

## Polaronic conduction in *n*-type BaTiO<sub>3</sub> doped with La<sub>2</sub>O<sub>3</sub> or Gd<sub>2</sub>O<sub>3</sub>

E. Iguchi, N. Kubota, T. Nakamori, N. Yamamoto, and K. J. Lee

*Department of Mechanical Engineering and Materials Science, Faculty of Engineering, Yokohama National University, Tokiwadai, Hodogaya-Ku, Yokohama 240 Japan*

(Received 30 July 1990; revised manuscript received 26 November 1990)

The dielectric properties and conductivities ( $\sigma$ ) of BaTiO<sub>3</sub> doped with 0.03 mol % of La<sub>2</sub>O<sub>3</sub> or Gd<sub>2</sub>O<sub>3</sub> were investigated in the temperature range of 10–300 K. A speculation over the experimental results, such as the temperature independence of conductivities below 30 K, linear Arrhenius relations between  $\sigma T^{3/2}$  and  $1/T$  with an activation energy of  $0.070 \pm 0.002$  eV above 50 K, and relaxation absorptions in the loss tangents with an activation energy of  $0.068 \pm 0.002$  eV leads to the conclusion that the dominant conduction in *n*-type BaTiO<sub>3</sub> is due to hopping motions of nonadiabatic small polarons. This conclusion is confirmed theoretically. Based upon polaron energies obtained experimentally, several parameters relevant to a nonadiabatic small polaron in this material are estimated.

The nature of electrical conduction in semiconducting polycrystalline *n*-type BaTiO<sub>3</sub> is still a subject of discussion as to whether the charge carrier is a small polaron or a conduction electron, in spite of its well-known characteristic, the PTC effect, the function of which is used in many practical applications. Most analyses as to the conduction in this material pertain to charge-carrier mobilities around the Curie point.<sup>1–6</sup> Although optical and thermopower results on this material,<sup>7,8</sup> suggest a high possibility of the conduction due to a hopping process of small polarons, there is no direct evidence, unfortunately. If such conduction takes place, an electron moves by hopping from one localized state to another and, consequently, an activation energy is required for each step because the localized states have energies extended over a certain range. Then, we can expect some dielectric relaxation behavior due to these motions in alternating fields. If we can observe such a relaxation experimentally, it would be direct evidence for the conduction due to a hopping process of small polarons. In fact, the dielectric relaxation related to the hopping motions of polarons is confirmed experimentally in WO<sub>3</sub> (Ref. 9) and Sm<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> glass.<sup>10,11</sup> From this point of view, we have carried out dielectric measurements of BaTiO<sub>3</sub> doped with La<sub>2</sub>O<sub>3</sub> or Gd<sub>2</sub>O<sub>3</sub>, along with dc-conductivity measurements in the temperature range of  $\sim 10$  to 300 K.

From x-ray measurements on related perovskite crystals such as Sr<sub>1-x</sub>La<sub>x</sub>TiO<sub>3</sub> and Pb<sub>1-x</sub>La<sub>x</sub>TiO<sub>3</sub> (Refs. 12 and 13) and chemical analysis,<sup>6</sup> most of the La<sup>3+</sup> ions are expected to substitute only for Ba<sup>2+</sup> ions. Then, the La-doped perovskite BaTiO<sub>3</sub>:La corresponds to the chemical formula Ba<sub>1-y</sub>La<sup>3+</sup><sub>y</sub>(Ti<sup>4+</sup><sub>1-y</sub>Ti<sup>3+</sup><sub>y</sub>)O<sub>3</sub>. The ionic radius of Gd<sup>3+</sup> compared with that of La<sup>3+</sup> suggests similar substitutions in BaTiO<sub>3</sub> doped with Gd<sub>2</sub>O<sub>3</sub>.<sup>14</sup>

The BaTiO<sub>3</sub> ceramic specimens doped with La<sub>2</sub>O<sub>3</sub> or Gd<sub>2</sub>O<sub>3</sub> (0.03 mol %) were prepared by the conventional solid state synthesis technique.<sup>15</sup> Powders of BaCO<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub> (Johnson Matthey, 5N grade) and TiO<sub>2</sub> (Aldrich Chemical, 4N grade) were used. Powder x-ray

measurements (Rigakudenki RAD-III B) indicate no other phases except BaTiO<sub>3</sub>, being independent of dopants. Flat surfaces of the specimens were coated with In-Ga alloy in 7:3 ratio by a rubbing technique for the electrode which gives a good ohmic contact. YHP 4272A and 4275A LRC meters were used for measurements of capacitances, while Keithley 619 Resistance Bridge or Advantest TR 6871 with a high-ohm unit TR 68704 were used for dc-conductivity measurements. The copper-constantan thermocouple precalibrated at 4.2, 77, and 273 K was employed for the temperature measurements.

As is well known, there are three phase transition points in BaTiO<sub>3</sub>; the first one is from the rhombohedral structure to monoclinic at  $\sim 200$  K, the second one from monoclinic to tetragonal at  $\sim 300$  K, and the third one from tetragonal to cubic at  $\sim 400$  K associated with the ferroelectric-paraelectric transition (Curie point) which induces the PTC effect. In our specimens, there appear the anomalies due to the phase transition at  $\sim 200$  K in both of dc-conductivities and dielectric properties. In the temperature range below 30 K, the conductivities contain nearly temperature-independent regions, which are predicted theoretically by Austin and Mott<sup>16</sup> for the small polaron conduction. On the other hand, the conductivities start to increase as the temperature rises above 30 K. Ihrig<sup>5</sup> suggests the electric conduction due to a hopping process of nonadiabatic small polarons between Ti sites in *n*-type BaTiO<sub>3</sub> in the temperature region where the PTC effect appears. If the conduction like this takes place also at low temperatures, the polaron theories<sup>16–18</sup> characterize the following temperature dependence of the conductivity:

$$\sigma = T^{-3/2} n_0 \exp[-(W_H + W_D/2 + W_0/2)/k_B T], \quad (1)$$

where  $W_H$  is the hopping energy of small polarons,  $W_D$  is the disorder energy,  $n_0 \exp(-W_0/2k_B T)$  represents the density of Ti<sup>3+</sup>, in the thermal equilibrium, nonadjacent to La<sup>3+</sup> or Gd<sup>3+</sup> substituted for Ba<sup>2+</sup> with the concentration of  $n_0$ , and we denote the potential energy of Ti<sup>3+</sup>

at the normal site compared to that of  $\text{Ti}^{3+}$  adjacent to  $\text{La}^{3+}$  or  $\text{Gd}^{3+}$  as  $W_0$ . Figure 1 demonstrates the linear relation between  $\ln(\sigma T^{3/2})$  and  $1/T$  in the temperature region of  $\sim 40$  to  $\sim 200$  K. Such a temperature dependence is likely to suggest conduction due to a hopping process of single polarons at low temperatures. The results in Fig. 1 yield a value,  $W_H + W_D/2 + W_0/2 = 0.070 \pm 0.002$  eV, which looks independent of dopants within the experimental errors.

Figure 2 demonstrates frequency dependencies of the absorption peaks in the loss tangent at low temperatures below 100 K. These results have the following remarkable features. The peak temperature,  $T_m$ , is found to move higher as the applied frequency increases. This fact suggests the absorption peaks due to dielectric relaxation processes. In most cases, a single relaxation time usually does not describe the relaxation process; rather, a distribution of relaxation times is required. The theoretical description of physical models exhibiting a distribution of relaxation times is often very complex. It is sufficient,

however, to quote the results of a simple model<sup>19,20</sup> in which the barrier heights involved for the polaron hopping are equally distributed between  $W_H$  and  $W_H + W_D$ . This model is also employed in Eq. (1). Then, the shift of the peak temperature,  $T_m$ , with increasing applied angular frequency,  $\omega$ , has a form

$$\omega \propto \exp[-(W_H + W_D/2)/k_B T_m]. \quad (2)$$

There are the linear relationships between  $T_m$  and  $\ln \omega$  and they yield a value,  $W_H + W_D/2 = 0.068 \pm 0.001$  eV. From the difference between the activation energy obtained in the conductivities and that in the dielectric loss angle, we have a value,  $W_0/2 \approx 2 \times 10^{-3}$  eV. Our experiments cannot separate  $(W_H + W_D/2)$  into individuals, but, in practice, the value of  $W_D/2$  is smaller than the experimental error in the determination of  $W_H$  as Dominik *et al.* suggested<sup>20</sup> and thus this is neglected. Then,  $W_H \approx 0.068$  eV. It is of great interest that the hopping energy of nonadiabatic small polarons in reduced barium titanate (0.074 eV) (Ref. 21) is very close in value to ours.

Figure 2 shows an increase of the loss angle value at maximum,  $(\tan \delta)_{\max}$ , with increasing frequency, i.e., the

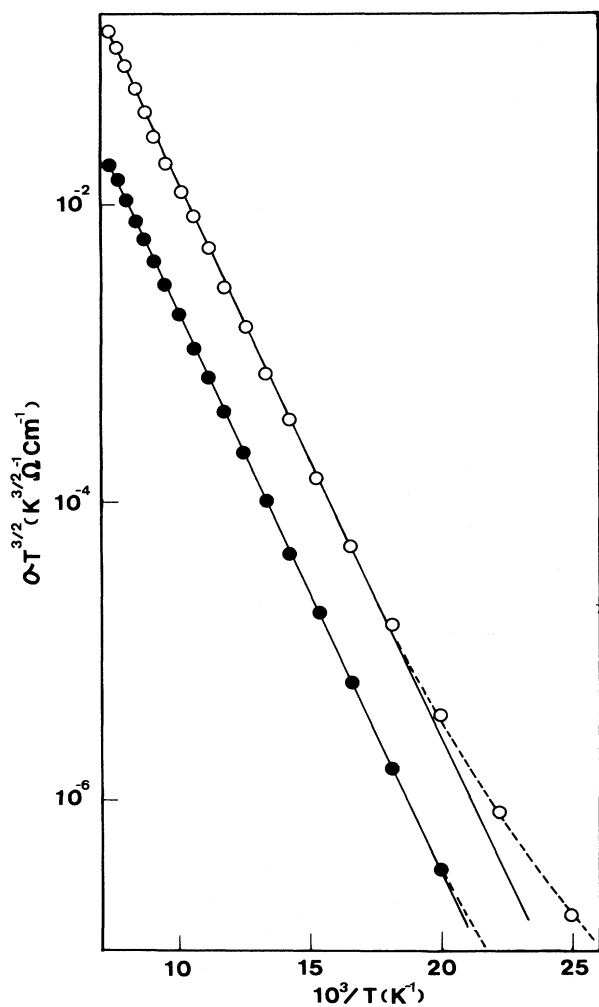


FIG. 1. The Arrhenius relations between  $\sigma T^{3/2}$  and  $1/T$  of  $\text{BaTiO}_3$  doped with 0.03 mol %  $\text{La}_2\text{O}_3$  (solid circles) and 0.03 mol %  $\text{Gd}_2\text{O}_3$  (open circles).

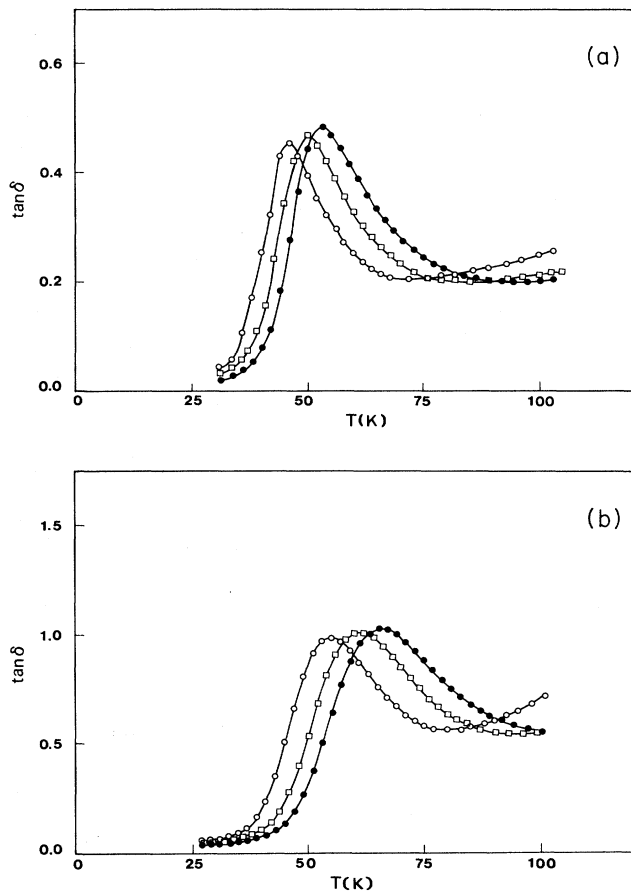


FIG. 2. The frequency dependencies of absorption peaks in loss tangent,  $\tan \delta$ , for the specimen doped with 0.03 mol %  $\text{La}_2\text{O}_3$  (a) and that doped with 0.03 mol %  $\text{Gd}_2\text{O}_3$  (b). Open circles represent the results at the applied angular frequency 10 kHz; squares, 40 kHz; and solid circles, 100 kHz.

increase in  $T_m$ . These behaviors are very similar to the results on  $\text{TiO}_{2-x}$  (Ref. 20) and  $\text{NiO}$ .<sup>22</sup> This effect is not predictable from the Debye theory if a constant number of oscillators is assumed. Alternatively, an activation energy was introduced by Dominik *et al.*<sup>20</sup> which can explain the thermal activation of the number of the oscillating dipoles. In our case, the  $\tan\delta$  value at maximum,  $(\tan\delta)_{\max}$ , is proportional to the polaron concentration,  $n_0 \exp(-W_0/2k_B T)$ . The linear Arrhenius relations of  $(\tan\delta)_{\max}$  and  $T_m$  are obtained and they yield a value of  $(1.6 \pm 0.1) \times 10^{-3}$  eV for the activation energy,  $(W_0/2)$ , which is in good agreement with the value obtained above, i.e.,  $W_0/2 \approx 2.0 \times 10^{-3}$  eV.

Although the speculation over the experimental results suggests a high possibility of the polaron hopping, a theoretical reconfirmation is required. Referring to the discussion of Ihrig *et al.*<sup>6</sup> that the conduction takes place by hopping of small polarons between Ti sites, we have the following conditions for the electron transfer integral between neighboring Ti ions in  $\langle 110 \rangle$ ,  $J_{\text{Ti-Ti}}$ , from the nonadiabatic polaron theories of Holstein<sup>17</sup> and Emin:<sup>23</sup>

$$J_{\text{Ti-Ti}} < 4W_H \quad (3)$$

and

$$J_{\text{Ti-Ti}} < (W_H k_B T / \pi)^{1/4} (\hbar\omega_{0L})^{1/2}. \quad (4)$$

There is another theoretical relation between the drift mobility and the electron transfer integral at sufficiently high temperatures subject to the "classical limit," i.e.,  $\hbar\omega_{0L}/k_B T \ll 1$ :<sup>17,24</sup>

$$\mu_D = [e(\sqrt{2}a_0)^2 J_{\text{Ti-Ti}}^2 \pi^{1/2} / 2\hbar W_H^{1/2}] \times (k_B T)^{-3/2} \exp[-(W_H + W_D/2)/k_B T], \quad (5)$$

where  $a_0$  is the cubic lattice constant (0.4007 nm) (Ref. 25) and  $\omega_{0L}$  is the frequency of the longitudinal optical mode for which we employed the experimental value,<sup>26</sup> i.e.,  $\omega_{0L} = 7 \times 10^{13}$  s<sup>-1</sup>. The "classical limit" indicates that Eq. (5) holds at temperatures  $T \gg \hbar\omega_{0L}/k_B = 534$  K. The drift mobilities and hall mobilities in  $\text{BaTiO}_3$  were obtained experimentally.<sup>1-4,27</sup> These mobilities and the hopping energy ( $W_H = 0.068$  eV) allow us to estimate the electron transfer integral. The mobilities,  $\mu_D = 0.10$  cm<sup>2</sup> V<sup>-2</sup> s<sup>-1</sup> at 1050 K, 0.20 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at 1000 K, and 0.5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at 400 K yield  $J_{\text{Ti-Ti}} = 0.019, 0.026$ , and

0.037 eV at each temperature, respectively. Then, the right-hand side in Eq. (4) is 0.026 eV at 1050 K, 0.025 eV at 1000 K, and 0.020 eV at 400 K. Although the inequality in Eq. (3) holds at every temperature because the right hand side = 0.27 eV, the inequality in Eq. (4) holds only at 1050 K and the lowest temperature subject to the "classical limit" looks to be about 1000 K in *n*-type  $\text{BaTiO}_3$ . Thus, Eq. (4) cannot hold at temperatures lower than 1000 K because of the "classical limit" employed. In view of the above, it is likely that the major carriers are nonadiabatic small polarons and our experimental results present the direct evidence for this conduction.

In order to understand the real feature of a nonadiabatic small polaron in *n*-type  $\text{BaTiO}_3$ , it is of interest to estimate several important physical parameters relevant to this. From the theoretical representation<sup>16</sup> for the rigid-lattice mass,  $m^*$ , corresponding to  $\langle 110 \rangle$  direction which connects neighboring Ti ions,  $m^* = \hbar^2 / 2J_{\text{Ti-Ti}}(\sqrt{2}a_0)^2$ , along with  $J_{\text{Ti-Ti}} = 0.019$  eV at 1050 K, we have a value,  $m^* \approx 6m_0$ , which is nearly equal to the magnitude obtained by Ihrig<sup>5</sup> ( $m^* \approx 3.5 \sim 5.4 m_0$ ), where  $m_0$  is the electron rest mass. The theoretical expression for the relation between the polaron binding energy,  $W_P$ , and the coupling constant,  $\alpha$ ,<sup>28,29</sup>  $W_P = 0.1\alpha^2 \hbar\omega_{0L}$ , yields that the coupling constant has a value of 5.4, being quite reasonable in comparison with  $\text{NiO}$  ( $\alpha \approx 6.3$ ) (Ref. 8) and some halides,<sup>30</sup> where we have used the approximation,  $W_P \approx 2W_H$ , which holds in the case of nonadiabatic small polarons.<sup>16</sup> There is a relationship between the polaron effective mass,  $m_P$ , and the coupling constant,<sup>16</sup> i.e.,  $m_P = 0.02m^*\alpha^4$ . Then, we have obtained a ratio of  $(m_P/m_0) \approx 105$ , which is compatible with the ratio in  $\text{TiO}_2$  (100 ~ 150),<sup>31-33</sup> and also with that in *p*-type  $\text{NiO}$  (150).<sup>34</sup>

#### ACKNOWLEDGMENTS

This project was supported, in part, by a Grant-in-Aid for Science Research (No. 62550517) from the Ministry of Education, Japan, and by the foundation from Sumitomo Metal Industries Ltd. The authors are very grateful to Dr. S. Kawado (Sony Research Laboratory, Yokohama) for the x-ray measurements and also to Mr. K. Akashi, Mr. K. Yamauchi, and Mr. H. Dodoro for their assistance to this project.

<sup>1</sup>P. Gerthsen, R. Groth, and K. H. Hardtl, Phys. Status Solidi **11**, 30 (1965).  
<sup>2</sup>P. Gerthsen, K. H. Hardtl, and A. Csillag, Phys. Status Solidi A **13**, 127 (1972).  
<sup>3</sup>C. N. Berglund and W. S. Baer, Phys. Rev. **157**, 358 (1967).  
<sup>4</sup>A. M. J. H. Seuter, Philips Res. Rep. Suppl. **3**, 1 (1974).  
<sup>5</sup>H. Ihrig, J. Phys. C **9**, 3469 (1976).  
<sup>6</sup>H. Ihrig and D. Hennings, Phys. Rev. B **17**, 4593 (1978).  
<sup>7</sup>E. V. Bursian, Ya. G. Girshberg, and E. N. Starov, Phys. Status Solidi B **46**, 529 (1971).  
<sup>8</sup>I. G. Austin, B. D. Clay, and C. E. Turner, J. Phys. C **1**, 1418 (1968).

<sup>9</sup>R. Gehlig and E. Salje, Philos. Mag. **47B**, 229 (1983).  
<sup>10</sup>A. Mansingh, J. M. Reyes, and M. Sayer, J. Non-Cryst. Solids **7**, 12 (1972).  
<sup>11</sup>H. A. A. Sidek, I. T. Collier, R. N. Hampton, G. A. Saunders, and B. Bridge, Philos. Mag. **59B**, 221 (1989).  
<sup>12</sup>T. J. Tien and F. A. Hummel, Trans. Br. Ceram. Soc. **66**, 233 (1969).  
<sup>13</sup>D. Hennings and G. Rosenstein, Mater. Res. Bull. **7**, 1505 (1972).  
<sup>14</sup>R. D. Shannon and C. T. Prewitt, Acta Crystallogr. Sect. B **26**, 1046 (1970).  
<sup>15</sup>O. Saburi, J. Phys. Soc. Jpn. **14**, 1159 (1959).

- <sup>16</sup>I. G. Austin and N. F. Mott, *Adv. Phys.* **18**, 41 (1969).
- <sup>17</sup>T. Holstein, *Ann. Phys. (N.Y.)* **8**, 343 (1959).
- <sup>18</sup>F. P. Koffyberg and F. A. Benko, *J. Non-Cryst. Solids* **40**, 7 (1980).
- <sup>19</sup>H. Fröhlich, *Theory of Dielectrics* (Clarendon, Oxford, 1958), p. 90.
- <sup>20</sup>L. A. K. Dominik and R. K. MacCrone, *Phys. Rev.* **163**, 757 (1967).
- <sup>21</sup>D. L. Ridpath and D. A. Wright, *J. Mater. Sci.* **5**, 487 (1970).
- <sup>22</sup>S. Van Houten and A. J. Bosman, in *Transition Metal Compounds*, 2nd ed., edited by E. R. Schatz (Gordon and Breach, New York, 1968), p. 123.
- <sup>23</sup>D. Emin, *Phys. Rev.* **4**, 3639 (1971).
- <sup>24</sup>D. Emin and A. M. Kriman, *Phys. Rev. B* **34**, 7278 (1986).
- <sup>25</sup>E. E. Havinga, *J. Phys. Chem. Solids* **28**, 55 (1967).
- <sup>26</sup>L. Gnininvi and J. Bouillot, *J. Phys. (Paris)* **33**, 1049 (1972).
- <sup>27</sup>J. Daniels and K. Härdtl, *Philips Res. Rep.* **31**, 489 (1976).
- <sup>28</sup>H. Fröhlich, *Adv. Phys.* **3**, 325 (1954).
- <sup>29</sup>G. R. Allcock, *Adv. Phys.* **5**, 412 (1956).
- <sup>30</sup>C. Kittel, *Introduction to Solid State Physics*, 4th ed. (Wiley, New York, 1971), p. 391.
- <sup>31</sup>V. N. Bogomolov, E. K. Kudinov, D. N. Mirlin, and Yu Firssov, *Fiz. Tverd. Tela (Leningrad)* **9**, 2077 (1968) [*Sov. Phys.—Solid State* **9**, 1630 (1968)].
- <sup>32</sup>V. N. Bogomolov and D. N. Mirlin, *Phys. Status Solidi* **27**, 443 (1968).
- <sup>33</sup>V. N. Bogomolov, E. K. Kudinov, S. T. Pavlov, and L. S. Sochawa, *Fiz. Tverd. Tela (Leningrad)* **10**, 2043 (1968) [*Sov. Phys.—Solid State* **10**, 1604 (1969)].
- <sup>34</sup>I. G. Austin, A. J. Springthorpe, B. A. Smith, and C. E. Turner, *Proc. Phys. Soc.* **90**, 157 (1967).