Dielectric response of disordered BaBi$_2$Nb$_2$O$_9$ perovskite ceramics

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Abstract. Studies of dielectric properties of BaBi$_2$Nb$_2$O$_9$ ceramics are reported. Considerable dispersion of $\varepsilon^*$ at low- and infra-low frequencies has been revealed in the region of the diffused phase transition. Dispersion of $\varepsilon^*$ is divided into “low-temperature” dispersion related to relaxation of polar formations and their boundaries and “high-temperature” dispersion (at $T \geq T_m$) the main contribution to which comes from Maxwell-Wagner relaxation.

1. Introduction

The structure of layered ferroelectrics is known to be substantially disordered broadening the phase transition at fluctuations of composition of the solid solution [1]. Properties of such compounds also depend on the concentration of admixture of rare earth elements. For example, at small concentrations the solid solution behaves as a typical ferroelectric turning into a relaxor at higher concentrations [2]. Therefore, the studies of such materials are of interest for applications as well as for fundamental research exposing the processes taking place at phase transition broadening in disordered solids.

The study presented hereafter has been focused on the mechanisms of low- and infra-low-frequency relaxation of polarization in the layered ferroelectric BaBi$_2$Nb$_2$O$_9$ in the region of the diffused phase transition.

2. Measuring techniques

For studies of the dielectric response within the 0.25 – 1000 Hz frequency interval the BaBi$_2$Nb$_2$O$_9$ samples were made as parallelepipeds 0.4 mm thick with the face area from 32 to 58 mm$^2$ bearing fired silver paste electrodes. The complex dielectric permittivity $\varepsilon^*$ was measured on a bridge at weak field intensity (E < 1 V/cm) and slow heating (1 °C /min) from the temperature of liquid nitrogen (-193 °C) to +220 °C the measurements being made at the temperature being kept constant within $\Delta T \approx 0.1$ °C. The dielectric permittivity $\varepsilon'$ was measured with accuracy within 0.5 %, the dielectric loss $\varepsilon''$ – within the accuracy of 1 %.

3. Results and discussion

Behaviour of the dielectric permittivity $\varepsilon'(T)$ curve over a wide range of temperatures including transition of BaBi$_2$Nb$_2$O$_9$ from the ferroelectric to paraelectric phase at different frequencies is seen in figure 1. At 500 – 1000 Hz frequencies $\varepsilon'(T)$ has a broad maximum in the range $T_m \approx 120 – 150$ °C. The contribution of high-temperature relaxation becomes more noticeable at lower frequencies – $\varepsilon'(T)$
increases over the whole range of temperatures. The growth of $\varepsilon'(T)$ is particularly pronounced at infra-low frequencies. The increase of the value of dielectric loss factor $\varepsilon''$ starts at lower temperatures. The so cold “tails” of $\varepsilon''(T)$ appear from 50 °C after the “low-temperature” maximums of $\varepsilon''(T)$ within a rather wide range: at 0.25 Hz – $T_{\max} \approx -20$ °C, at 1000 Hz – $T_{\max} \approx 50$ °C.

The maximums of $\varepsilon''(T)$ and corresponding behaviour of $\varepsilon'(T)$ at $T < T_m$ point to the presence of a substantial low- and infra-low-frequency dispersion of $\varepsilon^*$ in BaBi$_2$Nb$_2$O$_9$. Analysis of the dispersion shows it being well described by the Cole-Cole equation:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_s + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + (i\omega\tau)^{1-\alpha}},$$

where $\varepsilon_s$ and $\varepsilon_{\infty}$ are the low-frequency and high-frequency limits of $\varepsilon^*$, $\tau$ – the most probable relaxation time of polarization, $\omega$ – cycle frequency, $\alpha$ – parameter of distribution over the times of relaxation.

The $\varepsilon''(\varepsilon')$ curve is shown in figure 2 where experimental (solid line) and approximated (dotted line) values of the parameters are presented. The spectrum of the most probable relaxation frequencies is strongly broadened.

Dependence of the most probable relaxation frequency $\nu_r$ on reciprocal temperature (figure 3a), thermal behaviour of dispersion depths $\Delta\varepsilon = \varepsilon_s - \varepsilon_{\infty}$ (dotted line) (figure 3b) and distribution parameter $\alpha(T)$ (figure 3c) derived from approximation of experimental data to fit the Cole-Cole equation are presented. Effective dispersion depth $\Delta\varepsilon_{\text{eff}}$ (solid line) shown in figure 3b is defined as the difference between the values of $\varepsilon'$ at 0.25 Hz and 1000 Hz.

Analysis of $\nu_r(1/T)$ shows that it follows the Vogel-Fulcher equation below $T_m$:

$$\nu_r = \nu_o \exp\left(-\frac{E}{k(T-T_f)}\right),$$

where $\nu_r$ is the most probable relaxation frequency, $\nu_o \approx 2 \times 10^8$ Hz, $E$ – activation energy, and $T_f$ – the freezing temperature. The values of $E$ and $T_f$ are 0.2 eV and 264 K, respectively.

In the vicinity of $T_m$ the $\nu_r(1/T)$ curve is rather well described by the Arrhenius relation

$$\nu_r = \nu_o \exp\left(-\frac{U_a}{kT}\right),$$

where $\nu_r$ is the most probable relaxation frequency, $\nu_o$ – pre-exponential factor, and $U_a$ – activation energy. Within the range of temperatures around $T_m$, $U_a \approx 0.11$ eV.
As seen from figure 3b, the local maximum of the depth of effective dispersion \( \Delta\varepsilon_{\text{eff}} = \varepsilon_{0.25\text{Hz}} - \varepsilon_{1000\text{Hz}} \) appears in the region of \( T \approx 20 \, ^\circ\text{C} - 30 \, ^\circ\text{C} \), it is, within \( T_c < T < T_m \). The value of the parameter increases at heating from \( T \approx 100 \, ^\circ\text{C} \). The reason of such a raise of the value of \( \Delta\varepsilon_{\text{eff}} \) is the contribution of Maxwell-Wagner relaxation to polarization processes characteristic to heterogeneous structures, ferroelectric ceramics in particular [3]. The dotted line in figure 3b shows the depth of dispersion \( \Delta\varepsilon = \varepsilon_S - \varepsilon_\infty \) obtained from the Cole-Cole equation. The local maxima of \( \Delta\varepsilon_{\text{eff}} \) and \( \Delta\varepsilon \) practically occur at the same temperature. Farther on \( \Delta\varepsilon \), in distinction from \( \Delta\varepsilon_{\text{eff}} \), gradually decreases.

Such a distinction between \( \Delta\varepsilon_{\text{eff}}(T) \) and \( \Delta\varepsilon(T) \) suggests that dispersion depth \( \Delta\varepsilon \) derived from the Cole-Cole equation is characteristic to relaxation of polarization related to the nature of the phase of the material, for example, to the contribution of phase (or possibly domain) boundary oscillations of polar ferroelectric clusters. The decrease of this contribution at lower temperatures (\( T < 20 \, ^\circ\text{C} - 30 \, ^\circ\text{C} \)) most likely is related to “freezing” of that kind of relaxators, as suggested by the behaviour of
the distribution parameter \( \alpha(T) \) (figure 3c). The values of \( \alpha(T) \) substantially increase at temperatures below 100 °C, it is, below \( T_m \). Behaviour of \( \alpha(T) \) may be explained by interactions that start between polar nano-regions or relaxators thermally activated at \( T>T_m \) \( (U_a \approx 0.11 \text{ eV}) \), when the temperature declines and, consequently, polar ferroelectric clusters emerge the boundaries of which may be impinned by structure defects causing a considerable expansion of the spectrum of relaxation frequencies.

With account for the relaxation frequency, the depth of dispersion \( \Delta \varepsilon \), and the distribution parameter \( \alpha \), a possible contribution to the high-temperature relaxation to processes related to relaxation in the region of phase transition in BaBi\(_2\)Nb\(_2\)O\(_9\) has been estimated and the \( \varepsilon'(\nu,T) \) curves constructed (figure 4). Analysis of the dependence of \( \varepsilon'(T) \) on frequency or temperatures of “stepwise” anomaly \( \varepsilon'(T) \) shows a good agreement with the Vogel-Fulcher law where the values \( E \) are consistent with the data of dispersion derived from the Cole-Cole equation. As it follows from figure 4, the features of the dielectric response are close to those observed in typical relaxors PLZT and PMN [4]. At the same time, in case of BaBi\(_2\)Nb\(_2\)O\(_9\), a substantial shift of the stepwise anomaly of \( \varepsilon'(T) \) to infra-low frequencies allows to consider it as a material where the glass-like properties are most pronounced [5].

**References**

[1] Smolensky G A, Bokov V A, Isupov V A, Krainik N N, Pasinkov R E, Sokolov A I and Yushin N K 1985 *Physics of ferroelectric phenomena* (Leningrad: Science) 396 (in Russian)

[2] Pineda–Flores J L, Chavira E and Reyes–Gasga J 2003 *J. Eur. Ceram. Soc.* 23 839

[3] Turik A V, Radchenko G S, Chernobabov A I, Turik S A and Suprunov V V 2006 *Solid State Physics* 48 1088 (in Russian)

[4] Cross L E 1994 *Ferroelectrics* 151 305

[5] Levstik A, Kutnjak Z, Filipič C and Pirc R 1998 *J. of the Korean Phys. Soc.* 32 S957