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Structural, electrical and optical properties of lanthanum-doped barium stannate

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Abstract

$Ba_{1-x}La_xSnO_3$ compounds were prepared by a conventional solid-state reaction method and their structural, electrical and optical properties were analyzed in this work. X-ray diffraction investigations revealed that La substitution in $BaSnO_3$ led to the increase of cubic lattice parameters, whereas secondary phase appeared at $x=0.1$ or above. Evidences of the Sn^{4+} state and oxygen vacancies were clearly observed in X-ray photoelectron spectroscopy. The semiconductor behavior in temperature-dependent resistivity was found to obey the variable-range hopping conduction mechanism. With the help of absorption spectra, smaller band-gap energy and larger Urbach tail energy were observed in $Ba_{0.93}La_{0.07}SnO_3$, as compared with $Ba_{0.97}La_{0.03}SnO_3$, which was discussed in the frame of the role of structural disorder.

Keywords: C. Electrical properties; C. Optical properties; Transparent conductive oxides

1. Introduction

Transparent conducting oxides (TCO) [1,2] that simultaneously exhibit high visible light transparency and good electrical conductivity, are widely applied in a variety of products including photovoltaic cell, flat-panel displays, light-emitting diodes, etc. Until now, binary oxide materials (e.g., ZnO, SnO_2, In_2O_3, etc.) have been investigated as commercial TCO [3,4]. For instance, F-doped SnO_2 is the dominant choice for energy-efficient window coating, and the well-known Sn-doped In_2O_3 (ITO) is the most widely utilized material for flat-panel displays application. From the point of cost, there is an ongoing interest to develop alternatives to ITO for reducing the amount of indium used. On the other hand, the crystal structures of those binary oxide materials do not well match the ABO_3 perovskite family, which has always been the focus of scientific research due to their intriguing physical properties (e.g., superconductivity, ferroelectricity, piezoelectricity, colossal magnetoresistance, photocatalytic activity and multi-ferroic, etc.) [5–7]. Notably, such diverse physical properties can be utilized in the form of all-perovskite heterostrucutres for optoelectronic applications, where the high-performance property depends in part on the lattice and energy matching between the TCO and the active material. Extensive research effort should thus be performed to develop new transparent conductive oxide materials with perovskite structure.

Barium stannate ($BaSnO_3$) is known to form an ideal cubic perovskite structure and corresponds to a transparent wide-band-gap n-type semiconductor with an optical gap of 3.1 eV [8,9]. In order to improve the electrical property of $BaSnO_3$, both Ba and Sn sites were doped to form compounds, such as in single-crystal, polycrystalline or thin-film forms [10–18]. Compared to the low carrier mobility in La or Sb-doped polycrystalline or epitaxially grown $BaSnO_3$ samples, a high Hall mobility of $\sim 103\ cm^2\ V^{-1}\ s^{-1}$ was recently observed in La-doped $BaSnO_3$ single-crystal by Luo et al. [10] and subsequently the highest value of $\sim 320\ cm^2\ V^{-1}\ s^{-1}$ was reported by Kim et al. [11]. However, the detailed investigations of La-doped $BaSnO_3$ polycrystalline ceramics, thanks to the inevitable effect of grain boundaries, are not only of great interest for a variety of technologically important applications, but also provide compensatory explanations in other forms. Herein, we reported a carefully experimental study on the structural, electrical and

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optical properties of La-doped $BaSnO_3$ polycrystalline samples and established the role of structural disorder.

2. Experimental

The samples of $Ba_{1-x}La_xSnO_3$ ($x=0.03$, 0.07, 0.10 and 0.15; BLSx, abbreviated as BLS0.03, BLS0.07, BLS0.1, BLS0.15) were prepared via conventional solid-state reaction. $BaCO_3$, SnO_2 and La_2O_3 powders were used as raw materials and weighed with the stoichiometric ratio. The powders were ball-milled, followed by calcination at temperature of 1200 °C for 6 h in air. The calcined powders were ball-milled again and then pressed into pellets with diameter of 12 mm, followed by sintering at 1300 °C for 12 h. The pellets were coated by silver paste for electrical transport measurements.

The phase structures of the $Ba_{1-x}La_xSnO_3$ samples were characterized by X-ray diffraction (XRD) using θ–2θ scans with the Cu K_α radiation (D/max2200PC, Rigaku). The element valence states of the samples were checked using X-ray photoelectron spectroscopy (XPS) (ESCALAB 250) with Al K_α radiation. The transport properties of the samples were analyzed in the temperature range of 80–300 K. Raman spectra of the samples were measured by Renishaw inVia Raman microscope with excitation wavelength at 514.5 nm. Diffuse reflectance spectra were recorded by U3010 spectrophotometer with an integrating sphere in the wavelength range of 200–800 nm using $BaSO_4$ as the reference and then converted into absorption spectra according to the Kubelka–Munk method.

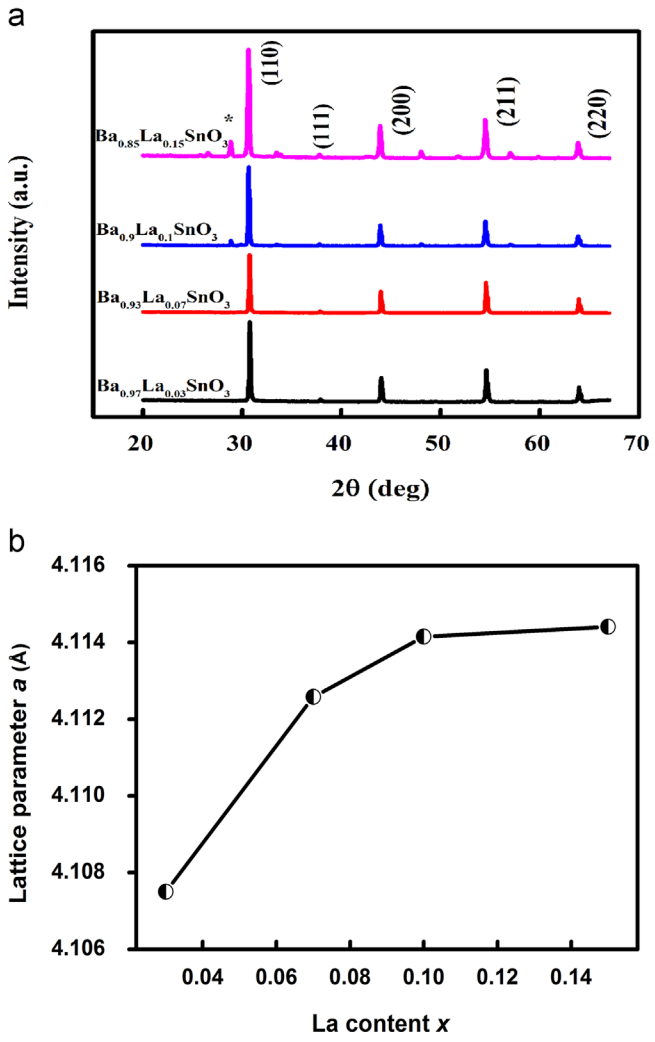

Fig. 1. (a) XRD patterns of the $Ba_{1-x}La_xSnO_3$ samples. An asterisk indicates the secondary phase. (b) Cubic lattice parameter for the $Ba_{1-x}La_xSnO_3$ samples.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the $Ba_{1-x}La_xSnO_3$ samples. First, the major diffraction peaks could be indexed to cubic phase $BaSnO_3$ crystal (JCPDS card no. 15-0780), and the La substitution does not cause any conspicuous change on the structure of $BaSnO_3$. Second, it is clear that a secondary phase (i.e., $La_2Sn_2O_7$) with the diffraction peak at $\sim$28.87° was observed in the BLS0.1 and BLS0.15 samples. This result demonstrates the solubility of La for Ba is less 10% in polycrystalline ceramics. Finally, the cubic lattice parameter was calculated for studying the effect of La doping using JADE 5.0 program, as shown in Fig. 1(b). Clearly, the lattice parameter increased with increasing the content of La dopant when $x<0.1$, and kept nearly constant for $x\geq 0.1$, which further demonstrates the solubility limit of La for Ba. If considering the ionic radius of La^{3+} (0.103 nm) is smaller than that of Ba^{2+} (0.135 nm) [19], this character is unique, and could be attributed to excess electrons into the conduction band composed of Sn–O anti-bonding orbitals via La doping, which results in expansion of the lattice due to the repulsive forces between Sn and O.

Raman spectroscopy is a versatile technique for detecting dopant incorporation and another phase in a host lattice. Despite the fact that pure $BaSnO_3$ with the space group $Pm\bar{3}m$ do not exhibit the first order Raman scattering [13], Raman modes are expected to appear when the dopant atoms and/or the oxygen vacancies affect the translational periodicity of the lattice. Fig. 2

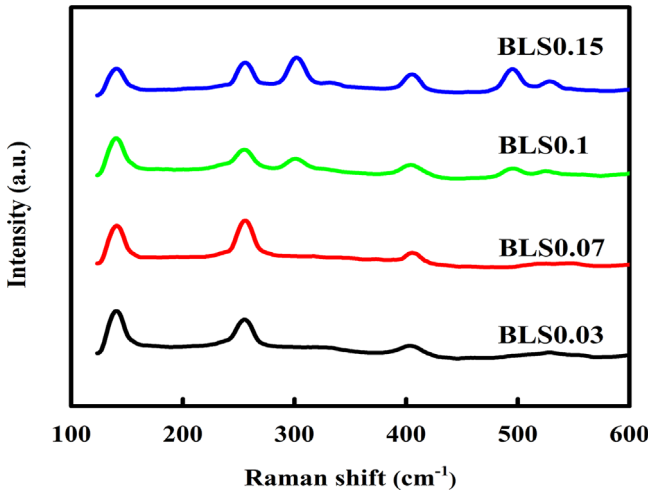

Fig. 2. Raman scattering spectra of the $Ba_{1-x}La_xSnO_3$ samples measured at room temperature.