Dielectric relaxation in pure and Co-doped $\text{Bi}_{12}\text{GeO}_{20}$ single crystals

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We report the results of investigation of dielectric spectroscopy study of single crystals of $\text{Bi}_{12}\text{GeO}_{20}$ and $\text{Bi}_{12}\text{GeO}_{20}$ doped with Co nanoparticles. The complex dielectric constant was measured in the temperature interval from 5 to 450 K and frequencies from 1 Hz to 1 MHz. The electrical conductivity of both samples was thermally activated with potential barriers of 0.55 eV and 0.59 eV, respectively. Doped samples had bigger complex dielectric constants and σ' exhibited slightly steeper temperature dependence than in the pure sample. The dielectric relaxation was observed in pure and doped single crystals and relaxation frequencies showed similar activation energies as electrical conductivities.

Keywords: Optical materials; crystal growth from melts; dielectric properties of solids and liquids; dielectric loss and relaxation.

1. Introduction

Bismuth germanate crystallizes in a sillenite structure type. It has potential applications in electro-optical devices as photorefractive material.¹ The character of photorefractive effect is determined by photogeneration and localization of electronic charge carriers. Because of that, it is important to study relaxation of $\text{Bi}_{12}\text{GeO}_{20}$ (BGO). Dielectric properties of this material were studied before.^{2–5} Electrical conductivity and dielectric relaxation in BGO single crystals and ceramics were studied recently⁶ in the temperature interval from 300 up to 1000 K. Microwave dielectric properties of ceramics of six sillenite compounds were investigated at 5.5 GHz and revealed the values of dielectric constant around 40 for all compounds.⁷ For ceramic materials it has been shown that addition of nanoparticles could increase significantly the dielectric constant of a composite material close to the percolation threshold (nanoparticles close to each other — almost touching).⁸ That is why it was also intriguing to check the change of the dielectric permittivity for this material while being doped with nanoparticles, since recently a new method of manufacturing dielectric matrices doped with nanoparticles has been shown. The developed technology uses the micro-pulling down method and nanoparticles direct doping.⁹ It enables manufacturing of glass matrices doped with metallic and nonmetallic particles⁹ as well as preliminary results has been shown for single crystalline matrices of BGO-doped with nanoparticles.¹⁰ In the present work, we study ac electrical conductivity and the dielectric dispersion in BGO and BGO doped with Co nanoparticles, in the temperature

interval from 5 to 450 K and frequencies range from 1 Hz to 1 MHz, in order to get information about the nature of the conductive process.

2. Experiment

BGO melts at 1203 K.¹¹ A stoichiometric mixture of high purity Bi_2O_3 and GeO_2 was used as starting material. The raw material was thoroughly mixed in a molar ratio 6:1. Then 10 wt.% of Co nanoparticles (Nanostructured & Amorphous Materials, Inc., US) was added to the mixture and mixed again. Powder X-ray diffraction (XRD) spectrum^{10,12} of the doped BGO crystal indicates the deficiency of the metallic Co nanoparticles and the excess of CoO nanoparticles (therefore sample was denoted as the BGO:nCoO sample). For the crystal growth the micro-pulling down method was used.^{13,14} This method has been developed originally for the growth of single crystal fibers.¹⁵ However, novel types of composites have been recently grown by this method as eutectic materials with potential application in photonics (metamaterials, photonic crystals, plasmonic materials).^{9,16–18} The method utilizes a crucible with a die at the bottom in which there is a centrally placed nozzle. The material is melted in the crucible. The melt passes through the nozzle and is touched with the seed crystal, and the crystal is pulled down. The crystallization was carried out under nitrogen atmosphere, with the Cyberstar Oxypuller equipped with r.f. generator. The temperature gradients in the system were controlled with afterheater placed at the bottom of the crucible and shields

[§]Deceased.

placed around the crucible and the afterheater. Rods of diameter of 3 mm were obtained and samples used in dielectric studies were cut perpendicularly to the growth direction. The samples faces, oriented perpendicularly to the growth direction, $\langle 110 \rangle$ crystallographic orientation,¹⁰ were covered by EPO-TEK EE129-4 silver-filled epoxy which was used as electrodes. After doping the crystals were still in one crystallographic orientation; so we can call it a single crystal doped with nanoparticles.

The complex dielectric constant $\varepsilon^*(\nu, T) = \varepsilon' - i\varepsilon''$ was measured between 5 K and 450 K in the frequency range of 1 Hz to 1 MHz, using a Novocontrol Alpha High Resolution Dielectric Analyzer. The amplitude of the probing ac electric signal was 1 V/mm. The temperature was stabilized within ± 0.1 K using an Oxford Instruments continuous flow cryostat. The real part of the complex ac conductivity $\sigma^*(\nu, T) = \sigma' + i\sigma''$ was calculated via $\sigma' = 2\pi\nu\varepsilon_0\varepsilon''$, with ε_0 being the permittivity of the vacuum.

3. Results and Discussion

The real and imaginary part of dielectric constant, ε' and ε'' , of BGO and BGO:nCoO sample as a function of temperature at different frequencies are presented in Figs. 1 and 2, respectively. There is almost no change on real part dielectric constant below 200 K, but at high temperatures the real and imaginary parts of dielectric constant increase with the increasing temperature. The values are very high and frequency dependent. Therefore, we plotted both quantities in the logarithmic scale. Both ε' and ε'' are bigger in doped samples.

The temperature dependence of the real part of the ac conductivity in the logarithmic scale, $\ln \sigma'$, of both samples is presented in Fig. 3. Above ~ 300 K the ac conductivity at 1 Hz can be well described with the activation type temperature dependence, $\sigma' \propto \exp(-E/k_B T)$, where E represents the apparent activation energy for the conduction process⁶ and k_B the Boltzmann constant.

Fig. 1. (a) Real part of dielectric constant, ε' , of BGO as a function of the temperature at different frequencies; (b) imaginary part of dielectric constant, ε'' , of BGO as a function of the temperature at different frequencies.

Fig. 2. (a) Real part of dielectric constant, ε' , of BGO:nCoO sample as a function of the temperature at different frequencies; (b) imaginary part of dielectric constant, ε'' , of BGO:nCoO sample as a function of the temperature at different frequencies.

Fig. 3. $\ln(\sigma')$, measured at the frequency of 1 Hz, of BGO and BGO:nCoO sample as a function of the inverse temperature.

The values of the activation energies are $E_1 = (0.55 \pm 0.01)$ eV for pure and $E_2 = (0.59 \pm 0.01)$ eV for the doped sample. Doped samples had bigger complex dielectric constants and σ' exhibited slightly steeper temperature dependence than in the pure sample.

The dielectric relaxation, which was observed in pure and doped single crystals, can be analyzed with the help of electrical modulus picture¹⁹ in order to determine the high frequency and static dielectric constants. Electrical modulus picture enables us to determine dielectric relaxation parameters even in the case when the conductivity at low frequencies is very high. Figure 4 represents dielectric dispersion in BGO single crystals at 300 K in the electric modulus M^* and dielectric constant ϵ^* picture. In this formalism an electric modulus M^* is defined as the reciprocal of dielectric constant ϵ^* as¹⁹

$$M^* = 1/\epsilon^* = M'(\nu) + iM''(\nu),$$

where

$$M'(\nu) = \frac{\epsilon'(\nu)}{(\epsilon'(\nu))^2 + (\epsilon''(\nu))^2}$$

and

$$M''(\nu) = \frac{\epsilon''(\nu)}{(\epsilon'(\nu))^2 + (\epsilon''(\nu))^2}$$

are the real and imaginary part of complex modulus, respectively.

M'' versus M' at 300 K in BGO is presented in Fig. 4(a). From the Cole–Cole diagram in an electric modulus picture it is possible to determine M'_∞ at high frequencies, M'_s at low frequencies, a characteristic frequency f_M , and a parameter h . Both parameters, at high and low frequencies, are well defined. From the values for $M'_\infty = 1/\epsilon_\infty$ and $M'_s = 1/\epsilon_s$ we can determine the static, ϵ_s , and a high frequency dielectric constant, ϵ_∞ , and a characteristic frequency, f_ϵ , in dielectric

(a)

(b)

Fig. 4. Cole–Cole diagrams of BGO in M^* and ϵ^* picture at 30 K.

constant picture [$f_M = f_\epsilon(\epsilon_s/\epsilon_\infty)^{1/(1-h)}$]. Thus, electric modulus picture enables us to determine dielectric relaxation parameters even in the case when the conductivity at low frequencies is very high. Figure 4(b) presents the same experimental data as in Fig. 4(a) in dielectric constant picture. M_s is determined with the better precision than ϵ_s .

The lines through experimental points (semicircles) in Figs. 4(a) and 4(b) are results of fitting with the Cole–Cole expression for $M^* = M_\infty + (M_\infty - M_s)/[1 + (i\omega\tau_M)^h]$, where $\tau_M = 1/2\pi f_M$ denotes the characteristic relaxation time.

In this way the temperature dependence of the characteristic frequency in BGO was determined. Similar dielectric dispersion was observed also in BGO crystals doped with CoO nanoparticles, and the same approach was used in order to determine the temperature dependence of the characteristic frequency.

Figure 5 presents the temperature dependence of the characteristic relaxation frequencies, $\ln f_\epsilon$, of BGO and BGO:nCoO sample. Below ~ 300 K the characteristic relaxation frequencies can be well described with the activation type temperature dependence $f_\epsilon \propto \exp(-E/k_B T)$, where E denotes the activation energy and k_B the Boltzmann constant. The values of the activation energies are $E_1 = (0.53 \pm 0.03)$ eV for pure and $E_2 = (0.64 \pm 0.03)$ eV for a doped sample. The

Fig. 5. Temperature dependence of the characteristic relaxation frequencies $\ln f_\epsilon$ of BGO and BGO:nCoO sample.

values of activation energies are close to the values determined from the temperature dependence of ac conductivity σ' measured at low frequency (1 Hz). The values of determined activation energies are comparable with the activation energy determined in BGO at high temperature ($E = (0.75 \pm 0.04)$ eV) recently.⁶

In order to describe the origin of dielectric relaxation and the conductivity mechanism of the single crystal or ceramics of $\text{Bi}_{12}\text{GeO}_{20}$ we followed the explanation of Macedo *et al.*⁶ They explained conduction mechanism as the hopping of charge carriers released from two different energy traps, which are related to defects arising from substitutional $\text{Bi}^{3+} + \text{h}^+$ in Ge^{4+} sites. Namely,⁶ in $\text{Bi}_{12}\text{GeO}_{20}$, the Ge^{4+} cations are tetrahedrally coordinated, occupying the cube corners and body-centered sites and linked by hepta-coordinated Bi atoms. Bi/Ge antisite defect was suggested to be the most plausible intrinsic defect, and in view of the chemical instability of Bi^{4+} , it was proposed that the Bi_{Ge} defect would consist of a Bi^{3+} ion associated with a hole. Due to the difference in the ionic radii of Bi^{3+} and Ge^{4+} , one may expect a local distortion of the tetrahedra. Holes residing in noncorrespondent Bi–O bonds would lead to different depth of hole traps. Similar explanation was given by Panchenko *et al.*²⁰ studying dielectric relaxation in Cr-doped $\text{Bi}_{12}\text{SiO}_{20}$ crystals. They found a reason for the dielectric relaxation in existence of impurity-vacancy-type quasi-dipoles. We think that by Macedo *et al.*⁶ adequately explained the origin of dielectric relaxation and the conductivity mechanism of single crystals or ceramics of $\text{Bi}_{12}\text{GeO}_{20}$. We also think that the same mechanism is valid also for $\text{Bi}_{12}\text{GeO}_{20}$ doped with Co nanoparticles. Namely, the Macedo *et al.*⁶ explained the prevailing mechanism which is not much changed by doping.

Another origin of the dielectric relaxation and the conductivity mechanism is connected with the homogeneity of the sample.²¹ If a dielectric sample is not homogeneous, but contains regions of different permittivity (such as may arise

from cracks in a solid sample, for example), misleading values of permittivity may be found experimentally. Because of these different conductivities, an apparent Maxwell–Wagner relaxation could be observed. As a result, the overall permittivity of the doped samples was higher than that observed for single crystals. That phenomenon explains that the doped samples had bigger complex dielectric constant than the pure crystals. But this mechanism does not influence much on dielectric relaxation and electric conductivities. The prevailing origin of the relaxation is the existence of the impurity-vacancy-type quasi-dipoles which is not much changed with the doping. Therefore, the observed dielectric relaxation in pure and doped single crystals and relaxation frequencies showed similar activation energies as electric conductivities.

4. Conclusions

Dielectric properties of single crystals of BGO and BGO doped with Co nanoparticles were studied in a wide frequency and temperature range. From the temperature dependence of σ' and characteristic relaxation frequency f_ϵ the activation energies in both single crystals were determined and the values are comparable with previous determination. Doped samples had bigger complex dielectric constants and σ' exhibited slightly steeper temperature dependence than in the pure sample. In this study, the dielectric relaxation is analyzed in M^* and ϵ^* picture as ϵ_∞ was different from zero which was not the case in previous work.⁶ Dielectric measurements show that the goal — embedding of metallic nanoparticles in a dielectric matrix and as a consequence control over the dielectric properties — was not entirely successful as during the synthesis some of the metal Co nanoparticles have reacted with the surrounding dielectric matrix and transformed into CoO nanoparticles, however still the complex dielectric constants of the sample doped with nanoparticles are bigger.

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