Journal of Alloys and Compounds 627 (2015) 238–243

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Effect of Sn content on dielectric, piezoelectric and ferroelectric properties for $Pb(Zr_{0.35}Ti_{0.65})_{1-x}Sn_xO_3$ ceramics near morphotropic phase boundary

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ARTICLE INFO

Article history:
Received 1 October 2014
Received in revised form 20 November 2014
Accepted 8 December 2014
Available online 15 December 2014

Keywords:
$Pb(ZrSnTi)O_3$
Piezoelectric ceramics
Rayleigh law
Domains

ABSTRACT

ABO_3 perovskite structure $Pb(Zr_{0.35}Ti_{0.65})_{1-x}Sn_xO_3$ (PZST) piezoelectric ceramics were synthesized by conventional solid state reaction method with the compositions near tetragonal to rhombohedral morphotropic phase of boundary (MPB). The influences of Sn content on dielectric, piezoelectric and ferroelectric properties of PZST piezoceramics were investigated while Zr/Ti ratio was fixed. With increasing Sn content, the c/a ratios and Curie temperatures T_C decrease monotonically. Rayleigh law was explored to evaluate the piezoelectric behaviors as a function of loading electric field strength. Both Rayleigh coefficients α_d and d'_{init} are increased with increasing Sn content, indicating that Sn content considerably increase the mobility of domain walls and also the piezoelectric nonlinear responses.

1. Introduction

Ferroelectric materials, which possess a spontaneous electric polarization and the polarization can be reversed by the application of an external electric field, have been widely used in many fields, such as sensors, actuators, non-volatile memories, and energy harvesting devices [1–6]. Among these ferroelectric materials, lead-based solid solution ceramics, represented by $Pb(Zr_{1-x}Ti_x)O_3$ (lead zirconate titanate, PZT) ceramics, have attracted many attentions for last few decades, because of their superior piezoelectric properties [1,5–7]. The phase structure of PZT is highly composition-dependent. For the composition with $Zr/Ti \approx 52/48$, a morphotropic phase boundary (MPB), in which both tetragonal and rhombohedral phase coexist, was identified. Interestingly, both dielectric and piezoelectric properties show maximum values at MPB [8–11]. It shown that enhanced polarizability arises from the coupling between the two equivalent energy states, allowing optimum domain reorientation during poling [12,13]. Furthermore, Noheda et al. attributed the enhanced properties to a third monoclinic phase, which assisted the polarization reversal between the tetragonal phase and rhombohedral phase readily [9,10]. Recently, Li et al. emphasized that the enhancement of piezoelectric coefficient d can be partly attributed to the increase of dielectric permittivity ε, since the coefficient d of perovskite ferroelectrics is proportional to $PQ\varepsilon$ (P, spontaneous polarization, Q is electrostrictive coefficient) [14]. The solid solution of $Pb(Sn_{1-x}Ti_x)O_3$ (PST) system has already been reported to exhibit some interesting properties which are different from PZT [15–21]. It has been found that when Sn content is in the range of 60–80 mol%, PST crystallizes into ferroelectric rhombohedral phase. However it cannot form perovskite phase at atmospheric pressure, when Sn content is higher than 80% [17]. Furthermore, for PST ceramics, similar to that of the PZT ceramics, their MPB separating the rhombohedral and tetragonal phases was observed with a Sn/Ti mole ratio of 50/50. Actually, the $Pb(ZrSnTi)O_3$ (PZST) solid solutions have received more general interest from the point view of fundamental research and application. The phase diagram of PZST is shown in Fig. 1 [1]. Adjusting the Zr/Ti/Sn mole ratio, different phase structures were obtained. From the point view of application, the compositions of PZST with high Zr concentration (Zr mol% > 60%) have been intensively investigated near antiferroelectric (A_T and A_O) to ferroelectric ($F_{R(LT)}$) phase transition region. However, another region between $F_{R(LT)}$ and F_T with high Ti concentration is not well understood. Although very little works have been conducted in this region, the piezoelectric and dielectric properties as a function of composition are not systematically studied.

To ferroelectric materials, properties come from both intrinsic and extrinsic contributions [22,23]. It is well accepted that the intrinsic contributions to dielectric and piezoelectric properties of a ferroelectric originate from field-induced changes of polarization

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http://dx.doi.org/10.1016/j.jallcom.2014.12.032
0925-8388/

and deformation within a single domain [24,25]. In contrast, extrinsic contributions to dielectric and piezoelectric properties include displacement of domain walls and other factors, such as, interphase boundary movement [26,27]. The nonlinear contributions from extrinsic mechanisms can be calculated from the field-dependent piezoelectric coefficients using Rayleigh law. Analysis of the dielectric and piezoelectric response with the framework of Rayleigh law enables us to describe quantitatively the contribution of irreversible movement of domain walls [28–30]. The Rayleigh law [28] for piezoelectric response can be expressed as:

$$d'_{33}(E_0) = d'_{\text{init}} + \alpha_d \cdot (E_0), \quad (1)$$

where E_0 is the amplitude of the driving field $E = E_0\sin(\omega t)$, d'_{init} is the initial piezoelectric coefficient, including the contributions from intrinsic piezoelectric effect of the lattice and the reversible domain walls vibration. The irreversible Rayleigh coefficient α_d represents irreversible displacement of domain walls. Although the linear description of piezoelectric coefficients is valid approximation at lower field and stress levels, normally the field strength is limited much lower than the coercive field (E_c); it becomes more and more inaccurate when higher external fields are applied [31]. The existence of threshold field E_t indicates that above which the piezoelectric coefficient and dielectric permittivity are expected to be constant with field [32,33]. The Rayleigh region is between the E_t and E_c. In the Rayleigh region, the piezoelectric coefficient and dielectric permittivity show linear increase with increasing the electric field strength [23,34].

In this work, the Sn content on phase structure and related piezoelectric and dielectric properties for the composition of $Pb(Zr_{0.35}Ti_{0.65})_{1-x}Sn_xO_3$ was systematically investigated. The Rayleigh law was applied to study the electric field dependence of the piezoelectric coefficients. It was found that both α_d and d'_{init} are increased with increasing Sn content, indicating that Sn content considerably increase the mobility of domain walls and also the piezoelectric nonlinear responses.

2. Experimental procedures

$Pb(Zr_{0.35}Ti_{0.65})_{1-x}Sn_xO_3$ piezoelectric ceramics were fabricated using conventional mixed oxide approach. The compositions studied in present work are given in Fig. 1, near the MPB region. High purity oxide powders: PbO (99%), ZrO_2 (99%), SnO_2 (99.5%), TiO_2 (98%) (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used as starting materials. The samples were sintered in sealed crucibles at temperature of 1220 °C for 2 h. The details of the ceramic processing can be found in Refs. [35,36].

The crystalline phases of studied samples were identified by X-ray diffraction (XRD, D/Max-IIIC, Rigaku, Japan) analysis using Cu Kα radiation on sintered powders operating at 40 kV and 100 mA. Scanning electronic microscopy (SEM, FEI Quanta 250 FEG, Hillsboro, Oregon, USA) was used to investigate the microstructures. The grain size was roughly estimated by the SEM photos using the interpolating method. A multi-frequency LCR meters (E4980A, Agilent, Palo Alto, CA, U.S.) was used to measure the dielectric permittivity as functions of temperature and frequency. Polarization–electric field (P–E) hysteresis loops and strain–electric field (S–E) curves were measured based on a Sawyer–Tower circuit (TF analyzer 2000, aixACCT, Aachen, Germany) combine with a photonic displacement sensor (MTI-2000, MTI Instruments, Washington, U.S.) at room temperature. Small signal piezoelectric coefficients were measured on disk samples using a Berlincourt d_{33} meter (ZJ-3A, Institute of Acoustics, CAS, Beijing, China).

3. Results and discussion

Room temperature XRD patterns of $Pb(Zr_{0.35}Ti_{0.65})_{1-x}Sn_xO_3$ ceramic powders with $x = 0.22$, 0.24, 0.26, 0.28 and 0.3 are shown in Fig. 2(a). The θ–2θ scanning angle is from 20° to 70°. It was found that only the peaks corresponding to a pure perovskite phase could be identified for the patterns collected from the calcined powders of all studied compositions. No pyrochlore or other secondary phase can be detected. As shown in Fig. 2(b), it was observed that with increasing Sn content, the (002) and (200) peaks moved closer gradually, indicating a decrease trend of tetragonality. According to Fig. 1, there is a rhombohedral–tetragonal phase boundary located around the composition with $x = 0.3$. Note that the (111) peak becomes broad as x increase. This phenomenon can be attributed to the existence of rhombohedral phase, since only the decrease of the tetragonality cannot result in such a broadening. Noheda et al. has found a monoclinic phase at MPB region in PZT ceramics, which display a similar diffraction feature as we observed in PZST ceramics [10]. However, as argued by Jin et al., a nanoscale coherent mixture of microdomains might be interpreted as an adaptive ferroelectric phase, while microdomain-averaged crystal lattice is monoclinic [37,38]. Therefore, whether there exist a monoclinic phase in PZST ceramics, further investigation is highly expected. As increasing the Sn content from 0.22 to 0.3, the composition approached the MPB region gradually. It can be seen in Fig. 2(c) that the c/a ratio decreased from 1.023 to 1.014, when the Sn content was increased from 0.22 to 0.30. The

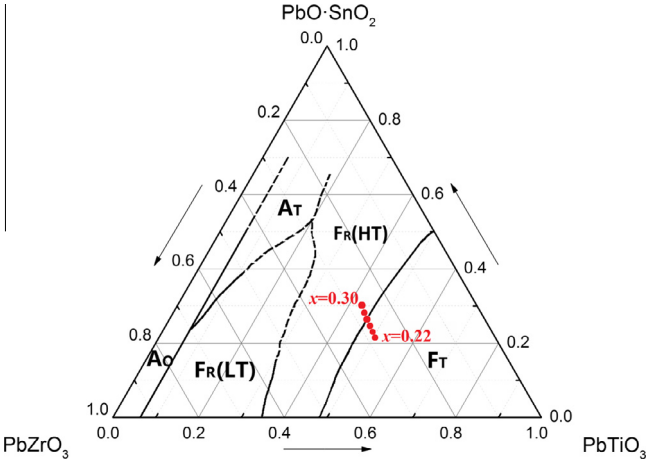

Fig. 1. Phase diagram of $PbSnO_3$–$PbZrO_3$–$PbTiO_3$ (PZST) ternary system [1] and the compositions studied in present work (red dot). A_T – tetragonal antiferroelectric phase; A_O – orthorhombic antiferroelectric phase; $F_{R(HT)}$ – high temperature rhombohedral ferroelectric phase; $F_{R(LT)}$ – low temperature rhombohedral ferroelectric phase; F_T – tetragonal ferroelectric phase. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

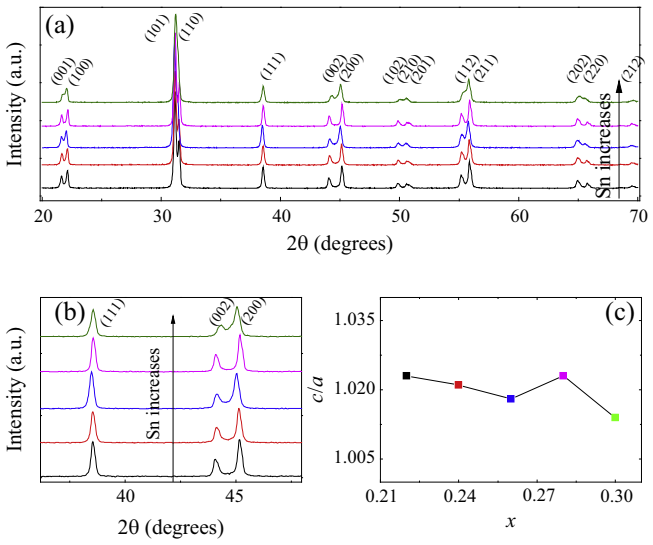

Fig. 2. Room temperature XRD patterns of $Pb(Zr_{0.35}Ti_{0.65})_{1-x}Sn_xO_3$ ceramic powders with different Sn content from $x = 0.22$ to $x = 0.30$ (a) $2\theta = 20$–$70°$, (b) $2\theta = 37$–$48°$, (c) and c/a ratio as a function of Sn concentration.