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Synthesis and Studies of High-Temperature Electrical Properties of $\text{Pb}_{0.8}\text{Bi}_{0.2}\text{Fe}_{0.734}\text{W}_{0.266}\text{O}_3$ Solid Solution

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Abstract. The $\text{Pb}_{0.8}\text{Bi}_{0.2}(\text{Fe}_{0.734}\text{W}_{0.266})\text{O}_3$ (PBFW) high temperature ceramic has been successfully synthesized by the modified columbite method. The phase purity was confirmed by the room temperature X-ray diffraction measurement and it confirms the formation of cubic structure with $Pm-3m$ space group. The lattice parameters were obtained from the Rietveld refinement technique, with $a = b = c = 3.9750 \text{ \AA}$. From the Scanning Electron Micrograph, the average grain size were measured about $1 \mu\text{m}$ and the Gaussian distribution showed uniform distribution of particles with small amount of porous nature. Temperature-dependent ferroelectric (P-E loop) measurement confirms the presence of polar Nanodomains along with leaky behavior owing to the conducting nature of the sample. A detailed study of frequency dependent permittivity and loss $\tan\delta$ evidenced the *Maxwell-Wagner* type of polarization. The Non-Debye type of relaxation in the PBFW was confirmed by analyzing the Impedance spectra and fitting the *Kohlraush-Williams-Watt* function to the electric modulus at few selected temperatures. The impedance spectra reveal that the grain boundaries are more resistive than grains. By fitting the *Johnscher's power law* to the ac conductivity and from the 'n' value, we conclude that the system has Correlated Barrier Hopping (CBH) conduction mechanism.

INTRODUCTION

The interaction of ferroelectric and ferromagnetic order parameters in magneto-electric multiferroics induces both polarization and magnetization in the system, which results in multifunctional properties. Due to this, over the decades, the multiferroic materials show a lot of potential for applications in spintronics, information storage, etc [1]. Among them, Lead-based complex structured perovskites $\text{Pb}(\text{B}'\text{B}'')\text{O}_3$ -type compounds have higher dielectric constants and lower sintering temperatures (as compared with BaTiO_3), along with wide range of Curie temperatures (T_C), thus have been studied widely as potential dielectric materials for ceramic chip capacitors, piezoelectrics, electrostrictions and PTC resistors exhibiting positive temperature coefficient of resistivity (PTCR) [1]. Lead iron tungstate, $\text{PbFe}_{0.67}\text{W}_{0.33}\text{O}_3$ (PFW) based materials are among the promising multiferroics as they exhibit very high ferroelectric, pyroelectric, and piezoelectric responses and can be sintered at relatively low temperatures [2, 3]. The main drawback in this material is low T_C and poor dielectric properties due to the formation of pyrochlore as a secondary phase. This is the most common problem encountered during the synthesis of PFW. These phases have a low dielectric permittivity, ϵ' , values and it is commonly believed that even a minor content of pyrochlore phase (about few %) reduces the dielectric constant considerably. Also, pure PFW is not a room temperature ferroelectric material, T_C is well below RT ($T_C = 150 \text{ K}$). Now by making substitutional solid solutions with similar compounds can enhance significantly both electric and magnetic properties. Similarly, BiFeO_3 (BFO) is a well-known RT multiferroic material with T_N and T_C well above RT. We made a solid solution of PFW and BFO with $x=0.2$ ie., $\text{Pb}_{0.8}\text{Bi}_{0.2}(\text{Fe}_{0.734}\text{W}_{0.266})\text{O}_3$ (PBFW). In this paper, we presented the synthesis of pure PBFW by using modified

columbite method and detailed studies structural and electrical properties through XRD, ferroelectric and frequency dependent dielectric measurements.

EXPERIMENTAL DETAILS

Mechanically activated two step solid state reaction method (Columbite method) was used to synthesize the pure PBFW and the details of synthesis are discussed elsewhere [3]. After obtaining the desired compound at RT, X-ray Diffraction was carried out using CuK α having a 1.5406Å wavelength (Model; RIGAKU ULTIMA IV, JAPAN) and 2 θ range of 20° ≤ 2 θ ≤ 80° in order to find the phase purity. Scanning Electron Microscopy was carried out (SEM, JEOL –JSM, Japan) to study the surface morphology, particle size and porosity of the sample. Ferroelectric (P-E) loop measurements were carried out at different temperatures (>300K, M/s Radiant Instrument) applying silver paste on both sides of the pellets as electrodes and immersed in the silicon oil to prevent the electric arcing at high applied voltage. Dielectric properties were measured in the temperature range of 313K – 528K at 100Hz to a 5MHz frequency range (Novo Control (Germany) Alpha AN analyzer with Quatro Cryo System).

RESULTS AND DISCUSSIONS

Figure1 (a) shows the Rietveld refined RT XRD pattern and it confirms Cubic phase with the space group of $Pm\bar{3}m$ (JCPDS # 40-374). The obtained structural parameters, bond length and R factors are listed in table 1. The RT lattice parameter (3.9750 (2) Å) of PBFW was decreased when compared with that of PFW ($a = 3.9776$ (4) Å). It is due to the smaller ionic radius of the Bi substituting at Pb site [4]. Figure 1(b) shows the SEM image and the Gaussian distribution of grain sizes (inset of Fig.1 (b)) show an average grain size of about 1µm. The image also shows the existence of porosity and is well reflected in XRD density (table 1).

TABLE 1. XRD Refined parameters of the PBFW Solid Solution

Composition	Lattice parameter	Bond length (Å)		χ^2	R_{wp}	R_p	Density(g/cm ³)	
	a=b=c (Å)	Pb/Bi-O	Fe/W-O				Theoretical	experimental
PBFW	3.9750 (2)	2.8107(4)	1.9875(3)	2.866	14.7	14.2	9.780	8.184

FIGURE 1. (a) RT Rietveld refined X-ray diffraction (b) Scanning electron micrograph and inset graph is distribution of the grain size of PBFW ceramic.

Figure 2 (a) shows the P-E hysteresis loop at few selected temperatures (300K, 337K, and 357K) measured at 200 Hz and up to 5 kV/cm applied field. The P-E loops show clear and well saturated loops at all the temperature along with some leaky behavior, though, the ferroelectric transition occurs at below RT. It indicates the existence of polar-nano domains. This mechanism can be explained with the existence of polar-nano domains, which are originated from the 1:1 B site ordered nano domains, containing the space charge polarization and these are thermally activated. The lossy nature occurs due to the formation of positively charged oxygen vacancies during the sintering. At these temperatures, electrons will start to hop from Fe²⁺ to Fe³⁺ state and transportation of oxygen vacancy charge carriers induces the conductivity. Frequency dependent dielectric constant and loss tangent were studied at few different temperatures (313K -528K) as shown in Fig. 2 (b) and its top inset, respectively. At lower frequency region, there is a rapid increase in the magnitude of permittivity and tan δ with increasing temperature.

This is attributed to the space charge polarization at the grain interface of the sample and it is thermally activated. Relaxation peak in the $\tan\delta$ at high frequency shows the shifting of peak maximum towards the higher frequency with increasing temperature. This indicates that Maxwell-Wagner type polarization is dominated in the dielectric material at these measured temperatures. Bottom inset of Fig. 2(b) shows the graph of peak frequency of $\tan\delta$ vs $1000/T$. The activation energy was estimated by fitting the Arrhenius equation (1), where f_0 is free exponential factor, E_a is relaxation activation energy and K_B is the Boltzmann constant. The calculated activation energy $E_a = 0.639$ eV, which relates the relaxation activation energy.

$$f = f_0 \exp\left(-\frac{E_a}{K_B T}\right) \quad (1)$$

Figure 3 (a) represents the cole-cole plot of Z' vs Z'' of the complex impedance at few selected temperatures [5]. The figure clearly shows two semicircles correspond to grain boundary and grains at low and high frequency regions, respectively. Predominantly, these semicircles were depressed and have their centers are below the real part Z' axis, hence it exhibits the non-Debye type of relaxation. The bulk (grain) and grain boundary resistance and capacitance (R_b , C_b , R_{gb} and C_{gb}) values were calculated by fitting the semicircle equation to Z' vs Z'' plot and are listed in table 2. Usually, the grain boundary resistance is more compared to grain due to the insulating nature. The interfacial polarization mechanism is confirmed by the grain boundary activation in the low frequency region. The resistance of both R_b and R_{gb} decreases with increasing temperature denotes the conducting nature in the sample.

FIGURE2. (a) Temperature-dependent P-E hysteresis (b) Frequency-dependent dielectric permittivity and top inset is $\tan\delta$ vs frequency and bottom inset is peak frequency vs temperature of PBFW ceramic.

TABLE 2. The calculated parameters from the P-E loop and Impedance spectra of the PBFW ceramic

From P-E loop				From impedance spectra				
Temperature (K)	P_r ($\mu\text{C}/\text{cm}^2$)	P_s ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)	Temperature (K)	R_g (Ω) $\times 10^5$	C_g (F) $\times 10^{-10}$	R_{gb} (Ω) $\times 10^5$	C_{gb} (F) $\times 10^{-10}$
301K	0.701	1.082	4.566	483K	2.601	2.406	4.276	6.940
337K	0.883	1.281	3.246	508K	1.222	1.825	2.025	2.163
357K	1.278	1.717	3.330	528K	0.478	1.796	0.566	3.292

Frequency-dependent complex impedance studies were studied at selected temperatures as shown in Fig.3 (b). There are two relaxation peaks located at high and low-frequency region related to the grain and grain boundary, respectively. The $M_{\max}$ peak shifted towards the high temperature with increasing temperature signifies the relaxation is dependent on temperature and also the system has intrinsic hopping charge carriers. Complex modulus data were fitted with the Kohlraush-Williams-Watt function as shown in equation (2). Where $\omega_{\max}$ is the frequency at $M''_{\max}$. The obtained β values are less than one at all temperatures which shows non Debye nature of relaxation, as shown in impedance spectra. The inset in Fig. 3 (b) shows the AC conductivity at selected temperatures, the mechanism of conductivity can be depicted by fitting the Johnson's power law and is given below [6].

$$M'' = \frac{M''_{\max}}{\left\{1 - \beta + \left(\frac{\beta}{1 + \beta}\right) \left[\beta \left(\frac{\omega_{\max}}{\omega}\right) + \left(\frac{\omega}{\omega_{\max}}\right) \right]^\beta \right\}} \quad (0 \leq \beta \leq 1) \quad (2)$$

Where n value decides the conduction mechanism in the material. From the fitting data, n value decreases with increasing temperature, hence the system exhibits a Correlated Barrier Hopping (CBH) conduction mechanism.

$$\sigma_{ac} = \sigma_{dc} + A\omega^n \quad (3)$$

The PFW-BFO solid solution exhibits the high conductivity at high temperature and frequency due to the vacancies of oxygen and electron hopping between Fe states.

FIGURE 3. (a) Nyquist plots at different temperatures (b) Imaginary part of electric modulus vs frequency at different temperatures and the inset shows the frequency dependent conductivity plot of PBFW ceramic.

CONCLUSION

The single phase PBFW was successfully achieved by the columbite method, which was confirmed through XRD. The grain size of about 1 μm observed by the SEM measurement and hence confirms the bulk nature of sample and with small amount of porosity. The RT P-E loops confirm the evidence of enhanced T_C compared to the pure PFW. In addition, lossy nature was explained with the presence of polar microdomains which contains thermally activated space charges. The grain and grain boundary contributions were separated by using the impedance spectroscopy. The electric modulus and impedance studies show the PBFW ceramic follows the Non-Debye type of relaxation. The frequency dependent conductivity reveals the grains are more conducting than the grain boundaries.

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