

Relaxor-like behavior of bismuth-based pyrochlores containing Sn

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Abstract Dielectric relaxation studies have been made in pyrochlore $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5-x}\text{Sn}_x\text{Nb}_{1.5-2x/3})\text{O}_7$ ceramics where $0 \leq x \leq 1.5$. The measurements of dielectric constant (ϵ) and dielectric loss ($\tan\delta$) are made in the frequency range from 1 to 1,000 kHz at low temperatures from 100 to 450K. Frequency dispersion associated with dielectric relaxation phenomena in polycrystalline cubic pyrochlore is analyzed. The effect of Sn on the dielectric relaxation behavior and the physical mechanism giving polarization is briefly discussed.

Keywords Pyrochlore · Tin · Dielectric relaxation · Disorder

1 Introduction

Pyrochlore (A_4X_7) is an anion-excessive compound in relation to perovskite (A_4X_6) or an anion-deficient compound in relation to fluorite (A_4X_8). The change in composition from (A_4X_8) to (A_4X_7) means that the structure of the compound may correspond either to defect-disordered fluorite (cubic space group $\text{Fm}\bar{3}\text{m}-\text{O}_h^5$), defect-ordered pyrochlore (cubic space group $\text{Fd}\bar{3}\text{m}-\text{O}_h^7$), or to a random mixture of fluorite and pyrochlore [1, 2]. The correlation between pyrochlore and neighboring structure (fluorite, pe-

rovskite) gives evidence for predisposition of the pyrochlore structure to random frustrations and disorder. Those facts can be the reason for the complicated behavior of the system on a temperature, spatial, and time scale and have to be taken into account when the physical properties of pyrochlores are analyzed [3].

In recent years, substantial interest has developed for bismuth-based dielectrics. As a member of the pyrochlore family of compound, bismuth zinc niobate has typical high-frequency dielectrics with high permittivity and low dielectric loss and can be applied as various devices, such as temperature-stable multilayer ceramics capacitors and microwave resonators and filters [4–6]. It is known that these compounds are neither dipolar glass nor relaxor ferroelectric. However, some interesting results were obtained on dielectric relaxation phenomena at low temperature (50–150K) in cubic pyrochlore of $\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ [7, 8] and $\text{Bi}_{1.5}\text{ZnTb}_{1.5}\text{O}_7$ [9]. Our previous works showed that dielectric relaxation character occurs below 170K for quaternary pyrochlore containing Ti [10]. There is no consequential relation between low-temperature dielectric relaxation behavior and ferroelectricity in, for example, the perovskite structure systems, Bi-doped SrTiO_3 [11]. It seems that there exist some common features in those different systems.

Dielectric relaxation studies are important to understand the nature and the origin of dielectric loss and which, in turn, may be useful in the determination of structure and defects in solids. Dielectric relaxation behavior in Bi-based pyrochlore ceramics was first observed by Cann et al. in 1996 [12]. Dielectric measurements on pyrochlore compounds have indicated that the dielectric dispersion does exist in the system at low temperature. The origin and the nature of dielectric losses in those materials have, therefore, been a matter of curiosity.

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The present paper reports the dielectric relaxation studies in pyrochlore with composition corresponding to $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5-x/3}\text{Sn}_x\text{Nb}_{1.5-2x/3})\text{O}_7$ system. Temperature and frequency dependence of dielectric permittivity and loss are studied in the frequency range from 1 KHz to 1 MHz and the temperature range from 100 to 405 K.

2 Experimental procedure

Ceramics samples were prepared by solid state reaction. Raw materials (Bi_2O_3 , ZnO , Nb_2O_5 , and SnO_2) were weighed according to the composition $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5-x/3}\text{Sn}_x\text{Nb}_{1.5-2x/3})\text{O}_7$, where $x=0, 0.25, 0.5, 1.0$, and 1.5 (designated as BZNS1, BZNS2, BZNS3, and BZNS4, respectively). The weighed batches were wet milled in an agate ball mill for 4 h. After drying, they were calcined from 750 to 820°C for 2 h. The calcined powders were milled again, dried, and pressed into disks. Finally, the samples were sintered from 1,080 to 1,180°C for 2 h in air and furnace-cooled. The higher the Sn contents, the higher the sintering temperature.

Samples for dielectric measurements were painted electrode with low-temperature-fired silver paste. The dielectric permittivity and dissipation factor of samples were measured using a high-precision LCR meter (HP 4284A). The temperature dependence of the dielectric constant was measured at four different frequencies (1 kHz, 10 kHz, 100 kHz, and 1 MHz) and temperatures varying from 100 to 450K by placing the discs in an automated measurement system consisting of a PC computer, a HP 4284A LCR meter, and a temperature chamber.

3 Results and discussions

Dense BZNS ceramics samples were obtained after sintering at temperatures of 1,080 to 1,180°C. The ceramic samples presented a homogeneous microstructure, and the relative density of the pellets was above 96%. The X-ray diffraction (XRD) results indicate that all samples are cubic with the

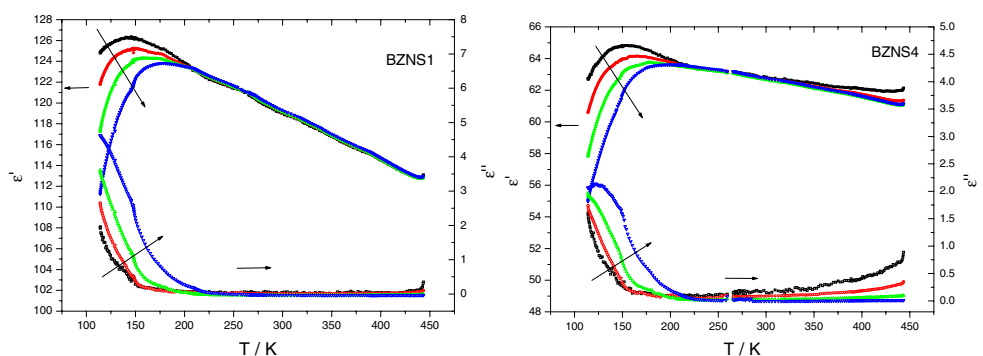
lattice parameter increasing linearly from 10.5515 to 10.5987 Å with increasing Sn content, indicating that Sn ions randomly occupy B site to form homogeneous solid solution phases. Considering the radius and valences of ions, it could be assumed that Sn^{4+} can cosubstitute Zn^{2+} and Nb^{5+} at B site. The following mechanism of substitution can be presented to satisfy the charge neutrality: $3\text{Sn}^{4+} \rightarrow \text{Zn}^{2+} + 2\text{Nb}^{5+}$.

Figures 1 and 2 show the temperature dependence of the dielectric properties as a function of frequency for BZNS. The frequency dispersion is seen in the real part of the dielectric permittivity and in the correlated peak of the dielectric loss. The temperature dependence of dielectric permittivity is studied at four fixed frequencies (1, 10, 100, and 1,000 KHz) of various BZNS compositions, as shown in Fig. 2. The permittivity is decreased with the increase of the Sn^{4+} substitution, and shows the minimum value of 65 at the $x=1.5$ composition, Sn-rich region. It is clear that dielectric permittivity exhibits typical relaxation behavior with strong frequency dispersion in the low-temperature range. Those curves are characteristics of typical relaxation behavior:

1. A broad temperature region of the permittivity peak and the peak value, ϵ'_{max} , decreases slightly with an increase of frequency.
2. When the frequency increases, the temperature of maximum permittivity, T_m , shifts towards higher temperatures.
3. The higher dielectric constant and larger negative temperature coefficient are also observed for the Sn-poor region.

Because measurements were limited to temperatures above 100 K, it was difficult to evaluate the dielectric dispersion characteristic of dielectric loss. However, it can be seen that the frequency dispersion is similar to that of BZNT ceramics and the temperatures of the maximum of the real and imaginary parts of the permittivity are shifted to the lower temperatures [10]. In addition, the dielectric loss increases with frequency and the onset of high loss shifts towards higher temperature. This dielectric relaxation phenomenon has also been observed in other bismuth

Fig. 1 Frequency dependence of dielectric response as a function of temperature for composition BZNS1 and BZNS4



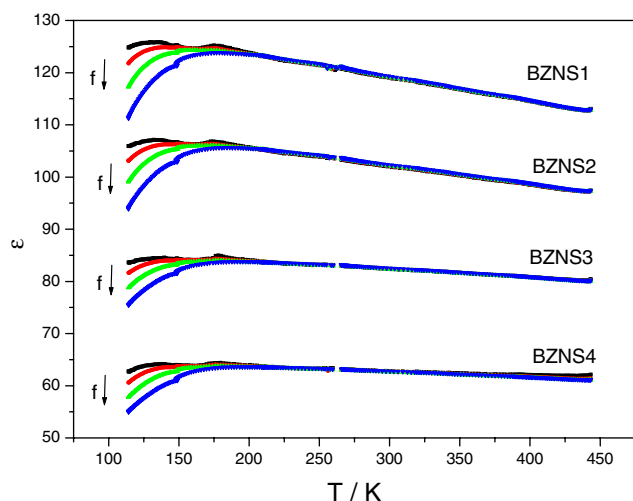


Fig. 2 Dielectric constant dependence of temperature measured at fixed frequencies for series compositions of BZNS

pyrochlore, such as C-BZN, C-BZT, and C-BZNT series solid-state compositions [7–10]. It should be emphasized that the temperature (T_m) where the dielectric permittivity maximum occurs is independent of Sn concentration. The permittivity peaks are quite diffuse with frequency dispersion present even for the sample with the smallest amount of Sn. With increasing Sn content, the peak value of the permittivity decreased remarkably with slightly decreased dielectric dispersion. The character above indicated that the relaxation behavior exhibit is more intensive for samples with less Sn concentration than that of Sn-rich compositions.

To characterize the dielectric dispersion, an empirical expression is proposed. The activation energies involved in the relaxation processes are approximated by the Arrhenius relation:

$$\nu = \nu_0 \exp\left(-\frac{E_a}{k_B T}\right)$$

where ν_0 is the attempt frequency, E_a the activation energy for relaxation, k_B the Boltzmann's constant, and T the absolute temperature. Figure 3 shows a straight-line plot according to the above equation yielding an activation energy value of 0.259 eV for BZNS4 samples. Table 1 lists the activation energy for bismuth pyrochlores. E_a of BZNS4 is reasonably close to 0.319 eV obtained for $\text{Bi}_2\text{Mg}_{2/3}\text{Nb}_{4/3}\text{O}_7$ pyrochlore by Cann et al. [12] and 0.202 eV obtained for $\text{Bi}_{3/2}\text{ZnNb}_{3/2}\text{O}_7$ pyrochlore by Kamba et al. [8]. The characteristic relaxation time, τ_m , obtained from the intercept of the straight-line frequencies axis of Fig. 3 and given by $\tau_0 = 1.22 \times 10^{-13}$ s for BZNS4.

The above results indicate that this system can be classified as a “dielectric relaxor.” The similar dielectric relaxation behavior in low temperature both for the C-BZN, C-BZT, and BZNS system and BZNT make it interesting to understand the nature of dielectric relaxation. To understand

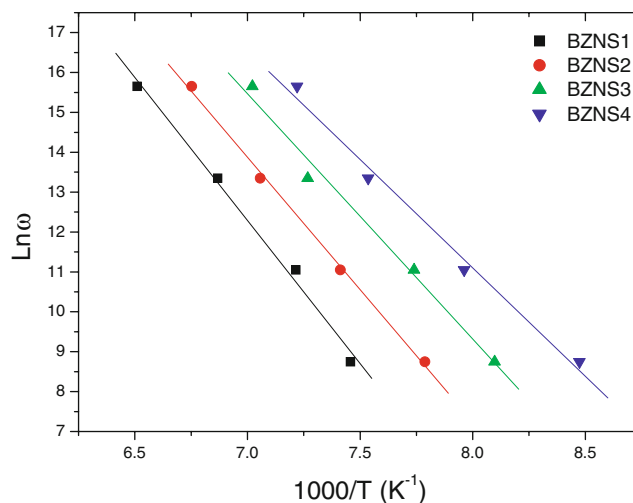


Fig. 3 Arrhenius plot of the experimental relaxation frequency dependence of temperature. The lines are the results of the best fits using the Arrhenius law

the physical nature of dielectric anomalies in Bi-based dielectrics, a question as to what the dielectric polarization species is should be discussed. Compared with the ferroelectric origin of $\text{Cd}_2\text{Nb}_2\text{O}_7$ and some perovskite oxides, more mechanisms should be evaluated for bismuth pyrochlore due to its complicated structure. The disorder structure or the reorientation of dipoles formed by the seventh oxygen with the A-site cations has been proposed as the origin of dielectric relaxation [8, 9, 12].

Studies of BZN using far-infrared spectroscopy conducted by Kamba indicated that the lowest-frequency $\text{O}'\text{--A--O}'$ bending mode provides the strongest contribution to the dielectric constant [8]. Further structural information obtained by Withers et al. [13] revealed that a highly structured, characteristic diffuse intensity distribution arises from static disordering caused by local short-range ordering of Bi and Zn ions on the pyrochlore A sites and associated structural relaxation of the A_2O substructure. Keeping in mind the specific nature of the pyrochlore structure, the relaxor-like behavior of bismuth pyrochlores may be ascribed to a dynamical disorder in alignment of the $\text{A--O}'$ dipoles at low temperature. Disorder inevitably produces

Table 1 The fitting parameters from the Arrhenius equation for bismuth pyrochlores.

Compositions	ν_0 (Hz)	E_a (eV)
$\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ [7]	3×10^{12}	0.136
$\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$ [8]	6.129×10^{12}	0.202
$\text{Bi}_{1.5}\text{ZnTa}_{1.5}\text{O}_7$ [9]	3.7×10^{12}	0.112
$\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Nb}_{0.5}\text{Ti}_{1.5}\text{O}_7$ [10]	1.133×10^{15}	0.195
$\text{Bi}_{1.5}\text{Zn}_{0.5}\text{Nb}_{0.5}\text{Sn}_{1.5}\text{O}_7$	8.196×10^{12}	0.259

random electric fields, which introduce some statistical distribution into the local potential barrier heights for charge hopping. Guintini proposed a model for dielectric relaxation in glasses [14] based on the hopping mechanism of charge carriers over the potential barrier between charged defect states. Each pair of sites is assumed to form a dipole that has a relaxation time depending on its activation energy. Thus, the activation energy should no longer be the same for all hopping ions, causing permittivity and loss peak broadening. This is observed in many dynamically disordered dielectric systems. This implies that the dielectric relaxation is strongly perturbed by local disorder and local chemical inhomogeneity.

Other possibilities are cooperative hopping of the loosely bound “seventh” oxygen ion or oxygen vacancies. In the hard (BO_6) octahedral-formed network, the positional A-site disorder with respect to static location of A-site ions and oxygen ions arises from fast reorientational motions of A-sites ions over the six equivalent off-center positions. The dipole reorientations may cause a change in the local electric field. Further investigation is needed on the influence of dielectric relaxation by annealing in oxidizing or reducing atmosphere.

In addition, it is also known that substituting a third cation species in pyrochlore solid solution in either the A site or the B site can also drive the system to order when the substitution increases the difference in the average radius of the species that occupy these sites [15]. In the system studied, the introduction of Sn decreases the size difference between the average radius of the A-site and B-sites species. The smaller difference in cation size may be the driving force for structural disordering. Therefore, we could reckon that local structural disorder and local chemical inhomogeneity in the A-site cations and anion sublattice increase when r_B approaches r_A in the BZNS compounds investigated.

The sample with less Sn concentration exhibits more intensive relaxation than that of Sn-rich compositions. It could be understood by the fact that the larger Sn-ions occupied at the center of oxygen octahedra lead to a weaker off-center displacement than the Nb-ions. In the case of the high-Sn-concentrations sample, the dielectric relaxation intensity tends to be suppressed. Therefore, we can infer that displacive disorder in BZNS pyrochlore dielectric is responsible for the dielectric relaxation phenomenon. Ongoing work is investigating these materials in more structural detail, together with related materials in the Sb and Zr systems.

Thus, the displacive disorder in the $\text{A}_2\text{O}'$ network and the hopping of off-centered cations most likely is the origin of the “glass-like” dielectric behavior observed for Bi-based pyrochlore systems. To clarify further the disorder structure

and the short-range interactions between reoriented dipoles, further investigations of Raman spectra and XRD structural refinement at low temperatures should be developed to understand the nature of the dielectric relaxation.

4 Conclusions

In summary, the observation of dielectric anomalies with relaxor-type behavior at cryogenic temperatures in a quaternary system of $\text{Bi}_2\text{O}_3\text{--ZnO--SnO}_2\text{--Nb}_2\text{O}_5$ solid solution was reported. The relaxation time follows the Arrhenius law and, given by τ_0 , is 1.22×10^{-13} s for BZNS4. The relaxation behavior of Sn-poor samples is more intensive than that of Sn-rich compounds. The similar dielectric relaxation behavior in low temperature both for ternary C-BZN, C-BZT, and quaternary BZNS system and BZNT make it interesting to understand the nature of disorder structure and the polarization mechanism of “hopping ions.” The dielectric relaxation is tentatively explained due to the displacive disorder in the $\text{A}_2\text{O}'$ network and the polarization mechanism of hopping of off-centered cations.

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