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Structural, Dielectric and Electrical Properties of Ba-modified PbWO4 Ceramics

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Polycrystalline samples of Ba-doped lead tungstate $Pb_1Ba_xWO_4$ (x = 0.0, 0.05, 0.10, 0.15) have been prepared by a high-temperature solid-state reaction technique. Preliminary X-ray diffraction studies of these compounds suggested the formation of a single-phase compound with the tetragonal crystal structure at room temperature. Detailed studies of dielectric constant (ε) and tangent loss (tan δ) as a function of frequency (400 Hz to 10 kHz) and temperature (room temperature to 598K) suggest that the above compounds are non-ferroelectric/non-polar with low activation energy, but interestingly contain space-charge polarization at high temperature.

Key Words: Dielectric, Electrical properties, Ceramics.

INTRODUCTION

Now-a-days, ferro-, piezo- and pyro-electric properties are found in a good number of oxides and non-oxides in a variety of structural families[1–3]. It has been observed that in spite of some structural, chemical and compositional[4-6] similarities of different members of some oxide families, they have many different structural and physical properties. Among them, some Pb-based pure and/or mixed oxides such as $PbTiO_3$ [7], $PbZrO_3$ [8], $LiNbO_3$, $Pb(ZrTi)O_3$, $(PbLa)(ZrTi)O_3$, etc.[9] are important for modern material science technology, because of their non-linear physical properties and existence of polarization (in ferroelectric phase) or in a wide range of temperature. Some molybdates and tungstates of Scheelite structured family of a general formula ABO_4 (A = alkali ions, B = W, Mo) have very unusual multiple phase transitions in a wide temperature range with high electrical conductivity and high dielectric loss but low dielectric constant[10]. $PbWO_4$ compound is a member of the Scheelite structural family with the C_{4h} point group symmetry of tetragonal crystal class and is suitable for laser applications[11]. From an extensive literature survey, it has been found that not much work has been done on the Ba-substituted $(Pb_{1-x}Ba_x)WO_4$ (x = 0.0, 0.05, 0.10, 0.15) ceramics. Therefore, preliminary investigations on structural, detailed dielectric and electrical properties of the compounds for the tailoring of the material properties and their better understanding for possible applications have been done.

EXPERIMENTAL

Polycrystalline samples of $Pb_{1-x}Ba_xWO_4$ with x = 0.0, 0.05, 0.10 and 0.15 were prepared from high-purity PbO (99.99%, Aldrich, USA), $BaCO_3$ (99.5% pure, BDH), MoO_3 (99.5% pure, BDH) using a high-temperature solid-state reaction technique. These materials were taken in a suitable stoichiometry form and mixed thoroughly in an agate mortar for 2 h. Dry powders of the compounds were calcined at 1053K in an alumina crucible for about 16 h. The mixing and calcination were repeated at 1073 K for 18 h. Finally, the fine calcined powder samples were used to make cylindrical pellets (10 mm diameter and 1–2 mm thickness) in an Uniaxial hydraulic press at a pressure of 5×10^7 kg/m^2. The pellets were sintered at 1193 K in an alumina crucible for 20 h. The density of the sintered pellets was measured by the Archimedes' method and was found to be 96–97% of $PbWO_4$ density. The formation and quality of the prepared compounds were checked by an X-ray diffraction (XRD) technique with a powder diffractometer (Philips PW1710, Holland) using CoKα radiation (λ = 1.789 Å) in a wide range of Bragg angles ($20° \leq 2\theta \leq 70°$) at room temperature with a scanning rate of 2° min^{-1} on calcined powders as well as on sintered pellets. High purity silver-paste was then painted on the flat polished surfaces of the sintered pellets to act as an electrode and then dried at 423K before taking any electrical measurements. The dielectric constant (ε) and tangent loss (tan δ) of the samples were obtained using a GR 1620 AP capacitance measuring assembly with a three-terminal sample holder as a function of frequency (400 Hz to 10 kHz) at room temperature (303 K) and in temperature range (303–598 K) at 10 kHz frequency. Existence of spontaneous polarization in the compounds was checked using laboratory-made modified Sawyer-Tower circuit.

RESULTS AND DISCUSSION

The XRD diffraction peaks of $Pb_{1-x}Ba_xWO_4$ in calcined powder as well as sintered pellets were sharp and single, which suggested the formation of good homogeneous and crystalline materials. All the peaks in XRD patterns (Fig. 1) were indexed, and cell parameters were determined in various crystal systems and cell configurations using a standard computer program package POWD MULT[12], with the observed d-values of strong, medium and low intensity reflections spread over a wide 2θ range. Finally, a particular unit cell was selected for which the difference in the observed and calculated d-values of the reflections, *i.e.*, $\Sigma\Delta d = \Sigma(d_{obs} - d_{cal})$, was found to be minimum. A good agreement between observed and calculated d-values (Table-1) suggests the correctness of the selected cell parameters of tetragonal crystal system at room temperature. The least -squares refined unit cell parameters of the compound with different x values are listed in Table-2. With the limited number of reflections, the exact space or point group of the compound could not be determined uniquely. The average

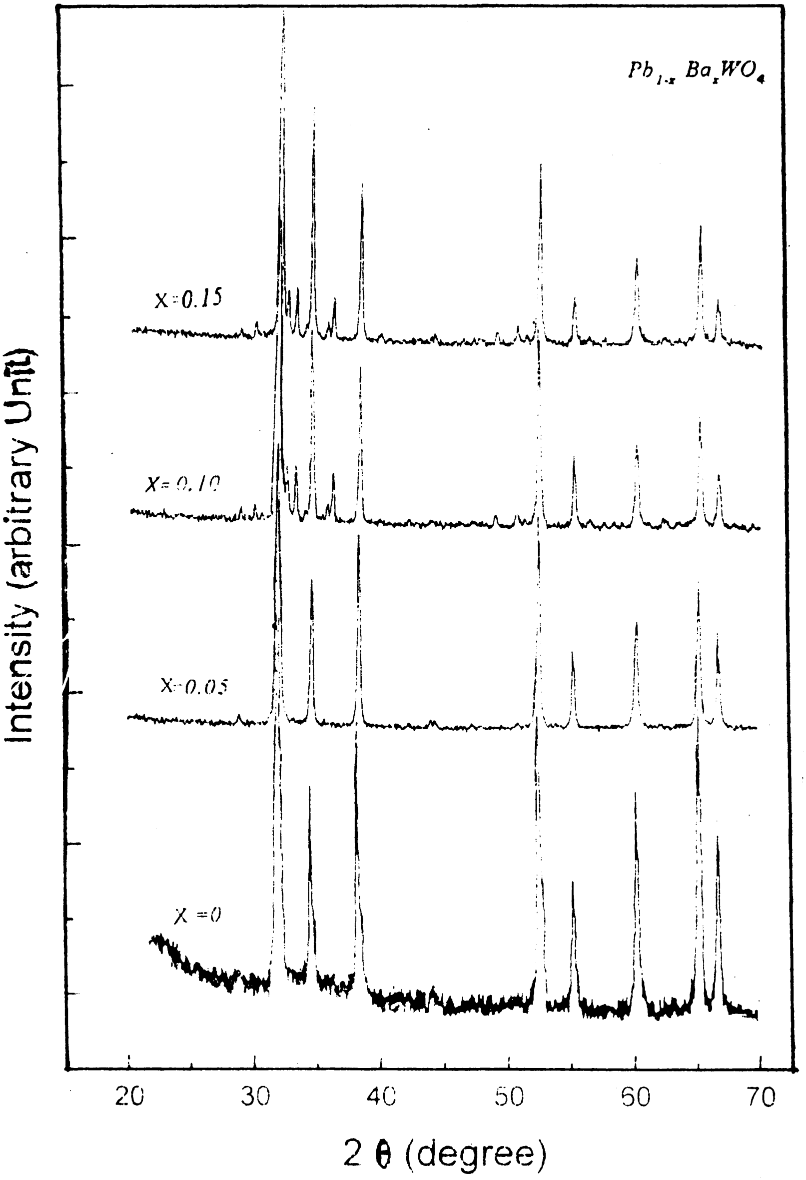

Fig. 1. Comparison of XRD patterns of $Pb_{1-x}Ba_xWO_4$ compounds at room temperature

crystallite size (P) of the compounds was found from strong, medium and low-intensity peaks (ignoring instrumental broadening) using Scherrer's equation, $P = 0.89/\beta_{1/2} \cos \theta$, where $\beta_{1/2}$ is the half peak width of the reflections. The average values of crystallite/particle size of the samples are given in Table-2.

TABLE-1
COMPARISON OF OBSERVED (O) AND CALCULATED (C) d-VALUES (IN Å) OF $Pb_{1-x}Ba_xWO_4$ COMPOUNDS WITH I/I_0 IN PARENTHESES

hkl	x = 0.0	x = 0.05	x = 0.10	x = 0.15
222, 310	(o) 3.4506 (16) (c) 3.4612	(o) 3.3263 (13) (c) 3.3270	(o) 3.4617 (12) (c) 3.4578	(o) 3.4561 (13) (c) 3.4564
104	(o) 3.2403 (100) (c) 3.2495	(o) 3.2403 (100) (c) 3.2561	(o) 3.2551 (100) (c) 3.2574	(o) 3.2551 (100) (c) 3.2556
312	(o) 3.1918 (17) (c) 3.1797	(o) 3.0335 (20) (c) 3.0296	(o) 3.1356 (18) (c) 3.1378	(o) 3.0292 (33) (c) 3.0314
223	(o) 2.9996 (30) (c) 2.9961	(o) 3.0080 (20) (c) 3.0159	(o) 2.8869 (7) (c) 2.8948	(o) 2.8831 (7) (c) 2.8933
055	(o) 2.7234 (35) (c) 2.7124	(o) 2.7234 (30) (c) 2.7208	(o) 2.7302 (32) (c) 2.7336	(o) 2.7337 (21) (c) 2.7325
522,334	(o) 2.0189 (51) (c) 2.0182	(o) 2.0224 (27) (c) 2.0243	(o) 2.0278 (23) (c) 2.0279	(o) 2.0314 (25) (c) 2.0297
442	(o) 1.9275 (23) (c) 1.9293	(o) 1.9307 (10) (c) 1.9310	(o) 1.9340 (16) (c) 1.9336	(o) 1.9356 (17) (c) 1.9386
540	(o) 1.7783 (30) (c) 1.7719	(o) 1.7809 (14) (c) 1.7792	(o) 1.7876 (12) (c) 1.7877	(o)1.7917 (11) (c) 1.7933
604, 444	(o) 1.6569 (40) (c) 1.6557	(o) 1.6603 (19) (c) 1.6609	(o) 1.6637 (18) (c) 1.6647	(o) 1.6659 (16) (c) 1.6652
208, 630	(o) 1.6239 (28) (c) 1.6248	(o) 1.6479 (23) (c) 1.6454	(o) 16307 (17) (c) 1.6300	(o) 1.6325 (16) (c) 1.6204

TABLE-2
COMPARISON OF UNIT CELL PARAMETERS, AVERAGE PARTICLE SIZE (P) AND ACTIVATION ENERGY (E_A) OF $Pb_{1-x}Ba_xWO_4$

The Estimated Error in Cell Parameter was ±0.0030

Composition x	a (nm)	c (nm)	P (nm)	E_a (eV)
0.00	0.5692	1.3562	15.0	0.31
0.05	0.5677	1.3565	15.3	0.27
0.10	0.5682	1.3551	14.9	0.43
0.15	0.5688	1.3557	17.1	0.24

Figs. 2 and 3 give the variation of dielectric constant (ε) and loss tangent (tan δ) as a function of frequency (400 Hz to 10 kHz) of $Pb_{1-x}Ba_xWO_4$ compound at room temperature. The nature of variation of these parameters shows that dielectric constant and tan δ decrease with the increase of frequency of all the compounds, which suggests a normal dielectric behaviour of the materials. This shows the presence of all the different types of polarizations (*i.e.*, electronic,

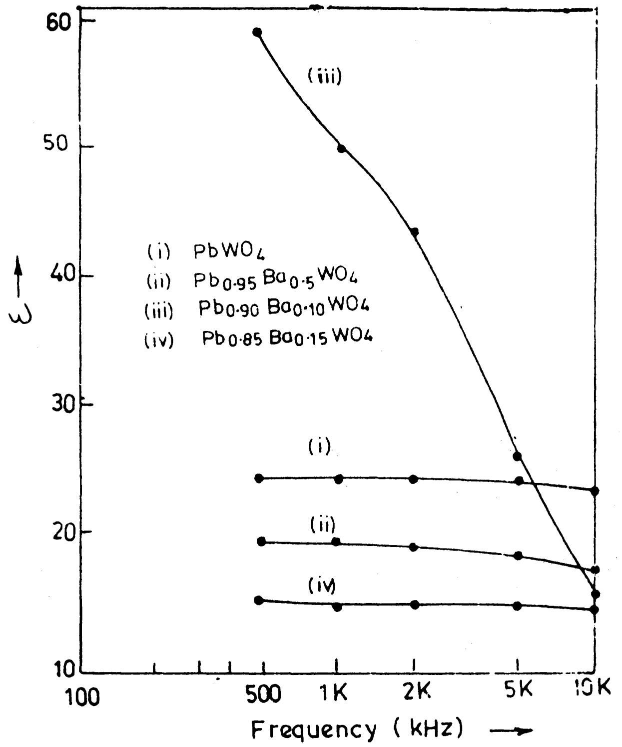

Fig. 2. Variation of dielectric constant (ε) of $Pb_{1-x}Ba_xWO_4$ as a function of frequency at room temperature

dipolar, interfacial, orientational etc) in the compounds at room temperature in the said frequency range. Fig. 4 shows variation of dielectric constant and tangent loss (tan δ) of the $PbWO_4$ compound with different x-values as a function of temperature at a frequency 10 kHz. It was found that the dielectric constant of $Pb_{1-x}Ba_xWO_4$ compounds increases very slowly, except in the case of $x = 0.15$ where ε increases at a faster rate and becomes very high beyond 543 K. The tan δ also shows similar behaviour with the temperature. The slow increase in dielectric constant in the low temperature region is due to lattice and/or ionic polarizability and faster increase of ε in high temperature region is due to space charge polarization[13]. In the high temperature region (> 553K) it is seen that with the increase in concentration of Ba, the dielectric constant increases faster and faster. Thus, it can be inferred that the space charge polarization starts early and increases fast for the higher concentration of Ba in lead tungstate compound. This behaviour is also observed in some other compounds of this family[14, 15]. Further, no hysteresis loop was observed at room temperature (as expected), which indicates the non-polar/non-ferroelectric properties of the compound.

The AC electrical conductivity σ and activation energy E_a of the samples was

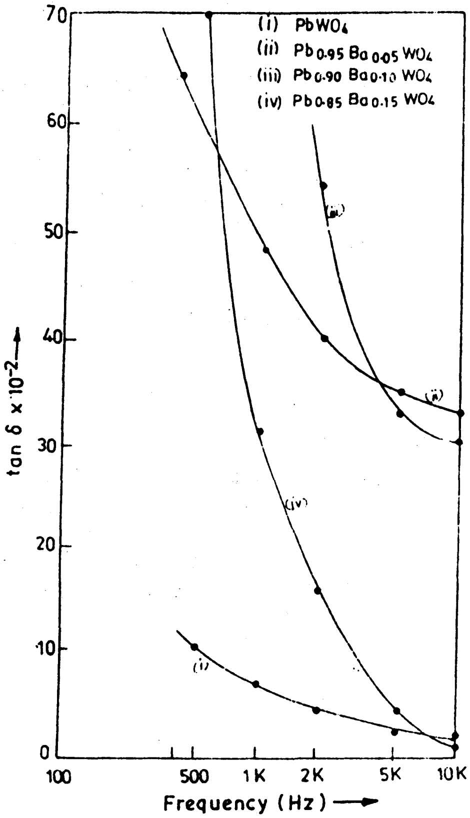

Fig. 3. Variation of tangent loss (tan δ) of $Pb_{1-x}Ba_xWO_4$ as a function of frequency at room temperature

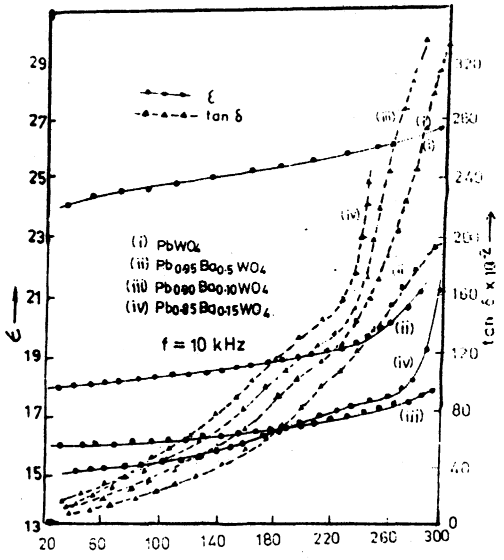

Fig. 4. Variation of dielectric constant (ε) and tangent loss (tan δ) of $Pb_{1-x}Ba_xWO_4$ with temperature at 10 kHz

calculated from the formulae $\sigma = \omega\varepsilon\varepsilon_0 \tan\delta$ and $\sigma = \sigma_0 \exp(-E_a/K_BT)$ where ε_0 = vacuum dielectric constant, ω = angular frequency and K_B = Boltzmann constant. The activation energy E_a in the high temperature region for all the samples has been obtained from the slope of the graph of log σ *vs.* 1/T (Fig. 5). The values of the activation energy of the samples have been given in Table-2. Low values of the activation energy are due to large ionic conductivity in the high temperature region supporting the existence of the superionic nature of all compounds studied[16]. Finally, it is concluded that the $Pb_{1-x}Ba_xWO_4$ compounds (where x = 0.0, 0.05, 0.10 and 0.15) have tetragonal centrosymmetric structure with no dielectric anomaly and hysteresis loop, but there is presence of space charge polarization at high temperature.

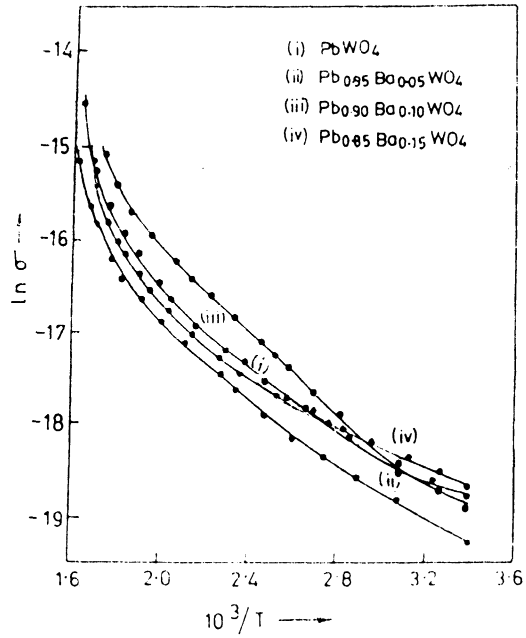

Fig. 5. Variation of ln σ as a function of inverse of absolute temperature (1/T) of $Pb_{1-x}Ba_xWO_4$ at 10 kHz

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