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Phase transition and conduction mechanism of rare earth based tungsten-bronze compounds

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ABSTRACT

The polycrystalline materials ($Li_2Pb_2R_2W_2Ti_4Nb_4O_{30}$ (R = Y, Eu)) of tungsten-bronze structural family have been synthesized using a high-temperature solid-state reaction (mixed-oxide) technique. The formation of the single phase compounds was checked using preliminary X-ray structural data/pattern. The nature and distribution of grains in the samples in the scanning electron micrographs (SEM) confirm the good quality of the samples used for electrical characterization. The phase transition (ferroelectric–paraelectric) in the materials was established through the detailed studies of dielectric, electric polarization and pyro-electric properties. Studies of pyroelectric properties show that the materials have reasonably high figure of merit useful for pyroelectric detector. The nature of frequency dependence of ac conductivity suggests that the materials obey Jonscher's universal power law.

1. Introduction

The discovery of ferroelectric phase transition with high dielectric constant and spontaneous polarization at room temperature in perovskite $BaTiO_3$ [1] in 1940s had prompted to examine many oxides of similar and/or different structural families in search of new materials for device applications. Among all the ferroelectric oxides examined and reported so far, some oxides of tungsten bronze (TB) structural family have been found very useful for piezoelectric [2], pyroelectric, microwave dielectric/resonators etc. devices at room temperature [3–13]. Rare-earth ion-doped compounds have particularly received a considerable attention [14–17] of researchers because of their better structural stability and enhanced properties. The TB structures of a general formula $[(A_1)_2(A_2)_4](C)_4[(B_1)_2(B_2)_8]O_{30}$ have complex chains of distorted BO_6 octahedral with three different types of interstices (A_1), (A_2) and (C) having 12-,15- and 9-fold coordination, respectively. The B_1 and B_2 sites, arising from two types of BO_6 octahedron, have C_{2v} and C_1 symmetry, respectively [15–19]. Moreover, the A-site is occupied by mono to tri-valence cations, B-sites occupied by tetra to hexa-valent ions (W^{+6}, Ti^{+4}, Nb^{+5}, Ta^{+5}, V^{+5}) and C-site either unfilled or occupied by small ions. As TB structure is complex, there is a large scope for modification at its different sites to tailor the physical properties required for devices.

Since the first report on ferroelectric properties in a tungsten bronze compound [4], a large number of compounds of the TB family have been investigated in the form of single crystal, ceramics and thin films. Structural, ferroelectric and electrical conductivity in some compounds related to this paper such as $Pb_3R_3Ti_5Nb_5O_{30}$ (R = rare earth ion) have already been reported by several workers [5,20–23]. Though studies of ferroelectric and related properties in some multi-valenced tungsten–bronze structure are reported earlier either in single crystal, ceramics or thin film [24,25], but not much information was available on ferroelectric phase transition and conduction mechanism of compounds having all the six valences. In order to tailor the ferroelectric properties in such type of compounds, we have studied $Na_2Pb_2Sm_2W_2Ti_4Nb_4O_{30}$ [6], $Na_2Pb_2Nd_2W_2Ti_4Nb_4O_{30}$ [7], and $Na_2Pb_2R_2W_2Ti_4V_4O_{30}$ (R = Gd, Eu) [8] which have provided many interesting properties useful for devices. Recently, pyro-electric properties of $Ba_5SmTi_3Nb_7O_{30}$ have been reported by Ganguly et al. [10]. More recently, ferroelectric phase transition and conduction mechanism in $Li_2Pb_2Pr_2W_2Ti_4Nb_4O_{30}$ was reported by Parida et al. [26]. Structural, dielectric and electrical properties of $K_2Pb_2Dy_2W_2Ti_4Nb_4O_{30}$ have been reported by Padhee et al. [9]. It is found that above compounds have very good ferroelectric and electrical properties studied from dielectric, polarization and impedance measurements. Though a lot of work has been done on TB structured compounds, no work has been reported on the ferroelectric and pyroelectric properties in the $Li_2Pb_2R_2W_2Ti_4Nb_4O_{30}$ (R = Y, Eu) complex system. Therefore, this work is an attempt to obtain new ferroelectric compounds with some interesting results useful for applications.

2. Experimental

The polycrystalline samples of $Li_2Pb_2R_2W_2Ti_4Nb_4O_{30}$ (R = Y, Eu) (LPRWTN) were synthesized by high-temperature solid-state reaction technique using high-purity (AR grade) ingredients: Li_2CO_3, TiO_2, Nb_2O_5 and WO_3 (99%, all from M/s LOBA Chemie Pvt. Ltd., India.), PbO (99.9%, M/s E. Merck India Ltd.), R_2O_3(R = Y, Eu)

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(99.9%, M/s Indian Rare Earth Ltd). These oxides and carbonate were grinded in dry (air) and wet (methanol) medium for several hours in agate mortar. The calcination temperature of the mixtures were decided and optimized (1100 °C) on the basis of repeated firing/mixing for 4 h in alumina crucible. The X-ray diffraction (XRD) pattern or diffraction data of calcined powders were obtained at room temperature using X-ray powder diffractometer (Rigaku Miniflex). The CuK_α radiation ($\lambda = 1.5405A^0$) was used to collect the XRD pattern/data of the above materials in a wide range of Bragg's angles (θ) ($20° \leqslant 2\theta \leqslant 80°$) at a scanning rate of 3 deg./min. The calcined fine powder of the materials was then cold pressed into cylindrical pellets (diameter 12 mm and 1-2 mm thickness) under a uni-axial pressure of 4×10^6 Nm^{-2} using a hydraulic press. Polyvinyl alcohol (PVA) was used as a binder to prepare pellets. The pellets were then sintered at an optimized temperature (1150 °C) and time (4 h) in air atmosphere. The sintered pellets were coated with high-quality silver paste, and dried at 160 °C for 8 h before measuring dielectric and electrical parameters. The surface morphology of gold-coated LPRWTN(R = Y, Eu) pellet samples were recorded by JEOL JSM-5800 scanning electron microscope (SEM). The dielectric (capacitance, dissipative factor), impedance and inductance parameters on sintered pellets were measured as a function of frequency (1 kHz to 1 MHz) at different temperatures (25–500 °C) using a computer-controlled impedance meter (PSM LCR 4NL, Model: 1735, UK) with a laboratory-designed and fabricated sample holder and furnace. A chromel-alumel thermo-couple and KUSAM MECO 108 digital milli-voltmeter were used to record the temperatures. The polarization (hysteresis loop) of the poled sample (electric field = 6 kV/cm, time = 8 h) was obtained at different temperatures using loop tracer (M/S Marine India, New Delhi). The pyroelectric current of the pellet samples was measured at different temperature (25–450 °C) by an electrometer (KEITHLEY INSTRUMENTS INC., MODEL 6517B) at the heating rate of nearly 2 °C/min. A constant voltage was applied across the sample to measure the dc conductivity.

3. Results and discussion

3.1. Structural analysis

The X-ray diffraction (XRD) patterns of LPRWTN recorded at room temperature on powder samples are compared in Fig. 1a. The diffraction patterns, consisting of a large number of sharp and single diffraction peak of the materials, are different from those of the ingredients of the prepared compounds exhibits better homogeneity and crystallization, and thus confirm the formation of single-phase new compounds [27]. As the TB structured compounds have either tetragonal or orthorhombic structure, attempts were being made to index all the observed peaks of the XRD patterns in these crystal systems with different unit cell configurations using a standard computer program package "POWD" [28]. Preliminary study of indexed reflections indicates that the materials can have Pma2 space group (polar point group mm2). However, with very limited powder diffraction data it is not possible to determine the space group uniquely. Further, the scattered crystallite or particle size (P) of the compounds was calculated using the broadening of some widely spread (over Bragg angles) strong and medium reflections in the Scherrer's equation: $P_{hkl} = \frac{K\lambda}{\beta_{1/2}\cos\theta_{hkl}}$ [29], where K (constant) = 0.89, λ = 1.5405 Å and $\beta_{1/2}$ = full width at half maximum (in radians). The average value of P is found to be 11 and 12 nm for LPYWTN and LPEWTN, respectively. The least-squares refined unit cell parameters are: a = 15.4956(16) Å, b = 14.3050(16) Å, c = 8.4076(16) Å and volume V = 1863.73 $Å^3$ for LPYWTN and those for LPEWTN are: a = 15.3625(19) Å, b = 14.2637(19) Å, c = 8.4016(19) Å and volume V = 1841.01 $Å^3$ (the number indicated in parenthesis is estimated standard deviation of unit cell parameters). As the ionic radius of lanthanide based compounds are known to decrease on increasing atomic number, consequently the cell volume of the studied compositions decreases when going from Y^{+3} to Eu^{+3}. The orthorhombic distortion calculated using unit cell parameters '+(a, b, c); $\delta = [b-a/b+a]$ will be 0.04 and 0.0371 for Y and Eu containing compounds, respectively.

Furthermore, the TB structure is built on five crystallographic sites. It is difficult to precisely determine the R^{+3} ions coordination (12- or 15-fold coordination) based on the current results. However, the previous structural studies show that the rare earth cations predominately prefer at the A_1 site [30].

Fig. 1b shows the surface microstructures/textures of LPRWTN. The nature and size of the grains suggest that the grain-growth during sintering is more or less completed. In spite of sintering at higher temperatures, some voids of irregular shape and dimension also seen. The small grains of varying dimension are homogenously distributed throughout the surface of the sample. The rod-as well as rectangular-shape of grains are found to be in the range of 3–10 μm. The rectangular grains impart ferroelectric switching property with large spontaneous polarization [31].

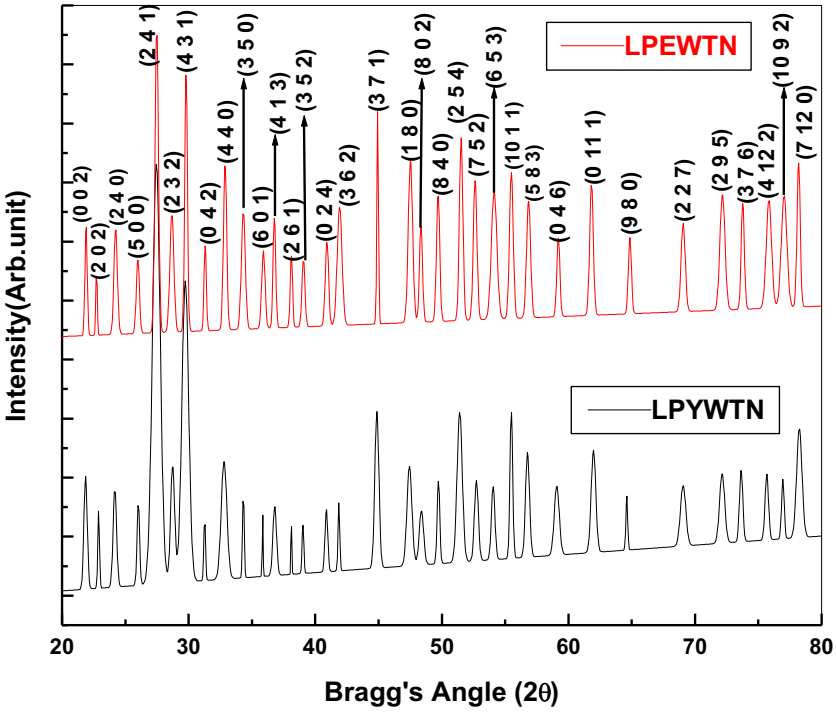

Fig. 1a. Indexed XRD pattern of LPYWTN & LEDWTN.