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Electrical Conductivity of $Bi_{12}SiO_{20}$ Single Crystals Doped with Os, Re, Ru, and Rh

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Abstract—$Bi_{12}SiO_{20}$ crystals doped with Os, Re, Ru, and Rh were grown by the Czochralski technique, and their conductivity (real and imaginary parts) was measured as a function of temperature and frequency. The results are interpreted as evidence that the charge transport in the crystals is due to hopping along chains of localized states.

INTRODUCTION

Photorefractive $Bi_{12}SiO_{20}$ (BSO) crystals (sillenite structure, sp. gr. *I*23) find wide application in optical information recording, storage, and processing systems [1, 2]. The key to optimizing the performance of BSO in various photorefractive applications lies in identifying the native and impurity defects determining the distribution of energy levels in the band gap of BSO. Such information can be gained from ac conductivity data. The conductivity of undoped BSO crystals has been measured at frequencies from 1 kHz to 100 MHz and temperatures from 290 to 600 K [3–6]. The conduction in BSO in this temperature range was shown to be due to hopping between localized states. Doping with Al, P, Fe, Cr, Mn, and Ni has a significant effect on the conductivity of BSO and the associated activation energy [7, 8].

In this paper, we report the first ac conductivity measurements on BSO crystals doped with Re, Os, Ru, and Rh.

EXPERIMENTAL

BSO single crystals were grown by the Czochralski process in the [001] direction in air from platinum crucibles, using a stoichiometric growth charge [9–11]. The starting materials used were extrapure-grade Bi_2O_3 and SiO_2. The dopants were introduced into the growth charge in the form of oxides. The grown crystals were 30–45 mm in diameter and 70–100 mm in length. The dopant concentration was determined by atomic absorption spectrophotometry (Perkin-Elmer Model 3030): Os 1.76×10^{20}, Re 1.80×10^{20}, Rh 1.63×10^{20}, and Ru 3.23×10^{20} cm^{-3}.

In conductivity measurements, we used polished single-crystal plates measuring $12 \times 12 \times 1$ (± 0.25) mm, cut normal to the [001] direction. Au electrodes were deposited by thermal evaporation. The electrode diameter was 10 ± 0.5 mm. The temperature (294–600 K) was maintained with a stability of ± 0.1 K by a digital controller. Conductivity was measured in the frequency range 10^4 to 10^7 Hz using a Hewlett-Packard 4275 bridge. The relative uncertainty in conductivity was 3% over the entire frequency range studied.

RESULTS AND DISCUSSION

The real part of 10-kHz conductivity, $\sigma = \sigma_1 + i\sigma_2$, of our samples shows Arrhenius behavior (Fig. 1), characteristic of thermally activated processes,

$$\sigma_1 = A\exp(-E_a/(kT)), \quad (1)$$

where A is the preexponential factor for the real part of conductivity and E_a is the activation energy of conduction. Doping was found to increase σ_1 by an order of magnitude. The conductivity curves can be divided into two distinct portions, 450–600 and 290–380 K. The activation energy of conduction in the crystals studied is $E_a' = 0.86$–1.08 eV in the high-temperature portion and $E_a'' = 0.07$–0.13 eV in the low-temperature portion (table). The present results differ insignificantly from the data reported earlier for undoped BSO [3, 7, 8], which leads us to conclude that the conduction in the doped crystals is due to hopping transport. In the range 290–380 K, our data attest to hopping between localized states near the Fermi level (conductivity is a weak function of temperature). At higher temperatures, the

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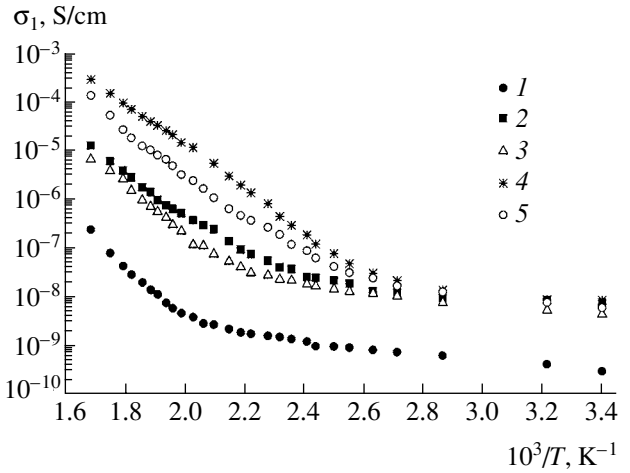

Fig. 1. Arrhenius plots of the real part of 10-kHz conductivity for (*1*) BSO, (*2*) BSO⟨Rh⟩, (*3*) BSO⟨Re⟩, (*4*) BSO⟨Ru⟩, and (*5*) BSO⟨Os⟩ crystals.

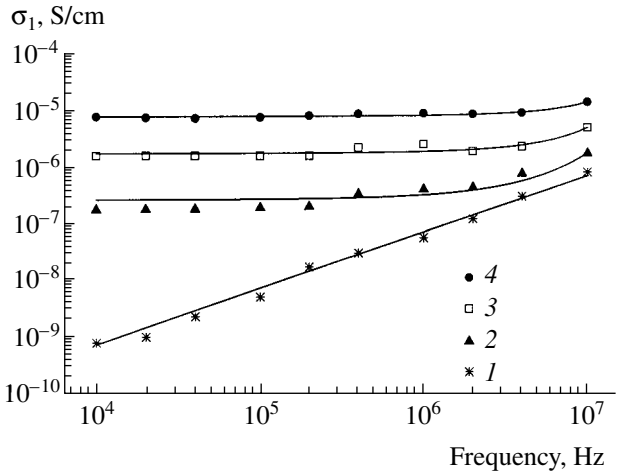

Fig. 2. Log–log plots of σ_1 vs. frequency for BSO⟨Rh⟩ at (*1*) 291, (*2*) 388, (*3*) 486, and (*4*) 575 K.

levels involved lie near the edge of the conduction or valence band (conductivity rises rapidly with temperature) [3, 12].

Figure 2 shows the log–log plots of σ_1 versus frequency for BSO⟨Rh⟩ at different temperatures. Similar data were obtained for the other samples. The observed behavior of conductivity is typical of hopping transport [13–15].

In the case of hopping conduction, σ_1 is related to frequency ω by

$$\sigma_1 \sim \omega^s T^l. \quad (2)$$

Here, s depends on the spatial and energy distributions of localized states and the localization radius of the wave function ($1 < s < 2$ [3], $s < 1$ (but $s \longrightarrow 1$) [7, 15], $0 < s < 2$ [16]) and $l = n - 1$, where n is the number of localized states in the chain, and l is the number of units in the chain ($l = 1$ if hopping occurs between two states) [17]. Using relation (2) and the log–log plots in Fig. 3, we determined l and n^2 (where n^2 is the number of jumps within the cluster) for undoped and doped BSO (table). From the $\sigma_1(\omega)$ data in the frequency range 10^4 to 10^7 Hz (Fig. 2), we evaluated s (table). The results for undoped BSO crystals at low temperatures differ little from those obtained by Avramenko *et al.* [3]. The shape of the $\sigma_1(\omega)$ curves and the calculated s values coincide with those reported in [7]. The l and n^2 data (table) indicate that, in both the undoped and doped BSO crystals, charge transport is due to multiple hopping over rather long chains of localized states.

Activation energy (E_a''), number of units in the chain of localized states (l''), and number of jumps per cluster (n''^2) at low (290–380 K) and high (450–600 K) (E_a', l', n'^2) temperatures and exponents s and t characterizing hopping conduction, evaluated from the data in Figs. 1–4

Sample	BSO	BSO⟨Rh⟩	BSO⟨Re⟩	BSO⟨Ru⟩	BSO⟨Os⟩
E_a', eV (450–600 K)	1.08	0.88	0.86	0.90	0.94
E_a'', eV (290–380 K)	0.07	0.12	0.11	0.13	0.13
l' (450–600 K)	23	19	22	22	20
$(n')^2$ (450–600 K)	576	400	529	529	441
l'' (290–380 K)	3.56	2.92	3.55	3.5	4.05
$(n'')^2$ (290–380 K)	25	16	25	25	25
s	0.98	0.99	0.98	0.97	0.97
t	0.99	1.0	0.98	0.98	0.97

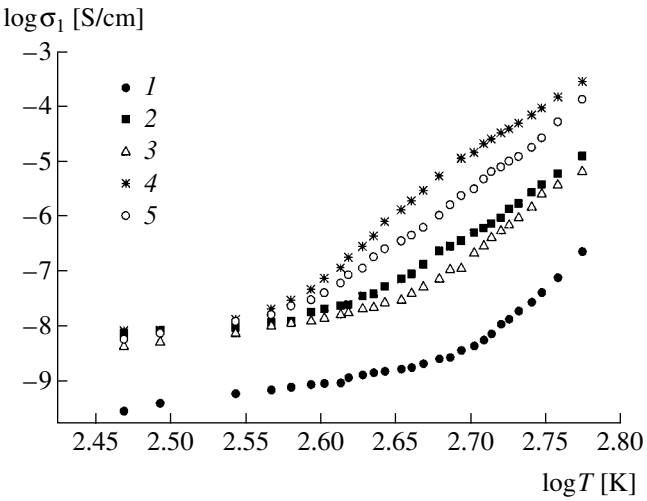

Fig. 3. Log–log plots of 10-kHz σ_1 vs. temperature for (*1*) BSO, (*2*) BSO⟨Rh⟩, (*3*) BSO⟨Re⟩, (*4*) BSO⟨Ru⟩, and (*5*) BSO⟨Os⟩ at frequency 10^4 Hz.

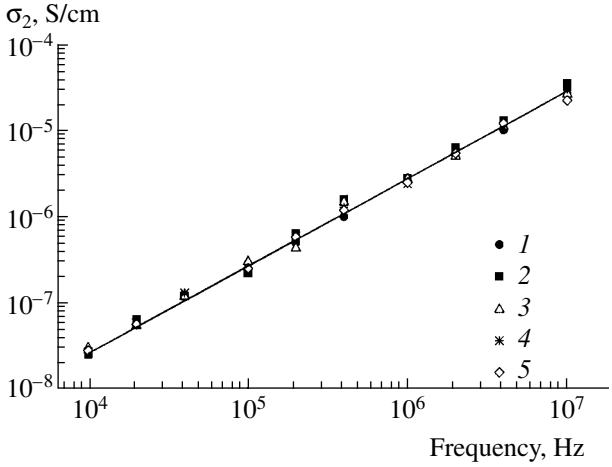

Fig. 4. Log–log plots of σ_2 vs. frequency for (*1*) BSO, (*2*) BSO⟨Rh⟩, (*3*) BSO⟨Re⟩, (*4*) BSO⟨Ru⟩, and (*5*) BSO⟨Os⟩ crystals.

Figure 4 shows the log–log plots of the imaginary part of conductivity, σ_2, versus frequency for undoped and doped BSO. We find that σ_2 is two orders of magnitude higher than σ_1 over the entire frequency range studied. The frequency dependence of σ_2 is similar to that of σ_1 and can be represented by [7]

$$\sigma_2 \sim \omega^t, \tag{3}$$

where t differs very little from exponent s in (2). The calculated values of t are also listed in the table. The room-temperature exponent for σ_2 is close to unity, which points to Ohmic behavior of the contacts. Note that t is sample-independent to within the present experimental uncertainty. The same refers to exponent s in (2).

The temperature dependence of σ_2 has an essentially constant slope, with a small bump at 580–590 K at low frequencies (10^4–10^5 Hz).

CONCLUSIONS

Our results indicate that the ac charge transport in BSO, BSO⟨Rh⟩, BSO⟨Re⟩, BSO⟨Ru⟩, and BSO⟨Os⟩ crystals is due to hopping between localized states. At this stage, it is not yet clear which defects, intrinsic or extrinsic, are involved in hopping conduction. In view of the inhomogeneous defect distribution over the crystal bulk, the present ac conductivity data for undoped and doped BSO crystals can be understood in terms of randomly distributed energy barriers in disordered solids.

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