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Microtructure and dielectric properties of $(1-x)Pb(Yb_{1/2}Ta_{1/2})O_3$–$xPb(Fe_{1/2}Ta_{1/2})O_3$, $0 \leq x \leq 0.2$ solid solution ceramics

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Abstract

Polycrystalline samples of $(1-x)Pb(Yb_{1/2}Ta_{1/2})O_3$–$xPb(Fe_{1/2}Ta_{1/2})O_3$ with $x = 0.0$, 0.1, 0.13, 0.15, 0.18 and 0.2 are prepared by solid state reaction method. The formation and structural changes are identified by X-ray diffraction studies. A uniform distribution of grains is observed from the microstructure by scanning electron microscopy. The dielectric measurement of the compounds is carried out at 1–200 kHz in the temperature range −100 to 300 °C. The substitution of Fe^{3+} ion at Yb^{3+} sites of $Pb(Yb_{1/2}Ta_{1/2})O_3$ significantly enhances the dielectric constant value, increases the diffuseness in the mode of phase transition and lowers the transition temperature. A detailed analysis of the dielectric response of the compounds is given in conjecture with their structural data.

Keywords: Ceramics; Doping effect; Grain boundaries; Phase transitions; X-ray spectroscopy

1. Introduction

Since last two decades, the intense research devoted to lead based complex perovskite ferroelectrics has been motivated by their varying phase transition properties and potential applications to various industries [1,2]. In the year 1959, Smolenskii and Agranovskaya proposed that a wide range of exogenous complex perovskite compounds can be prepared by keeping in mind the conditions of electrical charge neutrality, the properties of given a structure, the affinity of ions to a given co-ordination number and Goldsmith tolerance factor [3]. In this context, large number of compounds have been fabricated and well characterized. Several theoretical models [4–7] have been proposed by different groups to understand the various mechanisms involved in these compounds. However, certain problems still do exist for a complete study and need enhancement in their material properties for various applications.

Lead ytterbium tantalate $Pb(Yb_{1/2}Ta_{1/2})O_3$ (PYT) is a lead based antiferroelectric with highly ordered perovskite structure [8]. It was first reported by Yasuda and Konda [9] that similar to highly ordered $Pb(Yb_{1/2}Nb_{1/2})O_3$ [10] and $Pb(Ho_{1/2}Nb_{1/2})O_3$ [11], PYT displays a first-order phase transitions at T_a (=285 °C) from paraelectric to antiferroelectric, where the dielectric constant attains a maximum value. Below this transition temperature (T_a), another weakly diffused phase transition was suggested to occur from antiferroelectric to ferroelectric at T_b (=166 °C) [9]. The ferroelectricity in PYT below the second transition temperature (T_b) was confirmed from the observation of polarisation-electric field (P-E) hysteresis loops at room temperatures. They have observed from the temperature variation XRD data that the crystal symmetry of PYT is cubic in high temperature paraelectric phase and monoclinic at temperatures below T_b. Room temperature XRD pattern showed the presence of superlattice reflections due to B-site ordering and Pb antiparallel displacement. Later a few solid solution compositions containing polycrystalline PYT as one of the components like PYT–PT, PYT–PZ and PYT–PLN have been

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studied [12–14]. Park and Choo and Kim et al. reported that the splitting of structure sensitive peaks in low temperature (below T_b) XRD pattern could be interpreted as arising from orthorhombically distorted ABO_3 type sub cells with the pseudo-monoclinic cell [12,13]. Recently, Rout et al. reported that PYT undergoes a structural change to pseudo-cubic symmetry with the substitution of Ba^{2+} at the Pb^{2+} site [15]. In their report, the enhancement in dielectric properties of these compounds has been interpreted in terms of ionic radii (ionic radius of Ba^{2+} is larger than Pb^{2+}) and change in the degree of ordering at B-site influenced by the substitution at A-site.

$Pb(Fe_{1/2}Ta_{1/2})O_3$ (PFT) [16–18] belongs to the group of lead based complex perovskites where the B-site atoms are randomly distributed. From the structural study of the compound, Nomura et al. [19] revealed the absence of superlattice lines which indicated the disordered arrangement of Fe^{3+} and Ta^{5+} ions in the B-site of the perovskite structure. The dielectric properties of PFT were those of typical relaxor ferroelectrics showing significant dielectric dispersion and diffuse phase transition.

In the present work, consideration is given to the synthesis and characterization of $(1-x)Pb(Yb_{1/2}Ta_{1/2})O_3$–$xPb(Fe_{1/2}Ta_{1/2})O_3$ with $x = 0.0$, 0.1, 0.13, 0.15, 0.18 and 0.2 prepared by solid state reaction method. The study encompasses identification of single phase, microstructure analysis and dielectric property of PYFT ceramics.

2. Experimental procedure

In the process of investigation on the doping effect of Fe in PYT ceramic, the composition studied are represented by the general formula $(1-x)Pb(Yb_{1/2}Ta_{1/2})O_3$–$xPb(Fe_{1/2}Ta_{1/2})O_3$ (PFYT) with $x = 0.0$, 0.1, 0.13, 0.15, 0.18 and 0.2. All the samples are prepared by solid-state reaction method. Two-step process [20] was followed to prepare pure PYT to avoid the formation of additional phases and the details were given elsewhere [15]. For the preparation of Fe^{3+} substituted compounds high purity reagents of PbO (99.9%), Yb_2O_3 (99.9%), Fe_2O_3 (99. 9%) and Ta_2O_5 (99.9%) were mixed in a stoichiometric ratio with distilled water as medium. The powder was calcined at 900–950 °C for 2 h. Pellets were made after mixing polyvinyl alcohol (PVA) as binder using uniaxial press. The binder was removed by keeping the green pellets at 500 °C for more than 12 h and then sintered at 1025–1100 °C for 2 h. Care has been taken to minimise the lead loss. The density of the sintered pellets was measured by Archimedes liquid displacement method using an analytical balance and distilled water as the reference liquid. The X-ray diffraction spectrum of the samples was taken using Cu Kα radiation. The microstructure of the samples was observed on fractured surface using scanning electron microscope (SEM: JSM-840 scanning microscope JEOL). The pellets were electroded on the polishing surfaces with silver paint by firing at 500 °C for 1 h. The dielectric response of the samples was carried out at 0.1–200 kHz at the temperature range −100 to 300 °C using Zentech 1061 LCZ meter.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the X-ray diffraction patterns obtained for the bulk samples PFYT with $x = 0.0$–0.2. The samples are found to be well crystallised in single phase. There are no detectable secondary phases, indicating the complete solid solution of the PYT and PFT compositions. It can be observed that the splitting in the structure sensitive peaks starts merging for the higher value of x (=0.18, 0.2). This may be caused by gradual distortion of the unit cell as the solid solution is going towards pseudo-cubic phase for high value of x. This is expected since the crystal structure of PFT is cubic. It can be seen from the Fig. 1 that there is a slight shifting of the peaks for higher Fe concentration. The lattice parameters are calculated and listed in Table 1. The parameters resemble to monoclinic unit cell even at $x = 0.2$. This indicates that there is a mixture of two phases present in the system as we can see the splitting

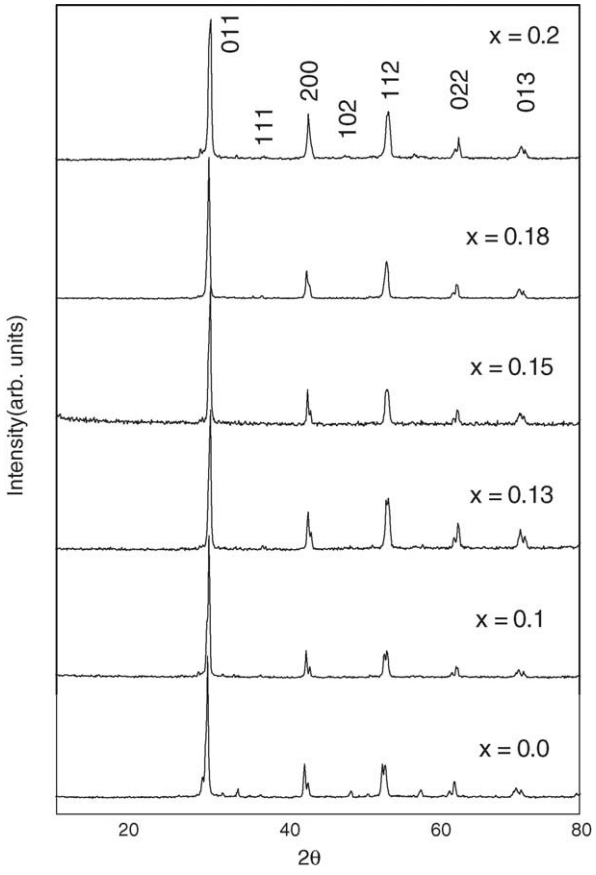

Fig. 1. XRD pattern of $(1-x)Pb(Yb_{1/2}Ta_{1/2})O_3$–$xPb(Fe_{1/2}Ta_{1/2})O_3$PFYT ceramics.