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ScienceDirect
Journal of the European Ceramic Society 30 (2010) 385–388
www.elsevier.com/locate/jeurceramsoc

Dielectric properties of cubic bismuth based pyrochlores containing lithium and fluorine

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Available online 17 July 2009

Abstract

In this work dielectric properties of $Bi_{1.5}Zn_{1-x}Li_xNb_{1.5}O_{7-x}F_x$ with $x = 0.25$ were investigated in a 20 Hz–12 GHz frequency and 120–500 K temperature range and compared to that of regular cubic BZN (when $x = 0$). Measurements showed that both ceramics have dipolar glass type dielectric dispersion with wide relaxation time distributions. Mean relaxation time follows Arrhenius law in the investigated frequency range, although Vogel–Fulcher law was anticipated.

Keywords: Dielectric properties; Traditional ceramics

1. Introduction

Low-temperature co-fired ceramics (LTCC) are widely used in wireless and other high-frequency applications. Because of numerous advantages, demand for materials which can be co-fired with metals and other ceramics is always huge. Bi_2O_3–ZnO–Nb_2O_5 (BZN) based pyrochlore ceramics are known for quite a while now, but recently they attracted more attention due to their excellent dielectric properties as promising candidates for LTCC and microwave applications.

BZN is a compound, which easily forms pyrochlore structured lattice. It was shown in previous works,[1,2] that lattice can be cubic or orthorhombic depending on oxides' ratio and sintering temperature. However, in later works (e.g. reference[6]) it is stated that structure is monoclinic instead of orthorhombic.

One of the most remarkable properties of BZN ceramics is low loss tangent despite high dielectric permittivity even in microwave range,[1–7] which must be a result of broad distribution of relaxation times.[4] Value of permittivity can be around 150 (in case of cubic BZN), around 80 (monoclinic), or any intermediate value depending on exact constitution and sintering temperature.

Several works[2–5] showed that frequency, at which loss is maximum, seems to follow Arrhenius law with activation energy around 0.15 eV. Moreover, in reference[4] it is stated that BZN exhibits dipolar glass type behavior.

An exhaustive summary on BZN-based ceramics can be found in reference.[10]

The aim of the present work was to investigate dielectric dispersion of $Bi_{1.5}Zn_{1-x}Li_xNb_{1.5}O_{7-x}F_x$ with $x = 0.25$ pyrochlore structured ceramics and compare it with pure compound.

2. Experimental

Ceramic samples were prepared by mix-oxides method with the starting materials of reagent-grade Bi_2O_3, ZnO, Nb_2O_5 and LiF. Powders were weighed according to chemical stoichiometric ratios for $Bi_{1.5}Zn_{1-x}Li_xNb_{1.5}O_{7-x}F_x$ ($x = 0$ and 0.25) and then mixed and milled for 3 h using a planetary mill with Zirconia balls (2 mm in diameter) as milling media. The slurry was dried and calcined at 750–800 °C for 2 h. After being crushed and re-milled for 3 h using ZrO_2 balls and deionized water, powder was pressed into cylinders (8 mm in diameter and 5 mm in height) in a steel die under uniaxial pressure of 20 kN/cm^2 with PVA binder addition. Samples were sintered at 960–980 °C temperature range for 2 h. Samples for dielectric measurements were machined and polished to the right size.

Measurements were performed using Hewlett Packard 4284A LCR-meter in 20 Hz–1 MHz frequency range using $0.6 \times 0.6 \times 4$ mm^3 size samples, coaxial line with a vector network analyzer Agilent 8714ET in 10–3000 MHz range

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doi:10.1016/j.jeurceramsoc.2009.06.032

using $0.6 \times 0.6 \times 0.3\,\text{mm}^3$ size samples, and waveguide setup with scalar network analyzer R2400, which is produced by "Elmika" company, in 8–12 GHz frequency band, using $0.4 \times 0.4 \times 11\,\text{mm}^3$ size samples.

3. Experimental results

First, let us discuss properties of pure cubic BZN. Its real and imaginary parts of dielectric permittivity at different frequencies are shown in Fig. 1. There is no clearly expressed maximum of real part of dielectric permittivity in whole investigated frequency range. From the imaginary part temperature dependence we can see that these ceramics exhibit dipolar glass-like behavior. The maxima of the imaginary part of dielectric permittivity shift to higher temperatures with the increase of the frequency. Similar dielectric behavior was observed in typical dipolar glasses BP/BPI[8] and RADP[9].

Loss tangent is relatively small even at its maxima, while the peak itself is quite broad, which suggests broad relaxation time distribution. The frequency dependence of the real and imaginary parts of dielectric permittivity confirms the dipolar glass behavior of this material (Fig. 2). All of this agrees very well with previously conducted works by other researchers.

Dielectric properties of cubic BZN with LiF are shown in Figs. 3 and 4. As we can see from these graphs, permittivity of these ceramics does not differ much from that of pure cubic BZN, despite the fact it contains quite big amount of admixtures. Dipolar glass-like behavior persists, and value of dielectric permittivity changes only a little.

To give proper characterization, frequency dependencies of dielectric permittivity of both ceramics were fitted with Cole–Cole equation:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + (j\omega\tau_0)^{1-\alpha}}. \quad (1)$$

In this equation $\Delta\varepsilon$ represents the strength of relaxator, τ_0 is the mean Cole–Cole relaxation time, α is the relaxation time

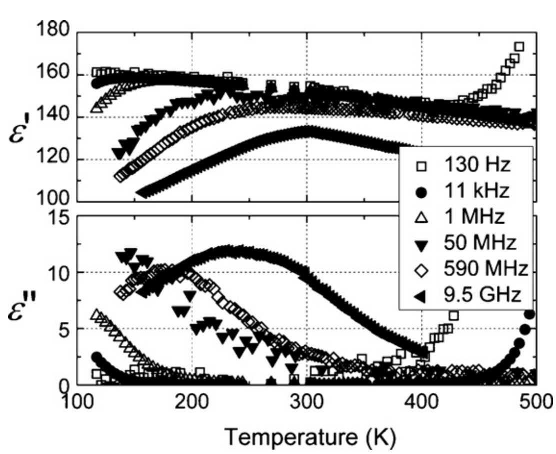

Fig. 1. Temperature dependencies of dielectric permittivity of pure cubic BZN (real and imaginary parts).

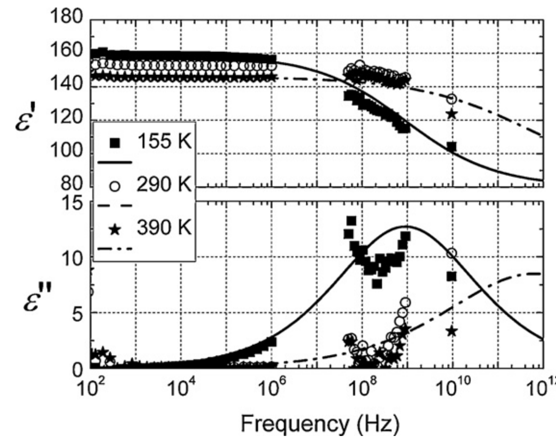

Fig. 2. Frequency dependencies of dielectric permittivity of pure cubic BZN (real and imaginary parts).

distribution parameter, and ε_∞ is the contribution of all phonon modes and electronic polarization.

When fitting, it was assumed that permittivity at infinite frequency ε_∞ is equal to 80 in both the cases. This value was chosen for two reasons—firstly, it seems logical from,[4] where properties at THz frequencies were studied, and secondly, it gave results

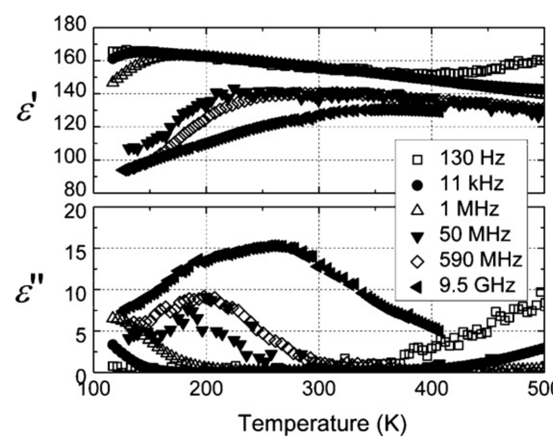

Fig. 3. Temperature dependencies of dielectric permittivity of BZN with LiF (real and imaginary parts).

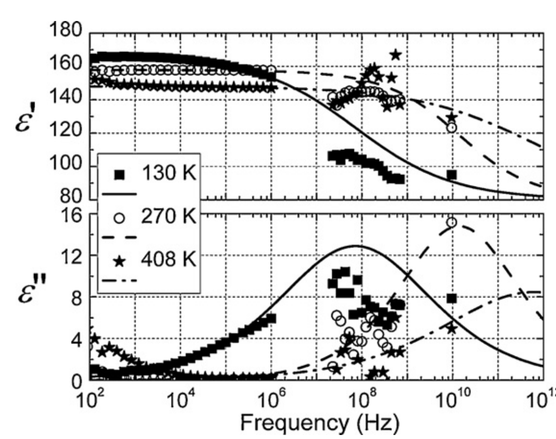

Fig. 4. Frequency dependencies of dielectric permittivity of BZN with LiF (real and imaginary parts).

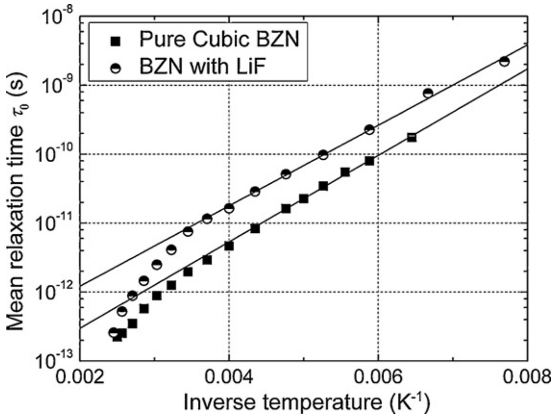

Fig. 5. Inverse temperature dependence of mean relaxation time.

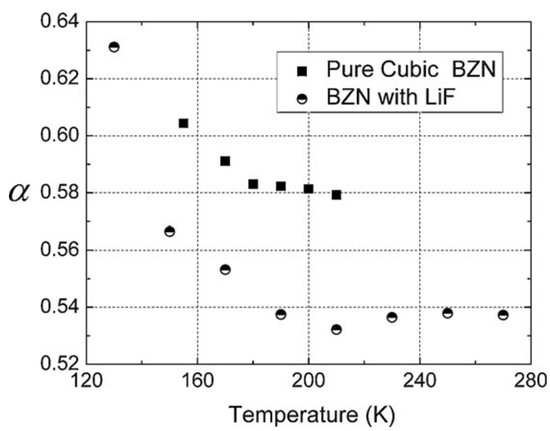

Fig. 6. Temperature dependence of α-parameter (only points, for which according mean relaxation time is longer than 10^{-11} s, are shown).

with smallest error. Fitting curves are presented in Figs. 2 and 4 as solid lines.

In such fits, the most information can be obtained from τ_0 and α parameters. Their values are displayed in Figs. 5 and 6.

From Fig. 5 we can see that mean relaxation time temperature dependence follows Arrhenius law (2) in both cases (solid lines):

$$\tau_0 = \tau_\infty \exp\left(\frac{E}{kT}\right), \tag{2}$$

where τ_∞ is the attempt relaxation time at infinite temperature and E is the activation energy. To obtain equation parameters, only points with mean relaxation time longer than 10^{-11} s were taken into account, since our highest measurement frequency was limited to 12 GHz.

For cubic BZN, the obtained parameters are: $\tau_\infty = 1.67 \times 10^{-14}$ s, and activation energy $E = 0.125$ eV, which corresponds to 1440 K. For BZN with LiF, the same parameters are as follows: $\tau_\infty = 8.31 \times 10^{-14}$ s and $E = 0.116$ eV (1340 K). The values, obtained for pure cubic BZN, correlate with those reported by other researchers. When relaxation time temperature dependence was fitted with Vogel–Fulcher equation instead of Arrhenius, the resulting freezing temperature was close to 0 K. This suggests that both of these ceramics have extremely low freezing temperature. To verify it, measurements at lower temperatures must be performed.

We must point that α-parameter in Cole–Cole equation is related to the width of relaxation time distribution. With addition of LiF, more random bonds were anticipated. This would result in the broadening of relaxation time distribution. But according to Fig. 6, we see the opposite. This suggests that the addition of LiF probably decreased random fields, which are a characteristic of dipolar glasses. Moreover, it seems that at higher temperatures the breadth of distribution of relaxation times remains constant, but on cooling from certain temperature dipoles start freezing, ceramics become more “glasseous”.

4. Discussion and conclusions

After performing detailed measurements, it became obvious that both pure and doped ceramics exhibit dipolar glass-like behavior. Despite the big amount of admixtures, both ceramics have quite similar properties. The pure BZN seems to have broader distribution of relaxation times. However, it was anticipated, that dopants would introduce more defects, which result in distribution broadening. In both the cases, mean relaxation time temperature dependence seems to follow Arrhenius law, although Vogel–Fulcher law is a characteristic of dipolar glasses. This suggests extremely low freezing temperatures of these ceramics. To verify it, measurements at lower temperatures (and probably at much lower frequencies) must be performed.

Acknowledgment

This work was supported by Lithuanian Science and Study Foundation.

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