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Citation: *Journal of Applied Physics* **88**, 6526 (2000); doi: 10.1063/1.1309045

View online: <http://dx.doi.org/10.1063/1.1309045>

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# Small polaron and bipolaron transport in antimony oxide doped barium hexaferrites

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(Received 24 April 2000; accepted for publication 13 July 2000)

Direct current electrical resistivity measurements on specimens with composition  $\text{BaO} (6-x) \text{Fe}_2\text{O}_3, x \text{Sb}_2\text{O}_3$  with  $x$  having values of 0.0, 0.025, 0.05, 0.1, and 0.3, respectively, were carried out in the temperature range of 120–300 K. Chemical analyses showed the presence of  $\text{Sb}^{3+}$  and  $\text{Sb}^{5+}$  ions as well as  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions in the doped specimens. The doped specimens were found to have reduced resistivities. The analysis of the data shows that the electrical conductivity in this system arises due to a combined contribution of both small polaron hopping between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  sites and bipolaronic transport between  $\text{Sb}^{3+}$  and  $\text{Sb}^{5+}$  sites. © 2000 American Institute of Physics. [S0021-8979(00)08320-1]

## I. INTRODUCTION

Semiconducting properties of glasses containing variable valency transition metal ions have been studied extensively during the last two decades.<sup>1–3</sup> In these systems the electrical transport has been explained as arising as a result of the migration of small polarons. The latter are defects formed in a covalent solid due to the presence of a charge carrier at a site which causes a large degree of local lattice distortion. In the case of bipolaronic conduction two electrons hop simultaneously between the defect sites. Antimony and arsenic ions with two valence states, i.e.,  $\text{Sb}^{3+}/\text{As}^{3+}$  and  $\text{Sb}^{5+}/\text{As}^{5+}$ , respectively, have been shown to contribute to bipolaronic conduction in oxide glasses.<sup>4,5</sup> Polaronic conduction in crystalline oxides has also been investigated in recent years.<sup>6–8</sup> We had earlier investigated the effect of antimony oxide as a dopant on the magnetic properties of barium hexaferrite.<sup>9</sup> Antimony ions substituted for iron and the magnetization were found to decrease as a function of the dopant concentration. We have now studied the dc electrical properties of these doped samples. A marked decrease in electrical resistivity in them compared to that of the base samples is noticed even if the doping level is small. The relative amounts of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Sb}^{3+}/\text{Sb}^{5+}$  present in these specimens have been determined by wet chemical analysis. An analysis of the electrical resistivity data shows the presence of both small polaron and bipolaron hopping in these specimens. The details are reported in this article.

## II. EXPERIMENT

The compositions of the different specimens can be represented by  $\text{BaO} (6-x) \text{Fe}_2\text{O}_3, x \text{Sb}_2\text{O}_3$  where  $x$  had values 0.0, 0.025, 0.05, 0.1, and 0.3, respectively. Analytical re-

agent grade  $\text{BaCO}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Sb}_2\text{O}_3$  were used as starting materials. A standard ceramic processing method was used to calcine the pelletized powder and for subsequent sintering. Details of the specimen preparation have been reported earlier.<sup>9</sup>

The crystalline phases present in the sintered specimens were identified from the x-ray diffraction patterns taken on a Rich and Seifert 2000P diffractometer with  $\text{Cr } K\alpha$  radiation. The diffractogram obtained in the case of the sample with  $x=0.05$  is shown in Fig. 1. It is typical of all the samples studied here. The diffraction peaks correspond to the interplanar spacings characteristic of barium hexaferrite. No other phase was present in these samples. Even for the sample with  $x=0.3$  no other phase could be detected.

The amounts of iron and antimony in different valence states were determined by wet chemical analysis. The sample was dissolved in HCl in an inert (dry nitrogen) atmosphere. To estimate  $\text{Fe}^{2+}$  and the total Fe in the solution  $\text{Ce}(\text{SO}_4)_2$  was chosen as the titrant because in the latter case antimony did not interfere in the estimation<sup>10</sup> and  $\text{Ce}(\text{SO}_4)_2$  oxidized only  $\text{Fe}^{2+}$  ions in the solution. The titration was carried out using a ferroin indicator. For estimation of the total Fe a certain volume of solution prepared as above was taken and  $\text{Fe}^{3+}$  ions were reduced to  $\text{Fe}^{2+}$  with the controlled addition of  $\text{SnCl}_2$  solution. The  $\text{Fe}^{2+}$  content of the resulting solution determined by titration delineated as above gave the total iron concentration in the sample. The concentration of  $\text{Sb}^{3+}$  was estimated by oxidizing a certain volume of aliquot by standard iodine solution.<sup>11</sup> Some tartaric acid was added to the solution to prevent antimony precipitating out as hydroxide. Some sodium hydrogen carbonate was added before the addition of iodine solution and the pH of the solution kept at a value of  $\sim 6.0$ . The latter was kept in darkness for the reaction to take place. The excess iodine was titrated with standard sodium thiosulfate solution using starch as the indi-

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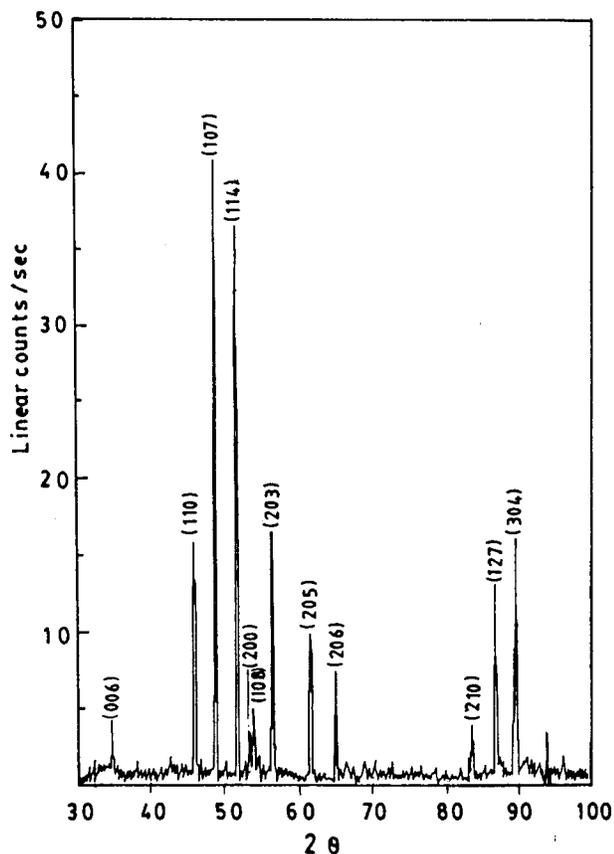


FIG. 1. X-ray diffractogram for a specimen with composition of BaO. 5.95 Fe<sub>2</sub>O<sub>3</sub> · 0.05 Sb<sub>2</sub>O<sub>3</sub>.

cator. The total antimony concentration was determined gravimetrically. All the antimony ions were precipitated as antimony sulfide by passing H<sub>2</sub>S gas through a certain volume of aliquot. The precipitate was then dried in an oven at 353 K and weighed. Typical values of [Fe<sup>2+</sup>]/[Fe<sub>total</sub>] and [Sb<sup>3+</sup>]/[Sb<sub>total</sub>] for the specimen with  $x=0.3$  were 0.022 and 0.672, respectively. The corresponding values for the specimen with  $x=0.10$  were 0.015 and 0.755, respectively.

For dc resistivity measurements the specimen surfaces were polished using silicon carbide powders of different mesh sizes. Electrodes on opposite faces were applied using silver paste supplied by M/s Acheson Colloiden BV, The Netherlands. Electrical measurements on specimens were carried out using a Keithley electrometer (model 617) over the temperature range of 120–300 K. The absence of barrier layers at the contacts was ascertained from the linear voltage–current characteristics before measurements.

### III. RESULTS AND DISCUSSION

Figure 2 shows the variation of log resistivity as a function of inverse temperature for all specimens. It is evident that the resistivity decreases dramatically as the Ba-hexaferrite sample is doped with even a small amount of Sb<sub>2</sub>O<sub>3</sub> ( $x=0.025$ ). Also, the resistivity variation appears to be controlled by an activated process. We have fitted the high temperature part of experimental data for the specimen

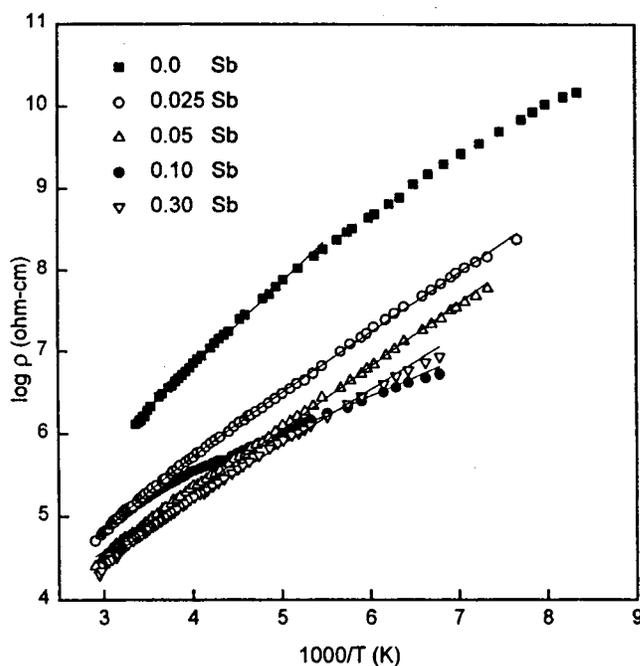


FIG. 2. Variation of resistivity as a function of inverse temperature for different specimens in the series BaO. (6-x) Fe<sub>2</sub>O<sub>3</sub> · x Sb<sub>2</sub>O<sub>3</sub>.

with  $x=0$  to Mott’s small polaron hopping model between localized states.<sup>12,13</sup> The expression for resistivity  $\rho_{sp}$  is given by

$$\rho_{sp} = \frac{kTR}{v_o e^2 c (1-c)} \exp(2\alpha R) \exp(W/kT), \quad (1)$$

where  $v_o$  is the optical phonon frequency,  $\alpha^{-1}$  is the localization length characterizing the localized states at each iron ion site,  $R$  is the average intersite separation,  $c$  is the ratio of [Fe<sup>2+</sup>]/[Fe<sub>total</sub>],  $W$  is the activation energy for the hopping conduction,  $e$  is the electronic charge,  $k$  is the Boltzmann constant, and  $T$  is the temperature. The solid line in Fig. 2 is the theoretically fitted curve. The values of the parameters  $v_o$ ,  $\alpha$ , and  $W$  obtained are summarized in Table I. In the fitting procedure we have taken the experimentally determined values of  $c(=0.01)$  and  $r_p$  the polaron radius ( $=3.14$  Å). The polaron radius  $r_p$  is related to  $R$  as follows:

$$r_p = \frac{1}{2} (\pi/6)^{1/3} R. \quad (2)$$

Specimens doped with antimony were found to contain Sb<sup>3+</sup> and Sb<sup>5+</sup> ions besides the Fe<sup>2+</sup> and Fe<sup>3+</sup> species. We therefore used a model in which both small polarons and bipolarons contributed to electrical transport. The overall resistivity  $\rho$  of the specimen can be written as

TABLE I. Parameters extracted by fitting Mott’s small polaron hopping model for a specimen with a composition of BaO. 6 Fe<sub>2</sub>O<sub>3</sub> ( $c=0.01$ ;  $r_p=3.14$  Å).

$W$ (eV)	$\alpha$ Å <sup>-1</sup>	$v_o$ s <sup>-1</sup>
0.22	1.25	$0.6 \times 10^{13}$

TABLE II. Parameters extracted by fitting a combined small polaron and bipolaron transport mechanism to dc resistivity data for specimens with composition BaO (6-x) Fe<sub>2</sub>O<sub>3</sub> · x Sb<sub>2</sub>O<sub>3</sub>.

$x$	$f$	$W_M$ (eV)	$W$ (eV)	$\alpha$ (Å <sup>-1</sup> )	$\frac{v_o}{(\text{s}^{-1})}$ (×10 <sup>13</sup> )	$c$	$r_p$ (Å)	$\frac{N}{(\text{cc}^{-1})}$ (×10 <sup>20</sup> )
0.025	0.997±0.005	0.73±0.01	0.17±0.02	0.84±0.05	4.2±0.1	0.013	3.14	1.4
0.05	0.995±0.003	1.2±0.05	0.17±0.02	0.79±0.05	1.2±0.1	0.014	3.15	2.4
0.10	0.99±0.001	0.93±0.02	0.10±0.03	1.61±0.04	0.2±0.1	0.015	3.16	4.4
0.30	0.987±0.003	1.30±0.06	0.14±0.04	1.5±0.02	1.0±0.1	0.022	3.18	12.8

$$\frac{1}{\rho} = \frac{f}{\rho_{\text{sp}}} + \frac{1-f}{\rho_{\text{bp}}}, \quad (3)$$

where  $f$  is the fraction contributing to the overall resistivity by a small polaron hopping mechanism,  $\rho_{\text{sp}}$  is given by Eq. (1) and the expression for  $\rho_{\text{bp}}$  is as<sup>14</sup>

$$\rho_{\text{bp}} = \frac{60kT}{v_o e^2 N^2 (R_p^5 - R_{\text{min}}^5)} \exp \left[ \frac{1}{kT} \left( W_M - \frac{2e^2}{\pi \epsilon \epsilon_0 R_p} \right) \right], \quad (4)$$

where  $N$  is the defect concentration (in the present case the concentration of antimony ions),  $W_M$  is the potential energy associated with a defect site,  $\epsilon$  is the dielectric constant of the solid medium,  $\epsilon_0$  is the free space permittivity,  $R_p$  is the critical percolation radius and is given by

$$R_p = \left( 2.7x \frac{3}{4\pi N} \right)^{1/3}, \quad (5)$$

and  $R_{\text{min}}$  is a lower bound for the hopping distance and given by

$$R_{\text{min}} = \frac{2e^2}{\pi \epsilon \epsilon_0 W_M}. \quad (6)$$

We have fitted the experimental data for antimony doped specimens to Eq. (3) using  $f$ ,  $W_M$ ,  $W$ ,  $\alpha$ , and  $v_o$  as the parameters. The values of  $N$ ,  $r_p$ , and  $c$  were obtained from the experimental data. The value of  $N$ , i.e., the concentration of antimony ions, was determined from the wet chemical analysis data and the measured density of the specimen system. The value of  $c$  was obtained from the wet chemical analysis of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions present in different specimens. The value of  $r_p$  was calculated from Eq. (2) after substituting the value of  $R$  obtained from the following equation:<sup>4</sup>

$$R = \left( \frac{1}{N} \right)^{1/3}. \quad (7)$$

In Fig. 2 the solid lines represent the theoretically fitted curves. Table II summarizes the extracted values of the above mentioned parameters. The values are consistent with the physical mechanisms involved. A small polaron consists of a charge carrier (electron) trapped at a defect site (in this case Fe<sup>2+</sup>) with the associated local lattice distortion. Small

polarons are usually highly localized and this is characterized by the localization length  $\alpha^{-1}$ . The values of  $\alpha$  extracted by the fitting procedure are  $\sim 1 \text{ \AA}^{-1}$  which confirms then a state of localization. Electrical conduction by this mechanism arises due to hopping of these polarons between the defect sites. The activation energy  $W$  as determined from the fitting procedure looks reasonable.<sup>1</sup> A bipolaronic hopping mechanism entails simultaneous hopping of two electrons between defect sites. The value of  $W_M$  which is the barrier height at infinite intersite separation ( $\sim 1.2 \text{ eV}$ ) is consistent with the values reported in the literature.<sup>1</sup> Also, the values of  $f$  derived suggest that most of the contributions accrue due to the small polaron transport. This is consistent with the very low level of antimony doping. At the same time the present model predicts the drastic reduction in overall resistivity with reasonable accuracy.

In summary, electrical resistivity of barium hexaferrites was found to decrease sharply as it was doped with antimony oxide. A careful chemical analysis showed the presence of Sb<sup>3+</sup> and Sb<sup>5+</sup> ions in the system besides the existence of Fe<sup>2+</sup> and Fe<sup>3+</sup> species. Electrical conduction is explained as arising as a result of the presence of both small polaron hopping between Fe<sup>2+</sup> and Fe<sup>3+</sup> sites as well as from the bipolaron hopping between Sb<sup>3+</sup> and Sb<sup>5+</sup> sites.

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