

Low-temperature dielectric relaxation in the pyrochlore $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Ta}_{3/4})_2\text{O}_7$ compound

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The dielectric behavior of the pyrochlore $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Ta}_{3/4})_2\text{O}_7$ compound has been studied. A low-temperature dielectric relaxation was observed in a low-permittivity matrix with $\epsilon \sim 60$. The dielectric relaxation process follows a modified Debye model in the vicinity of the relaxation peak, and the relaxation rate follows the Arrhenius law in the wide frequency range 10^2 to $\sim 10^{10}$ Hz. The temperature intensity of dielectric peaks are independent of dc bias (≤ 60 kV/cm). The dielectric relaxation is tentatively attributed to the hopping of Zn/Bi ions at A sites with more than one equivalent potential minima, and the reorientation of the dipoles probably formed through interactions with the "seventh oxygen" and the Bi/Zn A-site ions in the pyrochlore $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Ta}_{3/4})_2\text{O}_7$ compound. © 2002 American Institute of Physics.
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With recent development in microwave devices, the compatibility of the ceramic processing (mainly sintering) with metal electrodes is emphasized, but a moderate quality factor Q value is allowed.^{1,2} For this application, a type of microwave ceramics located in the ternary system $\text{Bi}_2\text{O}_3\text{-ZnO-Me}_2\text{O}_5$ (Me=Nb and Ta), which allow low temperature cofiring with silver electrodes is being developed.^{3,4} The dielectric properties and crystalline structure of the compounds change with the variation of compositions.¹⁻¹⁰ Two compounds, $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Me}_{3/4})_2\text{O}_7$ and $\text{Bi}_2(\text{Zn}_{1/3}\text{Me}_{2/3})_2\text{O}_7$, with different crystalline structures have been mostly studied. Compound $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Me}_{3/4})_2\text{O}_7$ has been indexed as a pyrochlore structure with a cubic symmetry, while compound $\text{Bi}_2(\text{Zn}_{1/3}\text{Me}_{2/3})_2\text{O}_7$ has been recently identified as a zirconolite structure with a monoclinic symmetry.³ It is known that these compounds are not ferroelectric. However, an interesting behavior is that a low-temperature (below room temperature) dielectric relaxation process was observed in cubic pyrochlore $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Me}_{3/4})_2\text{O}_7$, but not in zirconolite $\text{Bi}_2(\text{Zn}_{1/3}\text{Me}_{2/3})_2\text{O}_7$.^{1,3,4}

On the other hand, low-temperature dielectric relaxation behavior which has no relation to the ferroelectricity has also been observed in many systems with different crystalline structures, for example, the perovskite structure systems, Bi-doped SrTiO_3 ,¹¹ and La-doped SrTiO_3 .¹² It seems that there exist some common features in these different systems. For example, the relaxation rate follows an Arrhenius law. However, to date, no common explanation for the physical mechanism of the dielectric relaxation is available.

Obviously the understanding of the physical nature of the dielectric relaxation is both of technical and fundamental importance. In this letter, we focus on the study of the low-temperature dielectric relaxation behavior of the $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Ta}_{3/4})_2\text{O}_7$ compound with cubic symmetry, hereafter denoted as C-BZT. The physical characteristics

of the dielectric relaxation behavior are discussed.

The ceramic samples of $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Ta}_{3/4})_2\text{O}_7$ were prepared by the solid state reaction, as discussed elsewhere.⁴ Complex dielectric permittivity was measured using an HP 4284A LCR meter with an ac field of 1 V/mm. The temperature dependence of the dielectric properties was measured in the temperature range 10–423 K, while the specimen was being cooled or heated up at a typical cooling/heating rate of 1–2 K per minute. A dc voltage was applied to the samples and a blocking circuit was adopted to separate the high dc voltage from the LCR meter. The ring resonator and waveguide transmission techniques were adopted to measure the dielectric properties of the samples at microwave frequencies. The accuracy of the measurements was compared by the resonant post and split cavity techniques. The details of samples preparation and measurement were described in Ref. 4.

The temperature dependence of the dielectric constant (ϵ') and dissipation factor ($\tan \delta$) for C-BZT is shown in Fig. 1. With decreasing temperature, ϵ' first increases slightly, then decreases quickly. An obvious dielectric relaxation behavior is observed for both ϵ' and $\tan \delta$, and their relaxation rate as a function of inverse temperatures is plotted in the inset of Fig. 1. The data can be well fitted to the Arrhenius law:

$$\nu = \nu_0 \exp(-U/k_B T), \quad (1)$$

where ν_0 is the attempt frequency, U is the activation energy for relaxation, and T is the temperature. The fit parameters are $U = 112$ meV and $\nu_0 = \sim 3.7 \times 10^{12}$ Hz.

The curve of ϵ'' (the imaginary part of the permittivity) vs ϵ' at 93 K, at which the dielectric relaxation behavior is present in the measured frequency range, is shown in Fig. 2. It can be seen that the data points fit reasonably into a semi-circular arc with the center lying underneath the abscissa, deviated from the ideal Debye model. Hence, the modified Debye equation is adopted to evaluate the dielectric relaxation. The complex permittivity can be empirically described by the equation:¹³

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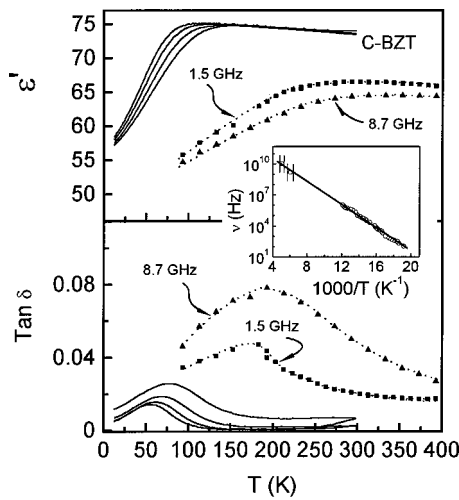


FIG. 1. Temperature dependence of ϵ' and $\tan \delta$ for the pyrochlore $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Ta}_{3/4})_2\text{O}_7$ compound: (a) ϵ' at 1, 10, 100, and 1000 kHz (solid curves, from top to bottom); (b) $\tan \delta$ at 1, 10, 100, and 1000 kHz (solid curves, from bottom to top). The microwave frequencies are labeled, the dotted curves are plotted to guide the eyes. Inset: Relaxation rate ν vs $1/T$ curve. Open circles: experimental data; solid lines: fitting to the Arrhenius law.

$$\epsilon^* = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) / [1 + (i\omega\tau)^\beta], \quad (2)$$

where ϵ_0 is the static permittivity, ϵ_∞ is the permittivity at high frequency, ω is the angular frequency, τ is the mean relaxation time, and $\beta = 1 - \alpha$, where α is the angle of the semicircular arc. The fitting data show that $\alpha = 0.24$, $\epsilon_0 = 75.6$, and $\epsilon_\infty = 45.4$. Although there are no data between the points at 1 MHz and 1 GHz for C-BZT, the curve of ϵ'' vs ϵ' for $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Nb}_{3/4})_2\text{O}_7$ (denoted as C-BZN) has been studied from 80 Hz to 1 GHz with more frequencies between 1 MHz and 1 GHz, and the results also show good fits to the Cole–Cole relation with the same level of α .¹⁴ This indicates that the present data for C-BZT are reasonable, and self-consistent with a similar polarization mechanism.

The real (ϵ') and imaginary (ϵ'') parts of the permittivity can be rewritten from Eq. (2) in the following way:

$$\epsilon' = \epsilon_\infty + (\Delta\epsilon'/2) \{1 - \sinh(\beta z) / [\cosh(\beta z) + \cos(\beta\pi/2)]\}, \quad (3)$$

$$\epsilon'' = (\Delta\epsilon'/2) \sin(\beta\pi/2) / [\cosh(\beta z) + \cos(\beta\pi/2)], \quad (4)$$

where $z = \ln(\omega\tau)$ and $\Delta\epsilon' = \epsilon_0 - \epsilon_\infty$.

The calculated frequency dependence of the dielectric constant and $\tan \delta$ is shown in Fig. 3, according to Eqs. (3) and (4), and $\tan \delta = \epsilon''/\epsilon'$ by using the data obtained from the Cole–Cole plot fitting. It can be seen that the calculated

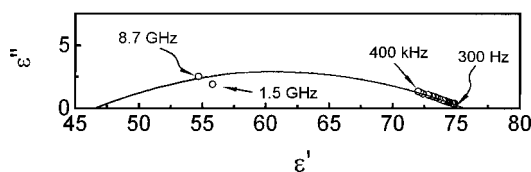


FIG. 2. Cole–Cole plot (ϵ'' vs ϵ') for the pyrochlore $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Ta}_{3/4})_2\text{O}_7$ compound at 93 K. (Open circles: experimental data; circular arc: fitting curve).

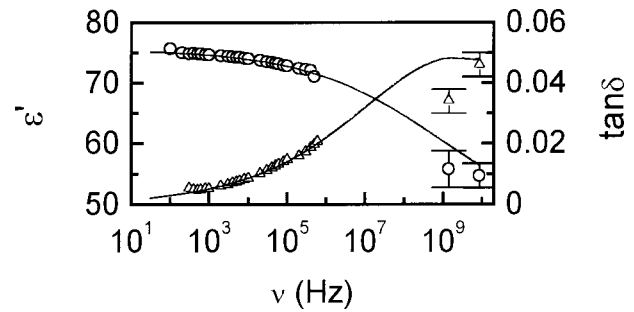


FIG. 3. Frequency dependence of ϵ' and $\tan \delta$ for the pyrochlore $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Ta}_{3/4})_2\text{O}_7$ compound at 93 K. The error bar is a fluctuation of data obtained from different measurement technique at microwave frequencies. Open symbols: experimental data; solid curves: fitting to Eqs. (3) and (4).

curve is in agreement with the experimental data. The results show that the dielectric spectra of C-BZT follows the modified Debye model.

In a recent report for C-BZN thin films by Ren *et al.*,¹⁰ a very small electric-field effect ($<10\%$) on ϵ is observed under very high dc fields (~ 800 kV/cm). We checked this behavior in bulk samples up to 60 kV/cm, and noted that the temperature and intensity of dielectric peaks are independent of dc bias for both C-BZT and C-BZN.

As discussed above, the dielectric relaxation process in cubic pyrochlore C-BZT(N) has three major characteristics:

(1) The first characteristic indicates the relaxation obeys the Arrhenius law as opposed to a Vogel–Fulcher law. This implies that there is very weak to no cooperation between the dipoles in the C-BZT system.

(2) The second characteristic of a suppressed semicircle shows a Cole–Cole plot with a relatively large α ; this indicates that there is broad distribution in the relaxation times. The source of this broadening is usually associated with many body interactions. We, therefore, assume that there is a weak interaction between dipoles, and is associated with large levels of disorder among many sites in the Bi-pyrochlore. This is consistent with recent structural studies in the C-BZN system, in which the C-BZT will strongly follow.

(3) The temperature of the dielectric peak is almost independent of dc bias. This characteristic implies that there are either no micropolar clusters or very weakly collaborated dipole clusters in pyrochlore C-BZT(N). This extrapolation can be supported by studies in KTaO_3 , CaTiO_3 , and $(\text{La},\text{Na})\text{TiO}_3$ under dc bias.¹⁵

Considering (1)–(3) the results indicate that this system can be classified as a “dielectric relaxor.”¹⁶ This implies that the dielectric relaxation is strongly perturbed by local disorder and local chemical inhomogeneity. In the pyrochlore $(\text{Bi}_{3/4}\text{Zn}_{1/4})_2(\text{Zn}_{1/4}\text{Ta}_{3/4})_2\text{O}_7$ compound, the partial substitution of Zn ions for Bi ions lead to more than one equivalent potential minima at A sites. The positional hopping of the cations and anions in these positions leads to the dielectric relaxation. This type of dielectric polarization mechanism is similar to the “dielectric-relaxor modes” observed in Bi doped SrTiO_3 , which are related to the movement of off-centered Bi ions.^{11,16}

In addition, it is also known that cubic pyrochlore structure $\text{A}_2\text{B}_2\text{O}_7$ oxides could be recognized as the cubic pyrochlore of $\text{A}_2\text{B}_2\text{O}_6$ -Z-type structure (Z denotes the “seventh oxygen” ions, which could be O, S, OH, or F). Because of

the special crystalline structural characteristics of $A_2B_2O_7$, the “seventh” oxygen ions are weakly bonded to the (BO_6) octahedra, which form the structural framework of the lattice. It is therefore feasible that the relative interactions between the cations (Zn/Bi ions) at disordered A sites and the “seventh” oxygen can lead to formation of unstable dipoles within the pyrochlore structure, and the reorientation of the dipoles under external ac fields causes the dielectric relaxation. The similar explanation has been applied to $Cd_2Nb_2O_7$.^{17,18} Solid solutions between pyrochlore structure ferroelectric $Cd_2Nb_2O_7$ and BZT(N) may lead to interesting dielectrics where the cooperative dipolar interactions are enhanced with Cd content. This could be similar to the behavior reported in Bi-doped $SrTiO_3$.¹⁶

Low-temperature dielectric relaxation behavior for the C-BZT compound was observed in a low permittivity matrix with $\epsilon \sim 60$ for C-BZT. The dielectric relaxation process follows the modified Debye model, Cole–Cole equation, where relaxation rate follows the Arrhenius law in the frequency window 10^2 to $\sim 10^{10}$ Hz. No influence of dc bias on the dielectric peaks was observed. The dielectric relaxation is tentatively explained due to the hopping of cations in the more than one equivalent potential minima of A sites, and the reorientation of dipoles formed through interactions with the “seventh oxygen” and the Bi/Zn ions in the C-BZT compound.

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