

# Diffuse phase transition of Fe doped lead ytterbium tantalate ceramics

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## Abstract

The effect of different concentration of Fe on the phase transition behavior of Lead ytterbium tantalate is investigated by dielectric and differential scanning calorimetry measurements. The samples are prepared through solid state reaction method and it has been found that the sintering temperature significantly lowered when the proportion of  $\text{Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$  increased. It has been observed that the doping in small amounts ( $0 \leq x \leq 0.2$ ) of Fe could meliorate the dielectric and ferroelectric properties. The diffuseness in the mode of phase transition increases and the phase transition temperature decreases as a function of Fe content. It is revealed that the dielectric data and heat capacity data follow a similar trend in the variation of the mode of phase transition and phase transition temperatures. The phase transition temperature values obtained from the heat capacity measurement well agreed with the values obtained from dielectric measurement.

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## 1. Introduction

In the recent years the oxides of complex perovskite structure  $\text{A}(\text{B}'_{1/2}\text{B}''_{1/2})\text{O}_3$  have been the subject of broad investigations from several point of view (structure and phase transition, inductive properties, non-linear optical properties, photo refractivity and electrochemical properties) [1,2]. Within the framework,  $\text{Pb}(\text{Yb}_{1/2}\text{Ta}_{1/2})\text{O}_3$  (PYT) [3] is a highly ordered lead based perovskite antiferroelectric similar to  $\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3$  [4] and  $\text{Pb}(\text{Ho}_{1/2}\text{Nb}_{1/2})\text{O}_3$  [5]. Yasuda and Konda have reported that PYT undergoes a first order phase transition at  $T_a$  ( $=310^\circ\text{C}$ ) from paraelectric (cubic) to antiferroelectric (monoclinic) and a weakly diffused phase transition from antiferroelectric to ferroelectric (monoclinic) at  $T_b$  ( $=177^\circ\text{C}$ ) [3]. Room temperature X-ray diffraction (XRD) pattern showed the presence of superlattice reflections due to B-site ordering and Pb antiparallel displacement. Later a few solid solution compositions such as  $\text{Pb}(\text{Yb}_{1/2}\text{Ta}_{1/2})\text{O}_3\text{-PbTiO}_3$  (PYT-PT) [6],  $\text{Pb}(\text{Yb}_{1/2}\text{Ta}_{1/2})\text{O}_3\text{-Pb}(\text{Lu}_{1/2}\text{Nb}_{1/2})\text{O}_3$

(PYT-PLN) [7] and  $\text{Pb}(\text{Yb}_{1/2}\text{Ta}_{1/2})\text{O}_3\text{-PbZrO}_3$  (PYT-PZ) [8] have been studied. Park et al. 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  $\text{ABO}_3$  type sub cells with the pseudo-monoclinic cell in PYT-PT and PYT-PLN, respectively, [6,7]. Sciau et al. suggested that the cubic phase of PYT belongs to the space group  $Fm\bar{3}m$  and the XRD pattern at 30 and  $220^\circ\text{C}$  are both in agreement with the space group  $Pbnm$  [9].

$\text{Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$  (PFT) belongs to the group of lead based complex perovskites where the B-site atoms are randomly distributed [10,11]. From the structural study of this compound, Nomura et al. revealed the absence of superlattice reflections, which indicated the disordered arrangement of  $\text{Fe}^{3+}$  and  $\text{Ta}^{5+}$  ions in the B-site of the perovskite structure [12]. The dielectric properties of PFT were those of typical relaxor ferroelectrics showing appreciable diffuse phase transition and dielectric dispersion.

In the present study, X-ray diffraction, polarization, dielectric and differential scanning calorimetry measurements are performed to investigate the effect of the different  $\text{Fe}^{3+}$  concentration on the phase transition behavior of  $\text{Pb}(\text{Yb}_{1/2}\text{Ta}_{1/2})\text{O}_3$ .

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## 2. Experimental procedure

Ceramics of  $(1-x)\text{Pb}(\text{Yb}_{1/2}\text{Ta}_{1/2})\text{O}_3-x\text{Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$  with  $x=0.0, 0.1, 0.13, 0.15, 0.18$  and  $0.2$  were prepared by solid-state reaction method. The two-step process proposed by Swartz and ShROUT [13] was followed to prepare pure PYT to avoid the formation of additional phases and the details were given elsewhere [14]. For the preparation of  $\text{Fe}^{3+}$  substituted compounds high purity reagents of  $\text{PbO}$  (99.9%),  $\text{Yb}_2\text{O}_3$  (99.9%),  $\text{Fe}_2\text{O}_3$  (99.9%) and  $\text{Ta}_2\text{O}_5$  (99.9%) were wet mixed in a stoichiometric ratio with distilled water as medium. The dried powders were calcined at  $900\text{--}950^\circ\text{C}$  for 2 h. The calcined powders were reground and then uniaxially pressed into pellets of 12 mm diameter and 1 mm thickness after adding poly vinyl alcohol (PVA) as a binding agent. The binder was removed by keeping the green pellets at  $500^\circ\text{C}$  for more than 12 h and then sintered at  $1025\text{--}1100^\circ\text{C}$  for 2 h in a controlled  $\text{PbO}$  atmosphere to minimize the loss of  $\text{PbO}$ . The XRD pattern of the samples was recorded by Philips X-ray generator (PW140) using  $\text{Cu K}_\alpha$  radiation. The bulk density of the sintered pellets was measured by Archimedes liquid displacement method using distilled water as the reference liquid and the relative density of the samples was calculated to be more than 94% of the theoretical density. The pellets were electroded on both the polishing surfaces with silver paint by firing at  $500^\circ\text{C}$  for 1 h. The dielectric response of the samples was carried out at  $0.1\text{--}200$  kHz at the temperature range  $-100$  to  $300^\circ\text{C}$  using Zentech 1061 LCZ meter. The  $P\text{--}E$  hysteresis loop measurement was carried out by using a Sawyer–Tower circuit (hysteresis loop tracer) at room temperature under AC field (amplitude  $60\text{ kV/cm}$  and frequency  $60\text{ Hz}$ ). The thermal properties of the specimens with differing Fe concentration were measured using differential scanning calorimetry (DSC). The specimen sample and the reference (sapphire pellet) sample of about diameter 4 mm and thickness 1 mm each were put in open Al crucible and heated in the temperature range  $40\text{--}350^\circ\text{C}$  at a rate of  $10^\circ\text{C/min}$ . Nitrogen gas in a flow rate of  $80\text{ ml/min}$  was constantly supplied as atmosphere. The heat of transition ( $\Delta H$ ) and corresponding entropy change were calculated for all samples by extrapolating a base line from the region outside the transition range, and determining the area between the base line and the measured thermal curve.

## 3. Results and discussion

### 3.1. X-ray diffraction

The XRD patterns of the sintered samples in the  $2\theta$  range  $40\text{--}60^\circ$  are shown in Fig. 1. It can be seen that the splitting present in the two structure sensitive reflection lines (200) and (112) for pure PYT sample, gradually starts merging as the concentration of Fe increases. This indicates that the structure of the system is going towards a higher symmetry and is expected to be cubic, as the symmetry of the end composition (PFT) is cubic. This can be evidenced by calculating the tolerance factor ( $t$ ) as a function Fe concentration. It is well known that the degree of distortion in the perovskite materials

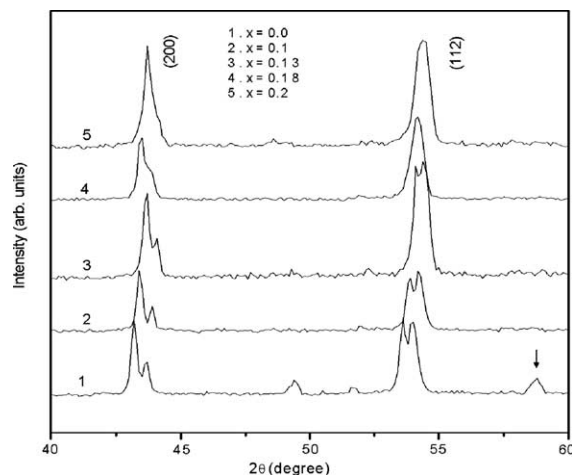


Fig. 1. XRD pattern of  $(1-x)\text{Pb}(\text{Yb}_{1/2}\text{Ta}_{1/2})\text{O}_3-x\text{Pb}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3\text{PFYT}$  ceramics at  $2\theta$  range  $40\text{--}60^\circ$ .

is determined by the tolerance factor ( $t$ ), given by

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (1)$$

where  $r_A$ ,  $r_B$  and  $r_O$  are the ionic radii of A, B and O ions. The tolerance factor,  $t=1$  corresponds to the ideal cubic structure and  $t < 1$  corresponds to the distorted perovskite structure. The tolerance factors are calculated by using the ionic radii given by Shannon [15]. The values are 0.814, 0.947, 0.948, 0.949, 0.951 and 0.952 for the compositions  $x=0.0, 0.1, 0.13, 0.15, 0.18$  and  $0.2$ , respectively. These values indicate that the distortion (monoclinic) from the ideal perovskite is more in case of PYT sample and gradually increase towards unity as the structure approaches cubic with increase of Fe content. It is also seen that the intensity of peak (indicated by an arrow in the XRD pattern) due to antiparallel displacement of Pb decreases with increase of Fe content.

### 3.2. $P\text{--}E$ Hysteresis measurement

Representative  $P\text{--}E$  hysteresis loops for  $x=0.0$  and  $0.2$  measured at room temperature are shown in Fig. 2. The loops

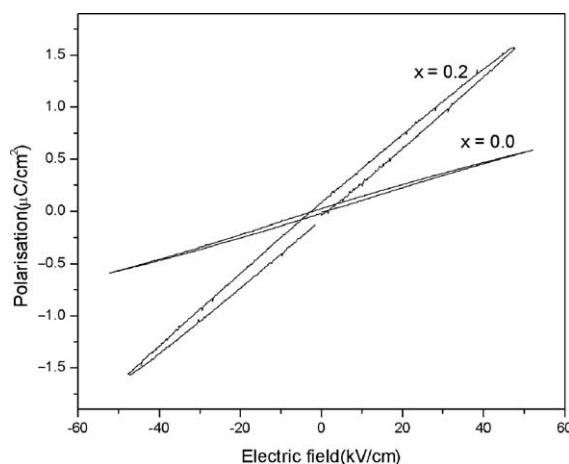


Fig. 2.  $P\text{--}E$  hysteresis loop of PFYT ceramics for  $x=0.0$  and  $0.2$ .

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