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Electrical Conductivity in $Ba_5RTi_{3-x}Zr_xNb_7O_{30}$ [R = La or Dy] Ceramics

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The polycrystalline samples of $Ba_5RTi_{3-x}Zr_xNb_7O_{30}$ [R = La or Dy; x = 0, 1, 2, 3] belonging to tungsten-bronze (TB) structural family were prepared by using conventional high-temperature solid-state reaction technique. Studies of electrical conductivity/resistivity as a function of biasing electrical field and a wide range of temperature have been carried out. The activation energy (E_a) of the compounds was calculated from the plot of dc resistivity and ac conductivity *vs.* absolute temperature. Dc resistivity studies show that the increase of Zr concentration enhances the resistivity characteristics of $Ba_5DyTi_{3-x}Zr_xNb_7O_{30}$ and decreases the resistivity characterisities of $Ba_5LaTi_{3-x}Zr_xNb_7O_{30}$ compounds. The compounds exhibit the negative temperature coefficient of resistance (NTCR) properties at higher temperature region.

Key Words: Electrical conductivity, $Ba_5RTi_{3-x}Zr_xNb_7O_{30}$, Ceramics.

INTRODUCTION

Though a large number of ferroelectric oxides of different structural families are now available, some compounds of perovskite and tungsten-bronze (TB) families[1-3] in pure and/or complex form, such as $BaTiO_3$, $LiNbO_3$, $PbTiO_3$, potassium lanthanum niobate etc., have been found to be very important because of their various physical properties suitable for fabrication of many devices. The tungsten-bronze structure has a general formula $[(A_1)_2(A_2)_4C_4][(B_1)_2(B_2)_8]O_{30}$ in which the charge and size tolerance is same as that of perovskite type in case of A and B sites. The C site being small (0.5 to 0.7 Å radius) often being vacant may be filled by monovalent/bivalent cation. With these interstices A, B and C a wide variety of substitution[4] is possible and hence it is possible to enhance the physical properties such as electro-optic, elasto-optic and pyro-electric for device parameters. Rare earth ion substituted BNN (*i.e.*, $Ba_2NaRNb_{10}O_{30}$)[5] was found to be more interesting from diffuse phase transition viewpoint. Studies of ferroelectric properties of some members of this TB-structural family, such as $K_2LaNb_5O_{15}$,[6] $Ba_4NaNb_{10}O_{30}$,[7] $Ba_5RTi_{3-x}Zr_xNb_7O_{30}$ [R = Nd, Y][8, 9] etc., showed that they have diffuse phase transition with a wide range of transition temperatue [*i.e.*, below and above room temperature]. As a result of important applications and structural complexity of the materials, a better understanding of their phase transition is essential for which we have studied extensively the structural and ferroelectric properties of titled compound[10, 11]. In this paper, we intend to report the electrical (ac conductivity and dc resistivity) properties of $Ba_5RTi_{3-x}Zr_xNb_7O_{30}$ [R = La or Dy].

EXPERIMENTAL

Polycrystalline samples of $Ba_5DyTi_{3-x}Zr_xNb_7O_{30}$ and $Ba_5LaTi_{3-x}Zr_xNb_7O_{30}$ (x = 0, 1, 2, 3), abbreviated as compounds A, B, C and D respectively in each group, were prepared by a standard high-temperature solid-state reaction technique using high purity ingredients, $BaCO_3$ (99.9%, Sarabhai Chemicals, India), La_2O_3 and Dy_2O_3 (99.9%, Indian Rare Earth Limited), TiO_2 (99.9%, Loba Chemicals Co.), ZrO_2 (99.9%, Aldrich Chemical Co.) and Nb_2O_5 (99.9%, BARC, Mumbai) in a suitable stoichiometry. The ingredient oxides and carbonates were mixed thoroughly in methanol and dried by slow evaporation technique. The dried powders were grounded and then calcined in an alumina crucible at 1273 K for 24 h. The process of mixing and calcination was repeated several times to get the desired compounds. Formation and quality of the compounds were checked with X-ray diffraction (XRD) technique. The fine powders of these compounds were used to make cylindrical pellets of 10 mm diameter and 1–2 mm thickness at a pressure of *ca.* 6×10^6 pa using a hydraulic press. The samples were sintered at 1473 K for 2 h in an air atmosphere. The sintered pellets were polished on fine emery paper in order to make both the faces flat and parallel. Finally, the pellets were electroded with high purity silver paste. The ac conductivity of all the compounds was measured as a function of temperature (180–673 K) with the help of H.P. 4342 A Q-meter. The dc conductivity of all the samples was determined as a function of the applied electric field (10–110 V cm^{-1}) and temperature (300–673 K) at 100 V cm^{-1} using a Keithley 617 programmable electrometer. Temperature measurement with accuracy of ±2°C was made with a chromel-alumel thermocouple.

RESULTS AND DISCUSSION

The ac conductivity can be obtained from a general expression[12] $\varepsilon^{11} = \varepsilon \tan\delta = (\sigma_{ac}/\omega\varepsilon_0) + \{((\varepsilon_s - \varepsilon_\infty)\omega\tau)/1 + \omega^2\tau^2\}$ where ε^{11} is the imaginary part of complex dielectric constant, ε_s the low-frequency static dielectric constant, ε_∞ the high-frequency dielectric constant for which ionic polarization becomes negligibly small and τ is the relxation time. At low frequency the first term, which represents the surface polrization due to ionic conductivity, is dominnt. Hence the ac electrical conductivity for all the samples at 10 KHz ws obtained from a conductivity relation, $\sigma = \omega\varepsilon\varepsilon_0 \tan\delta$, where ε_0 is the vacuum dielectric constant and ω is the angular frequency. Further, the variation of the electrical conductivity ($\ln \sigma$) with inverse of absolute temperature (Fig. 1, a and b) is governed by the relation $\sigma = \sigma_0 \exp(-E_a/K_BT)$, where K_B is the Boltzmann constant[13, 14]. In all these graphs there is a peak near the transition temperature. The value of activation energy (E_a) of all ceramics evaluated just below the transition temperature, *i.e.*, at the high temperature side, was found to decrease from 0.019×10^{-1} eV (for x = 0) to 0.067×10^{-1} eV (for x = 3) in the case of Dy-containing compounds and from 0.073×10^{-1} eV (for x = 0) to 0.031×10^{-1} eV in the case of La-containing compounds. This shows that with increasing Zr content, the activation energy decreases. The anomaly in the above curves was found close to the transition temperature (T_c) observed in our dielectric studies of the compounds[10, 11]. Such type of anomaly has been observed in many other ferroelectric ceramics[15, 16].

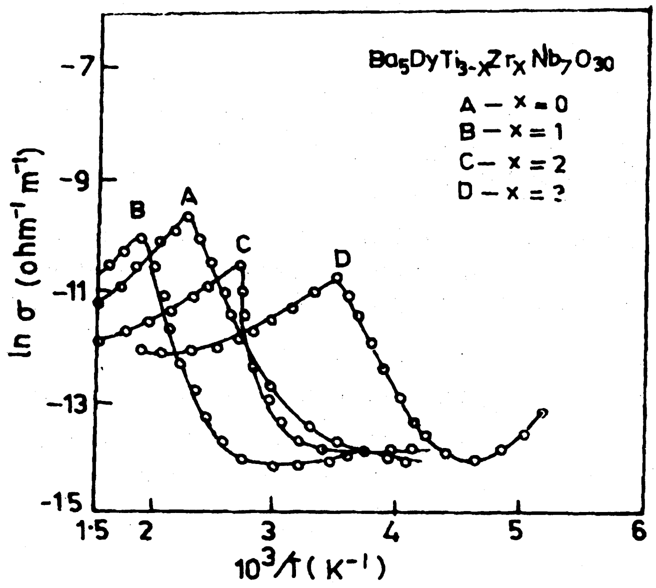

Fig. 1. (a) Temperature dependence of ac conductivity (ln σ) of $Ba_5DyTi_{3-x}Zr_xNb_7O_{30}$ (x = 0, 1, 2, 3) at 10 kHz

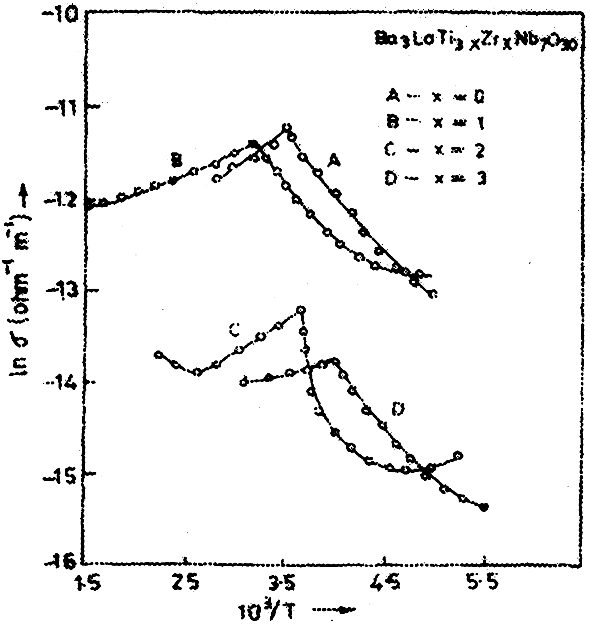

Fig. 1. (b) Temperature dependence of ac conductivity (ln σ) of $Ba_5LaTi_{3-x}Zr_xNb_7O_{30}$ (x = 0, 1, 2, 3) at 10 KHz.

The low activation energy in materials can generally be explained as follows. Typical ionic or doped solids possess a limited number of mobile ions, which are hindered in their motion by virtue of being trapped in relatively stable potential well. With increase in temperature the doped ions play an important role in the conduction process. The donors create a level in the vicinity of the conduction band. Therefore, to activate donors, a small amount of energy is required. On the other hand, a slight change in stoichiometry (*i.e.*, the metal to oxygen ratio) in multimetal complex oxides causes the creation of a large number of donors or acceptors, which may create donor or acceptor like states in the vicinity of the conduction or valence band. These donors or acceptors may be activated with less energy[17].

The variation of dc resistivity as a function of biasing electric field at room temperature (300 K) is shown in Fig. 2 (a and b) for all the ceramics. In all the cases resistivity was found to decrease smoothly with applied field. This may be explained on the basis of Heywang's model[18]. The resistivity of ferroelectric ceramics consists of two parts: (a) resistivity due to grain and (b) resistivity due to grain boundary. As it is known that in addition to the impurity level corresponding to the grain, there exist localised states in the forbidden gas which correspond to the surface states at the boundary. These surface states are due to surface imperfection and impurities. In absence of electric field some of these states are occupied by electrons resulting in a space charge region which generates potential barrier on either side of the boundary. On application of electric field

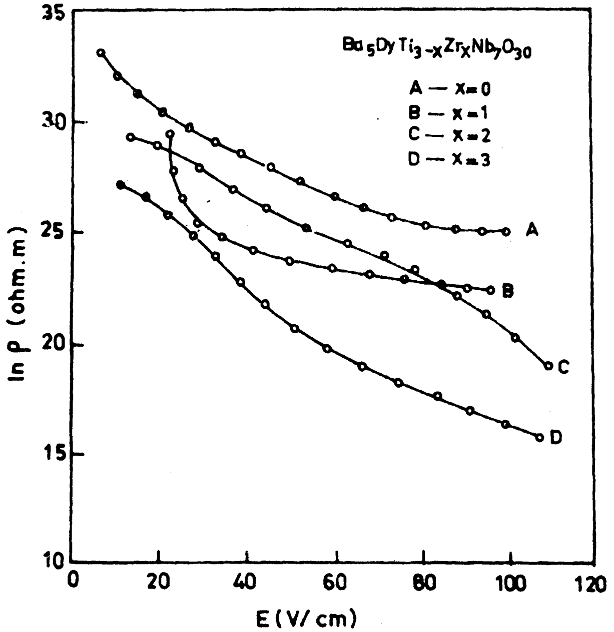

Fig. 2. (a) Applied electric field dependence of dc resistivity (ln ρ) of $Ba_5DyTi_{3-x}Zr_xNb_7O_{30}$ (x = 0, 1, 2, 3) at room temperature

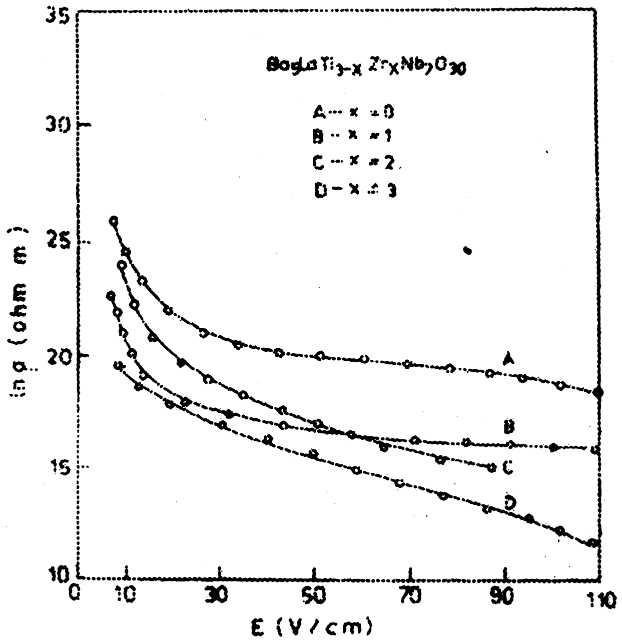

Fig. 2. (b) Applied electric field dependence of dc resistivity (ln ρ) of $Ba_5LaTi_{3-x}Zr_xNb_7O_{30}$ (x = 0, 1, 2, 3) at room temperature

the fermi energy level shifts and also the potential barriers are modified due to increase in electron concentration. This decreases the grain boundary resistance with electric field. The smaller is the grain size, the smaller is the local voltage to a single barrier with given external field. Thus it is clear from the figures that for the higher concertration of Zr, the resistivity decay is more prominent at higher voltage than in the lower.

Fig. 3 (a and b) shows the variation of dc resistivity (ln ρ) with temperature for all the compounds at constant electric field (100 V/cm). The value of resistivity increases with increase of the value of Zr in Dy-containing compounds and decreases with increase of the value of Zr in La-containing compounds. It has been also observed that the value of resistivity decreases with temperature in the higher temperature region and remains almost constant below 373 K in all compounds. The values of activation energy in the high temperature region are found to be 0.76, 0.73, 0.77 and 0.92 eV for A, B, C and D of Dy-containing compounds and 1.03, 0.86, 0.60 and 1.43 eV for La-containing compounds respectively. This can be attributed as follows: Due to the addition of thermal energy, electrons could be set free from oxygen ions. When an electron is introduced in the specimen, it may be associated with a cation which results in unstable valence states[19] and resistivity starts decreasing. This type of resistive behaviour is usually known as negative temperature coefficient of resistance at higher temperature, which is most desirable for developing highly sensitive thermal detectors, sensors, thermisters, etc.

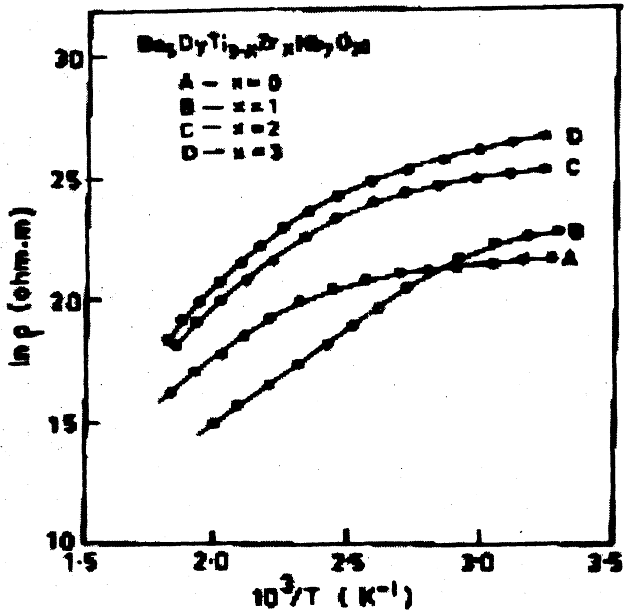

Fig. 3. (a) Temperature dependence of dc resistivity (ln ρ) of $Ba_5DyTi_{3-x}Zr_xNb_7O_{30}$ (x = 0, 1, 2, 3) at constant electric field

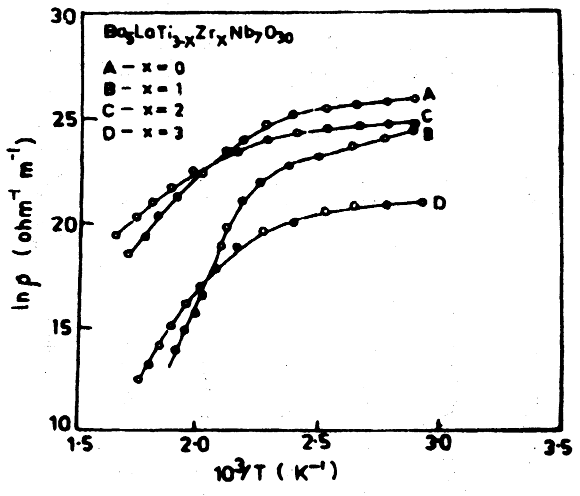

Fig. 3. (b) Temperature dependence of dc resistivity (ln ρ) of $Ba_5LaTi_{3-x}Zr_xNb_7O_{30}$ (x = 0, 1, 2, 3) at constant electric field.

Conclusions

(i) There is no change in basic struture of compound with substitution of Zr ions at the Ti site.

(ii) The compounds of $Ba_5RTi_{3-x}Zr_xNb_7O_{30}$ (R = La, or Dy : x = 0, 1, 2, 3) family has low activation energy in paraelectric region and behaves as negative temperature coefficient of resistane at higher temperature.

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