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Structure and dielectric behavior of (1-x)Pb($Sc_{1/2}Ta_{1/2}$)O_3-xPb($In_{1/2}Nb_{1/2}$)O_3 solid solution

Longhai Yang, Zhenrong Li*, Tingting Wang, Kexin Song

Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education and International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, China

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ABSTRACT

A solid solution system of (1-x)Pb($Sc_{1/2}Ta_{1/2}$)O_3-xPb($In_{1/2}Nb_{1/2}$)O_3 (x = 0.2, 0.4, 0.6, and 0.8) was synthesized by conventional solid-state reaction technique. The optimum sintering temperatures of ceramics with x = 0.2, 0.4, 0.6, and 0.8 were 1400 °C, 1400 °C, 1300 °C, and 1200 °C, respectively. At these temperatures, the densest samples and the maximum dielectric constant were obtained. With increasing x, the percentage of pyrochlore phase increased, indicating a decrease in the solubility of solid solution. For x = 0.2, with the sintering temperature increasing, the ordering degree decreased while the dielectric constant increased. For x = 0.6 and 0.8, at the highest sintering temperature, the most pyrochlore phase appeared and the minimum dielectric constant was obtained. In addition, the relaxor characteristics of solid solution ceramics were systematically investigated. It was found that the dielectric maximum decreased and the temperature at dielectric maximum shifted to higher temperature with x increasing. All compositions exhibited the second-order phase transition due to the analysis of dielectric behaviors on heating and cooling. Interestingly, the difference in dielectric maximum between heating and cooling became larger with PIN content increasing. The diffuseness exponents of all compositions were calculated to be in the range of 1.53–1.66, suggesting the typical relaxor. The polarization-electric field (P-E) hysteresis loops of all solid solutions showed the shapes of slim loop. Meanwhile, the coercive field and remnant polarization of all compositions were analyzed in detail.

1. Introduction

Over the past few years, A($B'_{1/2}B''_{1/2}$)O_3 complex perovskites were paid much attention because of the B-site order/disorder arrangement and potential applications in capacitors, actuators, and pyroelectric detectors [1–3]. Among A($B'_{1/2}B''_{1/2}$)O_3 compounds, Pb($Sc_{1/2}Ta_{1/2}$)O_3 was extensively studied [4–8]. Pb($Sc_{1/2}Ta_{1/2}$)O_3, usually abbreviated to PST, has Pb^{2+} cation at A-site, the B-site can be occupied by Sc^{3+} and Ta^{5+} cations with different ordering degrees [6–8]. Order/disorder structure of PST was confirmed by transmission electron microscopy and clearly reflected by superlattice diffraction peak in X-ray diffraction pattern [4,5]. The dielectric property of PST is affected by B-site ordering degree. A clear trend towards more diffuse and dispersive relaxor-type behavior occurs with decreasing long-range ordering [9,10]. Meanwhile, the transition temperature can be changed by adjusting B-site ordering degree. The temperature of the dielectric permittivity maximum ranges from − 5 °C to 25 °C, with the higher transition temperatures and lower dielectric permittivity occurring for the more highly ordered PST [11].

Additionally, Some Pb($Sc_{1/2}Ta_{1/2}$)O_3-based solid solutions were widely reported [12–15], such as (1-x)Pb($Sc_{1/2}Ta_{1/2}$)O_3-x$PbTiO_3$ [12,13], (1-x)Pb($Sc_{1/2}Ta_{1/2}$)O_3-x$PbZrO_3$ [14], and xPb($Sc_{1/2}Ta_{1/2}$)O_3-(1-x)Pb($Sc_{1/2}Nb_{1/2}$)O_3 [15]. The solid solution system (1-x)Pb($Sc_{1/2}Ta_{1/2}$)O_3-x$PbTiO_3$ illustrated the outstanding piezoelectric coefficient (d_{33} = 655 pC/N) and electromechanical coupling factors (k_t = 0.5, k_p = 0.61, and k_{33} = 0.73) accompanied by a low mechanical quality factor (Q_m = 30) [12]. In addition, some interesting phenomena were found in xPb($Sc_{1/2}Ta_{1/2}$)O_3-(1-x)Pb($Sc_{1/2}Nb_{1/2}$)O_3 system, the analysis of X-ray diffraction showed that the degree of compositional ordering increases with increasing x. Detail studies of dielectric properties exhibited that relaxor characteristics were observed for ceramics with x ≤ 0.3 and above this composition the solid solution simply displayed a diffuse phase transition [15].

According to the knowledge of PST-based solid solution, the (1-x)Pb($Sc_{1/2}Ta_{1/2}$)O_3-xPb($In_{1/2}Nb_{1/2}$)O_3 system was designed in this work. Except PST, Pb($In_{1/2}Nb_{1/2}$)O_3 (PIN) is also a typical A($B'_{1/2}B''_{1/2}$)O_3 perovskite, which has different degrees of chemical ordering in the arrangement of In^{3+} and Nb^{5+} at B-site [16]. It was reported that the

* Corresponding author.
E-mail address: zhrli@xjtu.edu.cn (Z. Li).

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phase transition from the paraelectric pseudo-cubic (Pm3m) phase to the ferroelectric rhombohedra (*R3m*) was present in disordered PIN, which exhibited the relaxor behavior with a broad dielectric maximum near 60 °C. The ordered PIN showed a first-order phase transition from a paraelectric phase (*Fm3m*) to an antiferroelectric phase (Pbam), occurring at ~ 180 °C with a sharp dielectric anomaly [17–19]. By mixing PIN with PST, it is expected that some interesting phenomena will be found due to the combination of the relaxor/normal ferroelectric phase for PST and relaxor/antiferroelectric phase for PIN. Meanwhile, with an increase in the amount of PIN, the difference in transition temperature between PST and PIN gives rise to the sequential transition temperatures for different solid-solution compositions. Moreover, it is known that synthesizing PST and PIN are very difficult due to the high sintering temperature (~ 1500 °C) for PST and the easy volatility of indium and lead for PIN, which may result in a challenge work for preparing solid solution. Besides, there is obvious difference in the sintering temperatures (1500 °C for PST and 1050 °C for PIN) [20], implying that different compositions of solid solution may have different sintering temperatures, the apparent difference in sintering temperature and the volatility of indium and lead may have some influences on the solubility of solid solution. Therefore, it is a meaningful work to investigate (1-x)$Pb(Sc_{1/2}Ta_{1/2})O_3$-x$Pb(In_{1/2}Nb_{1/2})O_3$ [(1-x) PST-xPIN] solid solution both in theoretical and practical interest.

In the present work, the (1-x)PST-xPIN solid-solution ceramics were prepared via the traditional solid-state reaction method. The preparation, structure, and dielectric properties for each composition were systematically investigated. In addition, the dielectric relaxation characteristics and hysteresis loop were discussed as well.

2. Experimental

The system of (1-x)PST-xPIN solid solution with compositions of x = 0.2, 0.4, 0.6, and 0.8 was prepared by solid state reaction. The raw materials were PbO (99.9%), Ta_2O_5 (99.0%), Sc_2O_3 (99.0%), Nb_2O_5 (99.0%), and In_2O_3 (99.0%). Compositions were initially prepared as powders employing a wolframite precursor method in order to reduce the occurrence of undesirable pyrochlore phases. Starting oxides Sc_2O_3 and Ta_2O_5 were mixed and calcined at 1400 °C for 6 h to form $ScTaO_4$ precursor. The mixture of Nb_2O_5 and In_2O_3 was calcined at 1100 °C for 8 h with 2 mol% excess In_2O_5 to form $InNbO_4$ precursor. Different compositions of solid solution were then formulated from PbO, $ScTaO_4$ and $InNbO_4$ precursor phases according to the stoichiometric ratio. The stoichiometric amounts of PbO, $ScTaO_4$ and $InNbO_4$ were mixed and ball-milled in ethanol for 24 h. Subsequently, the mixtures were dried and calcined at 900 °C for 4 h for every composition. The calcined powders were blended with approximately 5 wt% polyvinyl alcohol (PVA) and pressed into disk pellets after sufficient grind. Compacted specimens of compositions were sintered at temperatures from 1200 °C to 1400 °C for 2 h within sealed alumina crucibles containing PST/PIN source powders. For electrical characterization, the sintered disk pellets were surface-polished in most cases and then coated with silver paint and fired at 600 °C for 20 min.

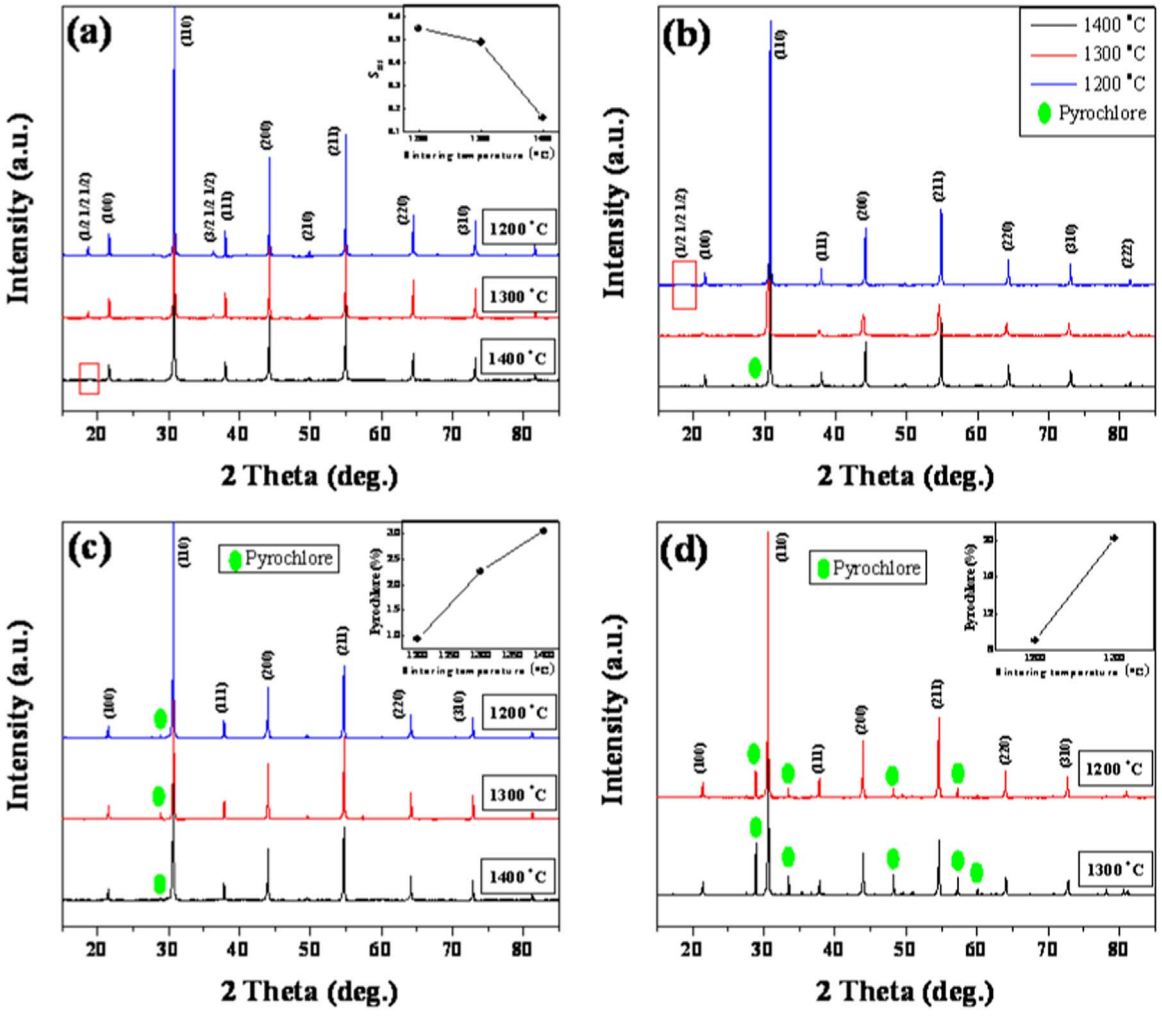

Fig. 1. XRD patterns of (1-x)PST-xPIN ceramics sintered at different temperatures. (a) x = 0.2; (b) x = 0.4; (c) x = 0.6; (d) x = 0.8. Inset (a) shows the relationship between ordering degree and sintering temperatures; Inset (c) and (d) show the percent of pyrochlore phase as a function of sintering temperature.