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STRUCTURE, SITE OCCUPATIONS AND DIELECTRIC PROPERTIES OF LA AND TM CO-DOPED BaTiO₃ CERAMICS

Yue Liang^{1,2}, Dayong Lu^{1*}¹Key Laboratory for Special Functional Materials in Jilin Provincial Universities, Jilin Institute of Chemical Technology Chengde Street 45, Jilin, China²College of Chemistry, Jilin University, Qianjin Street 2699, Changchun, China*Corresponding Author Email: dylu@jlicet.edu.cn

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ARTICLE DETAILS

ABSTRACT

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The nominal (Ba_{1-x}La_x)(Ti_{1-x}Tm_x)O₃ ($x = 0.01-0.15$) (BLTTm) ceramics were prepared at 1400 °C using a mixed-oxides method. The structure, solubility limit, site occupations, and dielectric properties were investigated using X-ray diffraction (XRD), Raman spectroscopy (RS), electron paramagnetic resonance (EPR), and dielectric measurements. The solubility limit of La/Tm in the BaTiO₃ lattice was determined by XRD to be $x = 0.08$. BLTTm has a tetragonal perovskite structure for $x \leq 0.03$ and a pseudo-cubic structure for $0.05 \leq x \leq 0.08$. The dielectric thermal behavior of BLTTm with $x = 0.05$ satisfied X6T specification, with $\epsilon'_{RT} = 1756$ and a very low $\tan \delta (< 0.02)$ below 100 °C. Tm³⁺ ions in BLTTm exhibited an asymmetric amphoteric behavior. Both reduction in Mn impurities of Mn⁴⁺/Mn³⁺ to Mn²⁺ and creation of high-intensity Ti vacancies are responsible for the very low $\tan \delta$ in BLTTm with $x = 0.05$.

KEYWORDS

La and Tm co-doped BaTiO₃ ceramics, site occupations, X-ray diffraction, dielectric properties, electron paramagnetic resonance.

1. INTRODUCTION

Since the discovery of high-permittivity La/Ce co-doped barium titanate ceramics with Y5V specification ($-82 \% \leq (\epsilon' - \epsilon'_{RT})/\epsilon'_{RT} \leq +22 \%$ in a temperature range -30 to 85 °C) in 2006, double rare-earth-doped BaTiO₃ ceramics were widely developed [1-9]. Some ceramics are applied in the luminescent field [2,3]. Most ceramics are applied in the dielectric field, such as BaTiO₃ co-doped with La/RE (RE = Tb, Dy, Ho, and Lu; this kind of ceramics requires higher sintering temperatures ($T_s \geq 1400$ °C) and both dopants can be sufficiently incorporated into the BaTiO₃ lattice [5-8]. The high-permittivity specifications above Y5V are often achieved in this kind of ceramics. Another kind of ceramics is core-shell structured ceramics prepared at low sintering temperatures ($T_s \leq 1320$ °C), such as La/Tm co-doped BaTiO₃ [9]. The La/Tm dopants are not incorporated into the BaTiO₃ lattice but locate on the surfaces of ferroelectric BaTiO₃ particles to form shells. This kind of ceramics generally satisfies X7R specification ($(\epsilon' - \epsilon'_{RT})/\epsilon'_{RT} \leq 15 \%$ in a range -55 to 125 °C). However, La/Tm co-doped BaTiO₃ ceramics with sufficient dopants incorporations has been never explored.

In this work, La/Tm co-doped BaTiO₃ ceramics were prepared at $T_s = 1400$ °C so as to form sufficient dopants incorporations. The structure, solubility limit, site occupations, and dielectric properties of BLTTm were investigated using XRD, RS, EPR, and dielectric measurements. The EPR technique was employed to explore vacancy defects and the site occupations of La and Tm in BLTTm.

2. EXPERIMENTAL

The initial materials were reagent-grade BaCO₃, TiO₂, La₂O₃, and Tm₂O₃. Ceramics were prepared according to the nominal formula (Ba_{1-x}La_x)(Ti_{1-x}Tm_x)O₃ ($x = 0.01, 0.03, 0.05, 0.08, 0.09, 0.15$) (abbreviated BLTTm) using a conventional mixed oxide method with the same conditions as described

elsewhere [1]. The final sintering condition was chosen as $T_s = 1400$ °C for 12 h in air.

Powder XRD measurements were performed between $20^\circ \leq 2\theta \leq 85^\circ$ and in steps of 0.02° using a DX-2700 X-ray diffractometer (Dandong Haoyuan) at room temperature (RT). All XRD data were collected at a collecting rate of 3 s per step. Unit-cell volume was calculated by software package (Accelrys Inc.) using Cu K α_1 radiation ($\lambda = 1.540562$ Å). Raman spectra of ceramics powders were used a LabRAM XploRA Raman spectrometer (Horiba Jobin Yvon) at room temperature, with a 532 nm laser. Temperature dependences of the dielectric permittivity and the dielectric loss were measured at 1 kHz from -75 to 200 °C at a heating rate of 2 °C/min using a Concept 41 Dielectric/Impedance spectrometer (Novocontrol) with an applied voltage of 1 V. EPR spectra were measured at RT using an A300 electron-spin resonance spectrometer system (Bruker BioSpin GMBH) at an X-band frequency of 9.86 GHz. The gyromagnetic factor (g) was calculated by the relationship $h\nu_0 = g\beta H$, where h is the Planck constant ($h = 6.626 \times 10^{-34}$ J·s), ν_0 is the microwave frequency, β is the Bohr magneton ($\beta = 9.262 \times 10^{-24}$ J/T), and H is the magnetic field strength.

3. RESULTS AND DISCUSSION

3.1 Crystalline Structure

The powder XRD patterns of BLTTm are shown in Figure 1. The main perovskite phase had been formed in all samples. BLTTm with $x \leq 0.03$ crystallized in the single phase and had a tetragonal perovskite structure; whereas for $0.05 \leq x \leq 0.08$, BLTTm converted to a pseudo-cubic structure.

When $x \geq 0.09$, a secondary phase of a small amount of Tm₂O₃ (JCPDS Cards No. 82-2416) remained in BLTTm, as shown in Figure 2. This result indicates that the solubility limit of La/Tm in BaTiO₃ was estimated to be $x = 0.08$.

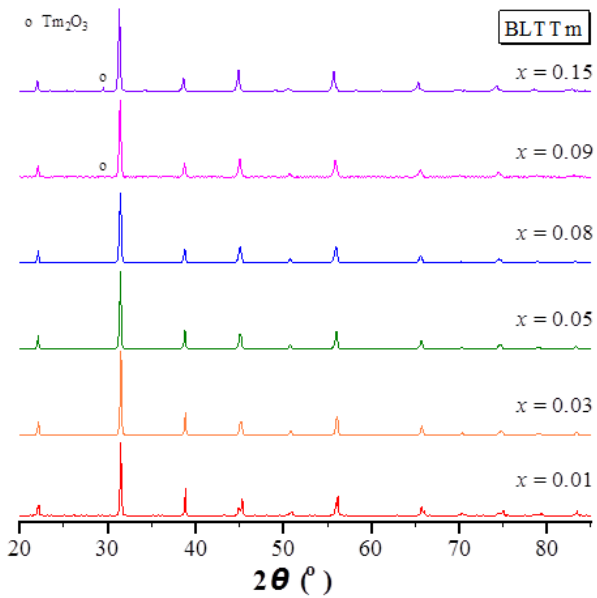


Figure 1: Powder XRD patterns of BLTTm ceramics with $x = 0.01$ – 0.15 .

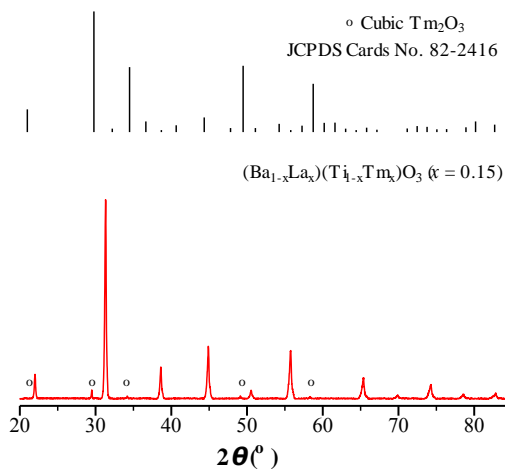


Figure 2: Powder XRD patterns of BLTTm with $x = 0.15$, and the simulated XRD pattern of the cubic Tm₂O₃.

The variations in lattice parameters (a , c) and unit-cell volume (V_0) as functions of x are shown in Figure 3. It has been known that La³⁺ is exclusively substituted for Ba-site [5–8]. The V_0 of BLTTm is greater than that of the tetragonal BaTiO₃ (JCPDS Cards No. 5-626) and increased with increasing x , revealing that Tm³⁺ ions were substituted dominantly for Ti-sites because 6-coordinate Tm³⁺ (0.88 Å) is larger than Ti⁴⁺ (0.605 Å) [10].

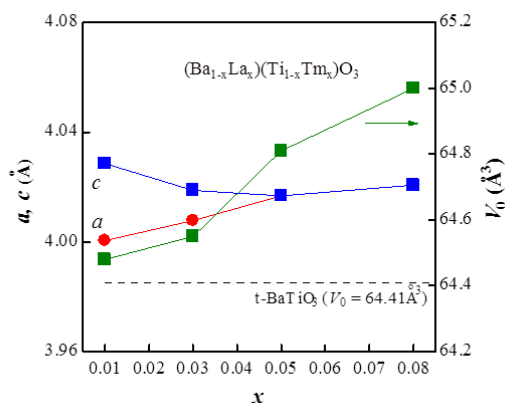


Figure 3: Variations in lattice parameters (a , c) and V_0 as a function of x for BLTTm

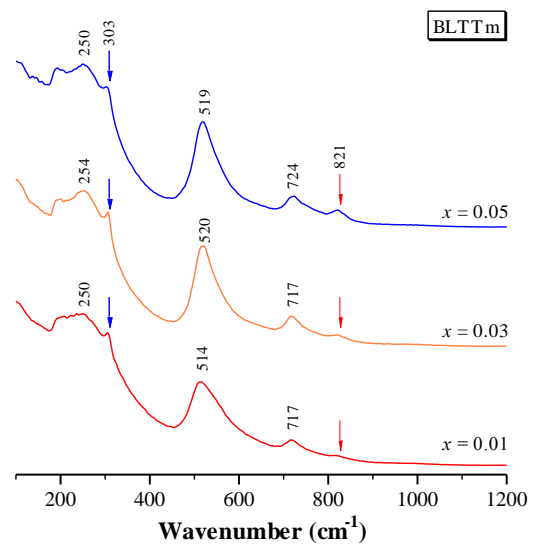


Figure 4: Raman spectra of BLTTm at RT.

The Raman spectra of the single-phase BLTTm at RT are shown in Figure 4. The tetragonal BaTiO₃ exhibits four common optical modes: ~ 260 [A_1 (TO_2)], ~ 305 [$B_1 + E$ ($TO+LO$)], ~ 520 [A_1 (TO_3)], and ~ 720 [A_1 (LO_3) + E (LO_3)], respectively [11]. The sharp band at 303 cm^{-1} is an indication of the ferroelectric tetragonal phase. The presence of this sharp band for $x = 0.05$ reveals that some ferroelectric phases such as tetragonal or orthorhombic existed in the pseudo-cubic BLTTm with $x = 0.05$. An additional band appeared at 821 cm^{-1} , which originates from the Raman charge effect [12]. The intensity of this band increased with increasing x , indicating an increase in the incorporation amount of both A-site and B-site dopants, which is in accordance with the XRD result.

3.2 Dielectric Properties

The temperature dependences of the dielectric permittivity (ϵ') and the dielectric loss ($\tan \delta$) for BLTTm with $x = 0.05$ are shown in Figure 5. The RT permittivity is $\epsilon'_{RT} = 1756$. This sample exhibited a more flattened diffuse phase transition (DPT) behavior with a dielectric-peak temperature of $T_m = 42$ °C and a very low $\tan \delta$ (< 0.02) below 100 °C, satisfying X6T specification ($-33\% \leq (\epsilon' - \epsilon'_{RT})/\epsilon'_{RT} \leq +22\%$ in a temperature range -55 to 105 °C) [13].

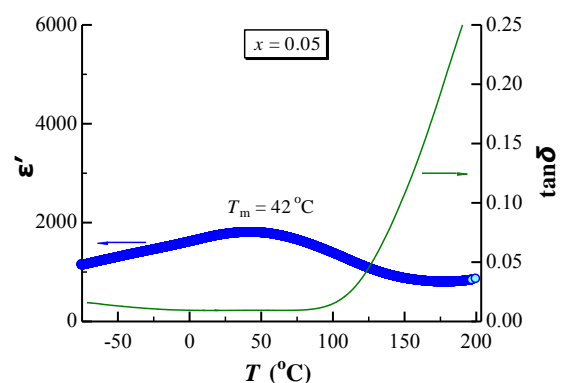


Figure 5: Temperature dependences of ϵ' and $\tan \delta$ for BLTTm with $x = 0.05$, measured at 1 kHz.

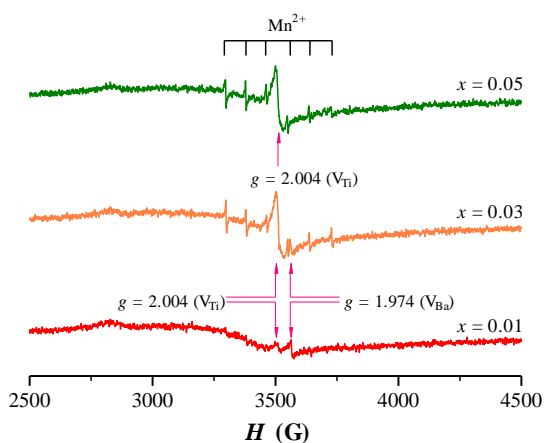


Figure 6: Room-temperature EPR spectra of BLTTm.

3.3 EPR Investigations

The room-temperature EPR spectra of BLTTm are shown in Figure 6. A $g = 2.004$ signal, which is associated with ionized Ti vacancies, appeared in all of the samples, and showed higher intensity for $x \geq 0.03$ [8,11]. This reveals that some Tm^{3+} ions entered Ba-sites in $(Ba_{1-x}La_x)(Ti_{1-x}Tm_x)O_3$, resulting in creation of Ti vacancies. A $g = 1.974$ signal associated with ionized Ba vacancy defects was observed only in BLTTm with $x = 0.01$ and 0.03 [14]. The line intensity of this signal decreased from $x = 0.01$ to 0.03 , and it disappeared at $x = 0.05$. This fact reveals that with Ba-sites were gradually filled with Tm^{3+} with increasing x . This further clarifies that Tm^{3+} in BLTTm exhibited an amphoteric behavior. A Mn^{2+} sextet signal was observed for $x \geq 0.03$. This signal originates from the reduction of Mn^{4+} or Mn^{3+} impurities in ceramics to Mn^{2+} . Thus, both reduction in Mn impurities of Mn^{4+}/Mn^{3+} to Mn^{2+} and creation of high-intensity Ti vacancies are responsible for the very low $\tan \delta$ in BLTTm with $x = 0.05$.

4. CONCLUSION

The nominal $(Ba_{1-x}La_x)(Ti_{1-x}Tm_x)O_3$ (BLTTm) ceramics were prepared at $1400\text{ }^\circ\text{C}$ by a mixed-oxides method. The solubility limit of La/Tm in the $BaTiO_3$ lattice was determined by XRD to be $x = 0.08$. BLTTm has a tetragonal perovskite structure for $x \leq 0.03$ and a pseudo-cubic structure for $0.05 \leq x \leq 0.08$. A small amount of Tm_2O_3 remained as a secondary phase in BLTTm with $x \geq 0.09$. BLTTm with $x = 0.05$ exhibits a more flattened diffuse phase transition behavior with $\epsilon'_{RT} = 1756$ and a very low $\tan \delta (< 0.02)$ below $100\text{ }^\circ\text{C}$, satisfying X6T specification. Tm^{3+} ions in BLTTm are substituted dominantly for Ti-sites and slightly for Ba-sites, and therefore exhibit an asymmetric amphoteric behavior. Both reduction in Mn impurities of Mn^{4+}/Mn^{3+} to Mn^{2+} and creation of high-intensity Ti vacancies are responsible for the very low $\tan \delta$ in BLTTm with $x = 0.05$.

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ABOUT THE AUTHORS

Professor Dayong Lu was born on July 31, 1967, in Liaoning, China. He earned a bachelor's degree in 1989 and a master's degree in 1996 from Jilin University and a PhD from Yamagata University in 2005. He taught at Jilin Institute of Chemical Technology (JLICT) in China. His research areas are high-permittivity ceramic materials, pharmaceutical analysis and quality control of traditional Chinese medicines, temperature-dependent measuring technology, and inorganic-organic composite materials. He is President of College of Materials Sciences and Engineering, Academic Leader of Materials Science and Engineering discipline, JLICT, Director of Key Laboratory of Special Functional Materials in Jilin Provincial Colleges and Universities. He was awarded New Century Excellent Talents in University, State Education Ministry (2007); Changbai Mountain Scholar Distinguished Professor (2016); and State Department Special Allowance (2015).

Yue Liang was born on February 12, 1994, in Gongzhuling, China. She earned a bachelor's degree from Tonghua Normal University of China in 2016. She is a postgraduate in Jilin University and is jointly-trained in Jilin Institute of Chemical Technology. Her research area is high-permittivity ceramic materials.