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ACOUSTIC LOSSES IN THE "PURE" AND Cr-DOPED $Bi_{12}SiO_{20}$ SINGLE CRYSTALS AT HIGH TEMPERATURES

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The acoustic losses has been measured from 300 up to 750°K and at frequency range 80 kGz-1 MGz in single crystals of "pure" bismuth silicon oxide $Bi_{12}SiO_{20}$ (BSO), for crystals doped with Cr and annealed in vacuo. Some relaxation loss peaks in these crystals have been observed, and correlation with dielectric measurements have been found. The contribution of acoustoelectronic coupling has been calculated in accordance with the Hutson-White theory. The data are discussed in terms of the ordering of point defects under external stress. A discussion is given of the possible defects which may produce the acoustic and dielectric losses.

INTRODUCTION

The bismuth silicon oxide $Bi_{12}SiO_{20}$ crystals have a useful combination of physical properties such as high electrical resistivity, strong piezoelectric effect, low velocity of sound, photoconductivity. All these made BSO promising material for application in optoelectronics. It is known that doping of some cations and annealing of BSO crystals at high temperature at vacuo leads to changing of many physical parameters of the crystals. But the state of the impurity ions and physical mechanism of their influence on physical properties is not clear. The ultrasonic decay in BSO has been investigated at 25–200 MGz range of frequency and from 4 to 300 K.[1,2]

This article consists results of studying by the internal friction method of "pure," Cr doped and annealed in vacuo BSO crystals from 300 up to 750 K and in 80 kGz–1 MGz frequency interval.

EXPERIMENTAL METHODS

Acoustic losses in our experiments has been investigated by the internal friction method using modified resonance bar scheme. The method based on the excitation of free ultrasonic oscillations in piezoelectric resonators by their piezoeffect.[3] Then the time of decrease of the free decay oscillations amplitude in *e* time is recorded. The dielectric constants and conductivity of the crystals has been measured on the same samples with automatic bridge TESLA BM 591. The resonance-antiresonance method have been used for measurement of the electromechanical coupling coefficient.

SAMPLES

Single crystals of BSO has been grown by Czochralski method. The content of Cr_2O_3 in the initial mixture was 0.1 weight percent. Annealing of the samples have been carried out at 700 K near 1 hour under pressure 3 Pa. Samples cut in shape of bars (12–18) × 1 × 1 mm, with Pt electrodes on (001) face has been used. Piezoelectric resonators has been suspended by thin (50×10^{-6} m) platinum wires, which has been fixed in the oscillations nodes. The use of special technique of making and fixing of the piezoresonators allow to run up the merit factor to 8×10^4, which corresponds to internal friction $Q^{-1} = 1.2 \times 10^{-5}$ ($\alpha = 2 \times 10^{-5}$ Np/sm).

RESULTS

The temperature dependences of acoustic decay and dielectric parameters of the "pure" BSO crystals are shown on Figures 1 and 2, accordingly. The weak linear increase of internal friction with temperature up to 450 K (Figure 1, curve 1) is in accordance with calculated temperature dependence of the losses in surface layers destroyed by mechanical treatment. The temperature dependence of the background internal friction at higher temperature is extrapolated by dash line on Figure 1 (curve 2). The activation energy value derived from this plot is about 0.4 eV.

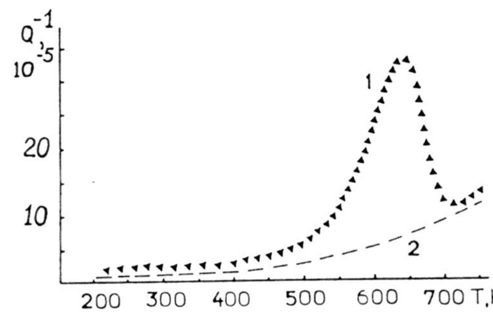

FIGURE 1 The temperature dependence of internal friction in "pure" BSO crystals. 1—experimental curve; 2—background internal friction.

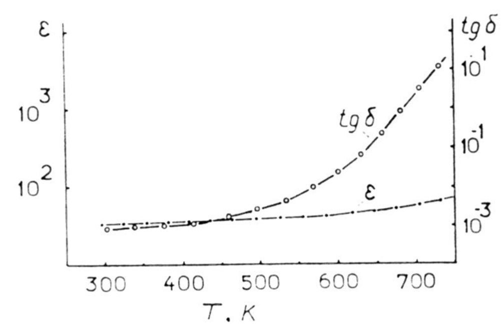

FIGURE 2 The temperature dependences of dielectric constant and losses in "pure" BSO crystals.

The exponential increase of the background internal friction with temperature is just come as for some other crystals such as the quartz. The exponential gain $Q^{-1}(T)$ may be explained by increase of the number of thermofluctuation defects and possibly, with the activation of some admixture atoms. The experimental date (Figure 1, curve 1) may be discussed in terms coupling of acoustic waves with electrical charges in piezoelectric crystals (acoustoelectronic coupling).[4] On the base of measurements temperature dependence of conductivity $6(T)$, dielectric constant $\varepsilon(T)$ (Figure 2) and constant of electromechanical coupling for piezoactive mode $K_{act.}(T)$ the losses of acoustoelectronic nature were calculated according to the theory Hutson-White from equation

$$Q^{-1} = \frac{K^2_{act.}}{2} \times \frac{6/(2\pi f_r \varepsilon\varepsilon_0)}{1 + [6/(2\pi f_r \varepsilon\varepsilon_0)]^2} \qquad (1)$$

where f_r = resonance frequency. The experimental data completely coincides to the theoretical ones. The activation energy of internal friction is 1.1–1.4 eV and it corresponds to the activation energy of the conductivity. It proves the acousto-electronics nature of the losses peak (Figure 1, curve 1). The results of the measuring of internal friction on Cr doped crystal are shown on Figure 3, curve 1.[5] There is some gain of the background of internal friction and there is peak at 530 K (150 kGz). The peak is shifted to higher temperatures with frequency increase. The activation energy calculated from this shift is 1.45 eV. The result of subtraction from experimental data (Figure 3, curve 1) the background internal friction (curve 2) and calculated from Equation (1) acoustoelectronic contribution (curve 3) is shown at Figure 3, curve 4. Dependence $Q^{-1}(1/T)$ has a symmetric Debye peak, caused by admixture of chromium. The activation energy calculated from half width of maximum losses is 1.54 eV. The similarity of two meanings of the activation energy reads that the relaxation processes are passing with single relaxation time.

The annealing of Cr-doped BSO crystals in vacuo change $Q^{-1}(T)$ dependence (Figure 4, curve 1). At 620 K there is the dominate peak of the internal friction as magnitude of 150×10^{-5} (frequency 117 kGz). This maximum has compound structure. Subtraction from the experimental data (curve 1) the background (curve 2), the contribution of acoustoelectronic coupling (curve 3) and the internal friction connected with Cr admixture (curve 4) points out the peak acoustic losses (curve

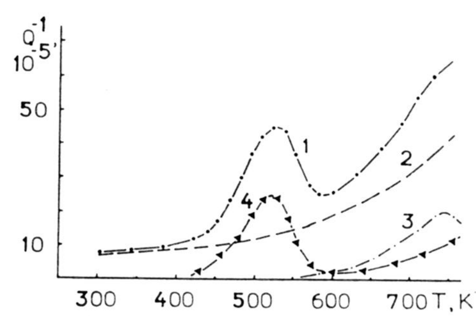

FIGURE 3 The temperature dependences of internal friction in BSO:Cr crystals. 1—experimental curve; 2—background internal friction; 3—contribution of acoustoelectronic coupling; 4—internal friction, due to Cr admixture.

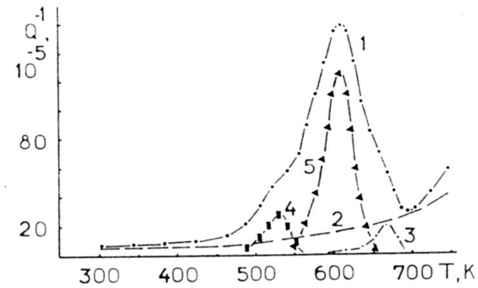

FIGURE 4 The temperature dependence of internal friction in BSO:Cr crystals after annealing in vacuo. 1—experimental curve; 2—background internal friction; 3—contribution of acoustoelectronic coupling; 4—internal friction due to Cr admixture; 5—internal friction due to Cr admixture and annealing in vacuo.

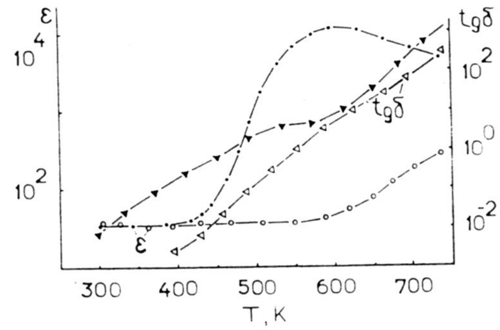

FIGURE 5 The temperature dependence of dielectric constant and losses in perfect crystals (○, △) and annealed in vacuo (●, ▲) BSO:Cr crystals.

5) which is connected with Cr admixture and annealing in vacuo. The activation energy for this peak is 1.6 eV.

The data of dielectric measurements which are necessary for the interpretation of the results of the internal friction experiments are shown at Figure 5. The comparison of the dielectric properties of the "pure" crystals BSO and the crystals BSO:Cr shows that doping do not lead to appearing the anomalies at ε (T) and Tan δ (T) dependences corresponding to $Q^{-1}(T)$ dependency. Annealing of the BSO:Cr crystals in vacuo produces the additional dielectric losses in the region 300–600 K and it leads to maximum of dielectric constant at 590 K (Figure 5).

DISCUSSION

The calculation of the contribution of the different mechanisms of acoustic losses[6] shows the only process that can cause the peaks of internal friction in the given temperature-frequency interval is relaxation process of ordering point defects in field of elastic stresses.[7]

BSO crystallizes in the body-centered cubic structure which belongs to the point group 23. In the tops and the center of cubic cell there are Si^{4+} ions, surrounded by oxygen tetrahedra. Besides that 56 ions of bismuth-oxide framework are in every crystals cell.

The experimental activation energy (1.5-1.6 eV) are typical for the ordering of ions. Chromium can be situated at different points of crystals cell. On the one hand Cr ions in interstitial position will cause deformation grating and increasing its potential energy. On the other hand simple Cr-ions themselves substituting Si ions can not couple contribution in an elastic relaxation because in this case they are situated in full symmetry positions. So we assume that Cr^{3+} ions which isovalently substitute the Bi^{3+} are responsible for the peak of internal friction in BSO:Cr crystals. Such isovalent substitution gives rise to elastic defects of monoclinic symmetry, which have an opportunity to order in the field of elastic stresses. But besides this, it gives no additional dielectric relaxation, that agrees with experimental results (Figure 5).

On the $Q^{-1}(T)$ dependence for annealed in vacuo BSO:Cr crystals the peak of internal friction duty the Cr admixture is conserved and new maximum appears. It testifies that the Cr ions occupy at least two nonequivalent positions in the grating. Moreover, in the second position Cr ions do not contribute to internal friction of original crystals, and display only after annealing in vacuo. The center of oxygen tetrahedra, which is occupied by Si ion in perfect crystal can be in the role of this position. If we suppose, that Si ions are substituted by Cr ions in 3+ valency, the formation of hole on one of oxygen ions from oxygen tetrahedra is possible.

The defect ($Cr^{3+} + h^{+}$) is elastic dipole trigonal symmetry and can cause peak acoustic losses at low temperatures.[1,2,8] In result annealing in vacuo the further breaking Cr—O bond and formation oxygen vacancy will occur. The defect tetrahedra (Cr^{3+} O_3^{2-}) formed here is equivalent to elastic dipole $Cr - V_0$ of trigonal symmetry. We assume, that it is the relaxation of this center in field of elastic stresses which cause the maximum of internal friction at 620 K in crystals BSO:Cr annealed in vacuo (Figure 4). By all means this defect must give rising to dielectric relaxation, which apparently leads to the anomaly on the ε (T) and Tan δ (T) dependences crystals annealed in vacuo (Figure 5).

CONCLUSION

The defect structure of BSO crystals doped Cr and annealed in vacuo is investigated by structure susceptible method internal friction. The defects model explaining the anomalies on temperature dependence of acoustic losses and dielectric properties are suggested.

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