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Studies on dielectric relaxation and high temperature conductivity of $Bi_{1.5}Zn_{1-x}Nb_{1.5}O_{7-x}$ ceramics

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Abstract The dielectric properties of cubic pyrochlore $Bi_{1.5}Zn_{1-x}Nb_{1.5}O_{7-x}$ (BZN) ceramics with high dielectric constant, low dissipation factor are strongly affected by their lattice defects. The dielectric properties of BZN sintered in various atmosphere including ambient, N2, and O2 are investigated. The equilibrium high temperature conductivity was examined.

Keyword Dielectric relaxation · High temperature conductivity

1 Introduction

Bi_2O_3–ZnO–Nb_2O_5 (BZN) based dielectric ceramics have recently found to be of great interests for low temperature sintering ceramic for high frequency applications. In BZN system, the dielectric properties of cubic pyrochlore structure depend on its composition and lattice defects.

It is well known that the molecular formulae of cubic pyrochlore oxides can be expressed as $A_2B_2O_6O'$. The A cations (usually ~1 A ionic radius) are eight coordinated to oxygen atoms and are located within scalenohedra. The B cations (usually ~0.6 A) are six coordinated to oxygen atoms and are located within trigonal antiprisms. In the BZN system, it is predicted that the Bi^{3+} cations occupy the A site for its large radius, the Nb^{5+} cations tend to occupy B site for its small radius, while the Zn^{2+} cations can occupy both A site and B site for its medium radius [1]. The accurate structure information is now available for a number of nonstoichiometric pyrochlore oxides including BZN oxides with excess oxygen or deficient cation have not been investigated in details. However, the nonstoichiometric pyrochlore oxides including BZN oxide with excess oxygen or deficient cation have not been investigated in details. Therefore, it is important to study the dielectric properties of the pyrochlore BZN ceramics with cation deficiency [2].

In this paper, the dielectric properties and high temperature ionic conductivity of BZN were investigated; the effect of lattice defects on the cubic pyrochlore BZN is discussed.

2 Experimental procedure

The starting material were reagent grade oxides of Bi_2O_3, ZnO, and Nb_2O_5.The compositions of $Bi_{1.5}Zn_{1-x}Nb_{1.5}O_{7-x}$ (x=−0.05, 0.05, 0.1, 0.15) were synthesized by conventional electroceramic processing technique. The constituent oxides were weighted in proper ratio and mixed with deionized water using ZrO_2 milling ball in polyethylene containers for 24 h.

The mixture was dried in an oven at 1100 °C for 24 h and then pressed into disks diameter of 10 mm. Ten percent organic binder approximately was added to assiter the pressing. Disks were sintered 1000 °C for 3 h in air, N_2, and O_2. The disks were polished, and then electroded with platinum paste.

Dielectric properties were measured at different temperature and using hp4284 LCR meter. The ionic conductivity in different partial oxygen pressure was measured by a high temperature conductivity test system.

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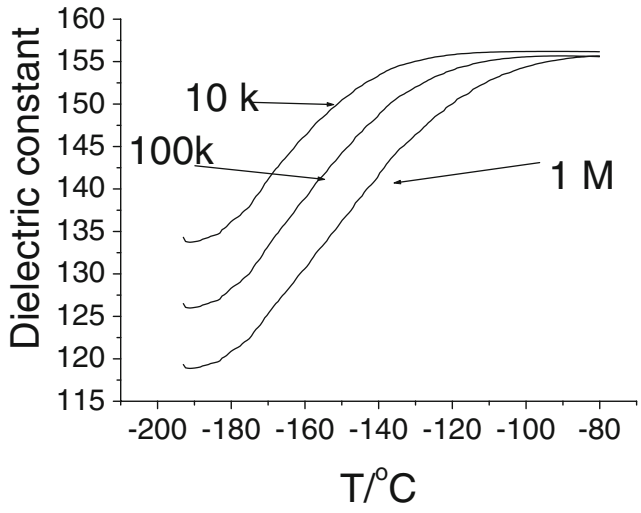

Fig. 1 Dielectric constant of $Bi_{1.5}Zn_{1.45}Nb_{1.5}O_{6.95}$ measured at 10 k, 100 k, 1 M

3 Results and discussion

3.1 Low temperature dielectric relaxation

The low temperature dielectric properties of $Bi_{1.5}Zn_{1-x}Nb_{1.5}O_{7-x}$ (x=−0.05, 0.05, 0.1, 0.15) were carefully measured. Figs. 1 and 2 are the temperature dependence of dielectric constant and dielectric loss of $Bi_{1.5}Zn_{1.45}Nb_{1.5}O_{6.95}$ (x=0.05) at low temperatures. The results for all the four samples are similar and are characterized with typical Debye relaxation of dielectric polarization. Based on the measurements, the activation energy U, relaxation time τ, frequency ν of dielectric relaxation can be calculated from the shift of the loss peak temperature T at two frequencies using the following Debye formula:

$$\tau = \frac{1}{2v} e^{U/kT} \tag{1}$$

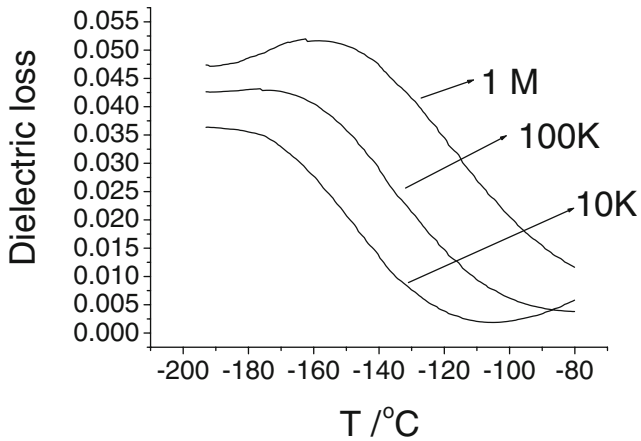

Fig. 2 Dielectric loss of $Bi_{1.5}Zn_{1.45}Nb_{1.5}O_{6.95}$ measured at 10 k, 100 k, 1 M

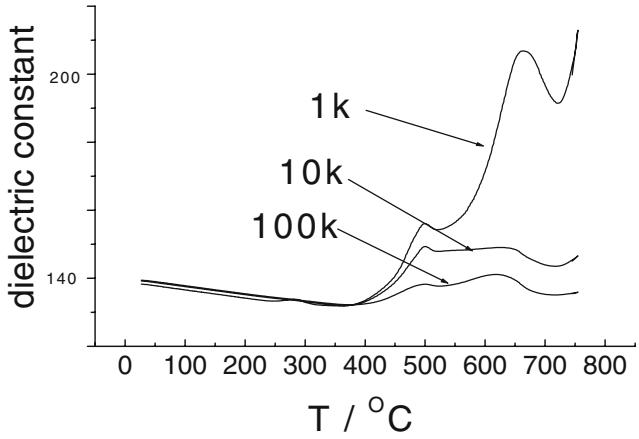

Fig. 3 Dielectric constant of $Bi_{1.5}Zn_{1.45}Nb_{1.5}O_{6.95}$ measured at 1 k, 10 k, 100 kHz

And

$$U = k\frac{T_1 \cdot T_2}{T_2 - T_1} In\frac{\omega_2}{\omega_1} \tag{2}$$

The activation energy of the four samples, $Bi_{1.5}Zn_{1-x}Nb_{1.5}O_{7-x}$ (x=−0.05, 0.05, 0.1, 0.15), are calculated as 0.151, 0.152, 0.158 and 0.169 eV.

It can be seen from the activation energy of low temperature dielectric relaxation is in the range of 0.15–0.17 eV and decreases with the x value decreasing.

3.2 High temperature dielectric relaxation and ionic conductivity

Figures 3 and 4 are the dielectric behavior of $Bi_{1.5}Zn_{1.45}Nb_{1.5}O_{6.95}$ (x=0.05) at high temperatures. All the four samples exhibit similar behaviors. Two dielectric relaxation processes can be observed in this high temperature region around 500 °C and 700 °C, however, due to the interference

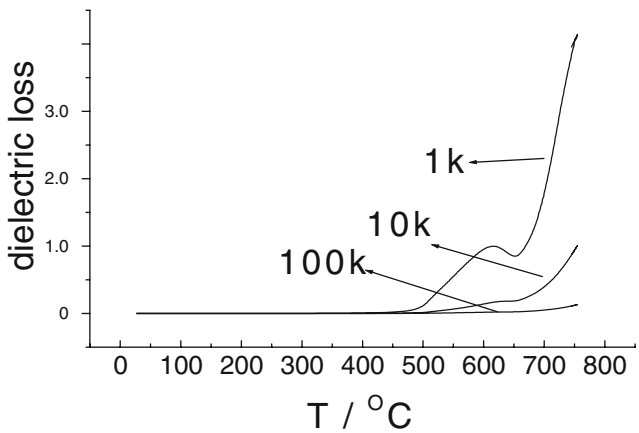

Fig. 4 Dielectric loss of $Bi_{1.5}Zn_{1.45}Nb_{1.5}O_{6.95}$ measured at 1 k, 10 k, 100 Khz

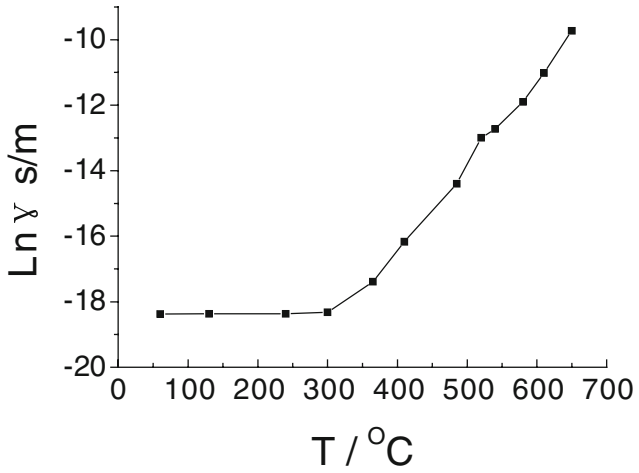

Fig. 5 Temperature dependence of conductivity of $Bi_{1.5}Zn_{1.45}Nb_{1.5}O_{6.95}$

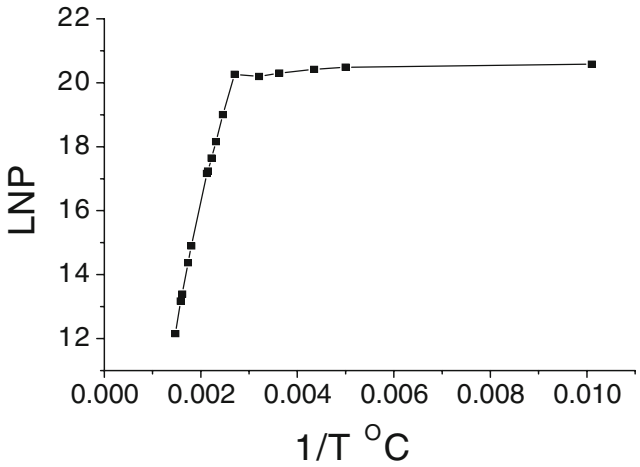

Fig. 7 ln$P$ vs $1/T$ (sintered in air)

of the ionic conductivity of the samples in this high temperature region. It is difficult to calculate the activation energy of dielectric relaxation.

Figure 5 is the temperature dependence of electric conductivity (in logarithm scale) of the sample $Bi_{1.5}Zn_{1.45}Nb_{1.5}O_{6.95}$ (x=0.05). There is an apparent transition of conduction at about 350 °C, which signifies the onset of ionic conduction of the material at elevated temperatures. At temperatures below 350 °C, the electrical conduction is mostly dominated by impurities of the system, while at high temperatures, the thermally activated lattice defects start to take over. The activation energy of conduction can be calculated and discussed in the following section.

3.3 Conductivity of cubic pyrochlore BZN and activation energy of conduction

It is well known that the temperature dependence of high temperature conductivity follows the logarithm law:

$$\mathrm{Ln}\,\gamma = \mathrm{In}\,A - E_c/KT = -\mathrm{Ln}\,P \tag{3}$$

Where γ is conductivity, P is resistivity, E_c is activation energy of conduction, T is absolute temperature, and K is the Boltzman constant. Then, the activation energy of conduction can be calculated by fitting the slope the curve of ln$P$ / (1 / T).

Again, $Bi_{1.5}Zn_{1-x}Nb_{1.5}O_{7-x}$ (x=0.5) is used as an example. For samples sintered in oxygen, air and nitrogen, the measured results of temperature dependence of resistivity are given Figs. 6, 7 and 8 respectively. The activation energy calculated from the test results using Eq. 3 is 1.38, 1.37, 1.35 eV. From the calculated results, it can be seen that there is no apparent difference of activation energy of conduction for samples sintered in different atmosphere, which suggests that the high temperature conduction mechanism is probably the same.

For $Bi_{1.5}Zn_{1-x}Nb_{1.5}O_{7-x}$ (x=−0.05, 0.05, 0.1, 0.15) samples with different chemical composition sintered in the same nitrogen atmosphere (N_2), the activation energy of conduction increases slightly from 1.32 to 1.48 eV with the decreasing of x.

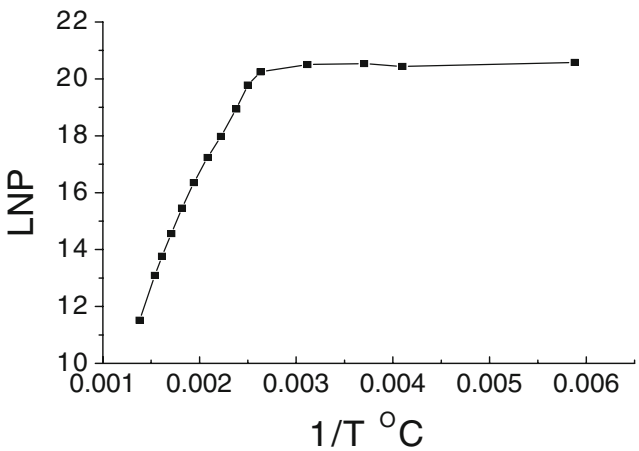

Fig. 6 ln$P$ vs $1/T$ (sintered in O_2)

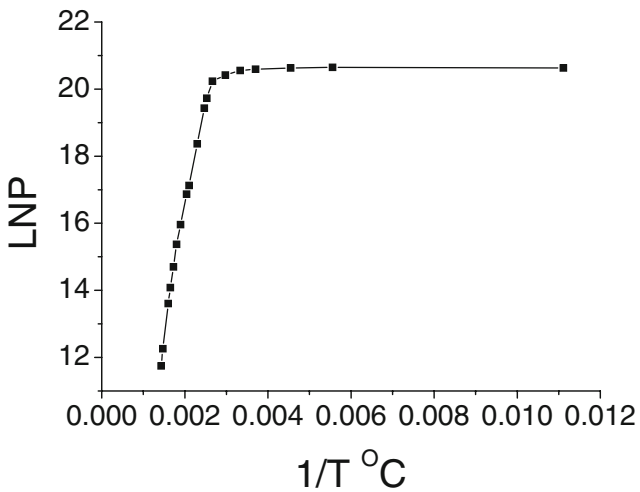

Fig. 8 ln$P$ vs $1/T$ (sintered in N_2)

The conduction activation energy of the four samples, $Bi_{1.5}Zn_{1-x}Nb_{1.5}O_{7-x}$ (x=−0.05, 0.05, 0.1, 0.15),are calculated as 1.48, 1.34, 1.32 and 1.32 eV.

In cubic pyrochlore BZN with formula $A_2B_2O_6O'$, the B_i^{3+} cation tends occupy the A site, and the Nb^{5+} cation tends to occupy B site, while the Zn^{2+} cation can occupy both A site and the B site. When BZN is sintered in different atmosphere, the number of oxygen vacancy changes. Based on the results obtained, it is possible to work out the defect structure of the system and its effect to their dielectric behavior. Works along this line is going on.

4 Conclusion

The dielectric property and high temperature conductivity of cubic pyrochlore BZN were measured. The activation energy of low temperature dielectric relaxation is in the range of 0.15–0.17 eV, and decreases with the x value and is affected by its nonstoichiometry. The activation energy of high temperature conduction of samples sintered in different atmosphere has no significant change, which suggests that the high temperature conduction mechanism of the cubic BZN ceramic is probably the same.

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References

1. H. Wang, H. Du, X. Yao, Mater. Sci. Eng. **b99**, 20–24 (2003)
2. Y. Hu, C.L. Huang, Ceram. Int. **30**, 2241–2246 (2004)