persist for millions of years in seafloor magnetite aligned by the Earth's magnetic field. Alloys used for the strongest permanent magnets are "hard" alloys made with many defects in their crystal structure where the domain walls "catch" and stabilize. The net magnetization can be destroyed by heating and then annealing the material without an external field, however. The thermal motion allows the domain boundaries to move, releasing them from any defects to return to their low-energy unaligned state.

As the temperature increases, thermal motion and entropy competes with the ferromagnetic tendency for dipoles to align. When the temperature rises beyond a certain point, called the Curie point, there is a second-order phase transition and the system can no longer maintain a spontaneous magnetization, although it still responds paramagnetically to an external field. Below that temperature, there is a spontaneous symmetry breaking and random domains form. The Curie temperature itself is a

critical point, where the magnetic susceptibility (χ) is theoretically infinite and, although there is no net magnetization, domain-like spin correlations fluctuate at all length scales.

Spinel is an important class of mixed-metal oxides, which has the general chemical composition of AB_2O_4 . Atom “A” is a divalent ion of radius between 80 and 110 pm, such as Fe, Mn and Cu; atom “B” is a trivalent atom of radius between 75 and 90 pm, such as Ti, Fe and Co. The majority of spinel compounds belong to the space group $Fd\bar{3}m$ ($F_{1/d}^4\bar{3}_{2/m}$; O_h^7 ; No. 227 in the International Tables). The structure consist of a cubic close-packed array of 32 oxygen ions, which forms 64 tetrahedral interstices and 32 octahedral interstices in one unit cell (containing eight formula units $(AB_2O_4)_8$) [10]. In a normal spinel structure, e.g. $MgAl_2O_4$, all the

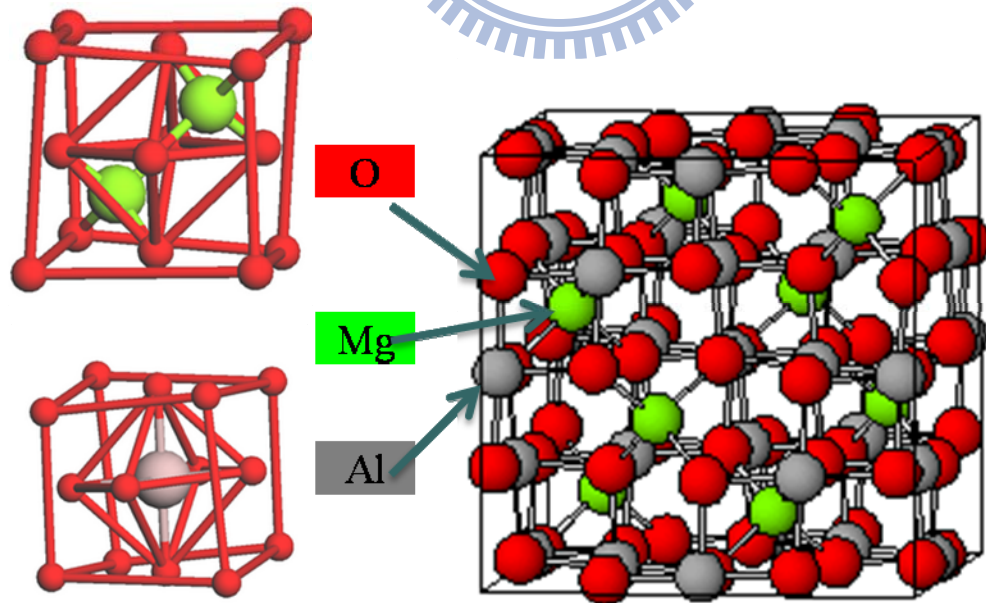


Figure 1.3: Arrangement of atoms within the $MgAl_2O_4$ unit cell.

trivalent cations (Al^{3+}) are located in half the octahedral sites, while all the divalent cations (Mg^{2+}) occupy 1/8 of the tetrahedral sites. Figure 1.2 shows a typical spinel structure. Notice the red oxygen atoms, the green “A” atoms are in the tetrahedral holes, and the grey “B” atoms in the octahedral holes.

Cobalt ferrite, CoFe_2O_4 (CFO), has an inverse spinel structure. The normal crystal structure of an AB_2O_4 spinel consists of the A^{2+} atoms occupying the tetrahedral coordination sites and the B^{3+} atoms occupying the octahedral sites [11].

An inverse spinel is an alternative arrangement where the divalent ions swap with half of the trivalent ions so that the Co^{2+} now occupy octahedral sites i.e. $\text{Fe}(\text{CoFe})\text{O}_4$. The Co cation occupies one half of the octahedral coordination sites and half the Fe^{3+} cations occupy the other half of the octahedral coordination sites as well as all of the tetrahedral coordination sites.

1.3 Multiferroic materials

Multiferroics displaying both ferroelectric and ferromagnetic properties is known possessing the magnetoelectric (ME) effect between the two parameters [12].

The ME effect in multiferroics possesses not only simultaneous magnetic and electric ordering but also interconversion of energies stored in electric and magnetic fields.

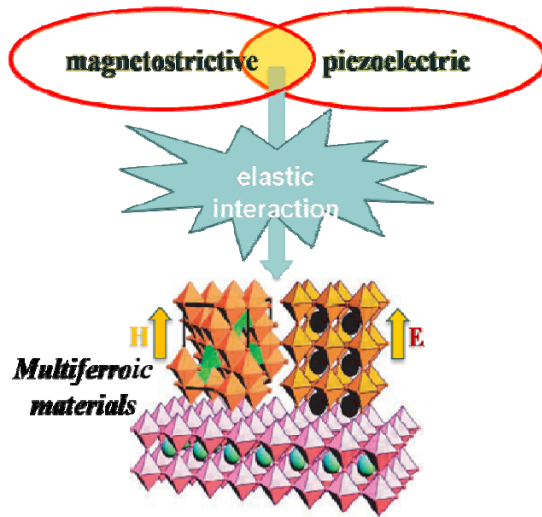


Figure 1.4: Schematic illustration of multiferroic material.

It is also an important mechanism in applications of transducers, actuators, and sensors [13, 14]. There are some theoretical studies [15-17] on calculating the coupling effect of different geometric structures and many experimental reports [13, 18] of ME effect in various types of materials, different geometric shapes, and operational modes. The coexistence of magnetic and electric subsystems engenders the material with the “product” property (i.e., the composite exhibits responses that are not available in the individual component phases), thus allowing an additional degree of freedom in the design of actuators, transducers, and storage devices. However, the choice of single-phase materials exhibiting coexistence of strong ferro/ferrimagnetism and ferroelectricity is limited [19, 20]. Van Suchtelen et al. [21] proposed that composites of piezoelectric and magnetostrictive phases can be electromagnetically coupled via stress mediation (see Fig. 1.4). The ME coupling

results from the elastic bonding at the interface and is transmitted through the stress/strain exerted by a magnetized magnetostrictive phase on a piezoelectric phase or vice versa along their boundary, hence it induces a net polarization or magnetization [12, 22, 23].

1.4 Motive

To develop a solution for integrated modulable devices, study on not only the emission properties of rare-earth (RE)-doped ferroelectric materials but also the various properties of host materials is strongly motivated.

1.4.1 Dependence of crystal structure on substitution, *size*, and *shape*

The physical properties of complex oxide perovskites have been dramatically influenced by various effects, such as temperature [24-26], pressure [25, 27], substitution [28], size, and shape [29-33]. With the development of miniaturization of electronics, recent advances in solid-state science have resulted in ferroelectric materials and devices with nanostructures with length scales less than 200 nm. The size dependence of Curie temperature and tetragonal distortion of the ferroelectric phase has been investigated theoretically based on the Landau-Ginsburg-Devonshire (LGD) theory in the case of isolated particles.[34-37] The change of the ferroelectric phase in isolated particles is mainly the consequence of the surface effect and a transition from the ferroelectric phase to a cubic paraelectric phase at room

temperature for a critical particle size from a few nanometers to a few tens of nanometers is predicted. However, it is often difficult in experiment to separate true size effects from other factors that change with the size. The fixity of the ferroelectric phase can be determined by additional factors like defect chemistry, incorporation of foreign atoms and bulk hydroxyl groups, aggregation level of the particles, porosity level, and residual stresses.[38-43] To avoid the disturbance of other causes, powders with uniform size therefore seems a more convenient system to study size effects. In this part, we synthesize BaTiO₃ nanocrystals with uniform crystal size less than 200 nm by using glycothermal synthesis method. We probe the size dependence of structure characterization with crystal size ranging from ~μm to ~10 nm by using the x-ray diffraction (XRD), scanning Electron microscope (SEM) and Raman scattering. The research topic will focused on the behavior of phonon modes, including the displacement of B cation and the coupling of phonon, as the crystal size decreases from ~μm to ~10 nm. We also attempt to synthesize BaTiO₃ nano-wires (nano-rods) by using molten-salt synthesis method.

1.4.2 Dependence of mechanism of luminescence on crystal structure in rare-earth ions doped materials

The different crystal field caused by structure symmetry of the host material would contribute to different perturbation terms for the rare-earth ions inner shell

transitions. Therefore, the crystal structure is a more important mechanism for not only emission efficiency in erbium-doped $\text{Pb}_{0.8}\text{La}_{0.2}\text{TiO}_3$ system, but also converting up-conversion (UC) green radiation to red radiation due to the EBT process in Er-Yb codoped ferroelectrics. In this part, we have studied the dependence of emission mechanism on the crystal structure of perovskites doped with rare-earth ions.

1.4.3 Dependence of coupling of electricity and magnetism on lattice mismatch

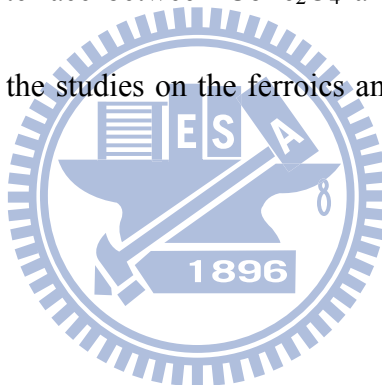
Multiferroics displaying both ferroelectric and ferromagnetic properties is known possessing the ME effect between the two parameters. Van Suchtelen et al. [21] proposed that composites of piezoelectric and magnetostrictive phases can be electromagnetically coupled via stress mediation. The ME coupling results from the elastic bonding at the interface and is transmitted through the stress/strain exerted by magnetized magnetostrictive phase on piezoelectric phase or vice versa along their boundary and hence it induces a net spontaneous polarization or magnetization [12, 22, 23]. Moreover, it is well known that the behavior of interfacial phonon is sensitive to the giant residual stress/strain resulting from the lattice misfit between the different media [44]. It is interesting and important to investigate the relationship between the ME effect and the behavior of interfacial phonon. Recent studies on phonon behavior of multiferroics were reported [45-47], but the results are inconclusive. In this part, we report on the stress dependence of the behavior of interfacial phonon and

the magnetic properties in three multiferroics consisting of the different geometric shapes of ferromagnetic CoFe_2O_4 (CFO) embedded in ferroelectrics PbTiO_3 (PTO) by using the micro-Raman spectroscopy and superconducting quantum interference device (SQUID).

1.5 Organization of this dissertation

In this thesis, I present investigations of the influence of perovskite structure on luminescence and characteristics of ferroics. The dissertation is organized as follows. I first describe the related theoretic background in Chapter 2, including a general concept of crystal structures, lattice dynamics, fundamental optical transitions, and magnetoelectric (ME) effect. In Chapter 3, I present the synthesis of the samples with different processes and also show the brief illustrations of characterization techniques. In Chapter 4, I discuss the dominant mechanisms on visible emission of the Er^{3+} doped $\text{Pb}_{0.8}\text{La}_{0.2}\text{TiO}_3$ polycrystalline films. Combining with examining the disappearance of Raman modes, I show destruction to a displacement of Ti in the short-range structure for doping concentration exceeding 7 mol%. The diminishing of symmetry breaking causes quench of Er^{3+} emission. As increasing Yb^{3+} co-doped concentrations in 6 mol% Er^{3+} doped PbTiO_3 , BaTiO_3 , and SrTiO_3 polycrystalline powder samples, the dominant mechanisms of visible upconversion emissions in Er-Yb codoped ferroelectrics are discussed in Chapter 5. In Chapter 6, I discuss the

attractive LO-TO splitting behavior and depict the low frequency TO spectral peak along with change of the tetragonal phase toward the cubic one for reducing diameter of BaTiO₃ nanocrystals from 140 nm to 30 nm. In Chapter 7, I discuss the characteristics of three different geometric forms of the PbTiO₃-CoFe₂O₄ multiferroics. The analysis of the magnetic and Raman measurements under different geometric forms indicates the dependence of magnetic property and interfacial phonon behavior on stress/strain due to the lattice misfit and the strongest chemical bonding at the interface between CoFe₂O₄ and PbTiO₃ matrices. In the final Chapter 8, I conclude the studies on the ferroics and propose the several topics worthy of the future work.



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Chapter 2 Theoretical Background

In this chapter, lattice vibration in crystals, optical transitions of rare earth, and multiferroic magnetoelectrics are reviewed. Lattice dynamics corresponding to lattice vibrational properties, the behavior of coupled phonon and, the mechanism of LO-TO splitting are discussed. Optical transitions in rare earth doped materials have been described, including the mechanism of fundamental optical transitions and upconversion.

2.1 Vibrational spectroscopy

2.1.1 IR absorption

For infra-red (IR) wavelengths, absorption must in some way be related to a variation in the charge distribution. This arises due to a change in the dipole moment associated with molecule. After bonding, one atom of the molecules has a local charge Δq then the rest of atoms have charge $-\Delta q$ and the dipole moment μ , is given by

$$\mu = \Delta q \times l, \quad (2-1)$$

where l is the separation of the charges (see Figure 2.1).



Figure 2.1: Diagram of dipole moment.

Electromagnetic wave can be absorbed or emitted by a medium if during its interaction there is a change in the charge distribution within the medium. During the interaction with photon, the dipole moment μ will change, thus one can rewrite the dipole moment as

$$\mu = \mu_0 + \frac{\partial \mu}{\partial Q} Q, \quad (2-2)$$

where $Q = (r - r_{eqm})$ is the displacement from the equilibrium position “ r_{eqm} ”.

In order to describe the excitation of a molecule from vibrational level, $v = i$ to $v = f$, as shown in Figure 2.2, an interaction Hamiltonian $H_{int} = E \cdot \mu$ that expresses the interaction of an atom with a photon is added to the unperturbed Hamiltonian H_0 to describe the total Hamiltonian,

$$H = H_0 + H_{int} \quad (2-3)$$

Thus the transition moment, R , can be written as

$$R = \int \psi_i H_{int} \psi_f = \langle i | H_{int} | f \rangle, \quad (2-4)$$

so,

$$R = \langle i | \left(\mu_0 + Q \frac{\partial \mu}{\partial Q} \right) \cdot E | f \rangle = \langle i | Q \frac{\partial \mu}{\partial Q} \cdot E | f \rangle \quad (2-5)$$

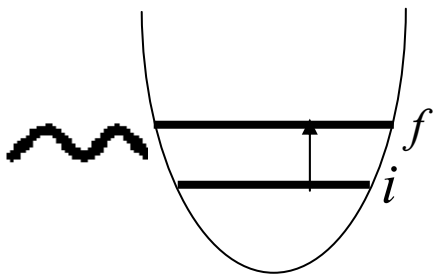


Figure 2.2: Transition from level i to f .

IR absorption occurs as the transition $R \neq 0$, in other words, there must be a change in the dipole moment due to vibration of the molecule which is induced by the applied field E , since the transition probability P is equal to $|R|^2$. The condition that an IR absorption or emission must be associated with a change in dipole moment is known as the dipole selection rule. The dipole selection rule plays an important role in IR spectroscopy because it tells us whether a molecule will be IR active or not.

2.1.2 Raman scattering

When light passes through a medium, most of the light is reflected, transmitted, absorbed, elastic or inelastic scattered. Raman scattering is an inelastic scattering process. When the light encounters the medium, it interacts inelastically with phonon (vibration) modes and produces outgoing photons whose frequencies are relatively shifted by an amount of energy correspondent to phonon energy from that of the incoming light. The scattered outgoing photons are called the Raman-scattered photons. If the light of frequency ν_0 is scattered by some media, the spectrum of the scattered light contains a strong line of frequency ν_0 and much

weaker lines of frequencies $\nu_0 - \Delta\nu_1, \nu_0 - \Delta\nu_2, \dots, \nu_0 + \Delta\nu_2, \nu_0 + \Delta\nu_1$, etc. Those lines on the low frequency side of the exciting lines (i.e., $\nu_0 - \Delta\nu_i, i = 1, 2, \dots$) are always matched by lines on the high frequency side (i.e., $\nu_0 + \Delta\nu_i, i = 1, 2, \dots$) but the latter are much weaker when the scattering medium is at room temperature. Raman scattering is inherently a weak process, but laser provides enough intensity that the spectra can be routinely measured. In analogy with terms used in the discussion of fluorescence spectra, lines on the low frequency side of the exciting line are known as Stokes lines and those on the high frequency side as anti-Stokes lines.

The incident photon loses its energy by producing a phonon (Stokes shifted), or gain energy and momentum by absorbing a phonon (anti-Stokes shifted), according to the energy conservation rules :

$$h\nu_i + W_1 = h\nu_s + W_2, \quad (2-6)$$

$$h(\nu_s - \nu_i) = h\Delta\nu = W_1 - W_2, \quad (2-7)$$

where ν_i and ν_s are the incoming and scattered photon frequencies, W_1 and W_2 are the energy of the molecule before and after the interaction, respectively.

Assuming that the scattering medium is in temperature equilibrium at temperature T , the distribution of the molecules over the energy states will be Boltzmann and the ratio of the number of molecules N_1 in a state of energy W_1 to the number of molecules N_2 in a state of energy W_2 is given by

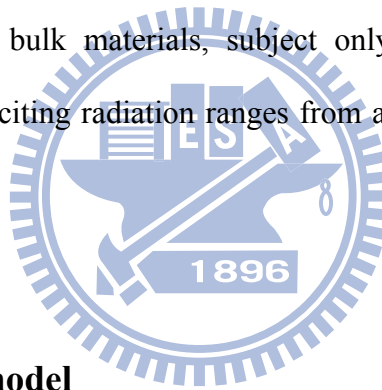
$$\frac{N_1}{N_2} = e^{-h\Delta\nu / kT}, \quad (2-8)$$

if degeneracy is neglected. If one includes the fact that scattered intensity is proportional to the fourth power of the frequency then the relative intensities of

Stokes to anti-Stokes lines and their temperature dependence be consistent with the ratio

$$\frac{I_{anti-Stokes}}{I_{Stokes}} = \left(\frac{\nu + \Delta\nu}{\nu - \Delta\nu} \right)^4 e^{-h\Delta\nu/kT} \quad (2-9)$$

All the Raman mode frequencies, intensities, line-shape, and line-width, as well as polarization behavior can be used to characterize the lattice and impurities. The intensity gives information on crystallinity. The line-width increases when a material is damaged or disordered, because damage or disorder occurs in a material will increase the phonon damping rate or relax the rules for momentum conservation in Raman process. All these capabilities can be used as a judgment for layered microstructure as well as bulk materials, subject only to the limitation that the penetration depth of the exciting radiation ranges from a few hundred nanometers to few micrometers.



2.2 Coupled phonon model

The Hamiltonian of an isolated system can always be brought to a diagonal form, which means that any coupling of the quantum states is reducible. Under this assumption, the reflectivity of the crystal with more than one infrared active mode is often quite well reproduced by a formula involving the sum of contributions from independent classical oscillators. However, no system above the temperature 0 K is isolated, for that we have least the blackbody radiation connecting it with the environment. In some notable cases, the Hamiltonian of the system is intrinsically

non-diagonal. The profile of the energy spectrum of such system is not composed of a set of Lorentzian peaks, but contains asymmetric interfering features.

Since the occurrence of coupling in the lattice modes was recognized by Barker and Hopfield to explain the infrared reflectivity of some perovskites, a handful of spectral anomalies in data on Raman, Brillouin and neutron scattering were observed and associated with phonon-phonon coupling. Because the coupling phenomenon is a temperature-induced effect, it seems probable that its occurrence will be more frequent in crystal showing other thermal anomalies in the phonon behavior. In fact, most of the crystals undergo a structural phase transition at some temperature not far from where the interference starts to be observable. BaTiO₃ presents three structural phase transitions, at -80, 0, and 130°C. In the tetragonal phase between 0 and 130°C the dynamics of the crystal is complicated. All the three A₁ modes of vibration are strongly coupled and two of them are heavily damped.

Because the three A₁(TO) modes are strongly coupled and two of them are heavily damped in the tetragonal phase of ABO₃, Sood, [1] and Chaves, *et al.* [2] have considered three coupled A₁(TO) modes to describe the complicated coupling phenomenon. The Raman intensity of the three coupled modes can be expressed by

$$I(\omega) = A [n(\omega) + 1] \text{Im}[\mathbf{T}^* \mathbf{G} \mathbf{T}], \quad (2-10)$$

where A is a constant, $n(\omega)$ is Bose-Einstein factor, \mathbf{T} is a vector involving Raman

scattering amplitudes, and the inverse matrix response is

$$\mathbf{G}^{-1}(\omega) = \mathbf{\Omega}^2 - \omega^2 \mathbf{I} - i\omega \mathbf{\Gamma}. \quad (2-11)$$

In Eq. (2-11), \mathbf{I} is the unit matrix, $\mathbf{\Omega}^2$ is the force constant matrix, and $\mathbf{\Gamma}$ is the damping matrix:

$$\mathbf{\Omega}^2 = \begin{pmatrix} \omega_1^2 & \omega_{12}^2 & 0 \\ \omega_{12}^2 & \omega_2^2 & \omega_{23}^2 \\ 0 & \omega_{23}^2 & \omega_3^2 \end{pmatrix} \text{ and } \mathbf{\Gamma} = \begin{pmatrix} \Gamma_1^2 & 0 & 0 \\ 0 & \Gamma_2^2 & 0 \\ 0 & 0 & \Gamma_3^2 \end{pmatrix}. \quad (2-12)$$

Here ω_i and ω_{ij} ($i, j=1,2,3$) are the uncoupled mode frequencies and the coupling strengths between modes i and j . The coupling between the lowest (ω_1) and the highest (ω_3) modes was set to zero ($\omega_{13} = 0$), to allow less fitting parameters; this is a reasonable approximation because they are too far from each other, having no spectral superimposition.

2.3 Born effective charges and LO-TO splitting

The total polarization in the crystal can be expressed as a sum of contribution from the displacements of the charged ions and from the displacements of electrons relative to their ionic nuclei

$$P^i = P_{ion}^i + P_{electron} \quad (2-13)$$

and

$$P_{ion}^i = \frac{N}{V} \sum_{\alpha} e_{\alpha} U_{\alpha}^i, \quad (2-14)$$

where i is the label of Cartesian coordinate, N is the number of primitive cells in the crystal volume V and e_α is the charge of the α th ions in a primitive cell, all ions of the same label suffering the same displacement U_α .

It is convenient to express the ionic polarization in terms of the normal coordinates. The polarization is a vector, and the vibrational modes that contribute to the polarization are limited to those with the same symmetry character as a polar vector. These polar modes can be chosen so that their contributions to the polarization are parallel to principal axes of the susceptibility tensor. Let ξ_σ be a unit vector parallel to the polarization contributed by the displacement of normal coordinates W_σ . Then one of the Cartesian components ξ_σ^i is unity and the other two are zero. The ionic polarization can be written as

$$P_{ion}^i = \frac{N}{V} \sum_{\sigma} Z_{\sigma} \xi_{\sigma}^i W_{\sigma}, \quad (2-15)$$

$$Z_{\sigma} \xi_{\sigma}^i \equiv \sum_{\alpha} \frac{e_{\alpha} c_{\alpha\sigma}^{i*}}{M_{\alpha}^{1/2}}, \quad (2-16)$$

where Z_{σ} is the effective charge of the normal mode σ and the mass of the α th atom is denoted by M_{α} . By simplifying equations of motion, we obtain

$$W_{\sigma} = \sum_{\alpha} W_{\alpha}^{1/2} c_{\alpha\sigma}^i U_{\alpha}^i, \quad (2-17)$$

where the transformation coefficients can be chosen to satisfy the orthonormality relations

$$\sum_{\alpha} c_{\alpha\sigma}^{i*} c_{\alpha\sigma'}^i = \delta_{\sigma\sigma'}. \quad (2-18)$$

The presence of an electric field E modifies the harmonic oscillator equation of the normal modes to

$$\ddot{W}_\sigma + \Gamma_\sigma \dot{W}_\sigma + \omega_\sigma^2 W_\sigma = Z_\sigma \xi_\sigma^i E^i. \quad (2-19)$$

The applied electric field of frequency ω , therefore, produces a steady-state normal-mode amplitude,

$$W_\sigma = \frac{Z_\sigma \xi_\sigma^i E^i}{\omega_\sigma^2 - \omega^2 - i\omega \Gamma_\sigma}, \quad (2-20)$$

and the ionic polarization can be written in a form proportional to the electric-field components. We assume that ω is in the vicinity of the vibrational frequencies and well below the frequencies of all electric transitions. The relative permittivity is then

$$\kappa^i = \kappa_\infty^i + \sum_\sigma \frac{NZ_\sigma^2 \xi_\sigma^{i2} / \varepsilon_0 V}{\omega_\sigma^2 - \omega^2 - i\omega \Gamma_\sigma}, \quad (2-21)$$

where κ_∞^i is a constant electric contribution to the relative permittivity, so that

$$P_{electron}^i = \varepsilon_0 (\kappa_\infty^i - 1) E^i. \quad (2-22)$$

The electric field and polarization of any electromagnetic wave frequency ω and wavevector q will satisfy the Maxwell's equation :

$$-\varepsilon_0 c^2 q(q \cdot E) + \varepsilon_0 (c^2 q^2 - \omega^2) E = \omega^2 P. \quad (2-23)$$

This equation is unfortunately very complicated in its most general form, but simplification can be made for most applications. The most striking simplification occurs when the frequency and wavevector satisfy $cq \gg \omega$. We obtained

$$\kappa^x q^{x^2} + \kappa^y q^{y^2} + \kappa^z q^{z^2} = 0. \quad (2-24)$$

By combining the equation for the divergence of the electrical displacement,

$$q \cdot (\varepsilon_0 E + P) = 0, \quad (2-25)$$

with Eqs. (2.23) and (2.24), we can obtain the general representation

$$\ddot{W}_\sigma + \omega_\sigma W_\sigma = - \frac{NZ_\sigma (q \cdot \xi_\sigma) \sum_\tau Z_\tau (q \cdot \xi_\tau) W_\tau}{\varepsilon_0 V (\kappa_\infty^x q^{x^2} + \kappa_\infty^y q^{y^2} + \kappa_\infty^z q^{z^2})}, \quad (2-26)$$

where τ is summed over all the polar modes. In cubic symmetry crystal, the polar-vector representation is threefold degenerate. The crystals are optically isotropic and the principal axes are not restricted to lie in any particular directions. For any direction of the wavevector of a threefold polar mode, it is permissible to choose two of the polarization vectors ξ_σ perpendicular to q and the third ξ_σ parallel to q . The two transverse polar modes have a frequency determined by the standard lattice dynamics calculation. The longitudinal polar mode has the associated macroscopic electric field, and its frequency is determined by the equation above, which reduces to

$$\kappa = 0 \quad (2-27)$$

in the cubic case. The simplest cases to consider first are the cubic crystals that have a single threefold polar mode. The relative permittivity has the isotropic form

$$\kappa = \kappa_\infty + \frac{NZ^2 / \varepsilon_0 V}{\omega_T^2 - \omega^2 - i\omega\Gamma}, \quad (2-28)$$

where the mode frequency ω_0 is replaced by ω_T to emphasize its transverse nature and redundant subscripts and superscripts are omitted. The longitudinal frequency obtained from the equation mentioned above with the damping removed is

$$\omega_L = \left(\frac{\kappa_0}{\kappa_\infty} \right)^{1/2} \omega_T, \quad (2-29)$$

where κ_0 is the zero-frequency value of the relative permittivity

$$\kappa_0 = \kappa_\infty + \frac{NZ^2}{\varepsilon_0 V \omega_T^2}. \quad (2-30)$$

This expression for the longitudinal frequency is the Lyddane-Sachs-Teller relation. The equation of motion for the longitudinal mode takes the form

$$\ddot{W} + \omega_T^2 W = -\frac{NZ^2 W}{\varepsilon_0 V \kappa_\infty}, \quad (2-31)$$

and leading to

$$\omega_L^2 = \omega_T^2 + \frac{NZ^2}{\epsilon_0 V \kappa_\infty}. \quad (2-32)$$

Resta *et al.* [3] have shown that polarization is linear in the change of the position vector of the basis atom to a good approximation. The Born effective charge tensor Z_m^* is rewritten through

$$\delta P = \frac{e}{\Omega} \sum_{m=1}^N Z_m^* \cdot \delta u_m. \quad (2-33)$$

Here, N is the number of atoms in the primitive unit cell, δu_m is the first-order change of the position vector of the m th basis atom, and Ω is the volume of the unit cell.

The Born effective charge tensor reflects the effects of the Coulomb interactions and is directly related to the LO-TO splitting. The general representation of the dynamical material for LO and TO modes at $q=0$ are related by

$$D_{mn}^{LO} = D_{mn}^{TO} + \frac{4\pi e^2}{\Omega} \frac{Z_m^* Z_n^*}{\epsilon_0}, \quad (2-34)$$

where D represents the dynamical matrix and is proportional to the square of the vibration frequency. Zhong, *et al.* [4] and Waghmare, *et al.* [5] have calculated that the softest TO mode is most associated with the hardest LO mode via Coulomb interaction to give rise to giant LO-TO splitting in ABO_3 compounds, especially for the ferroelectric phonon modes.

2.4 Optical transitions of rare earth doped materials and upconversion

2.4.1 Fundamental optical transitions

Trivalent rare-earth (RE) ions are well known for their special optical properties, which result from the fact that the electrons of the partially filled $4f$ -shell are shielded from the surrounding completely filled $5s$ and $5p$ shells. The energy levels of the $4f$ -shell have equal parity, and hence electric dipole transitions are forbidden. In a solid, the slight mixing with odd-parity wavefunctions makes the transition slightly allowed. The influence of the electric field around the ion removes the degeneracy of the $4f$ -levels, resulting in a Stark-splitting of the energy levels. However, due to the shielding by the outer lying shells, the magnitude of the splitting is small, resulting in relative narrow emission lines, of which the wavelength is almost independent of the host material.

The energy levels of the $4f$ -level arise from spin-orbit interactions and are often denoted using Russel-Saunders notation $^{2S+1}L_J$, in which S is the total spin angular momentum, L is the total orbital angular momentum quantum number and J the magnitude of the total angular momentum, $J=L+S$ according to vector model. There exist 14 rare-earth elements, that all have a different number of electrons in the incompletely filled $4f$ -shell. As a result, each rare-earth ion has its own specific energy levels, and hence typical luminescence lines. The rare-earth ion erbium (Er) has transition at $1.53 \mu\text{m}$, which is the standard wavelength used in optical

telecommunication. The energy level scheme of trivalent RE ions was presented in the classic work by Dieke and Crosswhite [6] and then was reproduced in many reviews. Figure 2.3 has shown the energy levels and laser transitions of trivalent rare-earth ions.

As already mentioned, the choice of host material in rare-earth doped components does not influence significantly the position of the energy levels of the rare-earth ions.

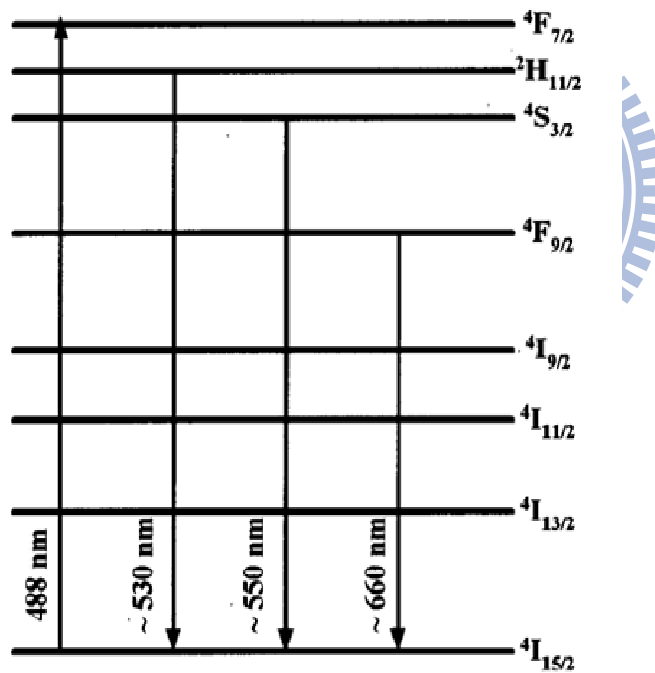


Figure 2.3: Energy level diagram of PLT:Er³⁺ thin films [6].

Therefore, in principle any material that little absorption at the pump and emission wavelengths can be used. Many different rare-earth doped materials have been

studied, like pure SiO₂, silicate and phosphate glasses, LiNbO₃, Al₂O₃, and GaN. By combining the excellent opto-electric properties and chemical stability, ferroelectric perovskite (Pb_{0.7}La_{0.3}TiO₃) is being considered in our research.

2.4.2 Upconversion

Upconversion (UC) in rare-earth (RE) ion-doped materials has been intensively studied in recent years of applications in laser devices [7], three-dimensional display [8], sensors [9], and biological fluorescent labels [10-12]. Energy UC of radiation can exist by intra-ionic successive absorption, cooperative energy transfer, and photon avalanche processes [13, 14]. The research of these mechanisms provides intellects on the physics of energy transfer processes and fluorescence converters. Recently, green and red UC radiation induced by a 980-nm diode laser excitation in Er³⁺-doped and Er³⁺—Yb³⁺ co-doped Y₂O₃ and ZrO₂ nanocrystals were reported [15-17]. It is known that the Er³⁺ ion absorbs one laser photon and jumps from the ground state ⁴I_{15/2} to the long-lived ⁴I_{11/2} state, which is termed the ground-state absorption (GSA). Then, the excited-state absorption (ESA) could happen to populate ⁴F_{7/2} state. Subsequently, the Er³⁺ ions at ⁴F_{7/2} state could further rapidly relax to the ²H_{11/2} / ⁴S_{3/2} state by multiphonon processes, from which the green UC emission arises. Thus, the green UC emission is a result of two-photon excitation (GSA followed by ESA) process. The codoped Yb³⁺ ions provide excitation of the ⁴I_{11/2}(Er³⁺) state by the

larger absorption cross section of Yb^{3+} ions.

The strong red UC emission is reported enabled by quenching the $^4S_{3/2}(\text{Er}^{3+})$ state to the saturation of the $^4I_{13/2}(\text{Er}^{3+})$ state through the so-called efficient energy back-transfer (EBT) process. [17] Through the exciting the nearest-neighboring Yb^{3+} ion at the ground state $^2F_{7/2}(\text{Yb}^{3+})$ to the $^2F_{5/2}(\text{Yb}^{3+})$ state, the excited Er^{3+} ion located at the $^4S_{3/2}(\text{Er}^{3+})$ state, which originally emits green UC radiation, will transit

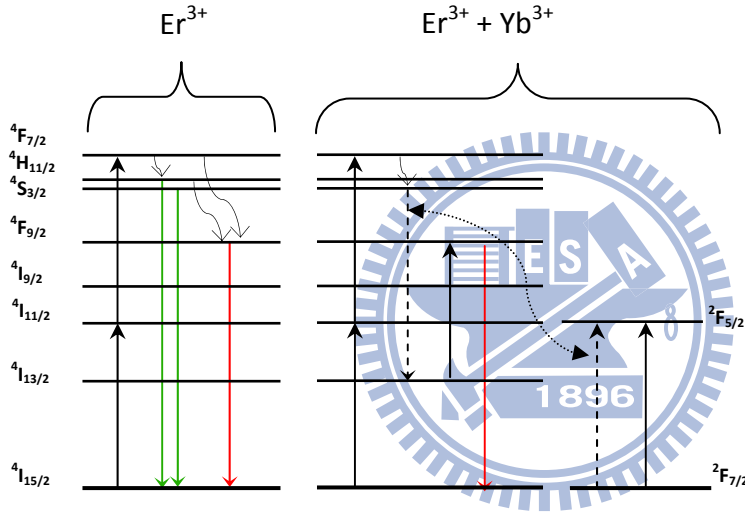


Figure 2.4: Energy level diagram of Er^{3+} and Yb^{3+} ions as well as the proposed mechanisms to produce UC spectra [17].

to the $^4I_{13/2}(\text{Er}^{3+})$ state. This excitation was expressed as: $^4S_{3/2}(\text{Er}^{3+}) + ^2F_{7/2}(\text{Yb}^{3+}) \rightarrow ^4I_{13/2}(\text{Er}^{3+}) + ^2F_{5/2}(\text{Yb}^{3+})$ and the energy diagram schematically presented in Figure 4 of Ref. 17 was duplicated in Figure 2.4 for making explanation clearer. Chen, *et al.* [17] reported that the energy mismatch in the EBT process is about 320 cm^{-1} and can be easily dissipated by one phonon of the ZrO_2 lattice (470 cm^{-1}). The excited

$^2F_{5/2}$ -Yb³⁺ ions can be further dissipated by another excitation that the Er³⁺ ions transited from the ground state to the $^4I_{11/2}(\text{Er}^{3+})$ state then further relaxed to the long-lived $^4I_{13/2}(\text{Er}^{3+})$ state by the EBT process. The higher Yb³⁺ ion concentration could provide the more Yb³⁺ ions nearly neighboring to the Er³⁺ ions to cause the efficient EBT process. The $^4I_{13/2}$ -Er³⁺ ion subsequently absorbs a laser photon from the $^4I_{13/2}(\text{Er}^{3+})$ state or directly relaxes from the high-lying states to populate $^4F_{9/2}(\text{Er}^{3+})$ state that the red UC emission arises. Thus, the efficient red UC radiation requires not only Yb³⁺ concentration but also level match of $^4S_{3/2} \rightarrow ^4I_{13/2}$ in Er³⁺ and $^2F_{7/2} \rightarrow ^2F_{5/2}$ in Yb³⁺ under assistance of phonon for efficient EBT process. Therefore, the red UC emission would be a mixing process of one-photon process [12] through the efficient EBT process and two-photon process through relaxing from the high-lying states after GSA and ESA.

2.5 Multiferroic magnetoelectrics [18]

The magnetoelectric response is the appearance of an electric polarization upon applying a magnetic field and/or the appearance of magnetization upon applying an electric field. This magnetic-field- induced electric polarization has been observed as an intrinsic effect at low temperature and high magnetic field in some natural material systems (e.g., in RMnO₃ with R=Tb, Dy [19-21]). Alternatively and with

greater design flexibility, multiferroic composites made by a combination of ferromagnetic and ferroelectric substances, such as combinations of piezoelectric ceramics [e.g., BaTiO_3 and lead-zirconate-titanate (PZT)] and ferrites or rare-earth-iron alloys (e.g., Terfenol-D), have been recently found to exhibit large magnetoelectric response at room temperature and low magnetic field [22-27]. The magnetoelectric behavior in these multiferroic composites is dependent on their microstructure and coupling interaction across ferromagnetic-ferroelectric interface [28, 29].

Most recently, nanostructured $\text{BaTiO}_3\text{-CoFe}_2\text{O}_4$ multiferroic composites have been deposited in a film-on-substrate geometry and magnetoelectric coupling has been observed for the first time in multiferroic nanostructures [30]. The coupling interaction between BaTiO_3 and CoFe_2O_4 in the multiferroic nanostructures has been found to be due to elastic interaction as was the case in bulk composites. However, the mechanical constraint arising from the film-on-substrate structures and the good bonding between the ferromagnetic and ferroelectric phases in the nanostructured films could significantly affect the coupling interactions, thereby the magnetoelectric effect and/or magnetic-field- induced electric polarization. Currently, a theoretical description on such multiferroic nanostructured films is lacking. The magnetoelectric effect is calculated in the nanostructured ferroelectric-ferromagnetic

composite films (e.g., BaTiO₃-CoFe₂O₄ films [30]) based on the Green's function is approach which had been successfully applied to bulk multiferroic composites [22, 23]. It provides the first phenomenological understanding of the magnetic-field-induced electric polarization in multiferroic nanostructures.

As the coupling interaction between ferroelectric and ferromagnetic phases in the multiferroic nanostructures is still an elastic interaction [30], the constitutive equations for the coupling magnetic-mechanical-electric interactions in the nanostructured films can be expressed by direct notation for tensors as

$$\begin{aligned}\sigma &= \mathbf{c}\varepsilon - \mathbf{e}^T \mathbf{E} - \mathbf{c}\varepsilon^{ms} - \sigma_s, \\ \mathbf{D} &= \mathbf{e}\varepsilon + k\mathbf{E} + \alpha\mathbf{H} + \mathbf{P}_s, \\ \mathbf{B} &= \mu(\varepsilon, \mathbf{E}, \mathbf{H})\mathbf{H} + \mathbf{M}_s,\end{aligned}\tag{2-35}$$

where σ , ε , \mathbf{D} , \mathbf{E} , \mathbf{B} , and \mathbf{H} are the stress, strain, electric displacement, electric field, magnetic induction, and magnetic field, respectively; \mathbf{c} and k are, respectively, the stiffness at constant fields and the dielectric constant at constant strain; the permeability μ strongly depends on ε and electric and magnetic fields; \mathbf{e} (\mathbf{e}^T being the transpose of \mathbf{e}) is the piezoelectric coefficient; and ε^{ms} is the magnetostrictively induced strain related with the magnetic field dependent magnetostriction constants (e.g., λ_{001} and λ_{111} [31]) of the ferromagnetic phase; is the magnetoelectric coefficient. These are the same as the case for bulk multiferroic composites [22, 23].

However, in comparison to the bulk composites, there exist remarkable residual stress σ_s (or residual strain ϵ_s), spontaneous polarization \mathbf{P}_s and magnetization \mathbf{M}_s in the multiferroic films.

The effective properties (denoted by the starred quantities below) of the multiferroic films can still be defined as usual [22, 23] in terms of the averaged fields (denoted by $\langle \rangle$), e.g., $\langle \mathbf{D} \rangle = \mathbf{e}^* \langle \epsilon \rangle + k^* \langle \mathbf{E} \rangle + \alpha^* \langle \mathbf{H} \rangle + \bar{\mathbf{P}}_s$. We considered the magnetic-field- induced electric polarization of such nanostructured films. Under only applied magnetic field, the effective polarization in the mechanically clamped films is $\bar{\mathbf{P}} = \alpha^* \langle \mathbf{H} \rangle + \bar{\mathbf{P}}_s$.



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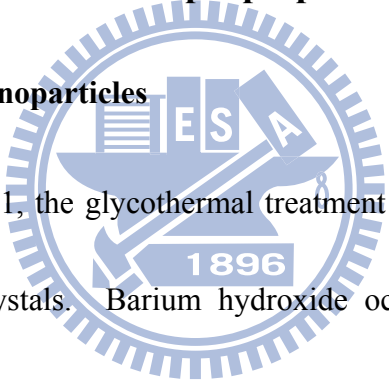


Chapter 3 Experimental procedures and characterization techniques

The chemical solution methods were adopted to prepare various ferroics with different geometric types to yield homogeneous samples with highly accurate composition. We will describe in detail the procedure of chemical solution methods and characterization techniques as follows.

3.1 Synthesis mechanism and Sample preparation

3.1.1 Barium titanate nanoparticles



As shown in Figure 3.1, the glycothermal treatment method [1] was adopted to synthesize BaTiO₃ nanocrystals. Barium hydroxide octahydrate (Ba(OH)₂·8H₂O) was used as the source of Ba and titanium tetrachloride (TiCl₄) was used as the source of Ti. Modification of titanium tetrachloride was achieved by adding deionized (DI) water to prepare transparent aqueous 0.1M TiOCl₂ solution. Amorphous titanium hydrous gel was prepared by adding 30 ml NH₄OH (24%) drop into 160 ml 0.1M TiOCl₂ solution at 60 °C for 2 h with stirring. The gel was separated and washed with DI water by 3 cycles of centrifugation for 4 min at 4000 rpm in a centrifuge. Excess water was decanted after final washing and the wet precursor was redispersed in a mixture of water and 1,4-butanediol. Ba(OH)₂·8H₂O then added into a mixture

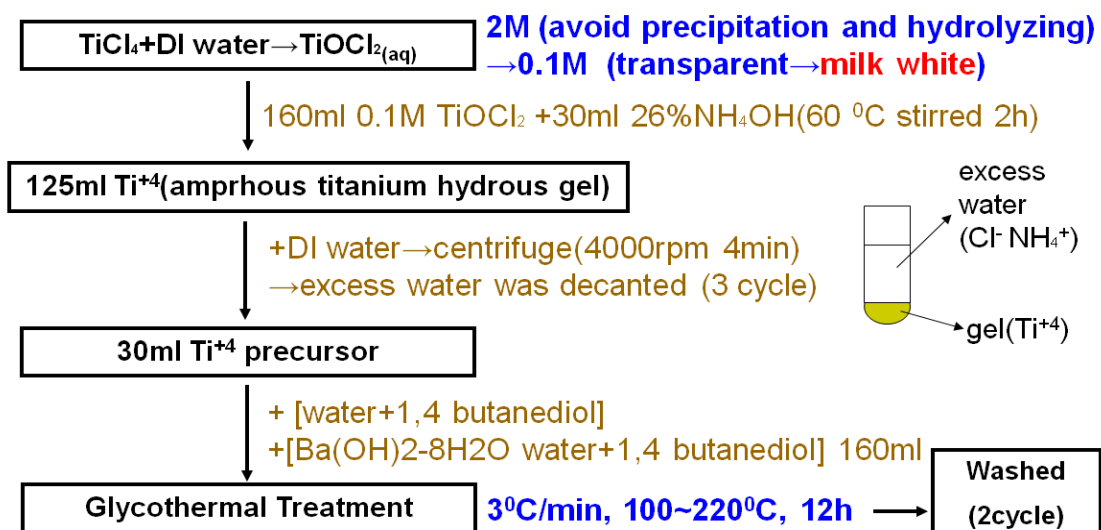


Figure 3.1: Flowchart of BaTiO₃ nanocrystals preparation by glycothermal treatment method.

of water and 1,4-butanediol (1,4-butanediol/deionized water: B/W = 1, Ba:Ti molar ratio=1). Total volume of the solvent was 200 ml. The resultant suspension was placed in 250 ml flask equipped with a stirred head heated to the desired temperature with a rate of 3 °C/min. To acquire BaTiO₃ particles with various grain sizes, reactions were carried out at the desired temperature from 100 to 220 °C for 12 h; the larger size of particles require the higher reaction temperature. After glycothermal treatment, the flask was cooled to RT. The powder was then washed with acetic acid solution to remove the residual BaCO₃ and the unreacted Ba ions in solution. The removal of residual BaCO₃ is crucial because its Raman spectra appear in the range of < 200 cm⁻¹ [2]. After washing, the recovered powder was dried at 60 °C in a hot plate for 48 h.

3.1.2 Barium titanate rods

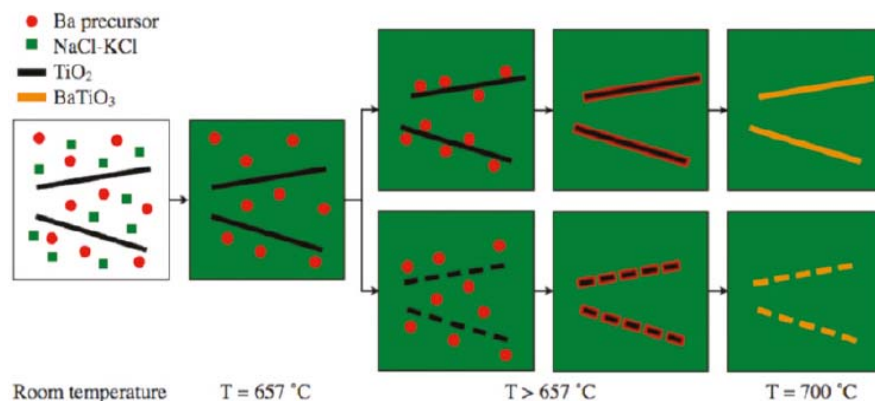


Figure 3.2: Proposed schematic diagram of the synthetic mechanism of BaTiO₃ rods.

The three-series products (BT-1, BT-2 and BT-3) were synthesized with different barium and multi-shaped titanium precursors. Proposed schematic diagram of the synthetic mechanism of BaTiO₃ rods is shown in Figure 3.2. BT-1 was synthesized by using BaCO₃ as the barium precursors reacted with the spherical TiO₂ in a eutectic mixture of NaCl-KCl flux. BT-2 and BT-3 were synthesized by using BaO and BaCO₃ (BaCO₃ will transform into BaO when heating over about 1450 °C which is much higher than the annealing temperature we used.) as the barium precursors reacted with the rod-shaped TiO₂ in NaCl-KCl flux respectively. The reagents we used were BaO, BaCO₃, TiO₂, KCO₃, NaCl and KCl, which were of A.R. grade without further purification. The rod-shaped TiO₂ was synthesized and derived from rod-shaped K₂Ti₄O₉. The mixture of K₂CO₃ and TiO₂ in the molar ratio of 1:3 was annealed at 1000 °C for 18 h in the combustion boat (Al₂O₃ boat). Then, the

as-synthesized product was washed with hot deionized water several times to remove the K_2CO_3 phase entirely and finally dried at 60°C overnight. The product in the meanwhile was rod-shaped $\text{K}_2\text{Ti}_4\text{O}_9$ verified by field emission scanning electron microscopy (FESEM) image and powder X-ray diffraction (XRD) pattern. The rod-shaped $\text{K}_2\text{Ti}_4\text{O}_9$ then was washed with hot 1M HCl solution for 2 h to get rid of K_2O phase. The residue phase is $\text{TiO}_2 \cdot n\text{H}_2\text{O}$, which was annealed at 700°C for 1 h for transforming into the rod-shaped anatase.

To synthesize BT-1, BT-2, and BT-3, the detailed synthetic procedure is as follows. For starters, the mixture of barium precursor and titanium precursor in the molar ratio of 1:1 was wet-mixed in the ethanol solution at 50°C for 1 h with magnetic stirring and then dried at 50°C for 6 h. Second, the mixture was mixed with NaCl-KCl flux (50% mol NaCl and 50% mol KCl, m.p.: 657°C), acting as a reaction medium, in the weight ratio of 1:1 by hand-grinding in a mortar and pestle for 0.5 h. Third, the as-synthesized mixture was placed into the combustion boat and heated at 700°C for 1 h in the furnace. The increasing rate was $5^\circ\text{C}/\text{min}$ and the product was taken out of the furnace for cooling naturally after reaction. Finally, the as-synthesized product was washed with hot DI water several times until no chloride ions were detected by silver nitrate solution to assure the residue of salt was removed exhaustively and then dried at 120°C overnight.

3.1.3 Rare-earth-doped perovskites

3.1.3.1 Er^{3+} -doped PLT poly-crystalline films

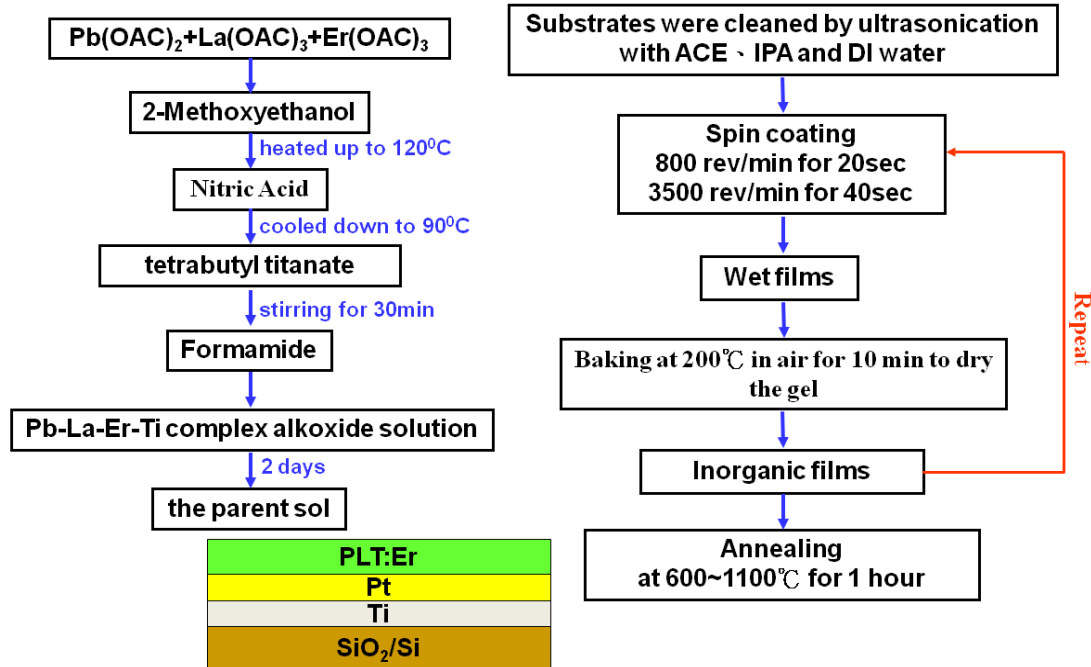


Figure 3.3: Flowchart of sol-gel derived Er^{3+} -doped PLT poly-crystalline films.

As shown in Figure 3.3, Er^{3+} -doped PLT poly-crystalline films were grown on the Pt/Ti/ SiO_2/Si substrates (supplied by) by the sol-gel method. The starting materials are high-purity lead acetate, lanthanum acetate, titanium isopropoxide, and erbium acetate, respectively. Lead acetate and lanthanum acetate with molar ratios of 8:2 and proper mole of erbium acetate were dissolved in 2-Methoxyethanol and stirred for 10 minutes at 110°C to remove the associated water of crystallization. The stoichiometric amount of titanium isopropoxide was then added into the sol at 80°C while stirring continuously for approximately 10 minutes.

The diluted solution was then spin-coated on the clean Pt/Ti/SiO₂/Si substrates, which were cleaned thoroughly in a series of organic solvents in an ultrasonic cleaner. The coated films were heated at 200°C in ambient atmosphere for 10 minutes to dry the gel. To accumulate the film thickness, we coated the samples by the aforementioned process ten times that corresponds to about 800 nm determined by the cross-section SEM. Finally, the samples were sintered in a furnace at various temperatures of 650~1100°C for 60 minutes.

3.1.3.2 Er-Yb codoped ferroelectrics

PbTiO₃, BaTiO₃, or SrTiO₃ powder samples simultaneously doped with 6 mol % Er³⁺ ions and 0 mol %, 6 mol %, and 12 mol % of Yb³⁺ ions, respectively, were synthesized according to a procedure described briefly as follows (see Figure 3.3). Lead acetate (or barium acetate, strontium acetate), erbium acetate, and ytterbium acetate with corresponding mole ratio of cations were first sufficiently stirred for 20 min at 90 °C for being completely dissolved in dehydrated acetic acid. Titanium isopropoxide was then added to the solution and kept stirring for another 20 min. We dried and solidified the solution under illumination of a 400 W infrared lamp for 36 h. The resultant solid was ground into powders and then sintered at 700 °C for 120 minutes in an Al₂O₃ crucible.

3.1.4 Multiferroic films

We used simple solution method to fabricate three different geometric forms of the CFO-PTO multiferroics, which are respectively disk-like CFO aligned in PTO matrix (disk-3 type), the CFO and PTO multilayered structure (2-2 type), and the CFO particles embedded in PTO matrix (0-3 type) as shown in Figure 3.4.

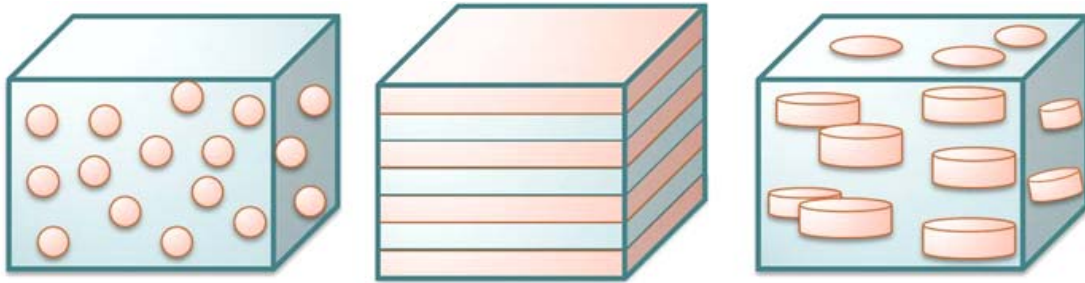
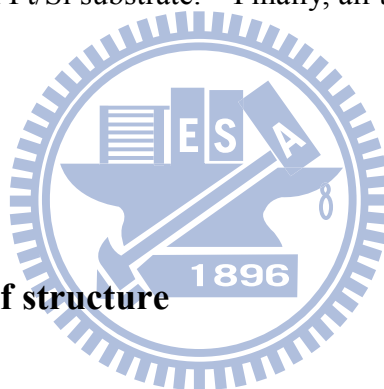


Figure 3.4: Schematic illustration of three thin films with different connectivity schemes: (a) the 0-3 type with CFO particles embedded in PTO matrix, (b) the 2-2 type with CFO and PTO nanolayers, and (c) the disk-3 type with CFO disc aligned in PTO matrix.

The gel of PTO was produced by dissolving lead acetate trihydrate and titanium isopropoxide into 2-methoxyethanol and stirring while heating for 30 min. The 0.3M CFO gel was made from the cobalt nitrate hexahydrate and iron nitrate enneahydrate by the same process. Pure PTO gel was spin-coated on Si and Pt/Si and CFO on Pt/Si substrate and then dried at 200°C for few times as the reference samples. The disk-3 type CFO-PTO samples were prepared by alternatively spin-coating PTO, drying then coating another CFO. Finally, we obtained

(4p/4c/4p)²/Pt/Si film, where “n”p and “n”c stands for successively coated and dried n times of PTO and CFO, respectively. The process of making the 2-2 type with (p/p/c/c)³/p/p/Pt/Si stacking layers is the same as the disk-3 type except that every single layer was individually annealed at 500 °C for 3 minutes. The 0-3 type is made of dispersing CFO particles in PTO matrix. The CFO particles of ~100 nm, obtained by drying CFO gel and annealed at 750°C, were then put into the PbTiO₃ solution with molar ratio 0.8:1 and shaken until they were well-mixed. The resultant solution was spin-coated 5 layers on Pt/Si substrate. Finally, all the samples were annealed at 750 °C for 1.5 h.



3.2 Characterization of structure

3.2.1 X-ray Diffraction

The XRD data of the prepared BaTiO₃ nanoparticles were collected on the imaging plate with transmission geometry using high intensity synchrotron radiation with wavelength of 0.56357 Å at beam line BL01C synchrotron radiation facility, NSRRC in Taiwan (see Figure 3.5). A single tetragonal-phase (*P4mm*) model was applied to refine the crystal structure with the XRD data by using the Rietveld analysis computer program GSAS (General Structure Analysis System) provided by National Institute of Standards and Technology (NIST) in USA. Furthermore, the

XRD data of the others were measured, using a Mac science M18X X-ray diffractometer equipped with a rotating anode (Cu- $k\alpha$ line of 1.5405 Å). Data were recorded between the angle range $20^\circ < 2\theta < 60^\circ$ with steps of 0.04° and rate of scanning is $4^\circ/\text{min}$. The resulting XRD patterns were Gaussian fitted to get the diffraction peaks and widths. By comparing with the JCPDS data, the fitted peak positions and corresponding reflection planes were used as the input of the refinement program [3]. In the next step, the lattice constants will be included in output files.



Figure 3.5: BL01C Experimental Station.

3.2.2 Field-Emission Scanning Electron Microscopy (FESEM)

The morphology of synthesized particles was observed using field-emission scanning electron microscopy (FESEM, JEOL 6500).

3.2.3 Raman spectroscopy

Raman spectroscopy consists of mainly three components: laser system, spectrometer, and computer. Figure 3.6 shows schematics of experimental setup. An-ion laser (Coherent INNOVA 90) provides an excitation source of a wavelength 488nm. The unwanted plasma lines were filtered out by a laser-line filter. A biconvex spherical lens with a focal length of 5cm was used to focus the laser beam onto the sample surface at 45 degree reflection geometry. The laser power on the sample surface is about 30~50 mW with beam spot size of 30~50 μm (in diameter). The scattered light was collected by a camera lens and imaged onto the entrance slit of a spectrograph (Spex triplemate1877C) which is equipped with a liquid-nitrogen cooled charge coupled device (CCD) detector array (Phometrics CC200) at 140K.

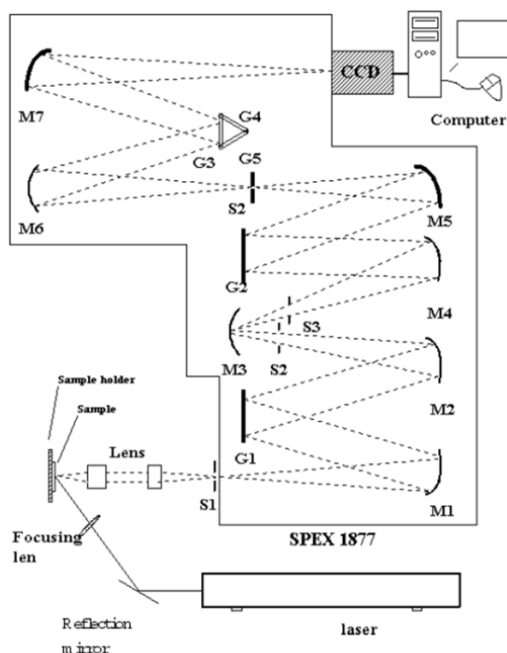


Figure 3.6: Setup of typical Raman and PL measurements.

3.3 Characterization of optical properties--Photoluminescence spectroscopy

Photoluminescence (PL) of Er-doped $\text{Pb}_{0.8}\text{La}_{0.2}\text{TiO}_3$ thin films were carried out by pumping with the 488 nm line of Ar^+ laser and the emitted UC fluorescence spectra of Er-Yb codoped ferroelectrics were performed by pumping with a 980 nm diode laser with maximal power output of 600 mW. The experimental setup is the same as that described in Raman measurement.

3.4 Characterization of magnetic properties--Superconducting Quantum Interference Device magnetometry

The magnetic properties were measured by Superconducting Quantum Interference Device (SQUID, MPMS-XL) system. The SQUID is very sensitive to magnetic field. By utilizing SQUID technology, the SQUID magnetometer can achieve superior measurement sensitivity. The standard deviation of measurement can achieve about 10^{-8} emu with Reciprocating Sample Option (RSO) and about 10^{-7} emu with traditional stepped-scan technique under 0.1 Tesla.

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Chapter 4 Destruction to the short-range disorder due to erbium dopant in $\text{Pb}_{0.8}\text{La}_{0.2}\text{TiO}_3$ films

Perovskites, the chemical formula of ABO_3 , are generally composed of a three-dimensional framework of corner sharing BO_6 octahedron and it is believed that there always exists disorder displacement of “B” ions in the skeleton. The characteristics of perovskites can be changed by replacing the “A” and “B” cations. In this chapter, we study on influence of perovskite structure due to the presence of substitution on luminescence and characteristics of Er^{3+} -doped $\text{Pb}_{0.8}\text{La}_{0.2}\text{TiO}_3$ (PLT) polycrystalline films. We show destruction to a displacement of Ti in the short-range structure by observing the disappearance of emission and Raman signals when the Er^{3+} concentration exceeds 7 mol% in sol-gel-derived PLT polycrystalline films. The disorder due to a displacement of Ti breaks the centrosymmetry to activate emission of rare earth ions such as Er^{3+} and Raman modes of perovskites. We found the symmetry breaking diminishes with introducing more Er^{3+} ions.

4.1 Crystal structure (results of XRD)

Figure 4.1(a) shows the XRD patterns of 7 mol% Er^{3+} -doped PLT films on Pt/Ti/SiO₂/Si at various sintering temperatures 650–1100°C and the pattern of un-doped

PLT film at 800°C is also presented for comparison. The Er³⁺-doped PLT film sintered at 650°C shows a perovskite phase with (100), (110), (200), (210) and (211) planes without obvious secondary phases. As the films were sintered at 800 °C and 950 °C, the diffraction peaks of the perovskite phase become more intense and their full widths at half maximum (FWHM) become narrower. It indicates that the films have better crystallinity at the higher sintering temperatures even though the weak secondary phases appear. We found small signatures of the secondary Er₂Ti₂O₇ phase appearing at $2\theta = 31^\circ$ and Er₂O₃ phase at 36° and 43.7° for sintering at 950°C. By further raising the sintering temperature to 1100°C, the strong peaks at 27° due to La₂Si₂O₇ consistent with the JCPDS data (# 722456) were recognized. It is believed that La₂Si₂O₇ phase appeared at the interface between Er³⁺-doped PLT thin films and silicon substrate during high-temperature sintering. And the peaks of the perovskite phase become weaker or even vanish, indicating the destruction of perovskite structure. The FWHM of (100) analyzed from the result of XRD pattern in Figure 4.1(a) tends to decrease from 0.28° to 0.22° , corresponding to the crystal size ranging from 28.9 to 36.8 nm, while increasing the sintering temperature from 650 to 950°C. The better crystallinity for the higher sintering temperature is universally known.

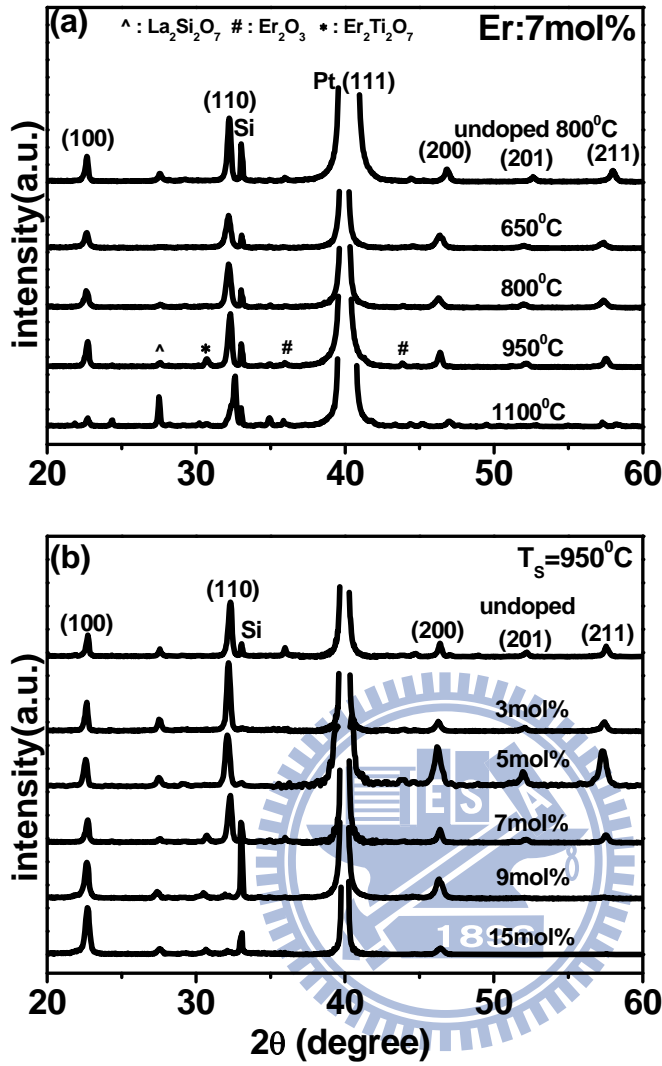


Figure 4.1: XRD patterns of Er^{3+} -doped PLT films with 7 mol% Er^{3+} doping at various sintering temperatures and with different Er^{3+} concentrations at sintering temperature 950°C.

Figure 4.1(b) shows the XRD patterns of PLT films on Pt/Ti / SiO_2 /Si doped with different Er^{3+} concentrations after being sintered at 950°C. All films exhibit good perovskite crystallinity, although several weak secondary phases appear. Due to the same charge state, Er^{3+} may take the positions of La^{3+} in the lattice. It indicates that

the Er^{3+} is dissolved in PLT by more than 15 mol% without destroying the crystallinity in the PLT system that exceeds the result of BST system⁸ of 3 mol%. Although the slight difference in the peak intensity of (110) and (211) for 9 mol% and 15 mol% Er^{3+} -doped samples may not be ascribed to alignments, the results still confirm a perovskite phase in these Er^{3+} -doped PLT powders.

In order to investigate the variation of long-range structures with the increase of Er^{3+} concentration, the resultant XRD patterns in Figure 4.1(b) were further analyzed with the refinement procedure. We have adopted the tetragonal structure for all samples to obtain the ratio of lattice constants c/a . The initial data of (100), (110), (200), (201) and (211) planes identified with the JCPDS data are input to the XLAT program.^[1] Plotted in Figure 4.2 are the FWHM of (100) and c/a versus the Er^{3+} concentration. The FWHM tends to linearly increase from 0.22° to 0.31° , corresponding to the crystal diameter ranging from 36.8 to 26.1 nm, as increasing the Er^{3+} -dopant from 0 to 15 mol%. It reveals degradation of the crystallinity for the higher Er^{3+} -dopant. On the other hand, the ratio of c/a , is between 1.001 and 1.007, which is much smaller than that of PbTiO_3 (1.067) but comparable or slightly larger than that ^[2] of BaTiO_3 (1.002). It indicates that the Er^{3+} -doped PLT films with different Er^{3+} concentrations of 0, 3, 5, 7, 9, and 15 mol% all belong to the tetragonal phase. We found that c/a is around 1.002 for the undoped sample, and slightly

increases and then declines to around 1.001 at 7 mol%, then increases to 1.007 for the samples with 9 and 15 mol%. The trend of c/a ratio with Er^{3+} concentration is similar to the results reported by Dobal *et al.* [3]. They reported that the tetragonality ratio c/a increases with increasing dopant concentration when $\text{Pb}_{0.90}\text{La}_{0.15}\text{TiO}_3$ was doped with Gd^{3+} . As the Er^{3+} -ion concentration increases or the host material possesses the higher tetragonality,

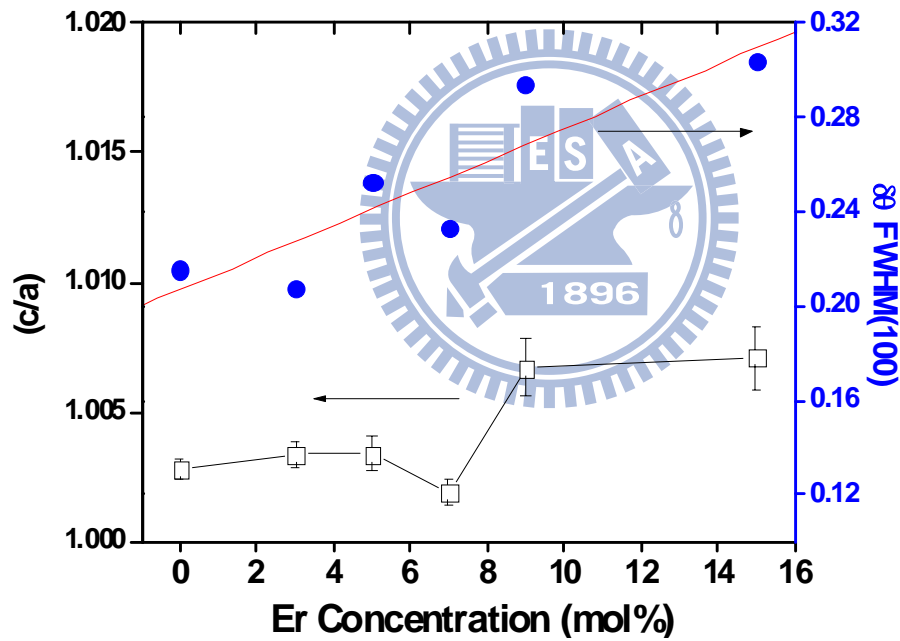


Figure 4.2: The ratio of lattice constants c/a after Rietveld refinement and the FWHM of (100) with different Er^{3+} concentrations at sintering temperature 950°C .

we expected that the stronger emission was observed. However, we will show shortly that the maximum emission was observed at 7 mol% but no emission for Er^{3+}

dopant larger than 9 mol%, which possess the higher tetragonality (non-centrosymmetry) than for the 7 mol% one.

4.2 Relationship between results of emission spectra and Raman spectra

Figure 4.3(a) shows the RT visible emission spectra of PLT films doped with 7 mol% Er^{3+} ions at sintering temperatures of 650, 800, 950 and 1100°C, respectively. All the visible emission spectra have similar shapes, but they possess the diversity of emission behavior. The strong green emission peaks at 530 and 550 nm are attributed to the Er^{3+} $4f-4f$ inner-shell transitions of $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, while the weak red emission centered at 660 nm is ascribed to $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$. The splits in emission peaks are attributed to the Stark splitting of the degenerate $4f$ levels under the crystalline field of the host material. As expected, the better crystalline (see Figure 4.1(a)), the higher emission as increasing the sintering temperature from 650 to 950°C, and weak emission was observed at 1100°C sintering.

The high Er^{3+} concentration also might mean the high emission efficiency, and Figure 4.3(b) displays the spectra of PLT films doped with different Er^{3+} concentrations of 3, 5, 7, and 9 mol% after sintered at 950°C. However, the emission intensity of the Er^{3+} -doped PLT films does increase as the activated Er^{3+} -dopant

increases until 7 mol%, but quickly decreases as the Er^{3+} -doping concentration exceeds 7 mol%. The quenching mechanism was thought to be a cross-relaxation process between two closely-placed Er^{3+} ions. [4-6]

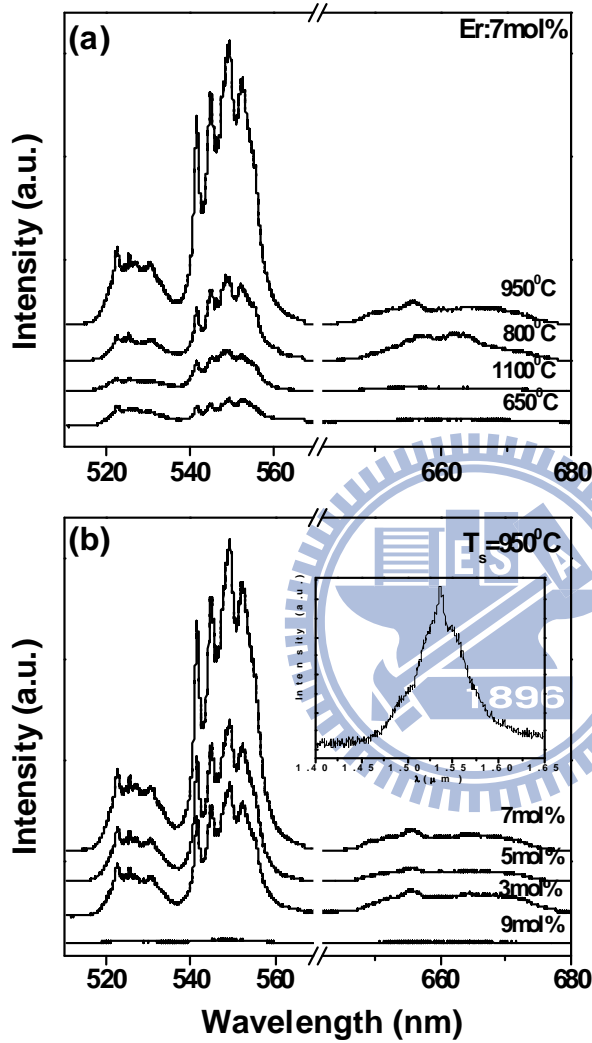


Figure 4.3: Dependence of the green emission intensities of Er^{3+} -doped PLT films on Er^{3+} concentrations and sintering temperature.

In this study, the ion density N of 3, 5, 7, and 9 mol % Er^{3+} doping is about 4.9×10^{20} , 8.2×10^{20} , 11.4×10^{20} , and $14.7 \times 10^{20}/\text{cm}^3$, respectively, and the mean

distance [7] among Er^{3+} ions estimated by $\gamma=0.62 \times N^{1/3}$ is 7.8, 6.6, 5.9, and 5.5 Å, correspondingly. The mean distance varies gently with increasing Er^{3+} concentration from 7 mol% to 9 mol%, while the emission efficiency decreases sharply. This indicates that the quenching mechanism would not be dominated by a cross-relaxation process, and therefore there may be other dominant factors responsible for decreasing emission efficiency in Er^{3+} -doped PLT system. Looking back on the result of Figure 4.2, because the 9mol% Er^{3+} -dopant films do possess higher tetragonality (non-centrosymmetry) than the 7mol% ones, the quenching mechanism also would not be dominated by the long-range structure and crystalline. As proposed by Tanabe *et al.*, that the emission efficiency has to do with the degree of local structure symmetry, [8] the quenching behavior is related to the local structure symmetry, which will be discussed with the results of Raman measurement later on. In addition, we also observed the RT IR-emission spectra of PLT films doped with 5 mol% Er^{3+} concentrations at 950°C sintering in the inset of Figure 4.3(b) under the excitation of 488-nm Ar-ion laser.

Figure 4.4(a) shows the Raman spectra of samples with different Er^{3+} concentrations in PLT sintered at 950°C. Besides the weak broad feature between 700 and 800 cm^{-1} we found another broad spectrum centered around 560 cm^{-1} that is attributed to $\text{A}_1(\text{TO}_3)+\text{E}(\text{TO}_3)$ phonon modes due to the reduced grain size and the

localized disorder of displacement of Ti ion from the center of

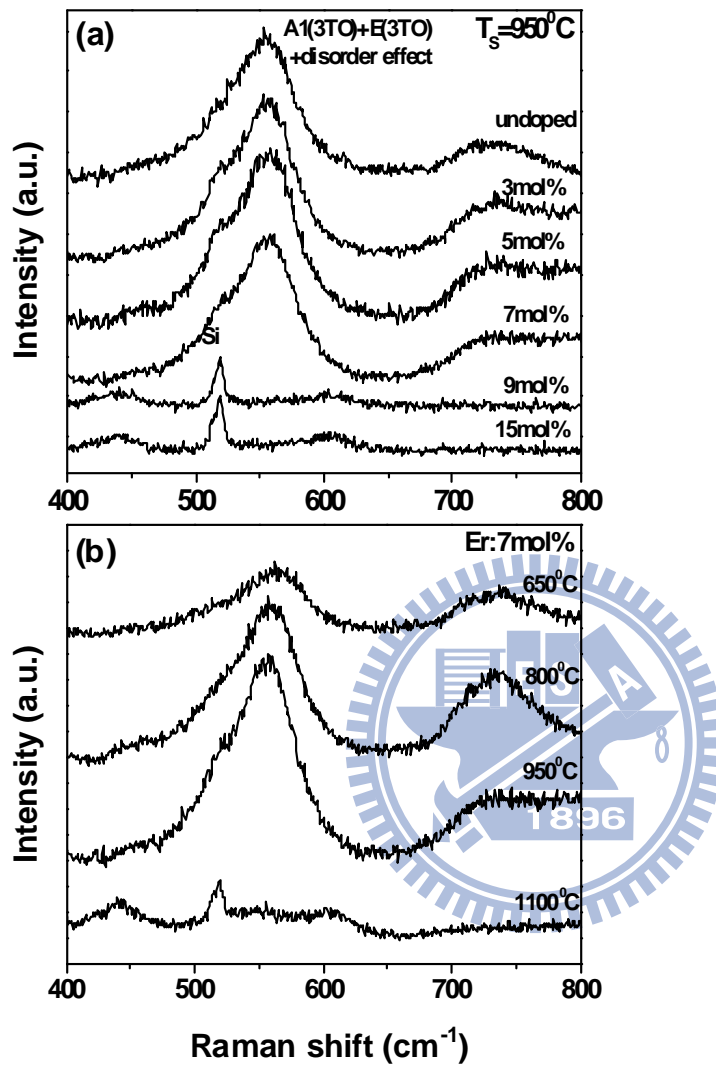


Figure 4.4: Raman spectra of Er^{3+} -doped PLT films with different Er^{3+} concentrations at sintering temperature 950°C and with 7 mol% Er^{3+} dopant at various sintering temperatures.

the BO_6 octahedron. [4-6] These peaks keep almost unchanged as Er^{3+} concentration increases from 3 mol% to 7 mol%, but vanish for samples with 9 and 15 mol% Er^{3+}

concentrations with only Si-LO phonon at 520 cm^{-1} from the Si substrate and phonon modes of amorphous native oxide around 440 and 600 cm^{-1} . The disappearance of Raman modes due to either weak ferroelectric phase or weak disorder effect (resulting from a displacement of Ti) is caused by decreasing the crystal diameter to result in the formation of a centrosymmetric structure [9] with increasing Er^{3+} concentration. By comparing with the results of XRD, we found weakening in disorder may be the dominant mechanism. In Figure 4.5, schematic representation of the mechanism illustrating that Ti atom displaces off its central position and moves towards one oxygen as Er^{3+} concentration is below or at 7 mol%. Nevertheless, it will return to its central position when the Er^{3+} concentration reaches or exceeds 9 mol%. Figure 4.4(b) shows change of the Raman spectra of Er^{3+} -doped PLT films at 7 mol % Er^{3+} ions, with increasing the annealing temperature from 650 to 1100°C . We found similar disappearance of these specific phonons resulting from destruction to a perovskite structure at sintering temperatures beyond 1100°C .

It is interesting to correlate the Raman spectra of Figure 4.4 with green emission emission of Figure 4.3. We found no variation in the ferroelectric and disorder modes from the Raman spectra, while the emission intensity of the Er^{3+} -doped PLT films increases as the Er^{3+} -dopant increases from 3 to 7 mol%. In contrast, by increasing the Er^{3+} concentration to 9 mol%, we found the green emission and the

disorder effect on Raman scattering suddenly diminish, indicating the selection rule is strongly reinforced to eliminate the short-range disorder, and the crystal structure becomes strictly centro-symmetric.

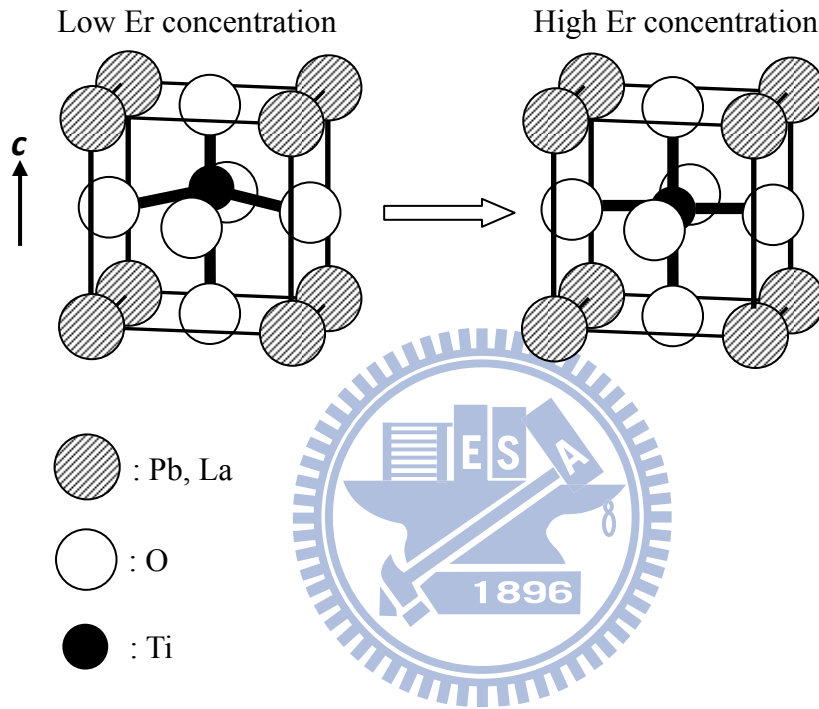
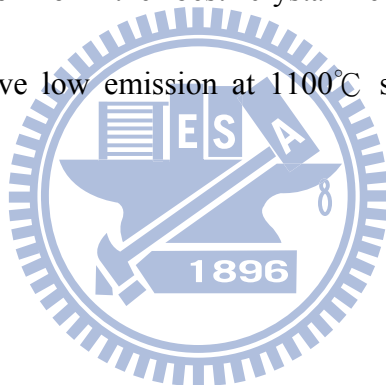


Figure 4.5: Schematic representation of the position of B atom in ABO_3 structure.

Looking back in Figure 4.3(b) and Figure 4.4(a), we found that the green emission becomes weaker and the disorder effect vanishes separately, but the crystal structure remains unchanged while increasing the Er^{3+} concentration above 9 mol%. It reveals the destruction to short-range disorder reduces the efficiency of emission, even though these films still possess good crystallinity. Thus, the symmetry on short

range of Er^{3+} -doped PLT crystal seems to influence the activity of Er^{3+} ions. The more symmetric structure of the host materials would reduce the transition probability within the 4f-inner shell of Er^{3+} ion.

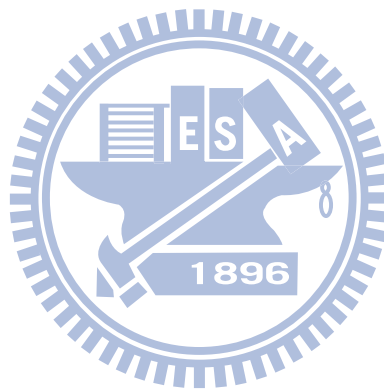
In contrast with the analysis of emission and Raman spectra, the films possess a good perovskite phase at sintering temperatures of 600°C , 800°C , and 950°C , so that they have similar visible emission spectral shapes and phonon modes. The weak perovskite phase at a sintering temperature of 650°C results in weak emission as strong emission originates from the best crystalline at 950°C -sintering. The unobvious split with relative low emission at 1100°C sintering is due to structure destruction.



4.3 Summary

The Er^{3+} -doped $\text{Pb}_{0.8}\text{La}_{0.2}\text{TiO}_3$ films with perovskite structure were manufactured on Pt/Ti/SiO₂/Si substrates by sol-gel method. The dependence of emission efficiency on Er^{3+} concentration and sintering temperature is dominated by solubility and symmetry of crystal structure. We showed that destruction to the short-range disorder displacement of B ions exists in the skeleton of BO_6 from the disappearance of emission and Raman signals when the Er^{3+} concentration exceeded 7 mol%, although the samples still possess good long-range structure, confirmed by X-ray

diffraction. The crystal field due to the disorder effect that contributes to the perturbation term for the $\text{Er}^{3+} 4f \rightarrow 4f$ inner-shell transitions is diminished when introducing more Er^{3+} concentration.



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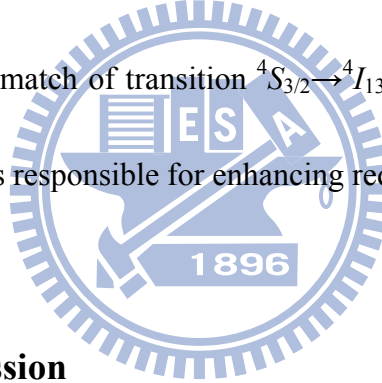
Chapter 5 Er-Yb codoped ferroelectrics for controlling visible upconversion emissions

UC emission in RE ion-doped materials has been intensively studied in recent years of applications in laser devices [1, 2], three-dimensional display [3], sensors [4], and biological fluorescent labels [5-7]. Following the influence of perovskite structure on luminescence with a **one-photon** process in Er^{3+} -doped PLT discussed in chapter 4, the mechanism of UC emission in RE ions co-doped materials has been discussed in this chapter. UC emission is a mixing process of one-photon process [8] through the efficient EBT process and two-photon process through relaxing from the high-lying states after GSA and ESA.

The different crystal field caused by structure symmetry of the host materials would contribute to different perturbation terms for the Er^{3+} and Yb^{3+} inner shell transitions. Whether the energy matches level spacing $^4S_{3/2} \rightarrow ^4I_{13/2}$ of the Er^{3+} ion and $^2F_{7/2} \rightarrow ^2F_{5/2}$ of the Yb^{3+} ion or not should be sensitive not only to assistance of phonon but also to the crystal field resulting from the crystal symmetry. Therefore, the crystal structure may be a more important mechanism for converting UC green radiation to red radiation due to the EBT process. In order to investigate the relationship between the crystal field and the match of energy levels, in this chapter,

we chose PbTiO_3 , BaTiO_3 and SrTiO_3 with different degrees of tetragonality as the host materials. Both PbTiO_3 and BaTiO_3 are ferroelectric perovskites which possess tetragonal phase at room temperature, while SrTiO_3 is a quantum paraelectric [9]. The tetragonality of PbTiO_3 ($c/a=1.065$) is higher than that of BaTiO_3 ($c/a=1.010$) according to the JCPDS-International Center for Diffraction Data No. 78-0298 and No. 83.1880.

In this chapter, UC emission spectra under a 980 nm laser pumping and X-ray diffraction confirm that the centrosymmetric crystal field arising from reducing tetragonality causes level match of transition $^4S_{3/2} \rightarrow ^4I_{13/2}$ of Er^{3+} and $^2F_{7/2} \rightarrow ^2F_{5/2}$ of Yb^{3+} . This level match is responsible for enhancing red UC emission.



5.1 Upconversion emission

Figure 5.1 shows the UC fluorescence spectra of PbTiO_3 [Figure 5.1(a)], BaTiO_3 [Figure 5.1(b)] and SrTiO_3 [Figure 5.1(c)] doped with 6 mol% Er^{3+} ions and various concentrations of Yb^{3+} ions under 980 nm excitation. As mentioned above and in the literature [8, 10], the emission bands around 550/565 nm (green) and 655/680 nm (red) originate from the intra $4f-4f$ electronic transitions $^2H_{11/2}/^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ of the Er^{3+} ions, respectively. The green and red bands in this study are

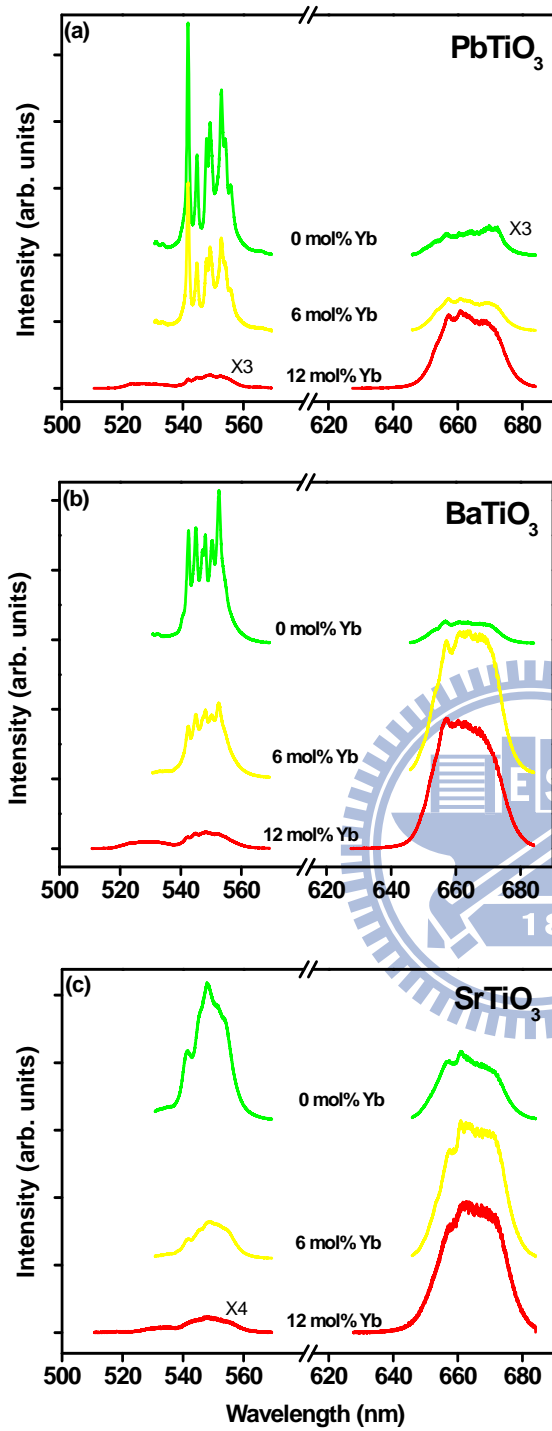


Figure 5.1: UC fluorescence spectra of (a) PbTiO_3 , (b) BaTiO_3 , and (c) SrTiO_3 doped with 6 mol% Er^{3+} ions and various concentrations of Yb^{3+} ions under the same pump power of 980 nm diode laser at 107 mW.

slightly shifted comparing to what appears in Ref. 8, we found the radiation peak positions and the spectral shapes of the red (around 665 nm) and the green fluorescent radiations (545/565 nm) are different from those in Ref. 8. It indicates that the different structure symmetry of host materials result in the different influence of crystal field on the energy levels of Er^{3+} and Yb^{3+} . The very weak red UC emission is a two-photon process at only Er^{3+} doping in various systems, which indicates a few population of $^4F_{9/2}(\text{Er})$ state. The bandwidths of the two UC labels are found about 30 nm. In these spectra, besides the quenching of green UC emission with increasing Yb^{3+} concentration, which indicates decreasing the population of the $^2H_{11/2} / ^4S_{3/2}(\text{Er}^{3+})$ state, we observed level splits in green UC emission of only Er^{3+} doping and co-doped 6 mol% Yb^{3+} ones in PbTiO_3 and BaTiO_3 . It is attributed to the Stark splitting of the degenerate 4f levels under the strong crystal field of the PbTiO_3 and BaTiO_3 [11]. The split in PbTiO_3 system is more obvious than that in BaTiO_3 system indicating the stronger influence of crystal field on the energy levels of Er^{3+} and Yb^{3+} in PbTiO_3 than in BaTiO_3 due to the larger asymmetric crystal field for the host material of larger tetragonality. On the other hand, the spectral shapes become smoother because of the weaker influence of the more centrosymmetric crystal field for high concentration Yb^{3+} (12 mol%) in both PbTiO_3 and BaTiO_3 systems and all samples in SrTiO_3 system. Figure 5.1 also shows unobvious splits in all of the red

UC emission spectra. It reveals that the underlying mechanism of the red UC emission differs from that of green one. The intensity of red UC emission greatly increases as the Yb^{3+} -ion concentration increases, that results from the increasing of the EBT process as reported by Chen, *et al.* [8]. The very weak red UC emission is a two-photon process at only Er^{3+} doping in various systems, which indicates a few population of $^4F_{9/2}(\text{Er})$ state; whereas, the strong red UC emission and almost complete quenching of the UC green emission are observed at co-doped 12 mol% Yb^{3+} . The energy mismatch in the EBT process is about 320 cm^{-1} that can be easily dissipated by the aid of one phonon of the ZrO_2 lattice with energy 470 cm^{-1} in [8]. If the energy mismatch in the EBT process were dissipated by one phonon of the PbTiO_3 lattice with energy 290 cm^{-1} or 510 cm^{-1} and the BaTiO_3 lattice with 310 cm^{-1} or 520 cm^{-1} , then the intensity ratios of the green UC and the red UC should make no difference for the same amount of Yb^{3+} in PbTiO_3 and BaTiO_3 . However, we observed that the red UC emission is stronger than the green one at co-doped 6 mol% Yb^{3+} in BaTiO_3 system, but weaker red UC emission in the PbTiO_3 system of the same doping. This reveals a weak EBT process in PbTiO_3 with 6 mol% Yb^{3+} co-doping. The observed spectral peak positions and shapes of green and red bands are slightly different from what observed in [8] that may be attributed to different crystal field. We observed a broad red emission around 665 nm with FWHM of 22

nm which is almost unchanged with crystal structure, but the position of maximal peak is at 544 nm (18382 cm^{-1}) at only Er^{3+} doping in PbTiO_3 while it changes to 555 nm (18018 cm^{-1}) at the same doping in BaTiO_3 . It indicates that the different structure symmetry of host materials resulted in the different influence of crystal field on the energy levels of Er^{3+} over a spectral range of 363 cm^{-1} . Therefore, the energy mismatch in the EBT process may be dissipated not only by the aid of phonons but also by Boltzmann distributed population within the manifold of $^4\text{S}_{3/2}$ or/and $^4\text{I}_{13/2}$ (Er^{3+}) state affected by the crystal field with different symmetries. The strength of EBT process depends on whether the energy match of level space $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$ of the Er^{3+} ion and $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ of the Yb^{3+} ion that strongly depends on crystal field due to structure symmetry [10]. The match can be achieved for centrosymmetric media but may not be so due to the asymmetric crystal field in tetragonal phase, thus to lower the strength of EBT process. We will discuss the influence of change of the crystal structure on the EBT process in the following using X-ray diffraction.

5.2 Mechanisms of upconversion emission

5.2.1 Crystal structure (results of XRD)

Figure 5.2 displays the x-ray diffraction patterns of various concentrations of Er^{3+} - and Yb^{3+} - doped PbTiO_3 [Figure 5.2(a)] and BaTiO_3 [Figure 5.2(b)] with

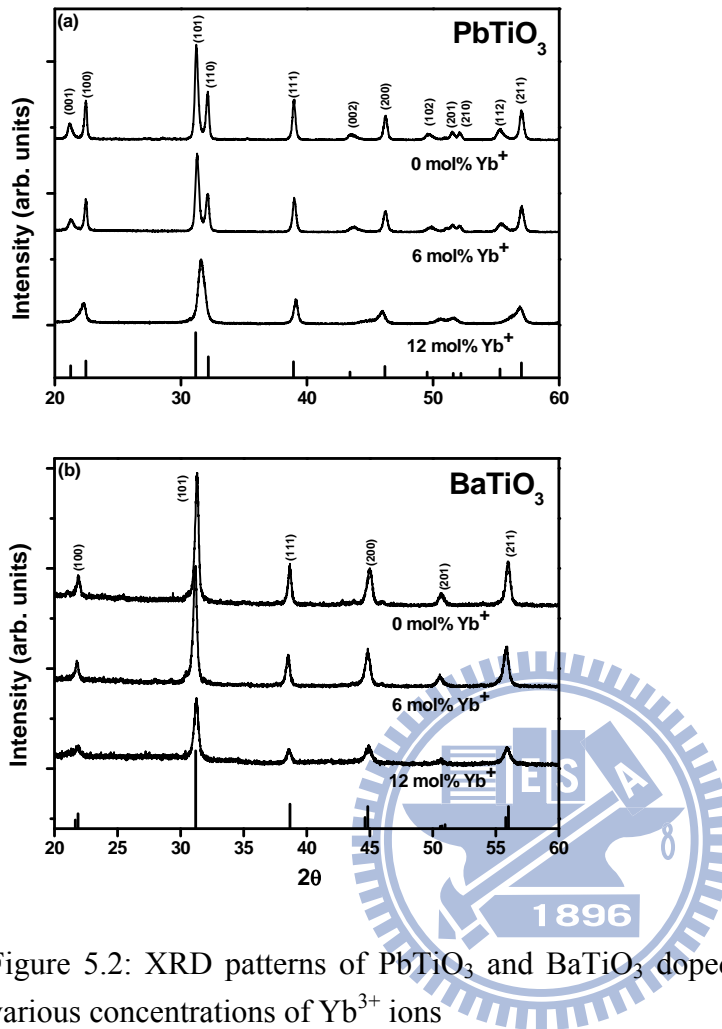


Figure 5.2: XRD patterns of PbTiO_3 and BaTiO_3 doped with 6 mol% Er^{3+} ions and various concentrations of Yb^{3+} ions

sintering temperature at 700°C . All the samples already show a tetragonal phase with various planes without obvious secondary phases, corresponding well to the standard powder diffraction pattern. To further investigate the variation of structures with the increase of Yb^{3+} concentration, a tetragonal single phase ($P4mm$) model was applied to refine the crystal structure with the XRD data. Here we just showed the refinement result of PbTiO_3 doped with 6 mol% Er^{3+} ions and 6 mol% Yb^{3+} ions in

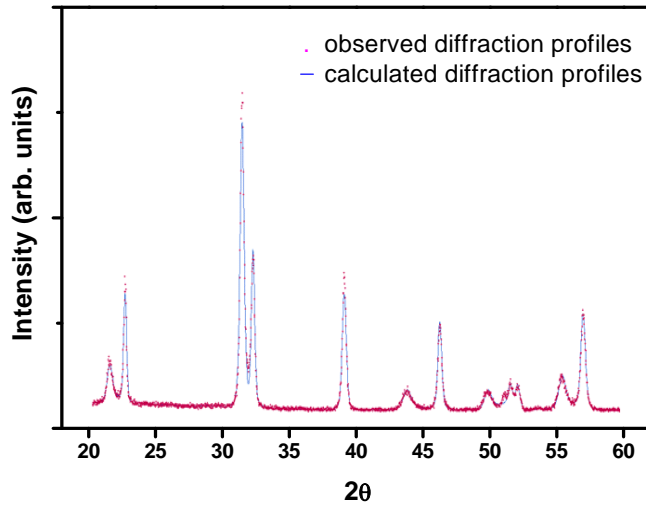


Figure 5.3: Rietveld pattern of PbTiO_3 doped with only 6 mol% Er^{3+} ions and 6 mol% Yb^{3+} ions.

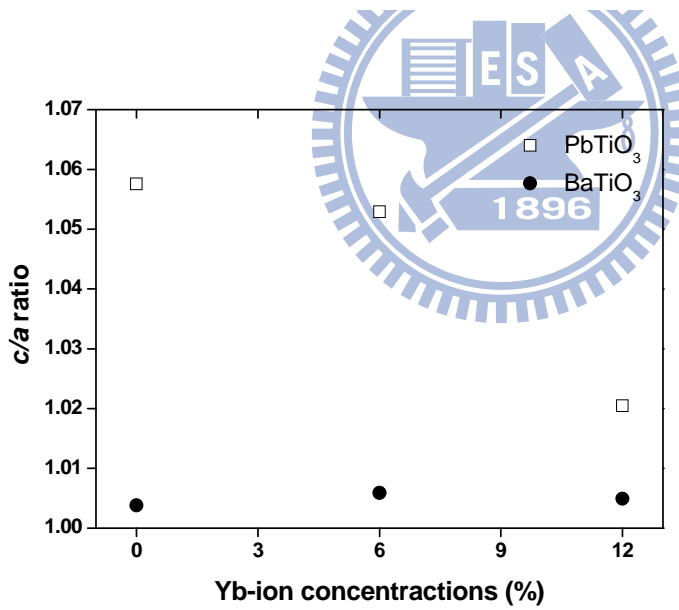


Figure 5.4: c/a (a and c are lattice constants) ratio as function of Yb^{3+} - ion concentrations after Rietveld refinement.

Figure 5.3 and the calculated profiles agree well with the observed ones. Figure 5.4 plots the Yb^{3+} concentrations dependence of the tetragonality, c/a , and lattice

constants following Rietveld refinement. As Yb^{3+} -ion concentration changes from 0, 6, to 12 mol %, the tetragonality (c/a) of PbTiO_3 system declines from 1.058, 1.053, to 1.020; moreover, c/a of BaTiO_3 system retains around 1.005. A Decline of tetragonality is due to the presence of substitution of Er^{3+} and Yb^{3+} ions in PbTiO_3 that is similar to the results reported by Kuo *et al.* [12].

5.2.2 Symmetry-dependent upconversion mechanism

The declining tetragonality of PbTiO_3 system as increasing Yb^{3+} concentration will result in weakening the crystal field on Er^{3+} and Yb^{3+} ions, in turn, it benefits the match of the level space $^4S_{3/2} \rightarrow ^4I_{13/2}$ of the Er^{3+} ion and $^2F_{7/2} \rightarrow ^2F_{5/2}$ of the Yb^{3+} ion to enhance the EBT process. These results are consistent with the observed split of spectral peaks of green UC emission in tetragonal phase as well as the quenching of green UC emission and enhancement of red UC emission for high Yb^{3+} concentration with low tetragonality.

As compared with PbTiO_3 system and BaTiO_3 system at 6 mol% at Yb^{3+} concentration, the larger asymmetric crystal field for PbTiO_3 of larger tetragonality on Er^{3+} and Yb^{3+} ions results in the mismatch of resonant photons. The weak strength of EBT process due to the larger asymmetric crystal field at 6 mol% at Yb^{3+} concentration in PbTiO_3 leads to weak red UC emission. It agrees with the result of the dependence of red UC emission on structure of host material at the same Yb^{3+}

concentration.

5.2.3 Pump power dependent upconversion

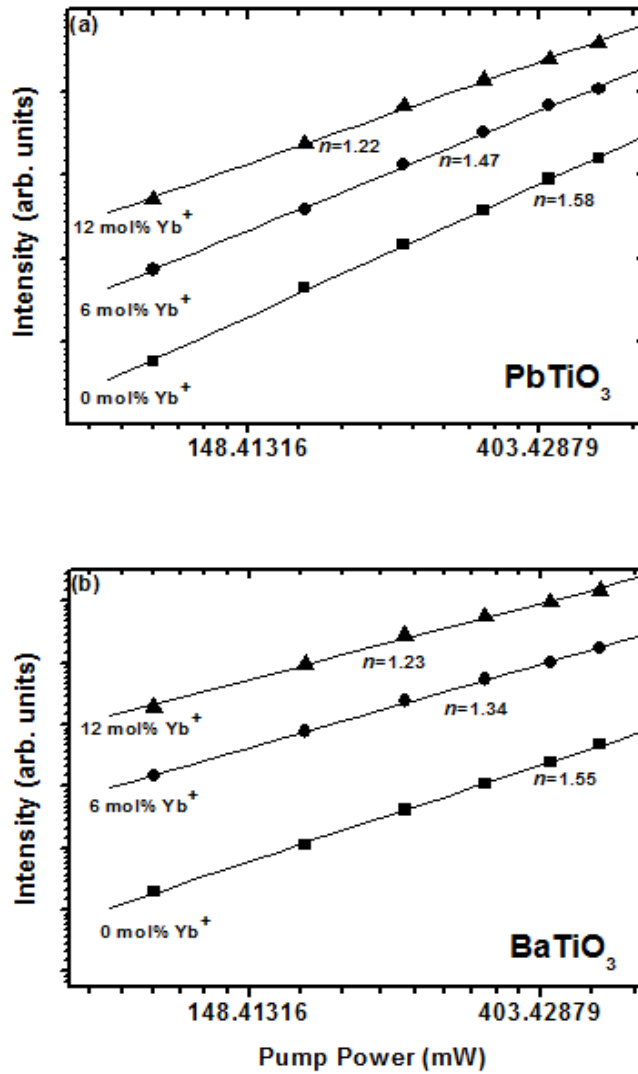


Figure 5.5: Pump power dependence of the red upconversion emission of PbTiO_3 and BaTiO_3 doped with 6 mol% Er^{3+} ions and various concentrations of Yb^{3+} ions in a logarithmic scale.

To verify the mechanism of red UC emission, we investigated the dependence of intensity (I) of red UC emission on the pump power (P). It is possible to determine

the number of photons (n) required for populating the emitting state according to [13, 14]:

$$I \propto P^n. \quad (5-1)$$

Similar to Ref. [8], the n value is close to 2 for the green UC emission. Because we are more interested in the mechanism of red UC emission, we plotted the logarithm diagram of I versus P for both PbTiO₃ and BaTiO₃ systems in Figure 5.5. As shown in Figure 5.5(a), the n value decreases from 1.58 for 0 mol % Yb³⁺-ion to 1.47 for 6 mol % Yb³⁺-ion concentration doped PbTiO₃, which indicate a mixing process of one- and two-photon for producing the red band with two-photon process being still the dominant mechanism. The EBT process is relatively weak because the strong crystal field due to the structure asymmetry contributes to the level mismatch between ⁴S_{3/2}→⁴I_{13/2} of Er³⁺ ion and ²F_{7/2}→²F_{5/2} of Yb³⁺ ion. However, for 12 mol% Yb³⁺ doping, the power law shows one-photon process dominant with n = 1.22, namely, the efficient EBT process takes over to effectively quench the ⁴S_{3/2}(Er) state and so to diminish the green band (see Figure 5.1(a)) in the more centrosymmetric host matrices at the highest Yb³⁺-ion concentration (Figure 5.2(a)). On the contrary, the n value is also 1.55 in Figure 5.5(b) for 0 mol% Yb³⁺ doped BaTiO₃, which is a two-photon process. It becomes 1.34 and 1.23 for Yb³⁺-ion concentrations of 6 and 12 mol%, respectively. Under this circumstance, the ⁴S_{3/2}(Er)

states, which the green UC radiation arises, were strongly quenched with low green emission in Figure 5.1(b) via the EBT process to saturate the $^4I_{13/2}(\text{Er})$ state through coupling with the transition $^2F_{7/2} \rightarrow ^2F_{5/2}$ of Yb^{3+} ion. And the strong red UC emission were observed dominated by the one-photon process in doped nearly cubic-phase BaTiO_3 (see Figure 5.2(b)). The efficient red UC radiation requires not only Yb^{3+} concentration but also level match of $^4S_{3/2} \rightarrow ^4I_{13/2}$ in Er^{3+} and $^2F_{7/2} \rightarrow ^2F_{5/2}$ in Yb^{3+} under assistance of Boltzmann distributed population within the manifold of $^4S_{3/2}$ or/and $^4I_{13/2}(\text{Er}^{3+})$ state affected by the crystal field with different symmetries for efficient EBT process. Declining tetragonality results in the centrosymmetric crystal field for high Yb^{3+} -ion to achieve the above-mentioned level matches, which may be difficult to be fulfilled with asymmetric crystal field in ferroelectric phase. It agrees with the results of XRD and of the dependence of red UC emission on structure of host materials at the same Yb^{3+} concentration.

5.3 Summary

As increasing Yb^{3+} co-doped concentrations in 6 mol% Er^{3+} doped PbTiO_3 , BaTiO_3 , and SrTiO_3 polycrystalline powder samples, we have observed the room-temperature green UC emission at 550 nm being quenched by the simultaneously enhanced red UC emission at 660 nm under the 980-nm laser

excitation. For codoping Yb^{3+} ions up to 6 mol% in PbTiO_3 and only Er^{3+} doped PbTiO_3 samples, which still possess relatively large tetragonality, the green UC emission is still much stronger than red one. In these cases, both the UC emissions are dominated by the two-photon process. But, as further increasing the Yb^{3+} ion concentration, the crystal structures tend to become cubic phase with enhancing red UC emission and almost diminishing in green emission. Since the pure BaTiO_3 crystal exhibits weaker tetragonality than PbTiO_3 , the stronger red emission and weaker green one were expected at the lower codoped Yb^{3+} concentration in BaTiO_3 system than in PbTiO_3 one. The observed quench of green radiation accompanied with enhancement of red radiation should be due to the efficient energy back-transfer process as reported by Chen, *et al.* by raising Yb^{3+} concentration [8]. The efficient EBT process requires not only Yb^{3+} concentration but also level match of $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$ in Er^{3+} and $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ in Yb^{3+} under assistance of Boltzmann distributed population within the manifold of $^4\text{S}_{3/2}$ or/and $^4\text{I}_{13/2}$ (Er^{3+}) state affected by the crystal field with different symmetries. As a result, declining tetragonality results in the centrosymmetric crystal field for high Yb^{3+} -ion concentration to achieve the level match required for the EBT process that may be difficult to be fulfilled with asymmetric crystal field in the tetragonal (ferroelectric) phase.

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Chapter 6 Size-dependent lattice dynamics of BaTiO₃ nanoparticles

Influence of the presence of substitution on the physical properties has been discussed in Chapters 4 and 5. It is similar to the results reported by Kuo *et al.* [1]. Furthermore, the physical properties have been dramatically influenced by various effects, such as temperature [2-4], pressure [3, 5], substitution [6], and size [7-11]. Continuous advance in miniaturization of ferroelectric devices, fine particles as ferroelectric materials have been applied in advanced electric devices [12] such as multilayer ceramic capacitor. Due to the close relationship between ferroelectric properties and crystal structure, the size dependence of structure is presently the major research topics.

In previous study of Ba_xSr_{1-x}TiO₃ (BST) system [1], the repulsion of giant LO-TO splitting with increasing “Sr” substitution, which causes crystal structure to change from tetragonal phase toward cubic phase, is due to decrease in the dimensions of the unit cell. In this chapter we report, in contrast to that in BST system, the attractive LO-TO splitting behavior and depict the low frequency TO spectral peak along with change of the tetragonal phase toward the cubic one for reducing diameter of BaTiO₃ nanocrystals from 140 nm to 30 nm.

By applying single tetragonal-phase model to refine the crystal structure and the coupled-phonon model to analyze transverse optical (TO) modes of BaTiO₃ nanocrystals, we found, upon decreasing the particle size from 140 nm to 30 nm, the tetragonality of BaTiO₃ nanocrystallites is reduced accompanied with expanding unit-cell volume, which is the dominant mechanism for reducing giant LO–TO splitting in BaTiO₃ system. The weakening coupling of two low-frequency modes among three A₁(TO) phonons leads to change the lowest one from a spectral dip to a peak; whereas the increasing coupling strength between two high-frequency modes, repels them farther so that the less reducing in spectral separation.

6.1 Size-dependent lattice constant of BaTiO₃ nanoparticles

BaTiO₃ nanoparticles shown in FESEM micrographs of Figure 6.1 have low aggregation and narrow size distribution with mean diameters of about 140, 60, and 30 nm, respectively. To analyze the crystal symmetry of BaTiO₃ nanoparticles, high resolution diffraction patterns of various sizes of BaTiO₃ nanoparticles were taken by using high-energy synchrotron radiation x-ray and refined by using the GSAS program; however, to retrench the layout of a printed page, here we just showed the refinement result of BaTiO₃ with a particle size of 60 nm in Figure 6.2. The XRD profiles around 32.5° in 2θ-scan for all sizes of BaTiO₃ particles indicate splitting of

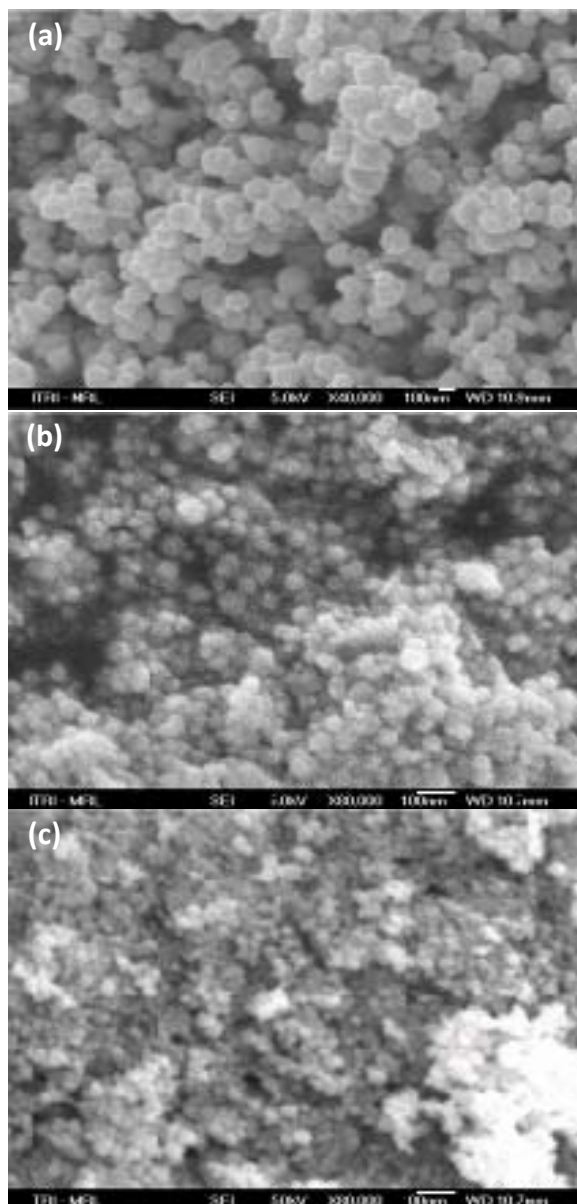


Figure 6.1: Microstructure (FESEM) of BaTiO₃ nanoparticles with average grain size of 140 ± 8 nm, 60 ± 6 nm, 30 ± 5 nm.

(004) and (400) peaks, thus, a tetragonal single phase ($P4mm$) model was applied to refine the crystal structure with the XRD data. As shown in Figure 6.2, the calculated profiles agree well with the observed ones. The refined structure parameters with very small deviations and reliability (R_{wp}) factors for various sizes of

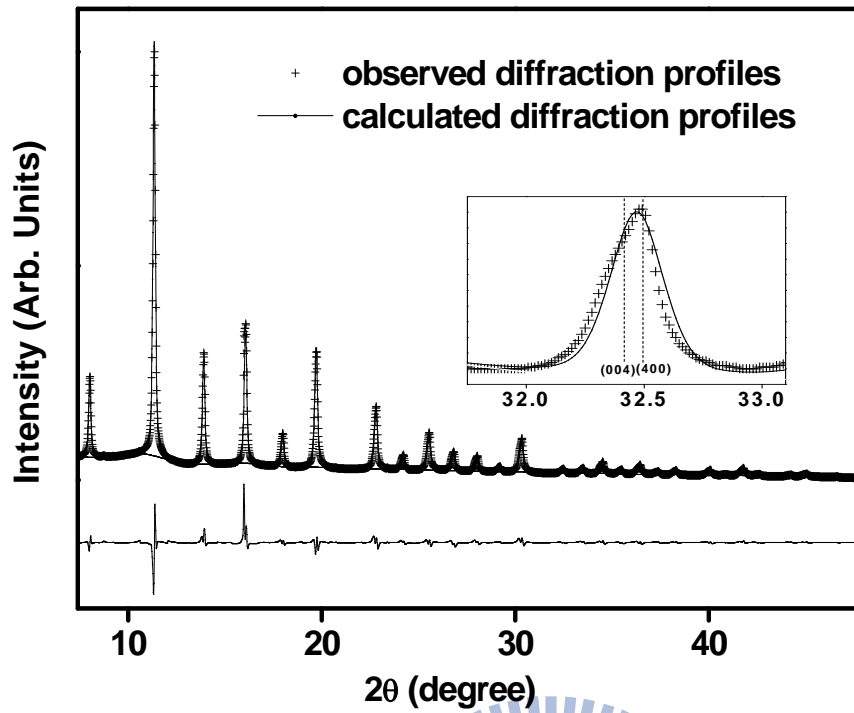


Figure 6.2: Rietveld pattern of BaTiO₃ nanoparticles with average grain size of 60 nm.

nanoparticles were listed in Table 6-1 and the results were plotted in Figure 6.3. It reveals that single tetragonal-phase model is suitable for particle size smaller than 100 nm and even gets better fitting with lower R_{wp} as decreasing particle size. It is consistent with the results of Yoon, *et al.* [13] that single tetragonal phase was used for 7.5 nm, although Yashima, *et al.* [11] reported that particles with a size of 40 nm identified to be a mixture of tetragonal and hexagonal phases. Besides, the ratio c/a is 1.0008 ± 0.0003 , which is still greater than 1, reveals the 30nm particle is still tetragonal, we will show later the results of Raman spectra provide auxiliary evidence

that the phonon modes specific to the tetragonal phase of BaTiO₃ as described in Ref. [14] still appear. We also fitted a cubic model to the XRD pattern of the 30 nm particles. The resultant lattice constant is 4.0341±0.0001 nm and reliability (R_{wp}) factors is 7.1%, which is acceptable but worse than 2.78% that fits with tetragonal model. Furthermore, the larger R-value for the larger particles may result from preferred orientation may exist in the larger particles that we did not consider in the refinement.

TABLE 6-1 Refined crystal parameters and reliability factors of BaTiO₃ nanoparticles.

Particle size	R _{wp}	a, Å	c, Å	c/a	Atomic coordinate	
					Ti	O(I)
~µm		3.9940	4.0330	1.0098		
140 nm	11.20%	4.0200	4.0304	1.0026	(0.5, 0.5, 0.5340)	(0.5, 0.5, 0.0299)
(± 7 nm)		(±0.0001)	(±0.0002)	(±0.00007)		
60 nm	7.46%	4.0285	4.0357	1.0018	(0.5, 0.5, 0.5201)	(0.5, 0.5, 0.0160)
(± 6 nm)		(±0.0004)	(±0.0008)	(±0.0002)		
30 nm	2.78%	4.0329	4.0362	1.0008	(0.5, 0.5, 0.5184)	(0.5, 0.5, 0.0061)
(± 5 nm)		(±0.0006)	(±0.0012)	(±0.0003)		

The lattice constants *a* and *c*, shown in Figure 6.3(a), simultaneously relax with decreasing the particle size from 140 nm to 30 nm. The results also show consistent with the assumption proposed by Ishikawa, *et al.* [15] that the tetragonality (*c/a*) declines from 1.0026 to 1.0008 with expanding unit-cell volume in Figure 6.3(b) as the particle size decreases. The observation is also consistent with the results

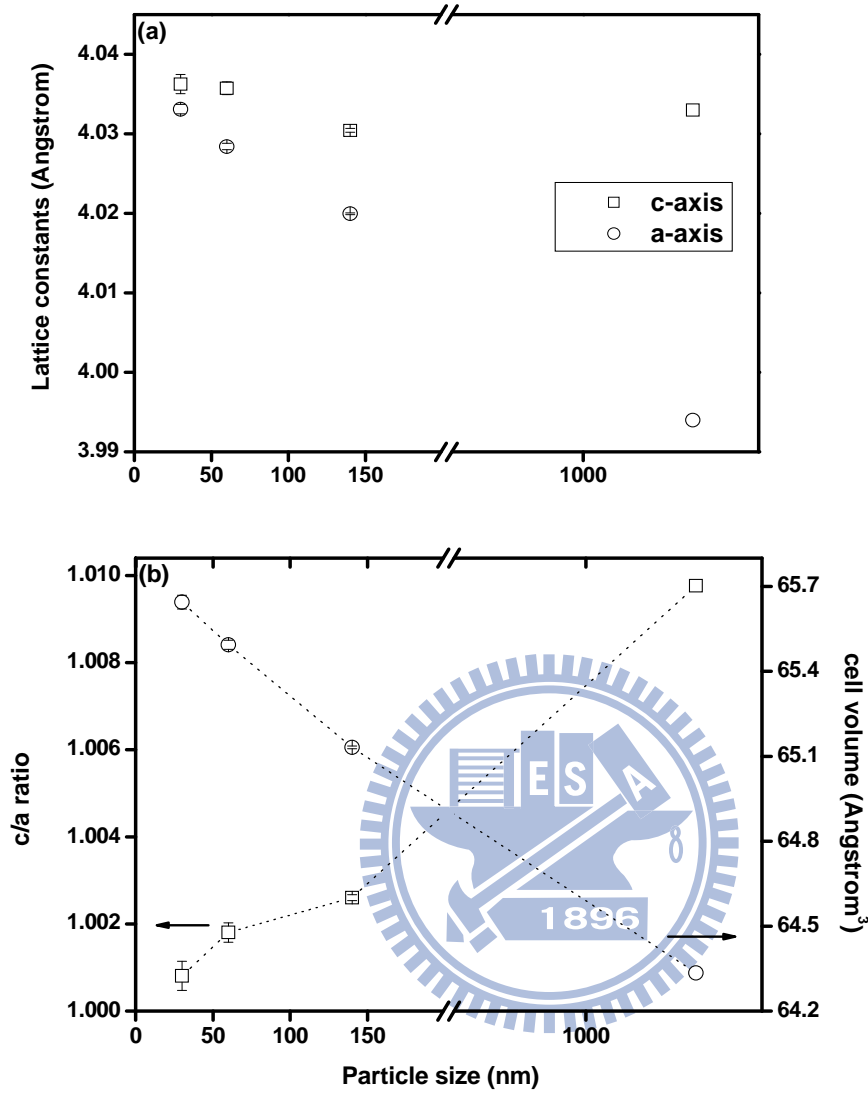


Figure 6.3: The lattice constants *a* and *c* of BaTiO₃ nanoparticles after Rietveld refinement procedure and the ratio of *c/a*.

presented in Figure 6.1 of Ref. [10] that *c* reduces from micrometer size to sub- μ m size then increases for further decreasing its size, whereas, *a* expands for decreasing crystal size. Nevertheless, our results of XRD refinement reveal the critical size of BaTiO₃ nanoparticles, which is the size of the phase transition from tetragonal to

cubic at RT, may be smaller than 30 nm that differs from the argument reported by Hoshina, *et al.* [10], in which the size-induced phase transition occurs between 40 nm and 30 nm. According to Table 6-1 the refined atom positions in a unit cell of the tetragonal BaTiO₃ nanoparticles reveal less displacement of titanium and oxygen [O(I)] atoms along the *c* axis with decreasing particle size. It also indicates, similar to the results due to the temperature effect [16], that the Ti-O₆ octahedron shows less distorted due to the less off-center displacement (Ti) resulting from the size effect.

6.2 Size-dependent Raman spectra of BaTiO₃ nanoparticles

The Raman spectra of BaTiO₃ nanoparticles taken at RT were plotted in Figure 6.4 with particle sizes of 30 nm, 60 nm, 140 nm, and > 1 μm, respectively. First of all, there is a spectral dip around 180 cm⁻¹ for micrometer-size sample but a spectral peak for all the nanoparticles that is assigned to *A*₁(TO₁) phonon mode. They are basically located at the same frequency of the destructive interference dip for the bulk BaTiO₃. A broad band around 260 cm⁻¹ attributed to *A*₁(TO₂) mode, a band at 305 cm⁻¹ to *B*₁+*E*(TO+LO) modes, the asymmetric band around 520 cm⁻¹ to *E*(TO) and *A*₁(TO₃) modes, and the highest frequency band around 720 cm⁻¹ to *A*₁(LO)+*E*(LO) phonon modes. The phonon modes at 305 and 720 cm⁻¹ specific to the tetragonal phase of BaTiO₃ as described in Ref. [14] become weak and broad with decreasing

particle size. The observed broadening and weakening of tetragonal Raman bands indicate that the crystal structure becomes progressively less tetragonal due to less displacements of Ti and O(I) atoms for the smaller particle size, which is consistent with the results of XRD. The Structural model of non-polar (cubic) and polar (tetragonal) ABO_3 crystal is shown in Figure 6.5. Ti atoms locate at the center of the Ti-O_6 octahedron when the octahedral units are perfect in the cubic-type structure.

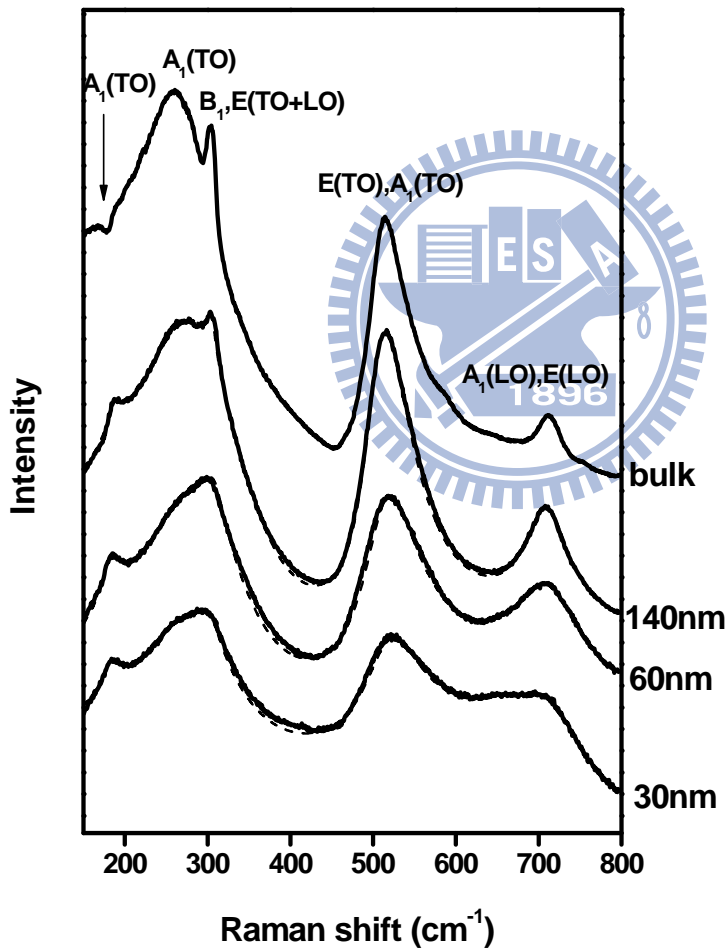


Figure 6.4: Size dependence of Raman spectra for BaTiO_3 bulk ($> 1\mu\text{m}$) and nanoparticles of diameter 140, 60, and 30nm, respectively.

Due to balance of the charges, the crystal is non-polar and Raman mode is inactive. On reducing temperature, the Ti-O_6 octahedron will be somewhat distorted with off-center displacement of Ti atoms toward one of the O(I) atoms while elongating the c -axis to the tetragonal structure and present spontaneous dipole. The refined atom positions in a unit cell of the tetragonal BaTiO_3 nanoparticles reveal less displacement of titanium and oxygen [O(I)] atom along the c axis with decreasing particle size so that the Ti-O_6 octahedron shows less distorted or less polar due to the less Ti off-center displacement resulting from the size effect.

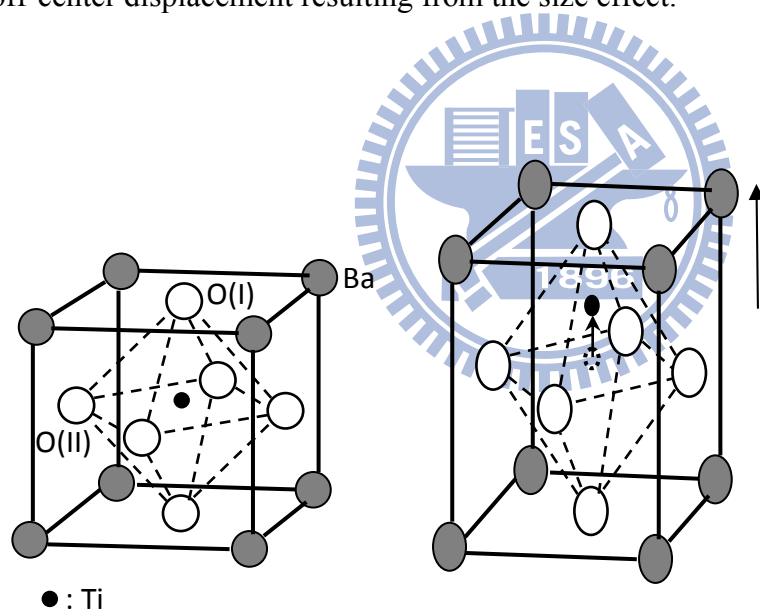


Figure 6.5: Structural model of the cubic- and tetragonal- phase occurring with bulk BaTiO_3 crystals.

Although we had also observed a weak peak around 810 cm^{-1} attributed to lattice OH group [17] and a very weak band around 930 cm^{-1} (not shown here) to the oxygen vacancy [18]. There are no reports on the OH groups and no direct evidence of

oxygen vacancy that would influence the frequencies of the observed Raman modes. The frequency shift observed in Ref. 31 should mainly results from the interface strain introduced between BaTiO₃ film and substrate rather than influence of oxygen vacancy, because spectra (b) and (c) in Figure 6.4 showed therein that the $A_1(\text{LO})+E(\text{LO})$ modes shifted to 715 cm⁻¹ before appearance of a very weak 930 cm⁻¹ band due to the oxygen vacancy. Finally, we did not observe 1060 cm⁻¹ peak attributed to BaCO₃ brought out by Pithan, *et al.* [19] so that we had prevented the BaCO₃ related peaks located in the spectral range below 200 cm⁻¹ by acetic acid washing.

Because the three $A_1(\text{TO})$ modes are strongly coupled and two of them are heavily damped in the tetragonal phase of ABO₃, Sood, [20] and Chaves, *et al.* [21] have considered three coupled $A_1(\text{TO})$ modes to describe the complicated coupling phenomenon. The Raman intensity of the three coupled modes can be expressed by

$$I(\omega) = A [n(\omega) + 1] \text{Im}[\mathbf{T}^* \mathbf{G} \mathbf{T}], \quad (6-1)$$

where A is a constant, $[n(\omega) + 1]$ is Bose-Einstein factor, \mathbf{T} is a vector involving Raman scattering amplitudes, and the inverse matrix response is

$$\mathbf{G}^{-1}(\omega) = \mathbf{\Omega}^2 - \omega^2 \mathbf{I} - i\omega \mathbf{\Gamma}. \quad (6-2)$$

In Eq. (6-2), \mathbf{I} is the unit matrix, $\mathbf{\Omega}^2$ is the force constant matrix, and $\mathbf{\Gamma}$ is the damping matrix:

$$\mathbf{\Omega}^2 = \begin{pmatrix} \omega_1^2 & \omega_{12}^2 & 0 \\ \omega_{12}^2 & \omega_2^2 & \omega_{23}^2 \\ 0 & \omega_{23}^2 & \omega_3^2 \end{pmatrix}, \mathbf{\Gamma} = \begin{pmatrix} \Gamma_1^2 & 0 & 0 \\ 0 & \Gamma_2^2 & 0 \\ 0 & 0 & \Gamma_3^2 \end{pmatrix}. \quad (6-3)$$

Here ω_i and ω_{ij} ($i, j = 1, 2, 3$) are the uncoupled mode frequencies and the coupling strengths between modes i and j . The coupling between the lowest (ω_1) and the highest (ω_3) modes was set to zero ($\omega_{13} = 0$), to allow less fitting parameters; this is a reasonable approximation because they are too far from each other, having no spectral superimposition.

The asymmetric broad band around 500-600 cm^{-1} is attributed to superposition of $E(\text{TO})$ and $A_1(\text{TO}_3)$ modes, so that one has to separate them before making coupled-mode analysis. These two modes are distinguishable by polarized Raman scattering in single crystals. From the results of polarized Raman study on the epitaxial BaTiO_3 film by Marssi, *et al.* [22], the $E(\text{TO})$ mode is situated at the low frequency shoulder with about 1/4 intensity of the $A_1(\text{TO}_3)$ mode. According to the process to refine the XRD data by using the GSAS, we can attain better fitting result in XRD analysis without considering any preferred orientation. Therefore, in our powder samples the particles should possess random orientation. We have to consider the angle dependent frequencies of these modes. It is well known that the frequency of $E(\text{TO})$ mode is independent of the observing angle with respect to the crystallographic axes, whereas, that of $A_1(\text{TO})$ mode depends upon the observing

angle according to: [23]

$$[\omega_{A_1}(\theta)]^2 = (\omega_{A_1})^2 \sin^2 \theta + (\omega_E)^2 \cos^2 \theta \quad (6-4)$$

Assuming the particles are completely randomly oriented, the scattering wave vector should also randomly orient with respect to the crystallographic axis.

Therefore, the observed $A_1(\text{TO}_3)$ frequency, after averaging over for Eq. (6-4) is

$$\text{well-defined between } \omega_{A_1} \text{ and } \omega_E \text{ or } \langle \omega_{A_1}(\theta) \rangle = \sqrt{\frac{\omega_{A_1}^2 + \omega_E^2}{2}} \text{ and } E(\text{TO}) \text{ and } A_1(\text{TO}_3)$$

modes are separable. It is reasonable to extract the contribution of the $E(\text{TO})$ mode

and the coupled $A_1(\text{TO}_3)$ mode for these randomly oriented nanoparticles. On the

other hand, $A_1(\text{LO})$ mode is inseparable from $E(\text{LO})$ mode for tetragonal structure around 720 cm^{-1} when the scattering wave vector makes an angle with respect to

crystallographic axes. It gives rise to mode mixing due to directional dispersion or

called the “oblique phonon”. The observed frequency shift of angle-averaged

oblique phonon in Figure 6.4 should not depend on the observing angle θ but other

effects, e.g., particle size. Therefore, other than Eq. (6-1) we added four Lorentzian

functions representing background signal (Rayleigh scattering) which depends on the

particle size, $B_1 + E(\text{TO} + \text{LO})$, $E(\text{TO})$, and $A_1(\text{LO}_3) + E(\text{LO})$ to fit the measured Raman

spectra.

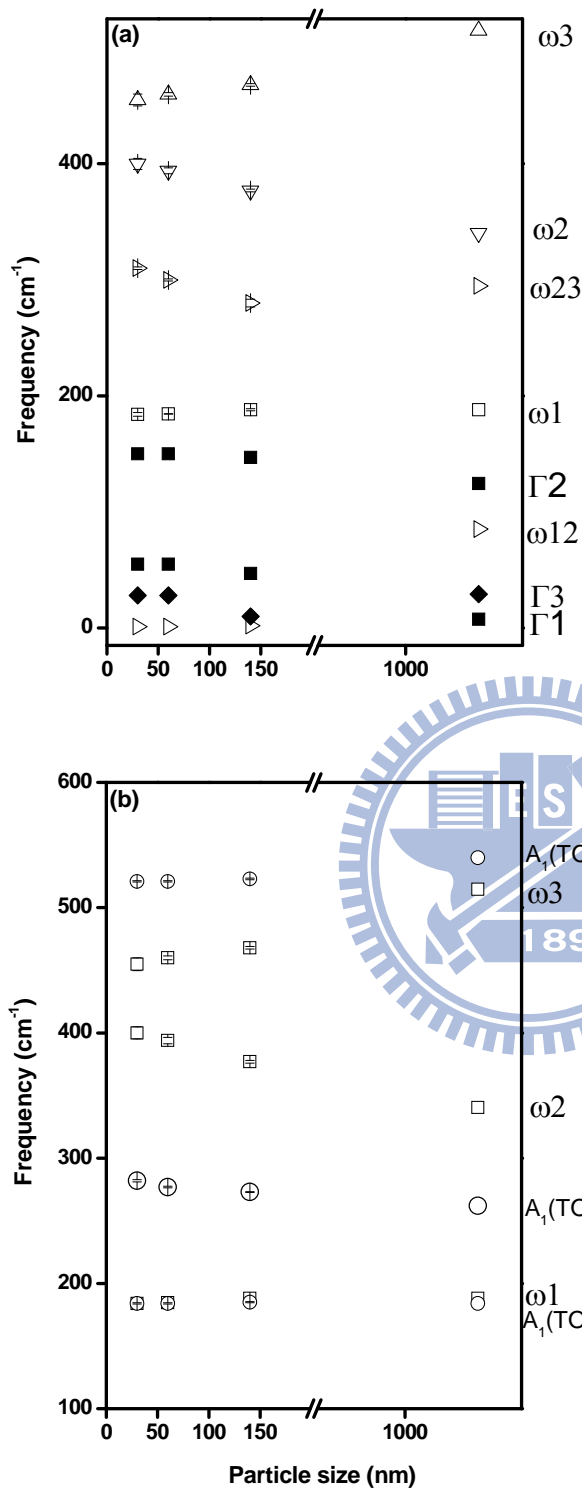


Figure 6.6: The fitted parameters using the coupled-phonon model as a function of particle size.

In order to attain the best fitting to our measured data, an extra band around 640 cm^{-1} has to be considered especially for 60-nm and 30-nm samples. This 640 cm^{-1} band was assigned to the grain-boundary regions [24] or was due to the hexagonal phase [11]. However, as aforementioned there is even better fitting with smaller R_{wp} for size of 30 nm in XRD analysis using single tetragonal phase, we therefore assigned the weak mode around 640 cm^{-1} to the grain-boundary regions for 60-nm and 30-nm samples rather than due to the hexagonal phase.

The fitting parameters of three coupled TO modes were plotted in Figure 6.6(a) that allows us to clarify the coupling behavior of phonon with decreasing particle size. We found that the coupling strength, ω_{12} , between ω_1 and ω_2 dramatically changes from 85 cm^{-1} to nearly zero as the particle size decreases from few micrometers to nanometer. The weaker (or zero) coupling between ω_1 and ω_2 in BaTiO_3 nanoparticles leads to observing a spectral peak around 180 cm^{-1} for the $A_1(\text{TO}_1)$ phonon mode rather than a dip at the same position. Figure 6.6(b) shows the plot of the as-read peak positions (hollow symbols and labeled as $A_1(\text{TO}_i)$, $i = 1, 2, 3$) of three A_1 -symmetric TO modes from our Raman data and those obtained from the coupled-phonon model as solid symbols. It can be seen that the size-dependent decoupled (calculated) phonon frequency ω_1 overlaps with the as-read one again indicating weak coupling strength ($\omega_{12} \sim 0$). With less tetragonality or small c/a due

to decreasing the particle size, we found that the approach of uncoupled ω_2 and ω_3 results in slightly increasing in ω_{23} . The larger coupling strength ($\omega_{23} \sim 300 \text{ cm}^{-1}$) repels these two modes farther such that the measured $A_1(\text{TO}_2)$ [$A_1(\text{TO}_3)$] peak only slightly shifts toward the higher (lower) frequency upon decreasing the particle size.

6.3 Born effective charge and LO-TO splitting in BaTiO_3 nanoparticles system

Furthermore, the dynamical matrices for the LO and TO modes, which have the same form of atomic displacements in a unit cell, are related by

$$D_{mn}^{LO} = D_{mn}^{TO} + \frac{4\pi e^2}{V} \frac{Z_m^* Z_n^*}{\epsilon_\infty(q)}, \quad (6-5)$$

where D represents the dynamical matrix that is proportional to the square of the vibration frequency, V is the volume of the unit cell, $\epsilon_\infty(q)$ is the optical dielectric constant, and Z^* is the Born effective charge of the corresponding vibration. The Coulomb interaction would play an important role in the behavior of LO-TO splitting.

Figure 6.7 shows the peak positions of $A_1(\text{LO})$ and $A_1(\text{TO}_1)$ modes versus BaTiO_3 particle size. We observed besides the expected softening of both $A_1(\text{LO})$ and $A_1(\text{TO}_1)$ modes, there is a decreasing trend of LO-TO splitting as the particle size decreases from $> 1\mu\text{m}$ to 30 nm. Since Ba-based ABO_3 perovskites basically

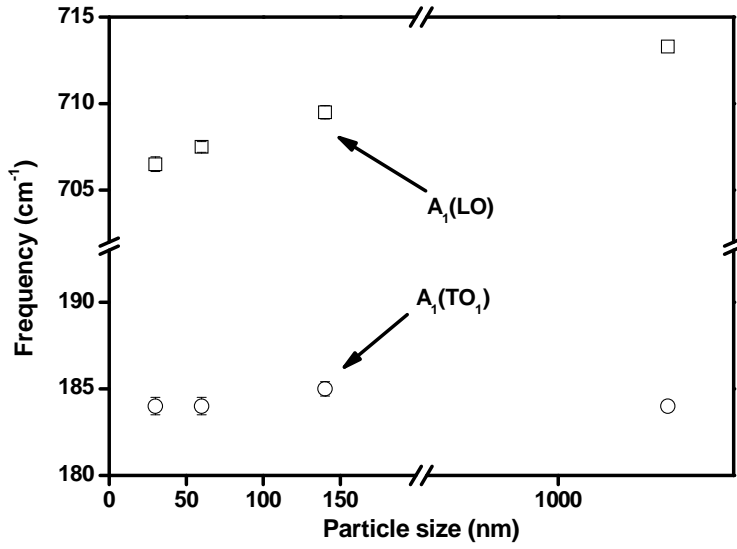


Figure 6.7: The LO-TO splitting of the $A_1(LO_3)$ and $A_1(TO_1)$ modes as function of particle size.

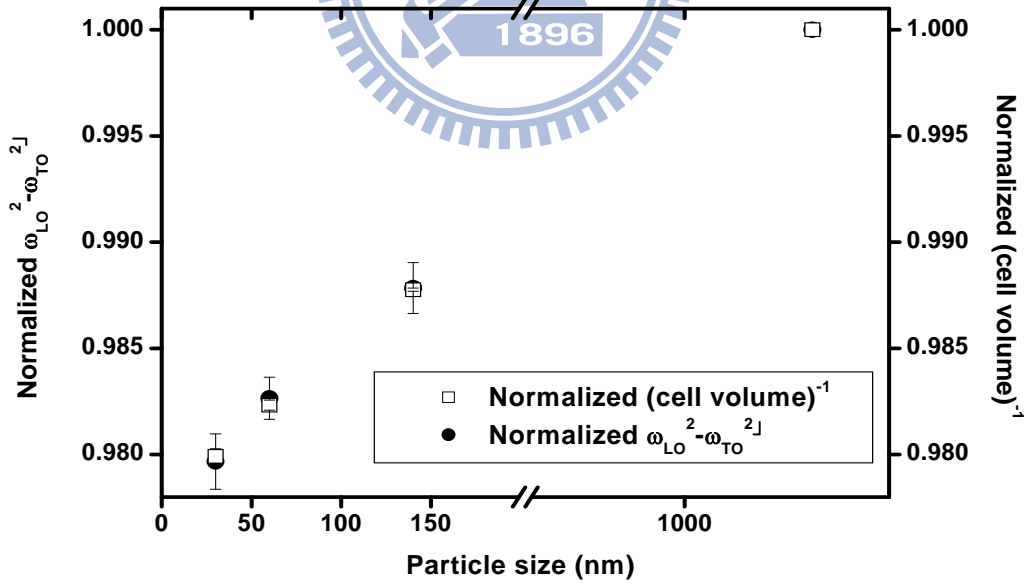


Figure 6.8: Normalized square difference of phonon frequencies of $A_1(LO_3)$ and $A_1(TO_1)$ and normalized reciprocal of unit cell volume for nanometer size samples to the micrometer size.

possesses ionic bonding [25, 26-28], the Born effective charge would not be influenced by change of structure [29, 27]. From the results of Figure 6.3(b) that the unit cell dimension of BaTiO₃ particles increases with the particle decreasing from micrometer size to 30 nm; we would expect reducing LO-TO splitting. Relatively, we previously reported that the tetragonality declines with unit-cell volume diminishing as x changes from 1 to 0.7 in polycrystalline Ba _{x} Sr_{1- x} TiO₃ [6]. Change of unit-cell volume was considered the dominant mechanism of increasing the LO-TO splitting in this system with negligible change of effective charge due to the substitution. In this study we directly observed the decreasing LO-TO splitting with the decline of tetragonality by decreasing the size of BaTiO₃ nanoparticles which causes expansion of the unit-cell volume.

Based on Eq. (6-5), we normalized the square difference of phonon frequencies of $A_1(\text{LO}_3)$ and $A_1(\text{TO}_1)$ for nanometer size samples to the one of micrometer-size and plotted in Figure 6.8 to compare with the normalized reciprocal of unit cell volume also to the micrometer-size one's. It shows that the normalized square difference of phonon frequencies of $A_1(\text{LO}_3)$ and $A_1(\text{TO}_1)$ almost coincides with the normalized reciprocal unit cell volume with less than 2% deviation. This result indicates that the

value of $\frac{4\pi e^2 Z_m^* Z_n^*}{\epsilon_\infty(q)}$ is a constant, namely, the Born effective charges should not be

influenced by change of structure or size, and the change of unit-cell volume is the dominant mechanism for the tendency of the LO–TO splitting in BaTiO₃ system without complication of ion replacement.

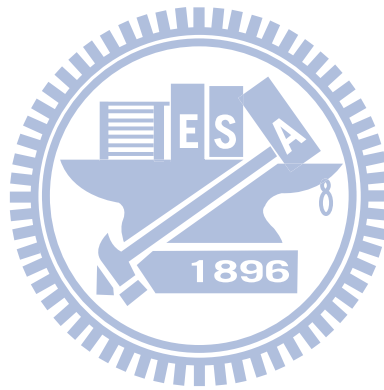
6.4 Summary

The size effect on structure for BaTiO₃ nanoparticles synthesized by the glycothermal method has been investigated using FESEM, synchrotron XRD, and Raman spectroscopy. We further applied a single tetragonal-phase model to refine the crystal structure and the coupled-phonon model to analyze the coupled $A_1(\text{TO})$ modes upon particle size decreasing from 140 nm to 30 nm. We explained that the weak strength of coupling between $A_1(\text{TO}_1)$ and $A_1(\text{TO}_2)$ leads to a change from a spectral dip at 180 cm⁻¹ for $A_1(\text{TO}_1)$ phonon to a peak at the same position and found that the approach of uncoupled ω_2 and ω_3 with less tetragonality due to decreasing the particle size results in slightly increasing in ω_{23} . The larger coupling strength repels these two modes farther so that the less reducing in spectral separation. According to the results of decomposition, we also observed the decreasing LO-TO splitting with the decline of tetragonality and expansion of the unit-cell volume. And the change of unit-cell volume is the dominant mechanism for the tendency of the LO-TO splitting in BaTiO₃ system without complication of ion replacement.

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Chapter 7 Correlating phonon frequency shift with magnetoelectric effect in the $\text{PbTiO}_3\text{-CoFe}_2\text{O}_4$ multiferroic system due to interfacial stress

We discussed the substitution effect on perovskite structure in Chapters 4 and 5 and size effect in the last chapter. In this chapter, we continue to discuss the influence of strain effect resulting from the lattice misfit between the different media on ferroics.

The ME coupling results from the elastic bonding at the interface and is transmitted through the stress/strain exerted by magnetized magnetostrictive phase on piezoelectric phase or vice versa along their boundary and hence it induces a net polarization or magnetization [1, 2, 3]. Moreover, it is well known that the behavior of interfacial phonon is sensitive to the giant residual stress/strain resulting from the lattice misfit between the different media [4]. It is interesting and important to investigate the relationship between the ME effect and the behavior of interfacial phonon. Recently, some studies about the behavior of phonon on multiferroics were reported [5-7] with lack of concrete conclusion.

In this chapter, we report on the stress dependence of the behavior of interfacial phonon and the magnetic properties in three multiferroics consisting of the different

geometric shapes (see Figure 7.1) of ferromagnetic CoFe_2O_4 (CFO) embedded in ferroelectrics PbTiO_3 (PTO) by using the micro-Raman spectroscopy and superconducting quantum interference device (SQUID). Their energy of interfacial phonon and ferromagnetic properties depend on stress due to not only the lattice misfit but also the degree of chemical bonding at the interface between CFO and PTO matrices. The disk-3 type structure, the self-assembled CFO disks embedded in PTO matrix, illustrates the strong elastic interactions between the two phases. The larger nonsymmetrical coercivity H_c and the absence of saturation magnetization M_s of CFO matches with the larger Raman shift of $A_1(\text{TO}_2)$ and $A_1(\text{TO}_3)$ modes of PTO found in the disk-3 type than the other types of the CFO and PTO multilayered structure and the CFO particles embedded in PTO matrix.

7.1 Microstructure and morphology

The top view images of the disk-3 type shown in Figure 7.2 by using OM and FESEM were found consisting of sub-10 μm CFO discs embedded in PTO matrix rather than nanometer sized CFO rods in PTO matrix [2]. It reveals the similar morphology as illustrated in Figure 7.1(c). Forming the CFO discs instead of CFO rods may be due to the cohesion of CFO gel is stronger than the adhesive force between CFO and PTO gels. According to the mechanism of synthesis, we may infer that the CFO and PTO multilayered structure (2-2 type) and the CFO particles

embedded in PTO matrix (0-3 type) as illustrated in Figure 7.1(a) and Figure 7.1(b), respectively.

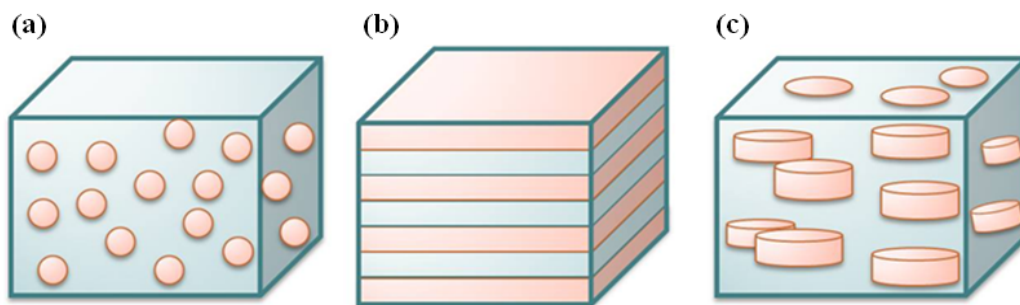


Figure 7.1: Schematic illustration of three thin films with different connectivity schemes: the 0-3 type with CFO particles embedded in PTO matrix, the 2-2 type with CFO and PTO nanolayers, and the disk-3 type with CFO disc aligned in PTO matrix.

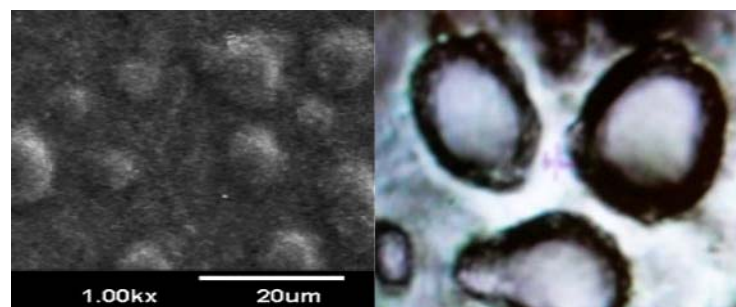


Figure 7.2: Top view of FESEM and OM images of the disk-3 type showing the CoFe_2O_4 disks in the PbTiO_3 matrix.

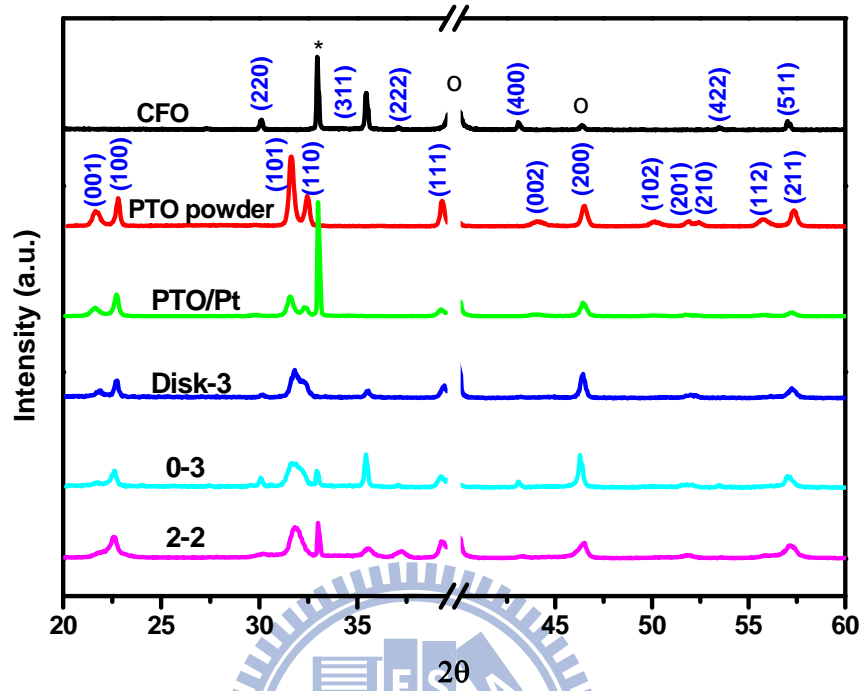


Figure 7.3: X-ray diffraction patterns of the 2-2, 0-3, and disk-3 multiferroics together with those of, pure CFO powder, pure PTO powder, and PTO on Pt/Si film for comparison.

The XRD patterns of the pure CFO and pure PTO powders, and three multiferroic films on Pt/Si substrates taken at RT as shown in Figure 7.3 reveal the correct phases with various planes without obvious secondary phases, and “*” and “O” represent Si and Pt signals from the substrates, respectively. By using the refinement analysis of XRD data, the refined structure parameters were listed in Table 7-1 and Table 7-2. We also define strain as variation in lattice constant in this study.

Table 7-1 The refined lattice parameters of PTO for the pure PTO powder and the films with different types

PTO						
Samples	$I_{(100)} / I_{(001)}$	$a(\text{\AA})$	Strain(%)	$c(\text{\AA})$	Strain(%)	c/a
Powder	1.9875	3.8616		4.0189		1.0407
PTO/Pt/Si	2.3722	3.8869	0.6552	3.9817	-0.9256	1.0244
disk-3/Pt/Si	2.9032	3.8871	0.6604	3.9814	-0.9331	1.0269
0-3/Pt/Si	3.1619	3.8872	0.6629	3.9470	-1.7890	1.0120
2-2/Pt/Si	3.6929	3.9078	1.1964	3.9422	-1.9085	1.0088

Table 7-2 The refined lattice parameters of CFO for the films with different types

CFO		
Samples	$a(\text{\AA})$	Strain(%)
CFO/Pt	8.3873	
disk-3/Pt/Si	8.3620	-0.3016
0-3/Pt/Si	8.3866	-0.0083
2-2/Pt/Si	8.3661	-0.2528

According to Table 7-1, the result of pure PTO powder agrees with the JCPDS-International Center for Diffraction Data No. 78-0298; and its intensity ratio of diffraction peaks (100) and (001) is close to 2, indicating the random orientation. On the other hand, prefer-oriented vertical a -axis growth with the c -axis lying on the substrate surface is obvious in the 2-2 type and the 0-3 type films but is less in the disk-3 type film and pure PTO/Pt/Si film. We also found that the a -axis of PTO matrix is lengthening with the compression of c -axis for all type films and PTO/Pt/Si film. The compression of c -axis is the most obvious in 2-2 type and is the least in PTO/Pt/Si film. The lattice constant of Pt is about 3.9240 Å and that of CFO is

about 8.3873 Å. For PTO/Pt/Si film, the tensile stress of lattice a and the compressed one of lattice c in PTO matrix arise from mismatch of the Pt lattice, whose lattice constant lies in between them. The strain/stress of PTO matrix is due to the interface of PTO and Pt substrate only. However, for three multiferroic samples, the stress in PTO matrix arises from both the interface of PTO and Pt substrate and that of PTO and CFO matrices.

There are more than twice as many lattice constant of CFO (8.3873 Å) to those of PTO (a : 3.8616 Å, c : 4.0189 Å). Having the larger mismatch along a of PTO with CFO than along c , CFO exerts the larger tensile stress on the a -lattice of PTO. Therefore, the PTO matrices in all the CFO-embedded PTO samples are strongly elongated in a -axis that leads to compress in the c -axis for preserving the unit cell volume. Consequently, the decreasing trend of c/a for PTO matrix is not difficult to comprehend as a result of the tensile stress induces a -lattice elongation with the compressive c -axis.

From the information of lattice parameters of PTO matrices in Table 7-1, it is difficult to differentiate the stress/strain due to the interface of PTO and CFO matrices from that of PTO and Pt layer. We therefore predict the lattice parameters of the CFO matrices for all types of samples in Table 7-2 and find that the lattices of CFO matrices are compressed for all types. Because in three multiferroic films the CFO

matrices only bond to the PTO ones, the stresses exerted in CFO matrices should be only on the interfaces of PTO and CFO matrices. As mentioned previously, more than twice as many lattice constant of CFO to the PTO ones, PTO exerts compressive stress on the lattice of CFO. From Table 7-2, we found the most obvious compression is in the disk-3 type and the least compression in the 0-3 type for these three types of samples. Therefore, the strain/stress caused by the lattice mismatch between the CFO and PTO matrices is the most pronounced in the disk-3 type and is the least in the 0-3 type that will be further confirmed by micro-Raman spectroscopy later on..

The ME coupling effect resulting from the elastic bonding at the interface [1, 2, 3] should also be transmitted through the stress/strain between the interface of CFO and PTO matrices. The magnetic properties in our CFO/PTO multiferroics should be influenced by the stress/strain, thus it is more important to directly observe the interfacial stress/strain using another appropriate probe of local behavior besides the peak shifts of XRD diffractions of CFO which covers mm^2 area and sub- μm depth. In the following study, we used SQUID to investigate the ferromagnetic properties in our multiferroics and the micro-Raman measurement system to probe the stress dependence of behavior of interfacial phonon, which is sensitive to the interfacial stress/strain.

7.2 Magnetic properties

We measured the RT magnetizations by applying the magnetic fields perpendicular and parallel to the surface of the films. Figure 7.4 shows the measured magnetic hysteresis loops for pure cobalt ferrite and different geometrical CFO contained multiferroics. The out-of-plane (Figure 7.4(a)) and the in-plane (Figure 7.4(b)) hysteresis loops of the 0-3 type are similar to that of the pure CFO powder in the values of coercivity H_c . It may result from the 0-3 type sample was made of dispersing pure CFO particles in PTO matrix, in which the chemical bonding between CFO particles and PTO matrix might not form. However, the saturation magnetization M_s of the 0-3 type for both the in-plane and out-of-plane loops is lower than that of the pure CFO powder. This discrepancy should result from the inaccuracy for estimating CFO volume % in the 0-3 type. Owing to inability to estimate CFO volume % of different geometric CFO contained multiferroics, we will not compare the values of saturation magnetization M_s among different types of samples.

The out-of-plane coercivity H_c under the positive magnetic field in Figure 7.4 are about 0.97, 1.01, 1.51, and 0.20 kOe in pure cobalt ferrite powder, 0-3, 2-2, and disk-3 types, respectively. Notice that the out-of-plane coercivity H_c of the disk-3

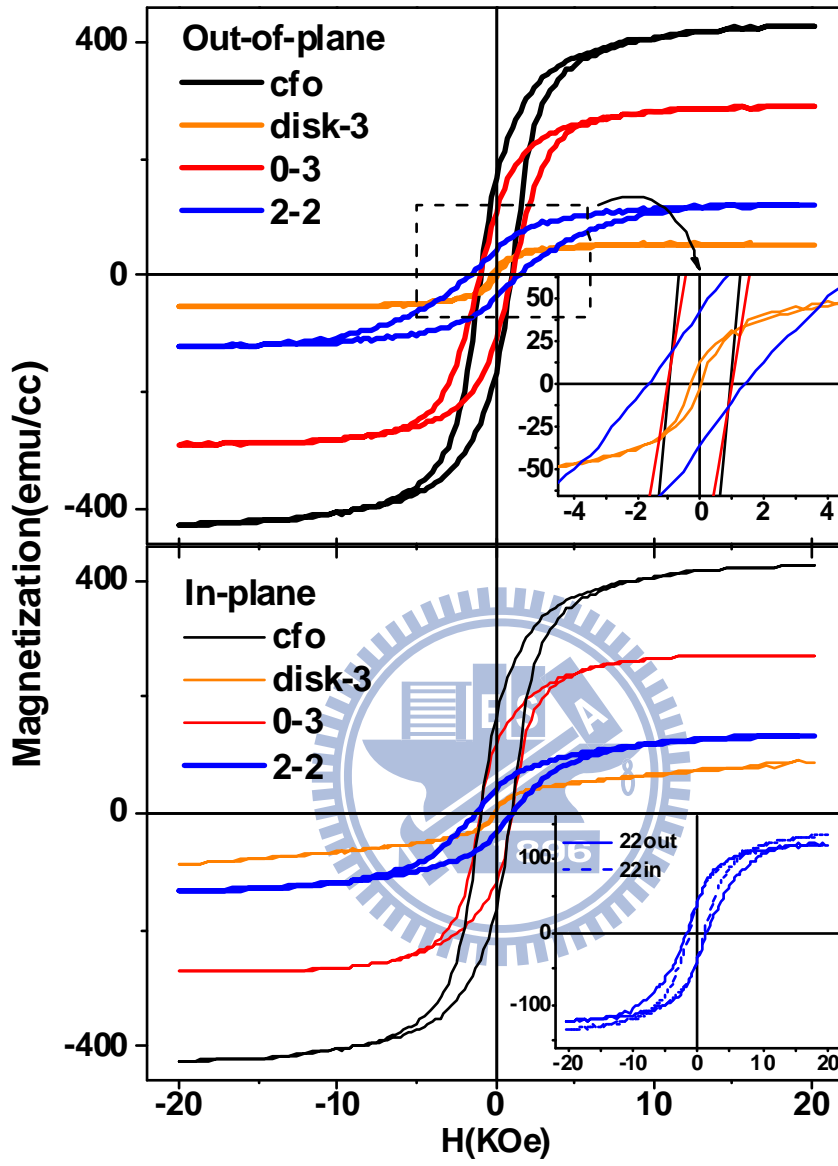


Figure 7.4: Hysteresis loops of out-of-plane and in-plane magnetization for the pure CFO, 0-3, 2-2, and disk-3 samples.

type is the lowest having only 0.2 kOe. O'Handley [8] proposed that the coercivity

H_c decreases with increasing defect size in fuzzy defect case, which is often defined

by strain fields. Wan *et al.* [2] also reported that the easier magnetization characteristic should contribute to the increase of the total magnetocrystalline energy related to the magnetoelastic coupling due to the compressive stress in the CFO phase caused by the lattice mismatch between the CFO and PTO matrices from our XRD results. Zhang *et al.* [9] also considered the reason that the lattice mismatch induces strains can indeed alter the magnetic properties.

The ME effect involves dynamic magnetoelastic coupling, key requirements for the ferrite phase are unimpeded domain motion and a large magnetostriction λ [10]. A soft initial permeability (low coercivity) is the main ingredient for strong ME effects. In magnetically hard CFO bulk, however, one has the disadvantage of a large coercive field that limits domain rotation. Since the ME effect originates at the interface, it is important to consider the influence of growth-induced stress and its effect on dynamics of domain motion. The lower inset of Figure 7.4 shows the hysteresis loops of the 2-2 type measured in-plane and out-of-plane with an external field up to 20 kOe. It reveals that the in-plane coercivity H_c is smaller than the out-of-plane one with nonsymmetrical values for the negative and the positive magnetic field. The differences in nonsymmetrical H_c reveal that it is easier to rotate the magnetic domain in horizontal direction than in vertical direction. It should contribute to the increase of the total magnetocrystalline energy related to the

magnetoelastic coupling due to the compressive stress in the CFO phase caused by the lattice mismatch between the CFO and PTO matrices [8].

As the coupling interaction between ferroelectric and ferromagnetic phases in the multiferroic is still an elastic interaction, the constitutive equations for the coupling magnetic-mechanical-electric interactions in multiferroics can be expressed by direct notation for tensors as [11]

$$\mathbf{D} = e\epsilon + \kappa\mathbf{E} + \alpha\mathbf{H} + \mathbf{P}_s, \quad (7-1)$$

$$\mathbf{B} = \mu(\epsilon, \mathbf{E}, \mathbf{H}) \mathbf{H} + \mathbf{M}_s, \quad (7-2)$$

where e , ϵ , κ , α , μ , \mathbf{D} , \mathbf{E} , \mathbf{B} , \mathbf{H} , \mathbf{P}_s , and \mathbf{M}_s are the piezoelectric coefficient, strain, dielectric constant at strain, magnetoelectric coefficient, permeability, electric displacement, electric field, magnetic induction, magnetic field, spontaneous polarization and magnetization, respectively. The magnetization \mathbf{M}_s in multiferroics is dependent on the direction of electric displacement, therefore, phenomena that the loop slightly shifts toward negative magnetic field should come from the ME effect between ferroelectric and ferromagnetic matrices.

We observed in Figure 7.4 the more apparent softening of initial permeability or low coercivity and asymmetric in-plane hysteresis loop for the disk-3 type. The in-plane negative and the positive coercive field H_c of the 2-2 type are about -1287.62 and 949.09 Oe; and those of the disk-3 type are -187.74 and 123.64 Oe. The

variation in the difference between the negative and the positive coercive field H_c of the disk-3 type is 34%, which is larger than that of the 2-2 type of 26%.

We speculate that the absence of saturation magnetization M_s in-plane loops of the disk-3 and 2-2 types may be due to the coupled interaction between ferromagnetic and ferroelectric materials. Under the magnetization process, the change of CFO structure resulting from magnetostriction could produce stress on the surrounding PTO structure. As the magnetic field increases, the strain imposed by CFO on PTO will increase. The strained PTO bonding along the interface should eventually affect the boundary structure of CFO matrix. Consequently, it not only lowers the values and increases asymmetry of the coercivity H_c but also causes more difficult to saturate the magnetization of CFO. Since the disk-3 type consists of the self-assembled CFO disks embedded in PTO matrix, it has the largest stress/strain due to the lattice misfit and the strongest chemical bonding between the CFO and PTO matrix, we observed the lowest H_c , the largest asymmetry of H_c , and the most difficult saturation of CFO magnetization in the disk-3 type.

7.3 Relationship between interfacial phonon behavior and magnetic properties

PTO belongs to the $C_{4v}^1 (P4mm)$ space group with tetragonal phase at RT [12], it has $3A_1(TO)$, $3E(TO)$, $3A_1(LO)$, and $3E(LO)$ Raman active modes. Figure 7.5 shows

the RT Raman spectra of the phonon modes of PTO assigned according to Foster *et al.* [13] to clarify the structural variation of PTO powder on Si (PTO/Si), PTO film on Pt pre-coated Si (PTO/Pt/Si), and three multiferroic films on Pt/Si substrates. $A_1(\text{TO})$

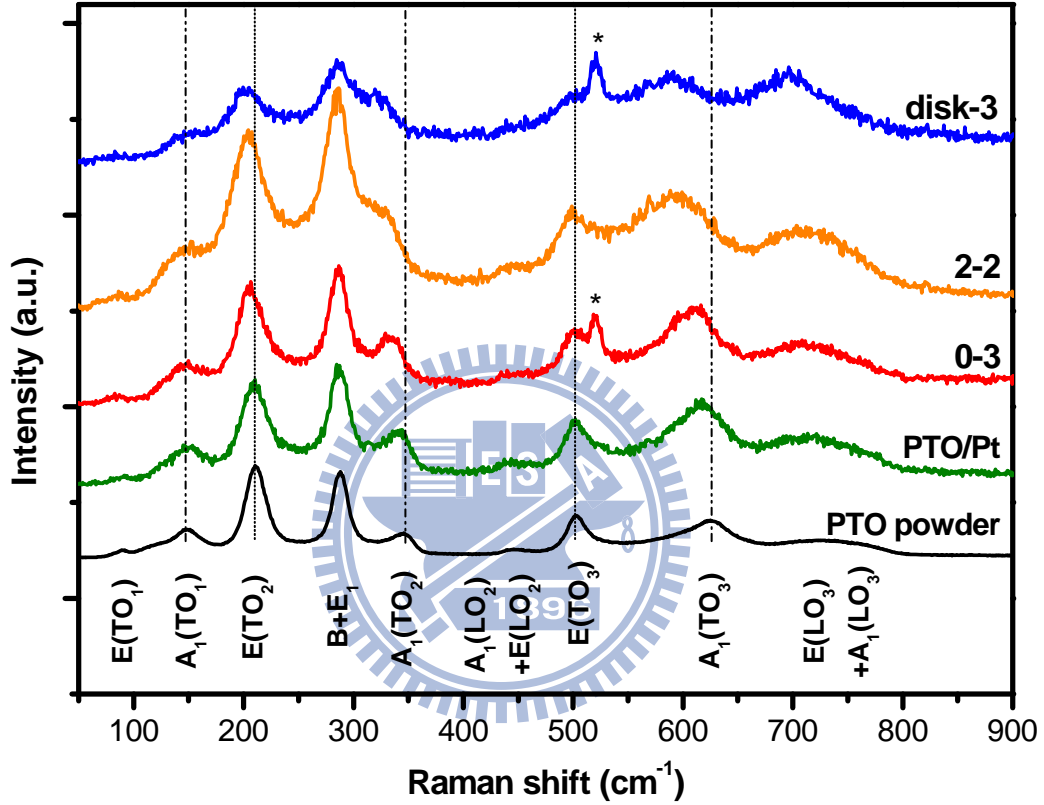


Figure 7.5: Micro Raman spectra of disk-3, 2-2, 0-3 multiferroics together with those of PTO on Pt/Si, and PTO powder for comparison.

mode is especially interesting, since the $A_1(\text{TO})$ mode consists of displacements of Ti and oxygen ions relative to the lead ions and is, with the $E(1\text{TO})$ mode, a soft mode.

On the other hand, CFO belongs to cubic phase (Space Group: $Fd3m$ (227)) [14-16]

and the Raman signal is hardly detected. Therefore, we shall concentrate on change

of Raman modes of PTO in various types of CFO/PTO structures.

The phonon modes have remarkable shifts in their frequencies for different types, the A_1 modes especially. The $A_1(\text{TO}_1)$, $A_1(\text{TO}_2)$, and $A_1(\text{TO}_3)$ modes of PTO having frequencies at 150, 350, and 630 cm^{-1} show significantly red-shifted and broadened while the E modes vary just marginally in all multiferroics as compared with the pure PTO powders. We speculated that the reasons for the above-mentioned frequency shifts are not from structure change but from the strain either between structures and substrate or intra-structures. The significant shift of A_1 mode with invariable E mode in this study is unlike the lattice dynamics of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ polycrystalline powder reported by Kuo *et al* [17], in which the presence of substitution Sr^{2+} ions on PbTiO_3 yields structure changes so that shifts in all types of phonon modes.

In order to investigate the mechanism of strain, we need to recognize whether the shift of A_1 mode in multiferroics in this study is due to strains between substrate and structure or intra structures by referring to the spectra of PTO on Pt and Si substrates. In Figure 7.5, we observed that all phonon modes of PTO on Pt and Si substrates are almost invariable or vary just a little bit as compared with ones of the pure PTO powder. It indicates that shift of phonon mode of PTO in three multiferroic samples do not result from interaction between substrates and PTO but from the interfacial stress between CFO and PTO matrices.

In order to further investigate the behavior of A_1 modes belonging to the PTO matrix in three multiferroic samples, Lorentzian line fitting was adopted to resolve the overlapping modes. The fitting results are in good agreement with experimental spectra (not shown) and the peak positions of $A_1(\text{TO}_1)$, $A_1(\text{TO}_2)$, and $A_1(\text{TO}_3)$ of various types were plotted in Figure 7.6. For PTO matrix, the results of XRD indicate prefer-oriented vertical a -axis growth with the c -axis lying. The oxygen atoms and cations (Pb and Ti) of PTO oscillate along c -axis in the $A_1(\text{TO})$ modes, while the atoms oscillate on the plane composed by a and b axes in the E modes. Undoubtedly, the A_1 modes, describing the vibration of atoms along c direction, could be significantly influenced by the strains resulting from the interfacial mismatch of PTO with CFO. However, owing to deficit of interaction with ferromagnetic materials, the behavior of E modes just like the pure PTO films having slightly shift in positions of their spectral peaks.

Further analyzing the phonon modes in three multiferroic samples, we observed the largest shift of $A_1(\text{TO}_2)$ and $A_1(\text{TO}_3)$ in the disk-3 type, whereas the smallest shift in the 0-3 type. It indicates that the Raman shift in the disk-3 type is due to the stronger coupling between BTO and CFO matrices resulting from existing most a -domain [18, 19], in which the c -axis of PTO matrix strongly bonds with CFO one. This result agrees well with the results of magnetic properties of multiferroics that

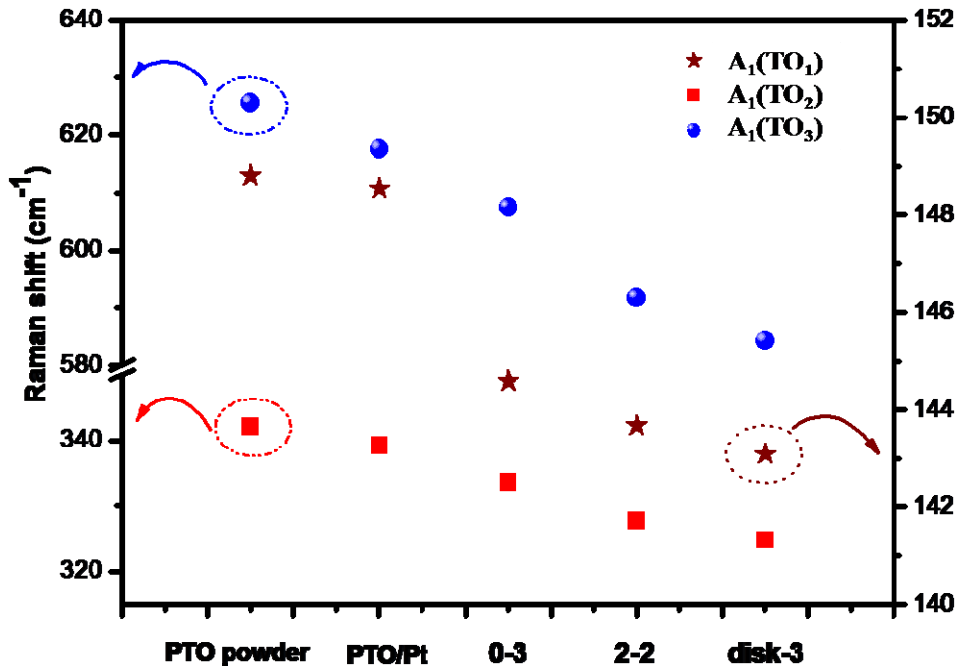


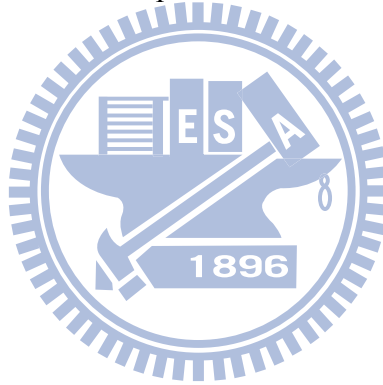
Figure 7.6: The fitted Raman shift of the $A_1(TO_3)$, $A_1(TO_2)$, and $A_1(TO_1)$ modes as a function of film type.

depends on the interface stress between CFO and PTO matrices which is also sensitive to the behavior of interfacial phonons. Therefore, the micro-Raman spectroscopy is a good probe for investigating the multiferroics and is under the way to study interfacial phonons under the applied magnetic field.

7.4 Summary

The characteristics of three different geometric forms of the $PbTiO_3-CoFe_2O_4$ multiferroics fabricated by the simple solution method has been investigated using OM, FESEM, XRD, SQUID, and micro-Raman spectroscopy. The analysis of the

magnetic and Raman measurements under different geometric forms indicates the dependence of magnetic property and behavior of interfacial phonons on stress/strain due to the lattice misfit and the chemical bonding at the interface between CoFe_2O_4 and PbTiO_3 matrices. The largest nonsymmetrical coercivity H_c and the absence of saturation magnetization M_s of CoFe_2O_4 consist with the largest shift of $A_1(\text{TO}_2)$ and $A_1(\text{TO}_3)$ modes of PbTiO_3 in the disk-3 type, the self-assembled CoFe_2O_4 disks embedded in PbTiO_3 matrix, than the other types of the CoFe_2O_4 and PbTiO_3 multilayered structure and the CoFe_2O_4 particles embedded in PbTiO_3 matrix.



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Chapter 8 Conclusion and Prospective

8.1 Conclusion

The major accomplishment of this work was the study on the influence of perovskite structure by substitution, size and strain effects on characteristics of ferroics, namely, Er^{3+} -doped $\text{Pb}_{0.8}\text{La}_{0.2}\text{TiO}_3$, Er^{3+} - Yb^{3+} codoped ABO_3 perovskites with different degrees of tetragonality (including PbTiO_3 , BaTiO_3 , and SrTiO_3), BaTiO_3 nanoparticles, and PbTiO_3 - CoFe_2O_4 multiferroics synthesized by chemical solution methods. All the results and discussions are summarized as follow:

Due to the substitution effect, the $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) system exhibits structural ordering transition points at $x \sim 0.4-0.5$ and $x \sim 0.75$ and $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ (PST) exhibits one structural ordering transition at $x \sim 0.5$. Our investigations indicate that the lattice ratio c/a is around 1.002 for the undoped $\text{Pb}_{0.8}\text{La}_{0.2}\text{TiO}_3$ (PLT) polycrystalline films, and slightly increases and then declines to around 1.001 at 7 mol% Er^{3+} -dopant, and then increases to 1.007 for the samples with 9 and 15 mol% in sol-gel-derived Er^{3+} -doped PLT polycrystalline films. However, our investigations also found that the maximum emission was observed at 7 mol% but no emission for Er^{3+} dopant larger than 9 mol%, which possesses the higher tetragonality than for the 7 mol% one. From the results of Raman spectra, the peak attributed to $\text{A}_1(\text{TO}_3)+\text{E}(\text{TO}_3)$ phonon

modes keeps almost unchanged as Er^{3+} concentration increases from 0 mol% to 7 mol%, but vanishes for samples with 9 and 15 mol% Er^{3+} concentrations. The disappearance of Raman modes due to weak disorder effect (resulting from a displacement of Ti ion is caused by decreasing the crystal diameter to result in the formation of a centrosymmetric structure with increasing Er^{3+} concentration. Finally, our investigation show destruction to a displacement of Ti in the short-range structure by observing the disappearance of fluorescence emission and Raman signals when the Er^{3+} concentration exceeds 7 mol% in sol-gel-derived Er^{3+} -doped PLT polycrystalline films.

For another study on the substitution effect, the mechanism of upconversion (UC) emission in Er^{3+} - Yb^{3+} co-doped ABO_3 perovskites was discussed. As increasing Yb^{3+} co-doped concentrations in 6 mol% Er^{3+} doped PbTiO_3 , BaTiO_3 , and SrTiO_3 polycrystalline powder samples synthesized by sol-gel method, we have observed the room-temperature green UC emission at 550 nm being quenched by the simultaneously enhanced red UC emission at 660 nm under the 980-nm laser excitation. For codoping Yb^{3+} ions up to 6 mol% in PbTiO_3 and only Er^{3+} doped PbTiO_3 samples, which still possess relatively large tetragonality, the green UC emission is still much stronger than red one. In these cases, both the UC emissions are dominated by the two-photon process. But, as further increasing the Yb^{3+} ion

concentration, the crystal structures tend to become cubic phase with enhancing red UC emission and almost diminishing in green emission. Since the pure BaTiO₃ crystal exhibits weaker tetragonality than PbTiO₃, the stronger red emission and weaker green one were expected at the lower codoped Yb³⁺ concentration in BaTiO₃ system than in PbTiO₃ one. The observed quench of green radiation accompanied with enhancement of red radiation should be due to the efficient energy back-transfer (EBT) process by raising Yb³⁺ concentration. The efficient EBT process requires not only Yb³⁺ concentration but also level match of $^4S_{3/2} \rightarrow ^4I_{13/2}$ in Er³⁺ and $^2F_{7/2} \rightarrow ^2F_{5/2}$ in Yb³⁺ under assistance of Boltzmann distributed population within the manifold of $^4S_{3/2}$ or/and $^4I_{13/2}$ (Er³⁺) state affected by the crystal field with different symmetries. As a result, declining tetragonality results in the centrosymmetric crystal field for high Yb³⁺-ion concentration to achieve the level match required for the EBT process that may be difficult to be fulfilled with asymmetric crystal field in the tetragonal phase.

Additionally, we report, in contrast to the substitution effect, the size effect on structure for BaTiO₃ nanoparticles synthesized by the glycothermal method. We applied a single tetragonal-phase model to refine the crystal structure and the coupled-phonon model to analyze the coupled $A_1(\text{TO})$ modes upon particle size decreasing from 140 nm to 30 nm. Our investigations indicate that the weak strength

of coupling between $A_1(\text{TO}_1)$ and $A_1(\text{TO}_2)$ leads to a change from a spectral dip at 180 cm^{-1} for $A_1(\text{TO}_1)$ phonon to a peak at the same position and found that the approach of uncoupled ω_2 and ω_3 with less tetragonality due to decreasing the particle size results in slightly increasing in ω_{23} . The larger coupling strength repels these two modes farther so that the less reducing in spectral separation. According to the results of decomposition, we also observed the decreasing LO-TO splitting with the decline of tetragonality and expansion of the unit-cell volume. And the change of unit-cell volume is the dominant mechanism for the tendency of the LO-TO splitting in BaTiO_3 system without complication of ion replacement.

Finally, regarding the strain effect, the characteristics of three different geometric forms of multiferroics fabricated by the simple solution method has been investigated using optical microscopy (OM), field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), superconducting quantum interference device (SQUID), and micro-Raman spectroscopy. We report on the stress dependence of the behavior of interfacial phonon and the magnetic properties in three multiferroics consisting of the different geometric shapes of ferromagnetic CoFe_2O_4 (CFO) embedded in ferroelectrics PbTiO_3 (PTO). Their energy of interfacial phonon and ferromagnetic properties depend on stress due to not only the lattice misfit but also the degree of chemical bonding at the interface between CFO and PTO matrices. The

disk-3 type structure, the self-assembled CFO disks embedded in PTO matrix, illustrates the strong elastic interactions between the two phases. The larger nonsymmetrical coercivity H_c and the absence of saturation magnetization M_s of CFO matches with the larger Raman shift of $A_1(\text{TO}_2)$ and $A_1(\text{TO}_3)$ modes of PTO found in the disk-3 type than the other types of the CFO and PTO multilayered structure and the CFO particles embedded in PTO matrix.

8.2 Prospective

In recent years, there are many theoretical studies and many experimental reports on physical properties dramatically influenced by various effects, such as substitution, shape, size, strain, etc. The continuous advance in miniaturization of devices, fine structure as a ferric material have been applied in advanced electric devices such as ferroelectric random access memory (FRAM), multilayer ceramic capacitor (MLCC), and in other integrated devices. Among these effects, the size dependence of properties with different shapes is presently one of the major research topics.

It is necessary for us to synthesize various high purity perovskite nanocrystals with uniform size and homogeneous shape. BaTiO_3 nanoparticles with uniform size were synthesized by glycothermal treatment and size-dependent properties were

discussed. Furthermore, much effort has been recently put into morphology controlled synthesis of crystalline ferroelectric oxide materials because the effects of a large nonlinear optical coefficient and a large dielectric constant are highly dependent on the size and shape. [1] Of various nanostructures low-dimensional nanostructures, such as nanoparticles, nano-wires, nanocubes and nanorods, have especially received great interest from the scientific and engineering communities [2, 3] because these structures exhibit distinct physical and chemical properties from bulk materials due to their smaller particle sizes and larger surface-to-volume ratios. Thus, many studies have probed the optical, [4] electronic, [5] and magnetic [6] properties of these nanostructures. Scientists expect one-dimensional (1D) structures, nano-rods, and nanowires to provide new alternatives for developing devices because of recent theoretical studies from the first principles and experiments on ferroelectric nanowires. This possibility primarily arises because the size-dependent ferroelectricity of 1D structures functions with much smaller diameters than do 0-D structures (nanoparticle), and the Curie temperature is reduced as the diameter of the 1D structure is reduced. [7-9] Wang *et al.* [10] also reported a method for studying the axial poling and switching in 1D BaTiO₃ nanowires by using piezoresponse force microscopy (PFM).

Therefore, we have proposed the novel insight into the nature of low-dimensional ABO_3 nanostructures related to the size and shape experimentally and theoretically. Because the ABO_3 1D nanostructure is difficult to obtain due to the isotropy of the ABO_3 crystal structure and the anisotropy of the 1D structure, the control of nucleation and growth of 1D nanostructure materials is still a big challenge. Presently, the three-series products (BT-1, spherical $BaTiO_3$; BT-2, cube-shaped $BaTiO_3$; and BT-3, rod-shaped $BaTiO_3$) were synthesized roughly with different barium and multishaped titanium precursors. (see Figure 8.1)

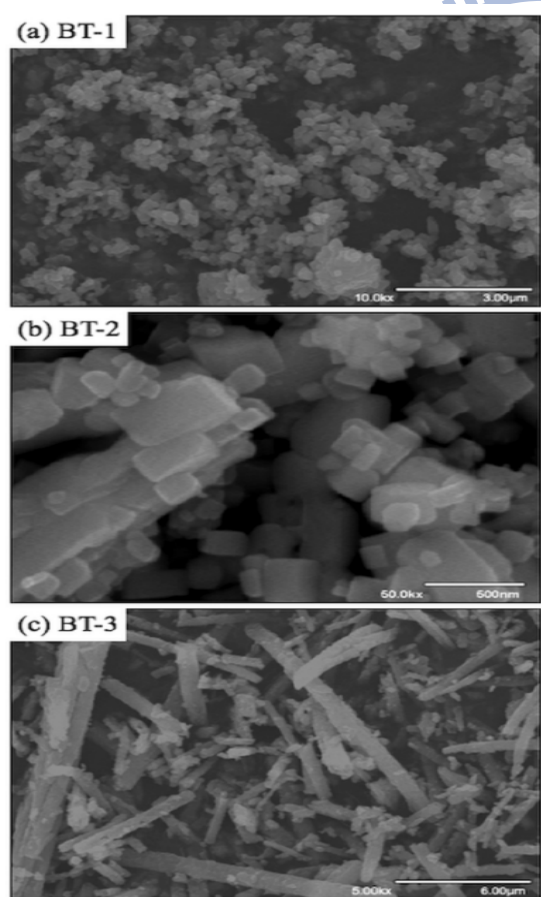


Figure 8.1: SEM images of the three-series products: BT-1, BT-2, and BT-3.

Magnetoelectric (ME) effect in multiferroics is an important mechanism in applications of transducers, actuators, and sensors. The ME coupling in bi-ferroic (e.g., $\text{PbTiO}_3\text{-CoFe}_2\text{O}_4$) self-assembled epitaxial nanostructures occurs indirectly via the elastic coupling. Although theoretical studies [11-13] point out the importance of the residual strains in the ME coupling, there is limited information on the lattice strains in ferromagnetic nanostructures in a ferroelectric matrix. We also reported on the relationship between local behavior of interfacial phonons and ferromagnetic properties in bi-ferroic ($\text{PbTiO}_3\text{-CoFe}_2\text{O}_4$). Their energy of interfacial phonons and ferromagnetic properties depend on stress due to not only the lattice misfit but also the degree of chemical bonding at the interface between matrices. At the same time, we still hope a detailed study of lattice strains for bi-ferroic nanocomposite heteroepitaxial structure could be continued experimentally and theoretically in the future based on the accomplishment have been done in this thesis.

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Publication list

I. Refereed Journal Publications:

1. **Tung-Ching Huang**, Mei-Tan Wang, Hwo-Shuenn Sheu, and Wen-Feng Hsieh, “Size-dependent lattice dynamics of barium titanate nanoparticles”, *Journal of Physics-Condensed Matter*, 19, 476212 (2007).
2. **Tung-Ching Huang** and Wen-Feng Hsieh, “Er-Yb Codoped Ferroelectrics for Controlling Visible Upconversion Emissions”, *Journal of Fluorescence*, 19, 511 (2009).
3. **Tung-Ching Huang** and Wen-Feng Hsieh, “Destruction of the short-range disorder due to erbium doping in $\text{Pb}_{0.8}\text{La}_{0.2}\text{TiO}_3$ films”, *Journal of Raman Spectroscopy*, accepted for publication (2009).
4. Kuan-Chih Huang, **Tung-Ching Huang**, and Wen-Feng Hsieh, “Morphology-Controlled Synthesis of Barium Titanate Nanostructures”, *Inorganic Chemistry*, 48(19):9180-4 (2009).

II. Conference:

1. **Tung-Ching Huang** and Wen-Feng Hsieh, “Decreasing Splitting of LO-TO Phonons in BaTiO_3 Nanoparticles Due to Unit-cell Volume”, in 2006 MRS Spring Meeting, San Francisco, USA, post paper (2006).
2. **Tung-Ching Huang** and Wen-Feng Hsieh, “Quenching green and enhancing red upconversion emissions of Er^{3+} by reducing tetragonality in Yb^{3+} co-doped ferroelectrics”, 2008 E-MRS Fall Meeting, Warsaw, Poland, oral paper (2008).
3. **Tung-Ching Huang** and Wen-Feng Hsieh, “Destruction to the short-range disorder due to erbium dopant in $\text{Pb}_{0.8}\text{La}_{0.2}\text{TiO}_3$ poly-crystalline films”, in Conference of Year 2005 Annual Meeting of Chinese Physical Society, Kaoshiung, TAIWAN, oral paper (2005).
4. Mei-Tan Wang, **Tung-Ching Huang**, and Wen-Feng Hsieh, “Grain size effect on the lattice dynamics of barium titanate nanoparticles” in Conference of Year 2007 Annual Meeting of Chinese Physical Society, Chunli, TAIWAN, oral paper (2007)
5. **Tung-Ching Huang**, Chung-Ting Li, Shou-Yi Kuo, and Wen-Feng Hsieh, in Proceedings of Optics and Photonics Taiwan'02, Taipei, TAIWAN, post paper (2002)