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Effect of Mn-doping on the structure and electrical properties of $(Pb_{0.325}Sr_{0.675})TiO_3$ ceramics

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ABSTRACT

$Pb_{0.325}Sr_{0.675}Ti_{1-x}Mn_xO_3$ ceramics (x = 0, 0.001, 0.005, 0.01, and 0.05) were successfully prepared by traditional solid-state reaction method. It was found that the lattice constant calculated through Rietveld refinement initially increased and then decreased with increasing Mn content, which was attributed to the variation in valence state of Mn and Ti ions. The microstructure gradually varied from the coexistence of large grains and fine grains for x = 0 to the uniform grain for x = 0.05 by increasing the doping Mn ions. With increasing Mn content from x = 0 to x = 0.05, the Curie temperature (*Tc*) dramatically decreased from 25 °C to − 40 °C and dielectric maximum decreased from 27,100 to 13,200. $Pb_{0.325}Sr_{0.675}Ti_{1-x}Mn_xO_3$ ceramics with x = 0.001 showed the lowest dielectric loss of 0.006 with a relatively high dielectric peak value of ~ 21,000. The grain boundaries resistance obtained from the complex impedance decreased with the increase of Mn content. The decrease in resistance was ascribed to oxygen vacancies and electronics produced by the change of ionic valence state. X-ray photoemission spectroscopy revealed that Ti ions were Ti^{4+} and the valences of Mn ions were deduced to be mainly in the form of Mn^{2+} and/or Mn^{3+} for ceramics with low content of Mn, while the Ti ions were in the form of Ti^{3+} and Ti^{4+} and Mn ions were diverse valence states with the coexistence of Mn^{2+}, Mn^{3+}, and Mn^{4+} for ceramics with x = 0.01 and 0.05.

1. Introduction

In recent years, much attention had been paid to the electric field enhanced pyroelectric materials due to the advantages offered by the pyroelectric detection of infrared radiation (IR): no need of cooling, fast response, and sensitivity over a large spectra bandwidth [1–3]. As a typical and popular pyroelectric material, $(Ba,Sr)TiO_3$ (BST) was extensively studied due to the high reversible pyroelectric coefficient under DC bias and tunable Curie temperature [4–10]. However, the development of BST ceramics was restricted by the evident grain size effect that the pyroelectric properties decrease rapidly with decreasing the grain size [8].

Previously, $(Pb,Sr)TiO_3$ (PST) was extensively investigated in the fields of V-shaped positive temperature coefficient effect (PTCR) and dielectric tenability due to the promising application in thermistor and wireless communication systems [11–17]. The high dielectric permittivity and the sudden change in dielectric constant at the ferroelectric-to-paraelectric phase transition were exhibited, which is helpful to obtain the large pyroelectric coefficient at phase transformation temperature [15]. The Curie temperature of PST can be controlled from − 220 to 490 °C by changing Pb/Sr ratio, which can be matched exactly to various ambient temperatures of detector [16,17]. PST ceramics exhibit the smaller grain size effect and the relatively low temperature comparing to BST pyroelectric ceramics. These make PST be a promising candidate for pyroelectric materials.

In this work, the composition $(Pb_{0.325}Sr_{0.675})TiO_3$ was selected to be studied due to the Curie temperature of ~ 25 °C, suggesting the potential application in room temperature IR detector. For an ideal pyroelectric material, the lower dielectric loss is needed in addition to the higher pyroelectric coefficient [10]. In order to reduce the dielectric loss, MnO, a type of "hard" acceptor dopant for $(Pb_{0.325}Sr_{0.675})TiO_3$ ceramics, was introduced in this work [18]. Mn is multivalence and acquires various valence states (Mn^{2+}, Mn^{3+} and Mn^{4+}) at different temperatures and ambient atmospheres [19]. These diverse Mn ions substitutions for Ti^{4+} will induce the formation of oxygen vacancies and/or Ti^{3+} in order to achieve charge neutrality. Meanwhile, these Mn ions of acceptor dopant and oxygen vacancies may generate the defect dipoles in the form of $(Mn_{Ti}^{2+\prime} - V_{\ddot{O}})$ and $(Mn_{Ti}^{3+\prime} - V_{\ddot{O}})^{\cdot}$, which tend to align along the spontaneous-polarization orientation during aging process [19,20]. These complex factors including the change in valence

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state, oxygen vacancies and defect dipoles may affect the electrical properties. Therefore, it is a meaningful work to investigate the influence of Mn substitution for Ti in $Pb_{0.325}Sr_{0.675}TiO_3$ ceramics on the structure and electrical properties both in practical and theoretical interest. In this article, $Pb_{0.325}Sr_{0.675}Ti_{1-x}Mn_xO_3$ (x = 0, 0.001, 0.005, 0.01, and 0.05) ceramics were prepared through the traditional solid-state reaction technique and the effects of Mn doping on the microstructure and electrical properties were systematically investigated. In addition, the related mechanism was discussed through X-ray photoelectron spectroscopy.

2. Experimental

$Pb_{0.325}Sr_{0.675}Ti_{1-x}Mn_xO_3$ (x = 0, 0.001, 0.005, 0.01, and 0.05) ceramics were prepared by a traditional solid-state reaction technique. The stoichiometric amounts of highly pure Pb_3O_4 (99.9%), $SrCO_3$ (99.9%), MnO (99.99%), TiO_2 (99.99%) were mixed and ball-milled with zirconium media for 10 h. Subsequently, the mixtures were dried and calcined at 900 °C for 2 h in air. The calcined powders were blended with approximately 5 wt% polyvinyl alcohol (PVA) and pressed to form disk-shaped pellets (12 mm diameter and 1.5 mm in thickness) with a uniaxial pressure of 100 MPa after sufficient grounding. These disk pellets were sintered at 1320 °C for 2 h in air. For electrical characterization, the sintered disk pellets were surface-polished in most cases and then coated with silver electrode and fired at 600 °C for 20 min.

The phase structure was analyzed by X-ray diffraction (Model D/Max-2400, Rigaku, Japan) with Cu Kα radiation and the microstructures were studied by scanning electron microscope (SEM, Quanta 200, Philips, Netherlands). The temperature dependence of dielectric spectrum was measured by using the LCR meter (Agilent E4980A) with a Delta temperature chamber. The complex impedance at room temperature were measured by Agilent 4294 A precise impedance analyzer within the frequency range of 40 Hz to 110 MHz. X-ray photoelectron spectroscopy were carried out on an ESCAPHI5400 (PerkinElmer, Santa Clara, CA) photoelectron spectrometer.

3. Results and discussion

3.1. Microstructure

Fig. 1 exhibits the SEM micrographs of $Pb_{0.325}Sr_{0.675}Ti_{1-x}Mn_xO_3$ ceramics. The pure $Pb_{0.325}Sr_{0.675}TiO_3$ ceramics present a duplex microstructure consisting of uniformly fine grains of ~ 3 μm and coarse grains of 20–30 μm that randomly locate among the fine grains. It is clearly seen that the microstructure changes dramatically with the content of Mn cationic substituted. With increasing Mn content, the percentage of fine grains gradually decreases. $Pb_{0.325}Sr_{0.675}Ti_{1-x}Mn_xO_3$ ceramics with x = 0.001, 0.005, and 0.01 display a wide range of the grain size distribution. When Mn content increases to the largest value of x = 0.05, uniform grain distribution and dense microstructure appear. However, some traces of precipitates were observed at grain boundaries. Therefore, the microstructure varies from the coexistence of large grains and fine grains for x = 0 to the uniform grain for x = 0.05 by doping Mn ions. Similar grain evolution was observed in the literature [21].

3.2. X-ray diffraction analyses

Fig. 2 shows the X-ray diffraction patterns of $Pb_{0.325}Sr_{0.675}Ti_{1-x}Mn_xO_3$ ceramics at room temperature. The phase structure of $(Pb_{0.325}Sr_{0.675})TiO_3$ ceramics was hardly changed by manganese doping. All diffraction peaks of ceramics with different manganese additions can be indexed by the cubic perovskite structure. No noticeable traces of impurities was observed, suggesting that Mn of all specimens has diffused into $(Pb_{0.325}Sr_{0.675})TiO_3$ lattice to form a solid solution.

In order to precisely estimate the influence of Mn doping on the lattice parameters of $(Pb_{0.325}Sr_{0.675})TiO_3$ ceramics, Rietveld refinement

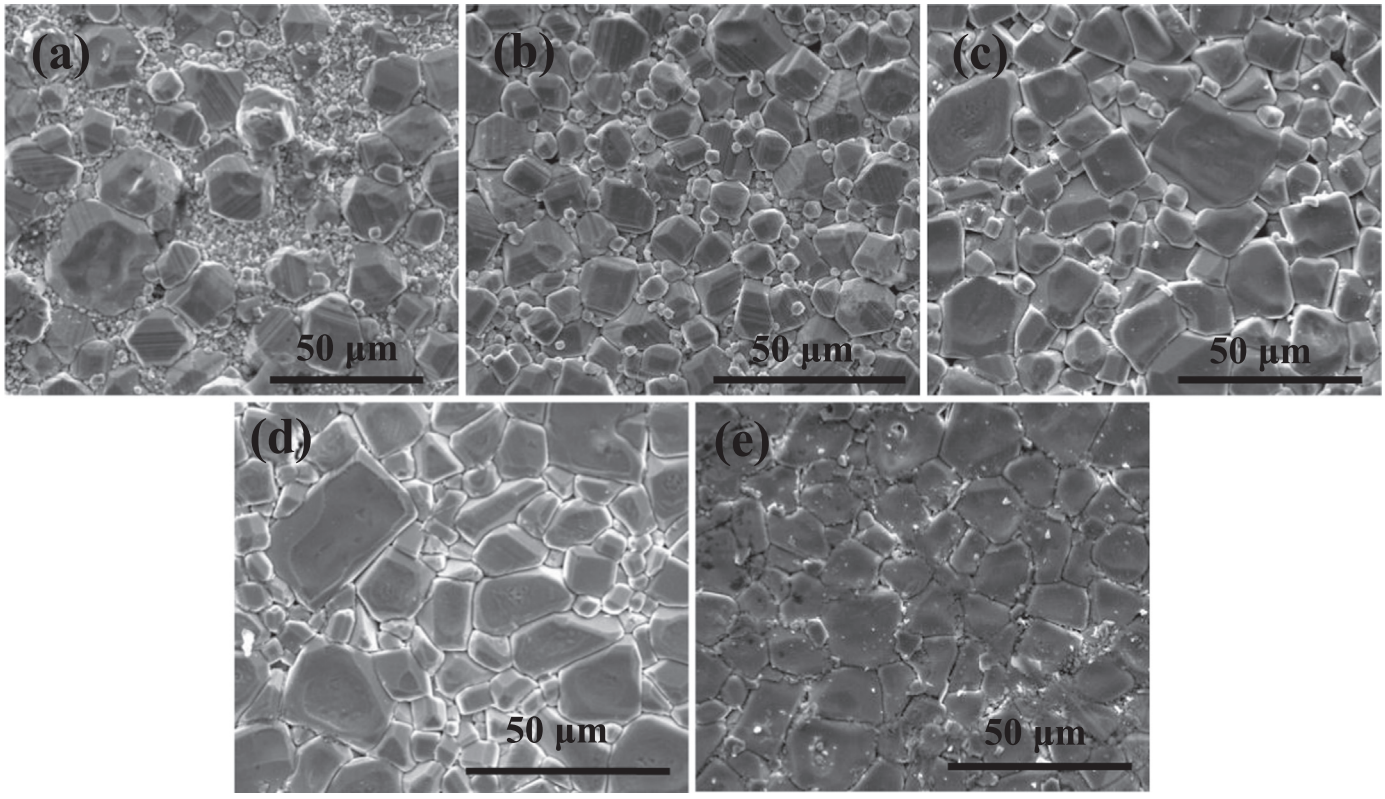

Fig. 1. SEM images of $Pb_{0.325}Sr_{0.675}Ti_{1-x}Mn_xO_3$ ceramics (a) x = 0; (b) x = 0.001; (c) x = 0.005; (d) x = 0.01; (e) x = 0.05.