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Short communication

Structural, magnetic and dielectric properties of $Bi_{5-x}La_xTi_3Co_{0.5}Fe_{0.5}O_{15}$ ceramics

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ABSTRACT

The $Bi_{5-x}La_xTi_3Co_{0.5}Fe_{0.5}O_{15}$ ($0 \leq x \leq 0.4$) ceramics were successfully synthesized by a modified Pechini process. The samples were characterized by X-ray diffraction and no impurity phase has been detected. The cell volume of the composites increases monotonously with the increase of La content, which indicates that La ions have been incorporated into the lattice of $Bi_5Ti_3Co_{0.5}Fe_{0.5}O_{15}$. The magnetic measurements show that La doping on Bi sites has enhanced the magnetization of $Bi_{5-x}La_xTi_3Co_{0.5}Fe_{0.5}O_{15}$ ($0 \leq x \leq 0.4$). Both the dielectric constants and loss tangent of all the samples decrease on increasing frequency and then become almost constant at room temperature. The La doped $Bi_5Ti_3Co_{0.5}Fe_{0.5}O_{15}$ samples exhibit improved dielectric and ferroelectric properties, with higher dielectric constant enhanced remnant polarization and lower losses at room temperature .

1. Introduction

Multiferroic materials, in which the ferroelectric and magnetic ordering coexist with intimately cross-coupling, have attracted intensive attentions due to their technological relevance and fundamental science challenges [1–6]. There are several kinds of materials exhibiting multiferroic behavior. The perovskite $BiFeO_3$ [7] and $BiMnO_3$ [8,9] were the most frequently investigated, offering ferroelectric order and spin order above room temperature. However, the multiferroics above room temperature are rare in naturally occurring single phase oxides [4], since ferroelectricity (FE) and ferromagnetism (FM) are mutually exclusive due to d^0 electronic structure of *B*-site elements. Theoretically, the layer-structured material can potentially avoid this factor, and reach high reliability above room temperature [10].

Aurivillius compounds, with the general formula $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$, are formed by layered intergrowths of fluorite-like $[Bi_2O_2]$ units alternating with perovskite-like $[A_{n-1}B_nO_{3n+1}]$ units, where *A* is a twelve coordinated cation, e.g., Na, K, Ca, Sr, Ba, Pb, Bi, and La, and *B* is an octahedrally coordinated cation such as Fe, Ti, Nb, Ta, and Cr [11,12]. Here *n* refers to the number of perovskite-like layers between Bi_2O_2 layers. In this compound series, a four-layered compound $Bi_5FeTi_3O_{15}$ was reported as antiferromagnetic having a T_N at 80 K [11] and exhibiting a magnetoelectric (ME) output of 16 mV cm^{-1} Oe^{-1} [13]. While seven-layered $Bi_8Fe_4Ti_3O_{24}$ showed ME signal of 0.35 mV cm^{-1} Oe^{-1} at room temperature [11]. Subsequently, Mao et al. have reported the coexistence of FE and FM remarkably above room temperature in half Fe^{3+} sites substituted by Co^{3+} ions in $Bi_5FeTi_3O_{15}$ [14].

The $Bi_5FeTi_3O_{15}$ also can be viewed as inserting $BiFeO_3$ into the three-layered FE compound $Bi_4Ti_3O_{12}$. It has been shown that lanthanum doping is effective in improving the dielectric property of many of these compounds, especially $Bi_4Ti_3O_{12}$ [15]. In this paper, the $Bi_{5-x}La_xTi_3Co_{0.5}Fe_{0.5}O_{15}$ ($0 \leq x \leq 0.4$) ceramics were prepared by a modified Pechini method, and enhanced dielectric and ferroelectric properties of $Bi_5TiCo_{0.5}Fe_{0.5}O_{15}$ have been obtained by La substituting for Bi ions according to the expectation. Moreover, the improved ferromagnetic property is detected.

2. Experiment

$Bi_{5-x}La_xTi_3Co_{0.5}Fe_{0.5}O_{15}$ ceramics were synthesized by a modified Pechini method. First, titanium isopropoxide $Ti[OCH(CH_3)_2]_4$, bismuth nitrate pentahydrate $Bi(NO_3)_3{\cdot}5H_2O$, iron nitrate enneahydrate $Fe(NO_3)_3{\cdot}9H_2O$, lanthanum nitrate hexahydrate $La(NO_3)_3{\cdot}6H_2O$ and cobalt nitrate hexahydrate $Co(NO_3)_2{\cdot}6H_2O$ were dissolved into the citric acid solution with glycol in stoichiometric proportions. Citric acid ($C_6H_8O_7$) in 1:1.25 molar ratio with respect to the metal nitrates was added to the solution as a complexant. Glycol was used for adjusting the viscosity and stability of the sol. Ammonia was added into the mixture of these solutions to adjust PH to 7 and the mixture was stirred until transparent. Then the precursor solution was evaporated and dried

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at 150 °C to obtain the xerogel powder. After that, the xerogel powder was grinded in an agate mortar. The obtained powder was heated at 600 °C for 6 h, sintered at 800 °C, and then pressed into pellets. Finally, the pellets were sintered to ceramics at 850 °C for 4 h. Electrodes were applied to both surfaces to measure electrical properties with silver paste.

The crystalline structure of the samples was examined by X-ray diffraction (XRD) (PANalytical B.V., X'Pert PRO, Holland) collected in a wide range of Bragg angles 2θ ($15^\circ \leq 2\theta \leq 60^\circ$) using Cu K$\alpha$ radiation ($\lambda = 1.5406$ Å). The particle size and morphology of the $Bi_{5-x}La_xTi_3Co_{0.5}Fe_{0.5}O_{15}$ ceramics ($x = 0$, 0.2, 0.3, 0.4) were characterized with a field emission scanning electron microscopy (SEM) (FEI, Sirion 200, Holland). The magnetic properties were investigated by a commercial physical properties measurements system (Quantum Design, ppms-9, America). The dielectric properties at room temperature were measured by a precision impedance analyzer (WK, 6500B, UK). The ferroelectric hysteresis loops at RT were measured by a standard ferroelectric tester (Radiant Technology, Precision Premier II, America).

3. Results and discussion

Fig. 1(a) displays the XRD patterns of $Bi_{5-x}La_xTi_3Co_{0.5}Fe_{0.5}O_{15}$ ($x = 0$, 0.2, 0.3, and 0.4). All the XRD peaks agree with an Aurivillius structure containing four perovskite layers clapped between two Bi–O layers in accordance with the standard XRD spectrum (JCPD 38-1257). There is no such evidence of the existence of any impure phase. The lattice constants of all the samples are evaluated from XRD spectra. The La content dependence of the lattice constants are shown in Fig. 1(b). With the increase in La content, the *a* axis is decreased, while *b*, *c* axes and the cell volume are slightly increased. This suggests that the La ions have been incorporated into the lattice without changing the Aurivillius structure.

The SEM images of the cross-sectional surface of the $Bi_{5-x}La_xTi_3Co_{0.5}Fe_{0.5}O_{15}$ ($0 \leq x \leq 0.4$) ceramics have been shown in Fig. 2. All the samples are composed of plate-like grains. This plate-like morphology of the grain is a characteristic feature of bismuth layer compounds. The plate like grains have edge length between 700 nm and 2 μm for $x = 0$, 700 nm and 1.5 μm for $x = 0.2$, 500 nm and 1 μm for $x = 0.3$, 400 nm and 700 nm for $x = 0.4$, while thickness are about 0.2 μm for $x = 0$, 0.2 and 0.3, 0.15 μm for $x = 0.4$, respectively. This indicates that La-doping significantly decreases the grain size of the ceramics. Rare-earth ions are known to suppress the grain growth in perovskites, which can be attributed to their lower diffusivity [16].

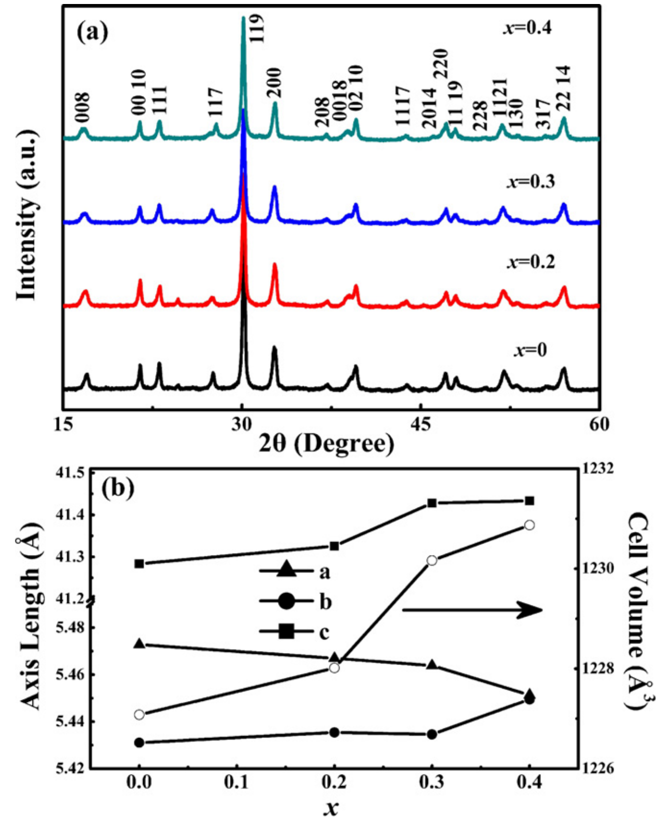

Fig. 1. The XRD patterns (a) and evolution of lattice parameters (b) for $Bi_{5-x}La_xTi_3Co_{0.5}Fe_{0.5}O_{15}$ ($0 \leq x \leq 0.4$) samples.

Fig. 3(a) and (b) shows the magnetization hysteresis loops for $Bi_{5-x}La_xTi_3Co_{0.5}Fe_{0.5}O_{15}$ ceramics ($x = 0$, 0.2, 0.3, and 0.4) measured at 300 K and 150 K. All the samples illustrate a typical ferromagnetic ordering. It is observed that both the remnant magnetization (*Mr*) and magnetization (*M* at 10 kOe and 20 kOe at room temperature and 150 K respectively) of the samples increase with increasing La content. At 300 K, the obtained the magnetization at 10 kOe are 0.056 and 0.086 emu/g, the coercive field H_c are 140 and 318 Oe for

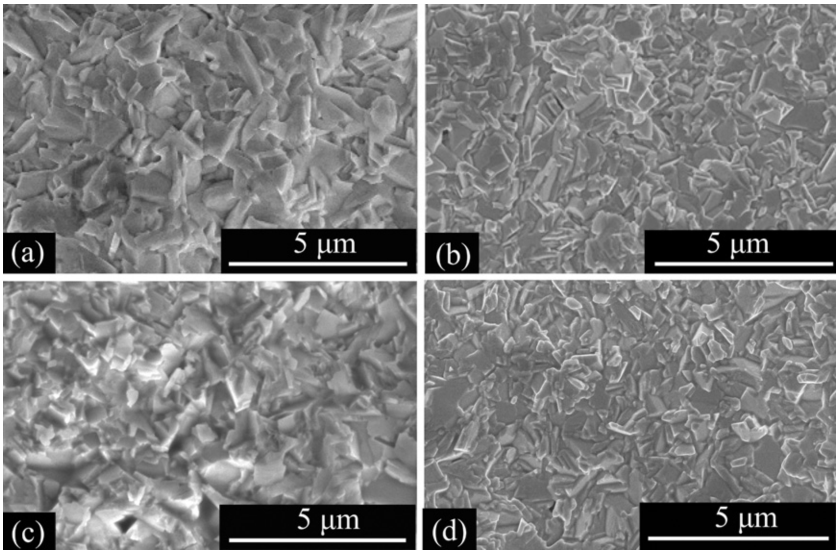

Fig. 2. The SEM images of $Bi_{5-x}La_xTi_3Co_{0.5}Fe_{0.5}O_{15}$ ceramics (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.3$, and (d) $x = 0.4$.