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A comparative study of dielectric and Raman spectroscopy of $Pb(Yb_{1/2}Ta_{1/2})O_3$ and $Pb(Yb_{1/2}Nb_{1/2})O_3$

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Abstract

A comparative study of the properties of two highly ordered lead based complex perovskites $Pb(Yb_{1/2}Ta_{1/2})O_3$ and $Pb(Yb_{1/2}Nb_{1/2})O_3$ has been carried out through x-ray diffraction, dielectric and Raman scattering measurements. These two compounds differ significantly in their structure, dielectric response and phonon vibration although the ionic radii and valencies are same for Ta and Nb. The room temperature x-ray diffraction pattern and Raman spectra show that the symmetry of lead ytterbium tantalate is lower than that of lead ytterbium niobate. The Raman spectra of $Pb(Yb_{1/2}Ta_{1/2})O_3$ also indicates the presence of local distortion in the lattice which may be one of the factors responsible for the existence of a secondary transition.

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1. Introduction

Lead based perovskites have been extensively explored for the last two decades because of their high dielectric and piezoelectric constants. Besides being beneficial for a variety of applications, these materials are of keen interest from a fundamental point of view due to their dielectric properties being extremely sensitive to the structure and chemistry [1,2]. Within this framework, lead based perovskites with formulae $Pb(B'_{1/2}B''_{1/2})O_3$ have been the subject of broad investigations from several points of view (structure and phase transition, inductive properties, non-linear optical properties, photo refractivity and electrochemical properties). The compounds like $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN), in which the B-site atoms are randomly distributed, are ferroelectric whereas the compounds like $Pb(Ho_{1/2}Nb_{1/2})O_3$ (PHN), in which the B-site atoms are highly ordered, are antiferroelectrics [3,4]. $Pb(Fe_{1/2}Ta_{1/2})O_3$ (PFT) behaves as a relaxor ferroelectric showing an appreciably diffuse phase transition and dielectric dispersion [5]. Interestingly some of these perovskites can exhibit ferroelectric, antiferroelectric or relaxor type behavior by altering the chemistry of the B-site cations. For example, in the systems like lead indium tantalate and lead scandium tantalate, the chemical ordering at the B-site induces a transition from relaxor to normal ferroelectric behavior in the compound [6,7]. However the influence of chemical order on the relaxor properties of these systems is not universal. It is generally accepted that relaxor behavior arises from a frustration of long-range ferroelectric coupling by some type of localized disorder in the crystal structure. The structure has been extensively studied by different experimental methods: X-ray diffraction, neutron diffraction, X-ray diffuse scattering, infrared and Raman spectroscopy, nuclear magnetic resonance, high resolution transmission electron microscopy and scanning force microscopy. In all the known $A(B'B'')O_3$ perovskite relaxors, the A or B sub-lattices are occupied by disordered or partially ordered mixtures of two (or more) different cations. The affinity to B-site ordering is generally determined from the valence and the ionic radii differences between B' and B'' cations. The importance of 1:1 B-site ordering

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for the dielectric response has been clearly demonstrated for the $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN) and $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) systems and the degree of ordering varies [8], although the ionic radii of Ta^{5+} and Nb^{5+} in a six coordination are the same (0.64 Å) [9]. Among the group of highly ordered lead perovskites, another pair of compounds that attracts much attention are $Pb(Yb_{1/2}Ta_{1/2})O_3$ (PYT) and $Pb(Yb_{1/2}Nb_{1/2})O_3$ (PYN) [10,11]. A lot of work has been carried out on PYN compared to that of PYT, but so far not a single comparative study seems to have been reported in the literature. In contrast to $Pb(Sc_{1/2}Ta_{1/2})O_3$ and $Pb(Sc_{1/2}Nb_{1/2})O_3$ or $Pb(Fe_{1/2}Ta_{1/2})O_3$ (PFT) and $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN), both PYT and PYN are highly ordered antiferroelectrics like PHN and $Pb(Mg_{1/2}W_{1/2})O_3$ (PMW) [4,12]. However PYT undergoes two successive phase transitions whereas PYN undergoes a single-phase transition [10,11]. It is interesting to do a comparative study of the phase transition behavior combined with the structure of these two compounds.

In this present work, a comparative study of X-ray diffraction, dielectric properties and phonon vibration modes of $Pb(Yb_{1/2}Ta_{1/2})O_3$ and $Pb(Yb_{1/2}Nb_{1/2})O_3$ has been performed to identify the possible factors that are responsible for the secondary diffuse phase transition present in PYT.

2. Experimental

The polycrystalline samples were prepared by a two-step solid-state reaction method [13]. The samples, $Pb(Yb_{1/2}Ta_{1/2})O_3$ and $Pb(Yb_{1/2}Nb_{1/2})O_3$, were calcined at 900 °C for 2 h and sintered at 1175 °C and 1100 °C for 2 h, respectively. The details of the preparation were given elsewhere [14–16]. The single-phase nature of the sample was confirmed through x-ray diffraction by a Philips X-Ray generator (PW140) using Cu Kα(λ = 1.5418 Å) radiation. The pellets (10.5 mm diameter and 1 mm thickness) were electroded on the polished surfaces with silver paint by firing at 500 °C for 1 h. The dielectric response measurement of the samples was carried out at 0.1–200 kHz in the temperature range from room temperature to 350 °C using a Zentech 1061 LCZ meter. The data were recorded in an interval of one degree by copper–constantan thermocouple connected with a Keithley nano-voltmeter. The Raman spectra of the samples were taken at room temperature in the frequency range 20–1020 cm^{-1}. The spectra were recorded in back scattering geometry using 200 mW output power of the 488 nm line of an Ar-ion laser. The scattered light was analyzed using a double monochromator (SPEX 14018) and detected with a photo-multiplier tube (Hamamatsu R120) operating in a photon counting mode. The position and full width at half maximum (FWHM) of the Raman peaks were obtained by fitting the spectra with Lorentzian line shapes (Jandel peak fit program).

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the x-ray diffraction patterns of PYN and PYT. The patterns confirm that the polycrystalline samples are formed in a single phase. The diffraction lines are indexed by comparing the present data with the data reported earlier [14–16]. In the present case also, we have observed clearly the super lattice reflections due to anti-parallel displacement of Pb^{2+} cations and B-site ordering, which are marked as open and closed circles respectively. The splitting of structure sensitive peaks in the pattern for PYT could be interpreted as arising from orthorhombically distorted ABO_3 type sub cells with the pseudo-monoclinic cell [15,17]. The lattice parameters were calculated as: $a = 4.247 \pm 0.001$ Å, $b = 4.151 \pm 0.001$ Å, $c = 4.166 \pm 0.001$ Å and $\alpha = \beta = 90°$, $\gamma = 90° 30'$. The symmetry of PYN at room temperature is found to be orthorhombic [16]. The lattice parameters are calculated as: $a = 5.918 \pm 0.001$ Å, $b = 23.453 \pm 0.001$ Å and $c = 8.221 \pm 0.001$ Å.

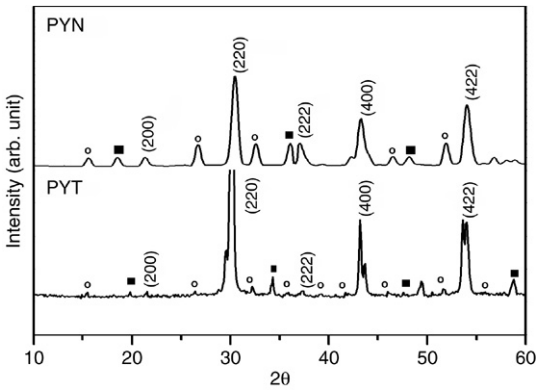

Fig. 1. X-ray diffraction patterns of PYN and PYT. The circles and squares represent the superlattice reflections due to antiparallal displacement of Pb and B-site ordering respectively. The patterns are indexed with respect to a double perovskite structure.

3.2. Dielectric constant measurement

Fig. 2(a) and (b) show the dielectric constant of PYN and PYT as a function of temperature and frequency. PYT undergoes two successive phase transitions: a primary paraelectric–antiferroelectric at T_C (562 K) and a secondary antiferroelectric–ferroelectric phase transition at T_m (448 K at 100 kHz). In a similar fashion PYN undergoes a primary paraelectric–antiferroelectric phase transition at T_C (578 K) whereas the secondary phase transition is absent. The maximum dielectric constant of the primary transition and the corresponding temperature (T_C) are larger in the case of PYN than that of PYT. In both cases the primary transition is of sharp first order in nature and the dielectric constant obeys Curie–Weiss law above T_C. The transition temperature, T_C is found to be independent of frequency for PYT and PYN. The secondary phase transition in PYT is diffuse and characterized by a frequency dependent transition temperature. The ferroelectricity below this transition is examined by E–P hysteresis measurement. Fig. 3 shows the E–P hysteresis loop measured at room temperature. The loop appears to be very slim indicating a weak ferroelectric phase. The remnant polarization (P_R) and the coercive field (E_C) are observed to be 0.023 μC/cm^2 and 0.35 kV/cm respectively. In analogy to the above observations it can be suggested that the antiferroelectric