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Dielectric relaxation and conductivity studies of $(K_{0.5}Bi_{0.5})(Fe_{0.5}Nb_{0.5})O_3$ ceramics

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ABSTRACT

The polycrystalline sample of $(K_{0.5}Bi_{0.5})(Fe_{0.5}Nb_{0.5})O_3$ was synthesized by a high- temperature solid-state reaction technique. The material crystallizes in cubic structure at room temperature. The dielectric properties of the material were investigated in a temperature range from 30-200 ºC in the frequency range (10^2–10^7 Hz). Impedance data is well fitted using proper equivalent circuit composed of a parallel resistance and capacitance in series with a parallel resistance, constant phase element and a capacitance. The compound shows a typical negative temperature coefficient of resistance type (NTCR) behavior like that of semiconductors. Modulus spectroscopy and dielectric conductivity formalism were employed to study dielectric relaxation phenomena in the material. The frequency dependence of conductivity is well fitted to Jonscher's single power law.

Keywords: Electroceramics; electrical properties; ferroelectrics; dielectric relaxation.

RNP Choudhary has actively been engaged in teaching and research for last 40 years at the institutes of national and international reputes such as IIT and NIT. He is one of the pioneer researchers and contributors in the field of ferroelectrics, and related materials in India and abroad. He has guided more than four dozens of PhD students and published more than 500 research papers in international/national journals. Professor Choudhary is an editorial board member and reviewer of many international journals. He has successfully completed many research projects.

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Introduction

Complex perovskite structured oxides with high dielectric constant play an important role in microelectronics and have numerous technological applications. Some of them are found to be useful for memory devices and capacitors. For these types of applications, materials of high dielectric constants are normally required. Most of the perovskite-structure dielectric materials useful for devices contain lead. The higher lead content of these materials is one of the major disadvantages due to the ecological restriction and hazardous. Lead-free ceramics are now in increasing demand to meet the above problem. A lot of lead free perovskite ceramics such as $(Bi_{0.5}Na_{0.5})TiO_3$, $(K_{0.5}Na_{0.5})NbO_3$ and $Ca(Al_{1/2}Nb_{1/2})O_3$ with their solid solutions have been investigated **[1-4]** with focusing efforts on finding alternatives to the lead-rich ceramics. Recently, extensive and systematic studies on dielectric properties of barium iron niobate $Ba(Fe_{1/2}Nb_{1/2})O_3$ (BFN) has been carried out **[5]**. Li et al. has studied the dielectric relaxor properties of $K_{0.5}Bi_{0.5}TiO_3$ **[6]**. Fabrication and electrical properties of textured $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ ceramics by reactive-template grain growth method were studied by Yan et al. **[7]**. Piezoelectric properties of $(K_{0.5}Na_{0.5})NbO_3$ ceramics were analysed by Du et al. **[8]**. Study of various properties of these lead free perovskite ceramics would be very interesting from both physics and application point of view. This has attracted our attention to fabricate similar systems.

Present work aims, analysis of dielectric and impedance properties of $(K_{0.5}Bi_{0.5})(Fe_{0.5}Nb_{0.5})O_3$ ceramic prepared by a solid-state reaction technique. Modulus spectroscopic analyses were also carried out to investigate and separate out different electrical processes occurring inside the material. Ac conductivity spectrum was analysed on the basis of Jonscher's single power law.

Experimental

The polycrystalline samples of $(Ki_{0.5}Bi_{0.5})(Fe_{0.5}Nb_{0.5})O_3$, (KBFN) were prepared with AR grade (≥99%) precursors: Bi_2O_3, K_2CO_3, Fe_2O_3 and Nb_2O_5 (M/s Loba Chemicals, India) using a standard solid-state reaction technique. The homogeneous mixtures of the ingredients were thoroughly mixed and calcined at 1000 °C for 8 h. The optimized sintering temperature and time of KBFN pellet is 1050 °C and 8 h respectively. Priliminary structural analysis was carried out with the help of X-ray powder diffraction data collected by Rigaku, Miniflex, Japan). Some electrical properties (i.e., capacitance, dissipation, impedance and phase angle) were obtained by using a computer-controlled impedance analyzer (PSM 1735) in conjunction with a laboratory-made sample holder as a function of frequency (100 Hz–1 MHz) at different temperatures (30–370 °C).

Results and discussion

Structural and micro-structural studies

The formation of the desired compound $(K_{0.5}Bi_{0.5})(Fe_{0.5}Nb_{0.5})O_3$ was checked by preliminary X-ray structural analysis. Room temperature X-ray powder diffraction pattern of the sample and the scanning electron micrograph (inset) are shown in **Fig. 1**. All the peaks of the XRD pattern were indexed in cubic and tetragonal system, and lattice parameters were determined with the help of a standard computer program 'POWDMULT' **[9]**. A good agreement between the observed (obs) and calculated (cal) inter-planer spacing [$\Sigma(d_{obs}-d_{cal})$=minimum] suggests that the compound has a cubic structure at room temperature with a=8.3117 (0.001) Å. The best agreement between the observed (obs) and calculated (cal) interplanar spacing (d) of the compound was found in a cubic system at room temperature. Using the refined lattice parameter, the interplanar spacing d of each reflection of the compound was calculated and compared with its observed value. The crystallite size of the sample was estimated from the broadening of the peak ($\beta_{1/2}$), using Scherrer's equation **[10]**; $P=K\lambda/\beta_{1/2}\cos\theta_{hkl}$, where K=constant=0.89 and λ=1.5405Å. Since a powder sample was used in recording the XRD pattern, broadening due to mechanical strain and instrumental factors was ignored. The average crystallite size of the compound was found to be 45 nm.

Fig. 1 (inset) shows the scanning electron micrographs of the sintered sample at room temperature describing its surface property and microstructure. The micrographs reveal the existence of a polycrystalline nature **[11]** of the sample with a certain degree of porosity. It is also found that the grains are homogeneously distributed throughout the surface of the material. Some of the grains are of rectangular shape. The average grain size of the compound is found to be 2-3 μm.

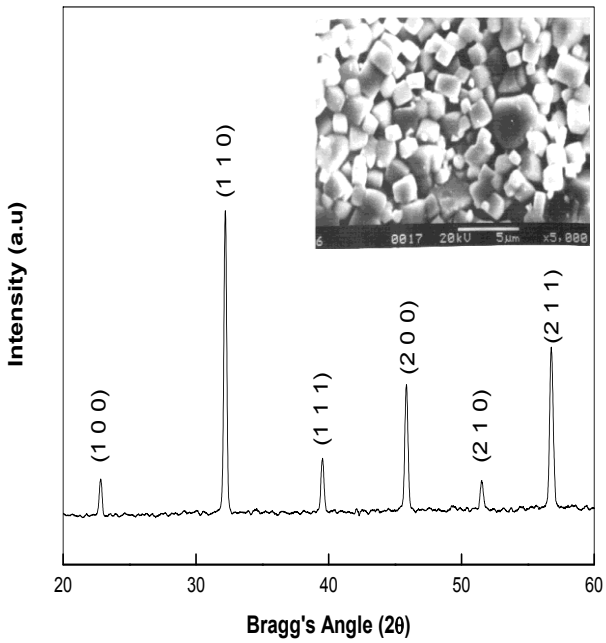

Fig. 1. The XRD pattern and SEM micrograph (inset) of $(K_{0.5}Bi_{0.5})(Fe_{0.5}Nb_{0.5})O_3$ ceramic.

Dielectric study

The variation of measured relative dielectric constant (ε_r) and loss tangent as a function of temperature at four fixed frequencies (10 kHz, 20 kHz, 50 kHz and 100 kHz) are shown in **Fig. 2(a)** and **(b)**. Slow dielectric relaxation is observed in ε_r–T curve **(Fig. 2(a))** in the range of 30–200

ºC reflecting a weak frequency dispersive nature. A single relaxation is observed from **Fig. 2(a)** which is accompanied by a peak in tanδ(T).

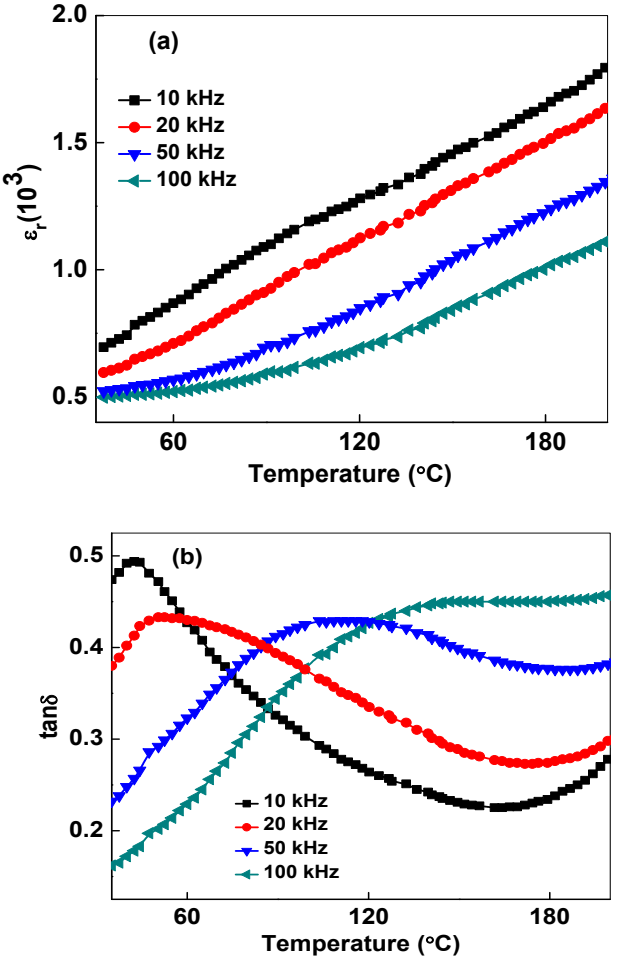

Fig. 2. (a) Variation of relative dielectric constant (ε_r) and (b) tangent loss (tan δ) as a function of temperature of $(Ka_{0.5}Bi_{0.5})(Fe_{0.5}Nb_{0.5})O_3$ ceramic at four different frequencies.

Impedance study: general formalism

CIS analysis was carried out to characterized different electrical processes occurring in a system on application of an ac signal. The output response appears in form of semicircles as follows:

a) the semicircular arc at the highest frequency generally represents the bulk (grain) contribution and

b) the semicircular arc at the intermediate frequency generally represents the grain boundary contribution

The equivalent circuit may be considered as two parallel RC elements connected in series and giving rise to two perfect semicircular arcs in complex plane. However, in practice, the semicircular arcs obtained are depressed with their centers below the real axis (i.e, Z' axis) which has to be taken care of by introducing a constant phase element (CPE). The CPEs demonstrates the 'power law' dependence of the impedance components on frequency. CPE has impedance, given by $Z_{CPE}=[A_0(j\omega)^n]^{-1}$, where $A_0=A/\cos(n\pi/2)$ and $j=\sqrt{-1}$. A and n are frequency-independent parameters which usually depend on temperature. The value of n lies between 0 and 1 (n=1 for an ideal capacitor and n=0 for ideal resistor) **[12, 13]**. The relative position of the two arcs in the complex plane can be identified by the frequency. The arc of bulk generally lies on a frequency range higher than that of grain boundary since the relaxation time $\tau_m=1/\omega_m$ for the grain boundary is much larger than that for the bulk.

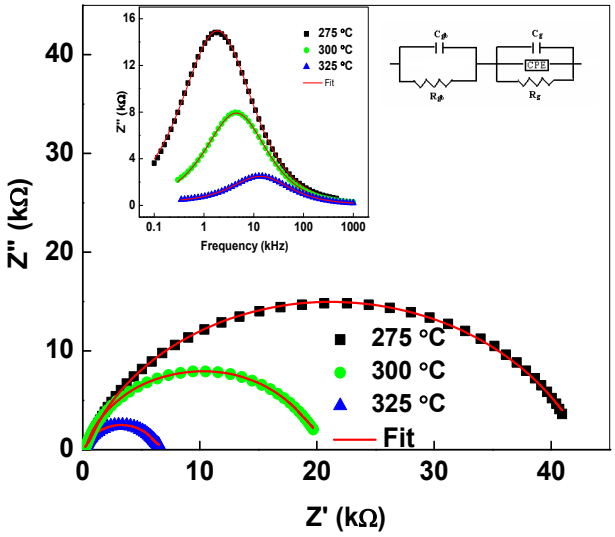

Fig. 3. Complex impedance plot (Nyquist plot) and variation of imagionary part of impedance with frequency (inset) of $(K_{0.5}Bi_{0.5})(Fe_{0.5}Nb_{0.5})O_3$ at different temperatures with corresponding equivalent circuit diagram in the inset.

Fig. 3 shows the complex-plane impedance plot (i.e., plot of imaginary part Z'' against the real part Z') and variation of imaginary part of impedance (Z'') with frequency (inset) at three different temperatures. Each curve of Z'' vs. frequency plot is characterized by the presence of a peak **[14]** at particular frequency and at a fixed temperature. The shift in peak frequency with increase in peak broadening is observed on increasing temperature. Asymmetric peaks suggest that the relaxation process in the material is temperature dependant. Relaxation time (τ) can be calculated using the equation $\omega_{max}\tau=1$. The equivalent circuit given in **Fig. 3** inset is for comparison of the complex impedance plot (point symbols) with fitted data contribution (line) using commercially available software ZSimp Win. Each component/element of the equivalent circuit has its own physical significance.

Modulus study

We have also adopted the modulus formalism to study the relaxation mechanism in KBFN. The importance of the modulus representation in the analysis of the relaxation properties has been demonstrated for polycrystalline ceramic **[15]**. In the modulus formalism, an electric modulus M*(ω) is defined in terms of complex dielectric permittivity ε*(ω) **[16]**,

$$M'(\omega) = 1/\varepsilon^* = M'(\omega) + jM''(\omega) \quad (5)$$

Fig. 4 shows the complex-plane impedance plot (i.e., plot of the imaginary part M'' against the real part M') and variation of imaginary part of impedance with frequency at five different temperatures. The first smaller arc in the plot of imaginary part M'' against the real part M' of the complex modulus M* is assigned to the grain boundaries, while the larger one is assigned to the grains. The values of M'' are determined by,

$$M'' = (\varepsilon_0 - \varepsilon_\infty)\frac{\omega\tau}{\varepsilon_0^{\,2} + \varepsilon_\infty^{\,2}(\omega\tau)^2} \qquad (6)$$

Fig. 5 shows the Arrhenius plot of M'' with activation energy 0.59 eV.

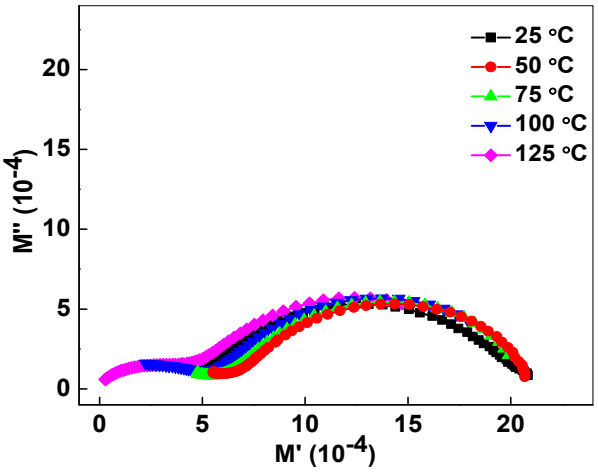

Fig. 4. Complex modulus plot of $(K_{0.5}Bi_{0.5})(Fe_{0.5}Nb_{0.5})O_3$ compound.

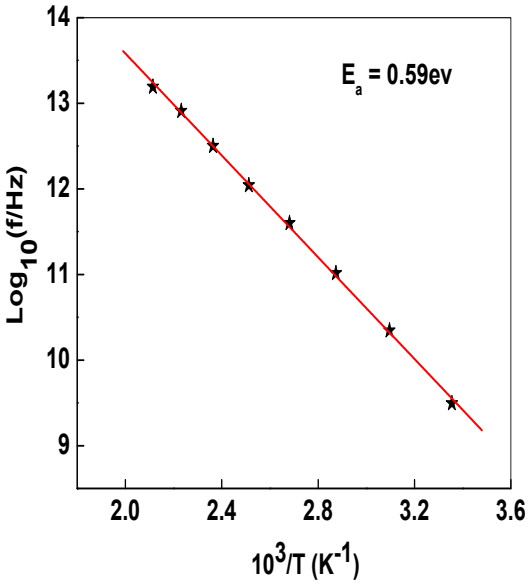

Fig. 5 Temperature dependence of the most probable relaxation frequency obtain from the electric modulus plots for $(Ka_{0.5}Bi_{0.5})(Fe_{0.5}Nb_{0.5})O_3$ ceramic. Symbols are the experimental points and solid lines are the least-square straight-line fits.

Ac conductivity studies

Fig. 6 shows the angular frequency-temperature dependence of ac conductivity (log σ) for KBFN at different measuring temperatures. The experimental conductivity data were fitted to Jonscher's single power law **[17]**.

$$\sigma_{ac} = \sigma_{dc} + A\omega^n$$

Significant low frequency dispersion has been observed in the ac conductivity plot. Decrease in frequency dispersion has been observed in the high frequency side on increase in temperature until all the curves merge with a single slope. Extrapolation of the conductivity curves at low frequency gives dc conductivity (σ_{dc}) values. The resulting σ_{dc} is plotted as a function of reciprocal temperature in **Fig. 6** (inset) which obeys the Arrhenius relation **[18]**,

$$\sigma_{dc} = \sigma_0 \exp(E_{cond}/KT) \qquad (7)$$

where σ_0 is the pre-exponential term and E_a is conduction activation energy, E_a=0.58 eV.

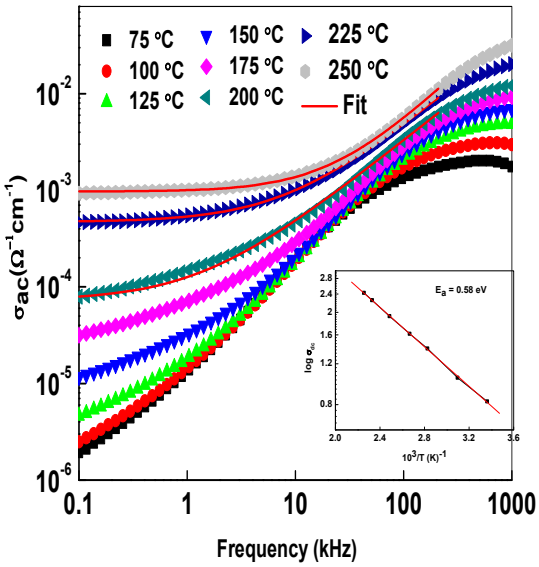

Fig. 6. Ac conductivity as a function of frequency at various temperatures for $(K_{0.5}Bi_{0.5})(Fe_{0.5}Nb_{0.5})O_3$ fitted to Jonscher's single power law with temperature dependence of dc conductivity for $(K_{0.5}Bi_{0.5})(Fe_{0.5}Nb_{0.5})O_3$ ceramics in the inset. Symbols are the experimental points and solid lines are the least-square straight-line fits.

Conclusion

$(K_{0.5}Bi_{0.5})(Fe_{0.5}Nb_{0.5})O_3$ (KBFN) ceramics were prepared by a simple solid state reaction method crystallizing in cubic structure. We have investigated the temperature dependence of dielectric and loss spectra of polycrystalline KBFN ceramics. One slow dielectric relaxation is observed in the whole temperature range followed by peak in tanδ(T) curve. Impedance data are well fitted using proper equivalent circuit. The compound shows a typical NTCR

behavior like that of semiconductors. Both modulus spectroscopy and dielectric conductivity formalism were employed to study dielectric relaxation phenomena in the material. The frequency dependence of ac conductivity is well fitted to Jonscher's single power law.

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