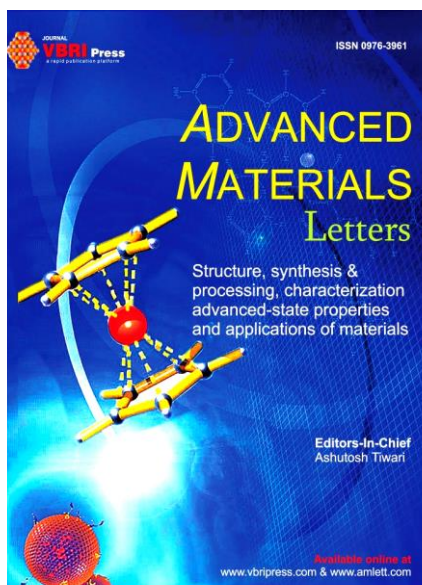


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Title	Electrical properties of $0.25\text{Ba}(\text{Bi}_{1/2}\text{Ta}_{1/2})\text{O}_3-0.75\text{BaTiO}_3$
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Electrical properties of $0.25\text{Ba}(\text{Bi}_{1/2}\text{Ta}_{1/2})\text{O}_3\text{-}0.75\text{BaTiO}_3$

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Abstract

The polycrystalline sample of $0.25\text{Ba}(\text{Bi}_{1/2}\text{Ta}_{1/2})\text{O}_3\text{-}0.75\text{BaTiO}_3$ was synthesized using conventional solid state reaction technique. XRD analysis indicated the formation of a single-phase orthorhombic structure. The SEM analysis shows the grain sizes to be 0.12 to 0.45 μm . Complex electric modulus analyses suggested the dielectric relaxation to be of non-Debye type. Dielectric studies indicated the relaxor behavior of $0.25\text{Ba}(\text{Bi}_{1/2}\text{Ta}_{1/2})\text{O}_3\text{-}0.75\text{BaTiO}_3$. The correlated barrier hopping model was employed to explain the mechanism of charge transport in the system. The ac conductivity is found to obey the Jonscher's power law. The nature of variation of dc conductivity with temperature suggested NTCR behavior with activation energy 0.36eV. The studied material can be a potential candidate for capacitor applications.

Keywords: Complex perovskite, Lead-free, Relaxor, Electric modulus, Ac conductivity.

Introduction

Since the discovery of ferroelectricity in BaTiO₃ in 1945, a large number of oxides of different structural families have been investigated in search of new materials for device applications. It has been found that each member of an oxide family has some interesting dielectric and electrical properties in spite of some similarities in their chemical formula or compositions [1-6]. Complex Perovskite electro ceramics are very important and many researchers have investigated the electrical properties of these compounds in detail during last few decades. Materials having a diffuse phase transition (relaxor behavior) have attracted the attention due to their broad maximum in the temperature dependence of their dielectric constant [7,8] due to the rich diversity of their physical properties and possible applications in memory storage devices, micro-electro-mechanical system, multilayer ceramic capacitors and recently, in the area of optoelectronic devices [9-11].

Most of the earlier discovered complex dielectric materials were containing lead. In recent times due to ecological restriction to the use of lead [12-19], new complex compounds with reduced lead content or without lead are in increasing demand and have been studied for various technological applications [20,21]. The objective of the present work has been to study the structural and electrical properties of a new lead-free solid solution of Ba(Bi_{1/2}Ta_{1/2})O₃ with BaTiO₃ to obtain a material with better dielectric properties. Accordingly, in this report, a new lead-free complex ceramic 0.25Ba(Bi_{1/2}Ta_{1/2})O₃-0.75BaTiO₃ has been synthesized by a high temperature solid state reaction technique and results on the structural, micro structural, dielectric, electric modulus and ac conductivity studies are reported for the first time as per the authors' knowledge.

Experimental

The conventional solid state reaction technique was employed for the synthesis of polycrystalline sample of 0.25Ba(Bi_{1/2}Ta_{1/2})O₃-0.75BaTiO₃ (abbreviated hereafter as BBT-BT). High purity (>99.9%) carbonates/oxides of BaCO₃ (Merck, Germany), Bi₂O₃ (Hi Media, India), Ta₂O₅ (Strem, USA) and BaTiO₃ (Aldrich, USA) were mixed in proper stoichiometry. The wet mixing of the ingredients was carried out with acetone as the medium for homogeneous mixing. Grinding was performed using mortar pestle for about 8h. Well-mixed powders were then calcined at 1200°C for 4 h under a controlled heating and cooling cycles. The calcined powders were compacted into thin circular disk with an applied uniaxial pressure of 650 MPa. The pellets were sintered in air atmosphere at 1240°C in alumina crucible for 4 h. The completion of reaction and the formation of desired compounds were checked by X-ray diffraction technique.

The XRD data were obtained with an X-ray diffractometer (XPRT-PRO, Pan Analytical) at room temperature, using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The scanning (2θ) was performed from 10° to 80° with a step of 0.02° at a scanning rate of $1.0^\circ/\text{min}$. The crystal structures, unit cell dimensions and hkl values were obtained using Crysfire software. The microstructures of the ceramics have been examined by scanning electron microscopy (SEM) technique. For electrical characterization, pellets were first polished and then electrodes were made using silver paste. The dielectric and impedance data were obtained using a computer-controlled LCR Hi-Tester (HIOKI 3532-50, Japan).

Results and discussion

Fig. 1 illustrates the XRD profiles for BBT-BT. Appearance of single and sharp peaks of the compound and no other peaks due to any component oxides/carbonates indicated the formation of single phase of the compounds. The compound shows a single phase orthorhombic structure. Therefore, addition of BaTiO_3 to $\text{Ba}(\text{Bi}_{1/2}\text{Ta}_{1/2})\text{O}_3$ changes the basic unit cell structure of the solid-solutions. This could be due to the partial replacement of pseudo-cation $(\text{Bi}_{1/2}^{3+}\text{Ta}_{1/2}^{5+})^{4+}$ with Ti^{4+} which produces some kind of disorder in the system and/or due to the difference in unit cell structure of $\text{Ba}(\text{Bi}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (cubic) [22] and BaTiO_3 (tetragonal). Besides, the difference in the ionic radii of pseudo-cation $(\text{Bi}_{1/2}^{3+}\text{Ta}_{1/2}^{5+})^{4+}$ and Ti^{4+} might have played an important role. The lattice parameters were found to be $a = 9.944 \text{ \AA}$, $b = 7.137 \text{ \AA}$ and $c = 4.796 \text{ \AA}$ with unit cell volume 340.43 \AA^3 . Also, some shifting in the peak positions and changes in the intensities of peaks could be observed (**Fig. 1**). Inset of **Fig. 1** shows the scanning electron micrographs of the fractured surface of BBT-BT ceramics. The photographs contain a very few voids suggesting the high density of the materials. The grains of different sizes $0.12\text{-}0.45 \mu\text{m}$ appear to be distributed throughout the samples. The ratio of the average particle size to the grain size for the composition is found to be of the order of 10^{-3} .

Fig. 2 shows the variation of (a) dielectric constant (ϵ_r) and (b) loss tangent ($\tan\delta$) with frequency at different temperatures. Dispersion with relatively high dielectric constant in the lower frequency region can be seen and the value of dielectric constant decreases continuously with increasing frequency showing the normal behavior of a dielectric. This implies that the crystal may have domains of different sizes with various relaxation times. The value of $\tan\delta$, in general, is found to decrease with increasing frequency **Fig. 2(b)**. The room temperature value of dielectric constant and loss tangent are found to be 1223 and 0.78 at 1 kHz, respectively. The temperature dependence of

dielectric constant of BBT-BT at different frequencies is shown in the inset of **Fig. 2(b)**. All the plots show a broad ferro-paraelectric phase transition (*i.e.* diffuse phase transition, DPT) and strong frequency dispersion, which indicate the relaxor behaviour of the compound. It is observed that the phase transition temperature (T_m) shifted to higher temperature side (from 305°C at 1 kHz to 390°C at 100 kHz), ϵ_r decreases (from 11237 at 1 kHz to 1598 at 100 kHz) with the increase in frequency. The above results obtained in BBT-BT, may usher it a possible potential candidate for device applications. A sharp decrease in dielectric constant with the increase in frequency can be explained in terms of the interfacial polarization. Contribution from interfacial polarizability comes due to the presence of two layers of materials of different conductivity.

Fig. 3(a) shows the variation of Z' with frequency at different temperatures. The dispersion region spreads in a high frequency region with increase in temperatures. The initial decrease in Z' value with frequency may be due to a slow relaxation process in the material probably due to space charges, at high temperatures; low frequency plateau region is observed. These frequency invariant (dc conductivity) electrical properties of the materials and the final merger of the patterns at higher frequency may be attributed to the release of space charge. Further, the impedance value is higher at lower temperatures in the low frequency region and decreases gradually with increase in frequency. The value of Z' also shows a decreasing trend with rise in temperature showing a nature typical to negative temperature coefficient of resistance (*i.e.* NTCR type) behavior as generally found in semiconductors. The variation of imaginary part of impedance of with frequency and temperature is shown in **Fig. 3(b)**. It is observed that all the curves display broad and low intensity peaks. A single relaxation for compound has been observed.

Fig. 4 shows the frequency responses of (a) M' and (b) M'' at different temperatures for BBT-BT. It is characterized by very low value of M' in the low frequency region and a sigmoidal increase in the value of M' with the frequency approaching ultimately to M_∞ , which may be attributed to the conduction phenomena due to short-range mobility of charge carriers. The variation M'' as a function of frequency is characterized by: (i) clearly resolved peaks in the pattern appearing at unique frequency at different temperatures, (ii) significant asymmetry in the peak with their positions lying in the dispersion region of M' vs. frequency pattern and (iii) the peak positions have a tendency to shift toward higher frequency side with the rise in temperature. The low frequency side of the M'' peak represents the range of frequencies in which charge carriers can move over a long distance *i.e.* charge carriers can perform successful hopping from one site to the neighboring site. The high frequency side of the M'' peak represents the range of frequencies in which the charge carriers are spatially confined to

their potential wells and thus could be made localized motion within the well. Therefore, the region where peak occurs is an indicative of the transition from long-range to short-range mobility with increase in frequency. Further, the appearance of peak in modulus spectrum provides a clear indication of conductivity relaxation. Also, $M''(\omega)$ curves get broadened upon increasing temperature suggesting an increase in non-Debye behavior. This particular behavior seems to be unique to electrical relaxation since all other relaxation processes (*e.g.* mechanical, light scattering) typically exhibit opposite behavior with tendency towards Debye behaviour with increasing temperature.

Fig. 5 illustrates the variation of σ_{ac} as a function of frequency at different temperatures for BBT-BT ceramics. It is observed that the patterns of the ac conductivity spectrum show dispersion throughout the chosen frequency range and with the rise in temperature, the nature of conductivity spectrum appears to be changed. The low frequency plateau becomes almost frequency independent at higher temperatures and the frequency dependence of real part of ac conductivity obeys the Jonscher's power law: $\sigma_{ac} = \sigma_o + A\omega^s$ [23]. The values of the index s can be obtained from the slopes of the plots ($\log \sigma_{ac}$ vs. $\log f$). It is observed that the values of s are always less than 1 and it decreases with the rise of temperature for all the compounds. Besides, the value of $s \rightarrow 0$ at higher temperatures indicates that the dc conductivity dominates at higher temperatures in the low frequency region, following $s = 1 + 4/\log(\omega\tau_o)$. The model based on correlated barrier hopping of electrons predicts a decrease in the value of the index with the increase in temperature. The experimental results follow the same trend. Therefore, the conduction in the system could be considered due to the short-range translational type hopping of charge carriers. Also, it is observed that the slope of the curves change with the temperature, which clearly indicates that the conduction process is dependent on both temperature and frequency. The frequency, at which there is a slope change, shifts to higher frequency side upon increasing temperature. The switch from the frequency-independent to the dependent regions show the onset of the conductivity relaxation phenomenon and the translation from long range hopping to the short range ion motion. Such dependence is associated with displacement of carriers which move within the sample by discrete hops of length R between randomly distributed localized sites. Furthermore, a decrease in the values of σ_{ac} is observed with the rise in temperature for all the compounds, thereby indicating the negative temperature coefficient of resistance (NTCR) character of the samples like that of semiconductors. This may happen due to the accumulation of charge species at the barriers (grain boundaries) which get thermally activated, that plays a dominant role at elevated temperature showing NTCR

characteristic. Inset **Fig. 5** depicts the variation of σ_{ac} with temperature which also supports the NTCR character of the compound. The value of activation energy, using linear least squares fit, is found 0.36 at 1 kHz.

Conclusions

Polycrystalline $0.25\text{Ba}(\text{Bi}_{1/2}\text{Ta}_{1/2})\text{O}_3-0.75\text{BaTiO}_3$ prepared using a high-temperature solid-state reaction technique, was found to have a perovskite-type orthorhombic structure. Dielectric study revealed that the compound possess a high dielectric constant 11237 at 1 kHz, which makes this composition, suitable for capacitor application. The compound shows a transition temperature $\sim 305^\circ\text{C}$ at 1 kHz with relaxor behavior. The ac conductivity study showed the NTCR character of the compounds. The ac conductivity is found to obey the universal power law and the correlated barrier hopping model is found to successfully explain the mechanism of charge transport in the system. These results are well supported by electric modulus data. Complex electric modulus analyses suggested the dielectric relaxation to be of non-Debye type.

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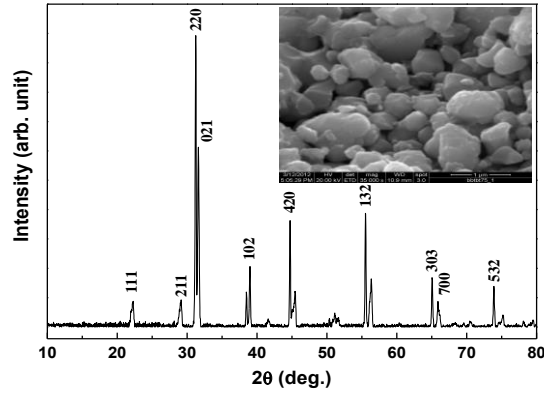


Fig. 1. XRD pattern at room temperature and SEM micrograph (Inset) of $0.25\text{Ba}(\text{Bi}_{1/2}\text{Ta}_{1/2})\text{O}_3\text{-}0.75\text{BaTiO}_3$.

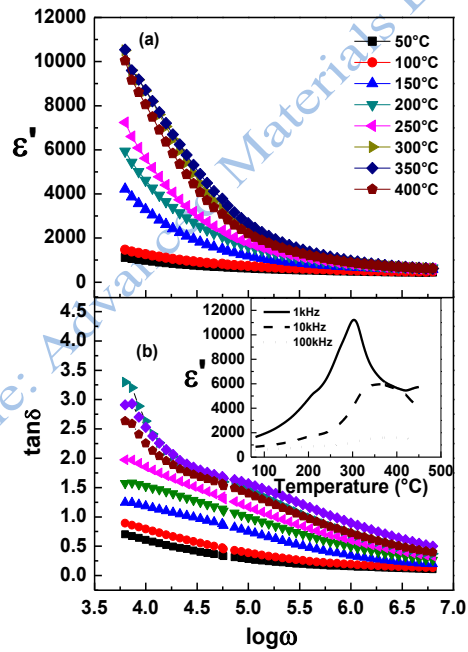


Fig. 2. Frequency dependence of (a) ϵ_r and (b) $\tan\delta$ at different temperatures of $0.25\text{Ba}(\text{Bi}_{1/2}\text{Ta}_{1/2})\text{O}_3\text{-}0.75\text{BaTiO}_3$. Inset: Variation of ϵ_r with temperature at different frequency.

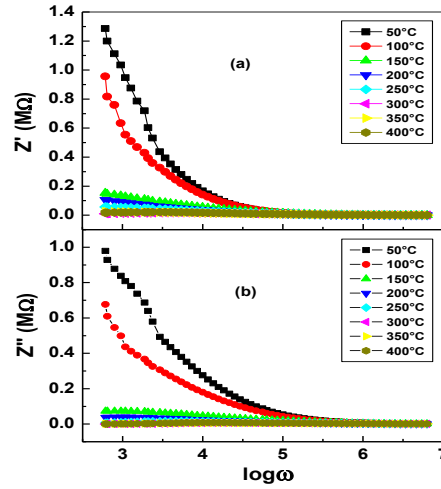


Fig. 3. Frequency dependence of (a) real and (b) imaginary parts of impedance of $0.25\text{Ba}(\text{Bi}_{1/2}\text{Ta}_{1/2})\text{O}_3\text{-}0.75\text{BaTiO}_3$.

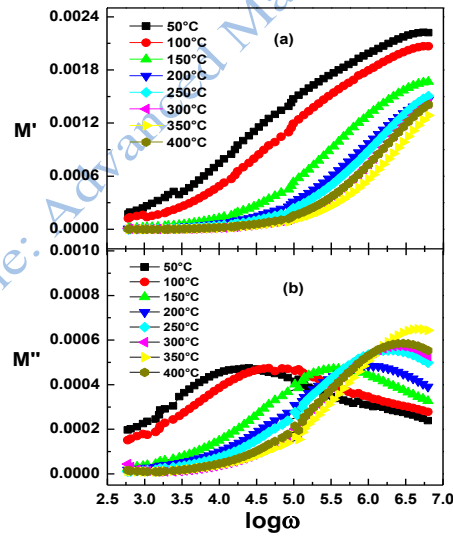


Fig. 4. Frequency dependence of (a) real and (b) imaginary parts of electric modulus of $0.25\text{Ba}(\text{Bi}_{1/2}\text{Ta}_{1/2})\text{O}_3\text{-}0.75\text{BaTiO}_3$.

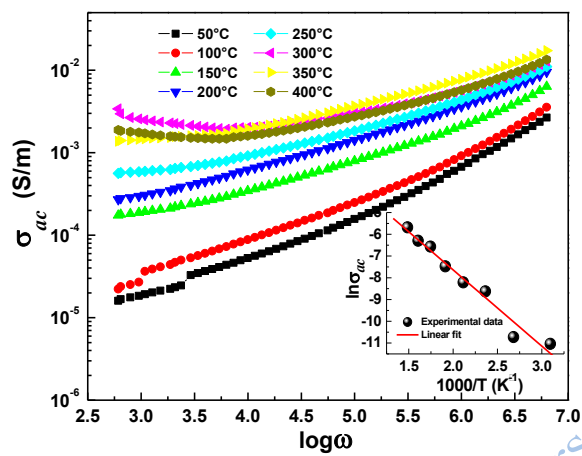


Fig. 5. Variation of ac conductivity with frequency of $0.25\text{Ba}(\text{Bi}_{1/2}\text{Ta}_{1/2})\text{O}_3\text{-}0.75\text{BaTiO}_3$ at different temperatures. Inset: Temperature dependence of the ac conductivity at 1 kHz.

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