

Electrical Transport Properties of La-BaTiO₃

A. I. Ali^{1,2}, Saleh H. Kaytbay³

¹Department of Basic Science, Faculty of Industrial Engineering, Helwan University, Cairo, Egypt; ²Department of Physics, Helwan University, Cairo, Egypt; ³Department of Production, Faculty of Industrial Engineering, Helwan University, Cairo, Egypt.
Email: ahmed_2010@Helwan.edu.eg, saleh952000@yahoo.com

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ABSTRACT

The Electrical properties as a function of temperature were investigated at elevated temperatures (300 K - 800 K) on quenched samples of donor doped La-BaTiO₃ system. The resistivity and carrier concentration increased with increasing temperature. The mobility of the sample shows exponential temperature dependence and the value of mobility is in well agreement with the theoretical values. From the conductivity data the activation energy was calculated (0.036 eV) and revealed that the conduction mechanism in this system is thermally activated.

Keywords: Hall Mobility, Electrical Resistivity, Microstructure and Donor Doped-BaTiO₃

1. Introduction

The BaTiO₃ system has attracted a great deal of attention due to its excellent dielectric properties, such as low dielectric loss and low temperature coefficients of dielectric constants. Most importantly is its potential technological application owing to its unique ferroelectric transitions. To understand the underlying physics, the electronic transportation properties of BaTiO₃ were extensively investigated by several researchers [1-4]. The total electrical conductivity of BaTiO₃, has been extensively documented against temperature and oxygen partial pressure, and the working model of its defect structure is available [5,6]. The chemical diffusivity is reported [7-11] as a measure of (oxygen) nonstoichiometry re-equilibration kinetics for “undoped” and 1.8 m/o Al-doped BaTiO₃, respectively. Subsequently, thermoelectricity of mixed ionic electronic conductor BaTiO₃ + δ is thermodynamically analyzed and measured across the mixed n/p regime of both undoped and 1.8 m/o Al-doped BaTiO₃ at elevated temperatures [12]. Later on, the electronic carrier mobilities of BaTiO₃ are reported [13]. The mobilities of electrons and holes over the temperature range 800°C - 1100°C were determined by measuring electrical conductivity and chemical diffusivity on undoped and 1.8 m/o Al-doped BaTiO₃, respectively, in their mixed n/p regimes. Later on, the factors that affect the shift of Curie temperature and the calculated evolution of overall polarization and dielectric constant of a BaTiO₃ crystal were examined [14]. Many of these reports focused on the carrier’s mobility, studied at low temperatures. How-

ever, the Hall mobility has received far less attention partially due to the difficulty of Hall experiment itself, as well as the low signal of Hall voltage emitted by the BaTiO₃ ceramic [15,16]. Recently there is considerable interest in the formation and characterization of the magnitude of the Hall mobility of the electrons in reduced BaTiO₃ single crystal and polycrystalline by Kolodiazhnyi [17]. The value of electron density is different from the expected value. They calculated the mobility from the relation;

$$\mu(T) = \frac{\sigma(T)}{\varepsilon N}$$

Assuming α constant electron density given by the electro neutrality condition. Unfortunately, all the measurements are only taken in the low temperature range of the frozen-in oxygen vacancy concentration; no direct determination of the mobility in the high temperature range has been reported yet, to my knowledge. For that reason, defect chemical constant like reduction enthalpy. In this work, we made La-BaTiO₃ in single phase, we characterized the samples by using XRD and SEM. We focused on the electronic transport behavior of lanthanum doped barium titanate ceramics, paying special attention to electrical resistivity and Hall mobility at a high temperature range (300 K - 800 K). Also, we found that the mobility of the reduced sample shows linear temperature dependence. In what follows, we discuss the conduction mechanism of the system, the Hall mobility as well as crystal growth using the theory of semiconductor physics. *In situ* high-temperature electrical conductivity and Hall

measurements have proven useful tools for establishing donor-doping efficacy in perovskite doped BaTiO₃ and to screen it for potential technological applications.

2. Experimental Work

La-doped BaTiO₃ (Ba_(1-x)La_xTi_(1-x/4)O₃; $x = 1.0 \text{ mol\%}$, $x = 0.01$) samples were prepared by a conventional powder processing unit. The powders (all from Aldrich, U.S.A.) of BaTiO₃ (99.99% pure), TiO₂ (99.99%), BaCO₃ (99.9%), and La₂O₃ (99.99%), were intimately mixed in an ethanol medium with zirconia's balls by stirring it in a high-speed turbine at 6000 r.p.m. for 24 hours. The slurring was dried at 100°C. Mixtures were crushed into powders and ground lightly in an agate mortar, and then sieved through a 100 micrometer mesh screen. The powder was fired at 1200°C for 5 hours. We repeated this process and then the powder was molded into a pellet (ca. 2.5 cm length, 1.4 cm width and 2 mm thickness) under a uni-axial pressure of 15 MPa. This was followed by cold-isostatically pressing under 150 MPa for 10 min. We drilled 4 holes in the plate to connect the platinum electrodes. Sintering at 1350°C for 5 hours followed. Then we quenched the sample to keep same structure. The thermodynamics condition is illustrated in **Figure 1(b)**. The quenched compacts were cut into thin pellets and connected with platinum wires, which were burned in at 1000°C, and platinum paste.

X-ray diffraction (XRD) patterns at room temperature confirmed the samples to be in single phase as in **Figure 1(a)**. An analysis of XRD patterns clearly indicated that all the synthesized samples were in cubic structure phase. All peaks has been indexed and there is no residuals of the original constituent oxides.

Micrographs of a La-BaTiO₃ sample which was sintered at 1350°C for 5 h in air and another La-BaTiO₃ sample reduced at 1380°C under around 10⁻¹⁴ atom of oxygen partial pressure, are shown in **Figures 2(a)** and **2(b)**, respectively. These figures indicate that, the sintered sample at 1350°C (5 h) in air, has small sized grains (around 0.72 ± 0.14 μm) as depicted in micrograph (a). In contrast, the reduced sample at 1380°C in the oxygen environment has large sized grains. In addition, large grains (around 60 μm) and fine grains (around 10 μm) were observed. The average grain size is 43.33 ± 17.93 μm, indicating that grain growth happen during the reduction process (Micrograph b). The grain growth phenomenon observed in this sample can be attributed to the reduction process.

The bulk density of the samples D_b was determined on the basis of the Archimedes principle. According to the principle, the theoretical density value is 6.08 gm/cm³. In this study the apparent density is 5.908 ± 0.001 gm/cm³ and the bulk density is 5.904 ± 0002 gm/cm³. Thus, the

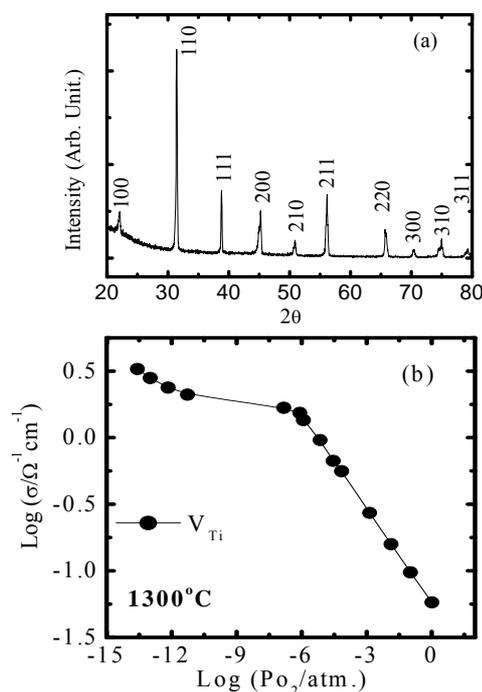


Figure 1. (a) X-ray diffraction patterns at room temperature for La-BaTiO₃; (b) The thermodynamics conditions for La-BaTiO₃ quenched sample.

experimental value is 97.1% of the theoretical value.

The electrical conductivity (σ), the carrier concentration (N), and the Hall mobility (μ) were measured using the Hall measurement system. The applied Hall voltage was in the range of few (μV), which was measured by using a Multi-meter (Keithley 2000). The electric currents required for the experiments were obtained from a constant current source (Keithley 240). With the same purpose, the magnetic fields were applied using 1.3 T magnetic field density permanent magnets of NdFeB. The sample was put in a furnace in which a constant temperature can be maintained. The furnace was homemade and had heating and cooling systems to keep the temperature constant by preventing any thermal effect on the sample. The temperature range could be varied from 280 K to 800 K.

A specimen was mounted on a sample holder, made of an alumina multi-bore tube. The sample holder was placed into a heating coil which was wound around quartz tube. The setup was thermally isolated with special ceramic fibers and alumina wool and placed inside the cooling system. The whole system was placed into the air gap between the magnet's poles.

It should be noted that the electrical contacts produced considerable noise, obscuring the Hall signal. The small fluctuations in temperature caused changes in the potential drop across the Hall contacts. To reduce the margin

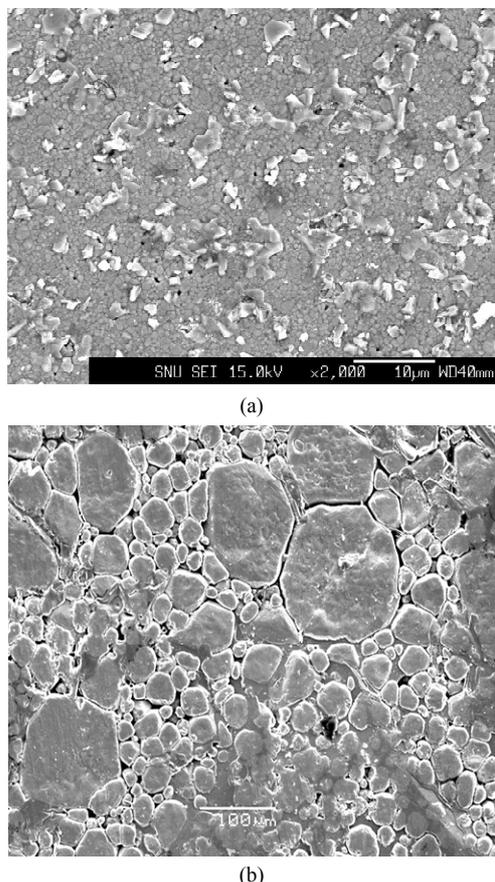


Figure 2 (a). SEM microstructure of La-BaTiO₃ sample sintered in Air at 1350°C; **(b).** SEM microstructure of La-BaTiO₃ sample sintered at 1350°C in Air and then quenched after reducing at 1380°C and around 10⁻¹⁴ atm Oxygen partial pressure.

of error, we took every precaution to create stability in temperature and we repeated the experiment several times to confirm the results.

3. Results and Discussion

The electrical resistivity of the quenched La-BaTiO₃ was measured and shown in **Figure 3(a)**. The resistivity is strongly depended on the degree of previous reduction, before the measurements of electrical resistivity, the sample was heated in atmosphere which possessed a well-defined partial oxygen pressure (as in **Figure 1(a)**) and this sample cooled rapidly to room temperature. The results proved that the resistivity of the La-doped shows saturation depending on the reduction degree. Also, the measurements of resistivity below 800 K revealed that, the curves were completely reversible. And no measurable change of composition appeared during the measurements. The resistivity of the reduced sample gradually decreases with temperature and there is no any discontinuous change in resistivity observed at the temperature

of the phase transition.

Figure 3(b) shows the plots of the dc electrical conductivity as ($\log \sigma_{dc}$) versus temperature as ($10^3/T$) over the temperature range from room temperature to about 800 K. The conductivity behavior for all samples was similar; it rose linearly with increasing temperature. Indicating that the conduction due to thermal activation. The activation energy for the conduction process was calculated from the slope of line according to Arrhenius relation;

$$\sigma = \sigma_0 \exp\left(\frac{-E_g}{KT}\right)$$

where σ_0 is a pre-exponential constant, T is the absolute temperature, K is the Boltzmann's constant (which have a unit of electron volt per degree) and E_g is the activation energy for electric conduction. The activation energy for the conduction process is equal 0.036 eV. $E_g \sim 0.048$ eV.

Figure 4 (a) shows the plots the carriers concentration versus temperature as ($10^3/T$) over the temperature range from room temperature to about 800 K. It seems that, the carriers are nearly temperature independent. The sample was quenched under reducing conditions from different

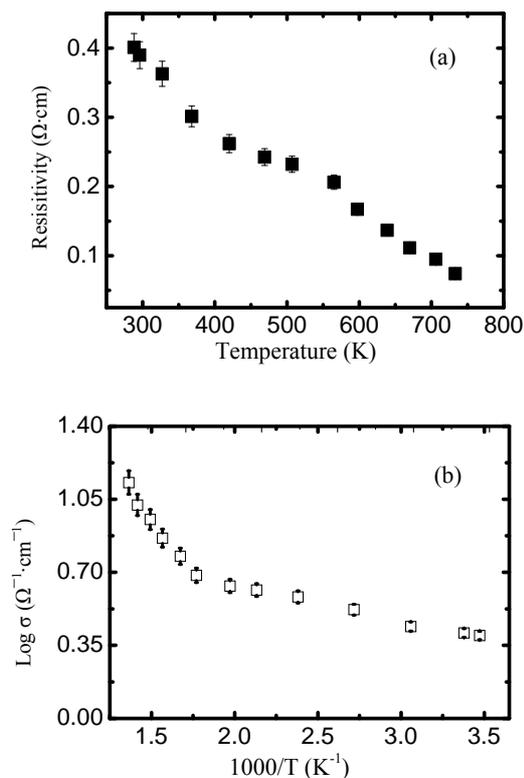


Figure 3. (a) the resistivity as a function of temperature (K) and **(b)** the logarithms of conductivity ($\log(\sigma)$) against $1000/T$ (K⁻¹) for the quenched sample of La-BaTiO₃.

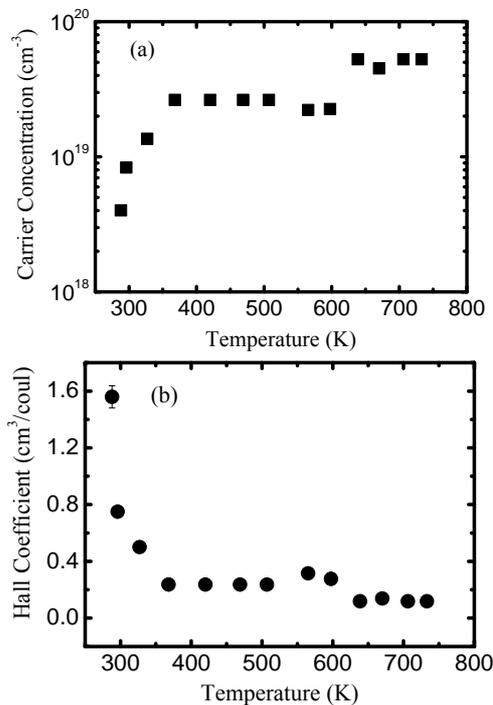


Figure 4. (a) The carriers concentration against temperature (K); (b) the Hall Coefficient as a function of temperature (K).

temperatures and/or oxygen partial pressures (as in **Figure 1(b)**) lead to a well-defined frozen-in oxygen vacancy concentration. Assuming a constant electron density given by the electroneutrality condition $N = [\text{La}]^{3+}$.

In our work, the experimental carrier concentration $(1 - 7) \times 10^{20}/\text{cm}^3$ is different from analytical value $(1 - 7) \times 10^{21}/\text{cm}^3$, this may be due to the quenching condition. All samples measured had carrier concentrations between from 10^{17} to $10^{20} \text{ cm}^{-3}/\text{coul}$. Hall voltages were relatively small. Typical data is shown in **Figure 4(b)**, the accuracy of the Hall coefficient measurements on these samples is no better 10%.

As in **Figure 5**, the mobility is decreasing with the temperature in the low temperature range (300 K - 400 K). One can confirm that, as the temperature increases the mobility nearly constant from around 400 K to 800 K. It can be concluded that the mobility is essentially independent of carrier concentration and that the Hall coefficient is constant within experimental error over the temperature range from 400 K - 800 K. This is due to the donors in BaTiO₃ are fully ionized over the studied range of temperature. The sintering and also quenching condition for the samples as in **Figure 1(b)** made the carrier concentration constant with the high temperature phase.

4. Conclusions

Single phase of samples made with out any impurity. The electrical resistivity decreased with increasing tempera-

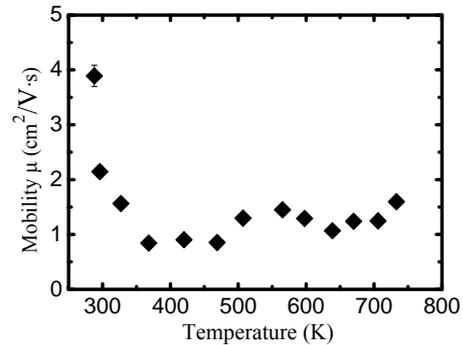


Figure 5. The Hall mobility as function of temperature (K) for quenched sample La-BaTiO₃.

the activation energy was calculated. The conduction mechanism of La-BaTiO₃ is thermally activated. The mobility of the system increased with increasing the temperature indicating that the increase of the charge carrier's token place. The carrier's concentration was calculated with increasing of the temperature and the value of the mobility is in agreement with the previous finding. The all data proven that the doner-doped BaTiO₃ is stable at high temperature range of measurements. Moreover the carriers concentration is quit constant which make these samples useful for technological applications

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REFERENCES

- [1] B. D. Cullity, "Element of X-ray Diffraction," Addison-Wesley, London, 1959, p. 329.
- [2] C. N. Berglund and W. S. Baer, "Electron Transport in Single-Domain, Ferroelectric Barium Titanate," *Physical Review*, Vol. 157, No. 2, 1966, pp. 358-366. doi.org/10.1103/PhysRev.157.358
- [3] E. K. Chang, A. Metha and D. M. Smyth, "Electro-Chemical Society," In: H. L. Tuller and D. M. Smyth, Eds., *Proceedings of the Symposium on Electro-Ceramics and Solid State Ionics*, Princeton, 1988, p. 35.
- [4] ASTM, "International Standard Technology Measurements," V10.50, Designation F76, Annual Book of ASTM Standards, 1999.
- [5] J. Nowotny and M. Rekas, "Defect Structure, Electrical Properties and Transport in Barium Titanate VII. Chemical diffusion in Nb-doped BaTiO₃," *Ceramics International*, Vol. 49, 1991, pp. 135-154.
- [6] J. Y. Kim, C. R. Song and H. I. Yoo, "Nonohmic Properties of Zinc Oxide Ceramics," *Journal of Electro Ceramics*, Vol. 1, 1997, p. 27. doi.org/10.1023/A:1009994230779

- [7] C. R. Song and H. I. Yoo, "Solid State Ionics: Science & Technology," In: B. V. R. Chowdari, *et al.*, Eds., World Scientific Publishing Co., Singapore, 1998, p. 149.
- [8] C. R. Song and H. I. Yoo, "Chemical Diffusivity of BaTiO₃- δ : I. Experimental Determination," *Solid State Ionics*, Vol. 120, No. 1-4, 1999, pp. 141-153. [doi.org/10.1016/S0167-2738\(99\)00012-0](https://doi.org/10.1016/S0167-2738(99)00012-0)
- [9] C. R. Song and H. I. Yoo, "Chemical Diffusivity of BaTiO₃- δ : Defect Chemical Analysis," *Physical Review B*, Vol. 61, No. 6, 2000, pp. 3975-3982. doi.org/10.1103/PhysRevB.61.3975
- [10] C. R. Song and H. I. Yoo, "Chemical Diffusivity of BaTiO₃- δ : III. Conductivity-Nonstoichiometry (δ) Correlation in a Mixed n/p Regime," *Solid State Ionics*, Vol. 124, No. 3-4, 1999, pp. 289-299. [doi.org/10.1016/S0167-2738\(99\)00226-X](https://doi.org/10.1016/S0167-2738(99)00226-X)
- [11] C. R. Song and H. I. Yoo, "Chemical Diffusivity of BaTiO₃- δ : IV. Acceptor-Doped Case," *Journal of the American Ceramic Society*, Vol. 83, No. 4, 2000, pp. 773-779. doi.org/10.1111/j.1151-2916.2000.tb01273.x
- [12] H. I. Yoo and C. R. Song, "Thermoelectricity of BaTiO₃+ δ ," *Journal of Electroceramics*, Vol. 6, No. 1, 2001, pp. 61-74. doi.org/10.1023/A:1011425920963
- [13] H. I. Yoo, C. R. Song and D. K. Lee, "Electronic Carrier Mobility of BaTiO₃," *Journal of the European Ceramic Society*, Vol. 24, No. 6, 2004, pp. 1259-1263. [doi.org/10.1016/S0955-2219\(03\)00504-1](https://doi.org/10.1016/S0955-2219(03)00504-1)
- [14] Y. Su and G. J. Weng, "The Shift of Curie Temperature and Evolution of Ferroelectric Domain in Ferroelectric Crystals," *Journal Mechanical & Physical Solid*, Vol. 53, No. 9, 2005, pp. 2071-2099. doi.org/10.1016/j.jmps.2005.03.008
- [15] R. Moos and K. Heinz, "Electronic Transport Properties of Sr_{1-x}La_xTiO₃ Ceramics," *Journal of Applied Physics*, Vol. 80, No. 1, 1996, p. 393. doi.org/10.1063/1.362796
- [16] R. Moos and W. Menesklon, "Hall Mobility of Undoped N-type Conducting Strontium Titanate Single Crystals between 19 K and 1373 K," *Applied Physics A: Materials Science & Processing*, Vol. 61, No. 4, 1995, pp. 389-395. doi.org/10.1007/BF01540113
- [17] T. Kolodiaznyi, A. Petric, M. Niewczas, C. Bridges, A. Safa-Sefat and J. Greedan, "Thermoelectric power, Hall effect, and Mobility of N-type BaTiO₃," *Physical Review B*, Vol. 68, No. 8, 2003, pp. 1-5. doi.org/10.1103/PhysRevB.68.085205
- [18] Z. L. Cheng and B. Bergman, "Processing and Structure Relationships in Electro Spinning of Ceramic Fiber," *Journal of American Ceramic Society*, Vol. 25, No. 4, 2005, p. 441.
- [19] J. S. Forrester, E. H. Kisi and A. J. Studer, "Effect of Interface Mechanical Properties on Pullout in a SiCO₃ Fiber Reinforced Lithium Aluminum," *Journal of American Ceramic Society*, Vol. 25, No. 4, 2005.