# Effect of the Crystallinity of BaTiO<sub>3</sub> Powders Prepared Using the Merker Method on the Properties of PTCR Ceramics

V. N. Shut, S. V. Kostomarov, and V. L. Trublovsky

Institute of Technical Acoustics, Belarussian Academy of Sciences, pr. Lyudnikova 13, Vitebsk, 210023 Belarus e-mail: shut@vitebsk.by

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**Abstract**—Barium titanate powders differing in particle size (110-740 nm) were prepared by calcining barium titanyl oxalate precipitated by the Merker method. The powders were sintered to produce PTCR ceramics with the composition  $100(Ba_{0.89}Ca_{0.08}Pb_{0.03})TiO_3 + 0.8TiO_2 + 0.7Y + 0.1Mn + 2.5SiO_2$  and electrical properties of the ceramics were studied. The results demonstrate that improving the crystallinity of the barium titanate powder suppresses recrystallization of the ceramics and has a significant effect on their resistance ratio and electric strength. We found the optimal range of calcination temperatures (950–1000°C) for barium titanyl oxalate which ensures the highest electric strength of thermistors with a resistance of 31  $\Omega$ . The average crystallite size of the parent barium titanate powder is ~250–320 nm.

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## INTRODUCTION

Positive temperature coefficient of resistance (PTCR) semiconducting barium titanate ceramics are used to produce PTC thermistors, which find application in industrial and consumer electronics [1-3]. The wide range of applications for such materials leads to a variety of requirements on their electrical characteristics, which stimulates extensive research into their property–composition relationships. No less important is the effect of the characteristics of the starting materials and fabrication procedure on their electrical properties [4, 5]. This issue has recently attracted increased attention.

The most commercially successful approach to the preparation of barium titanate powder is solid-state synthesis. "Classic" precursors are titanium dioxide and barium carbonate. The key features and capabilities of this process have been studied in sufficient detail. The best known alternative approach is oxalate route [6]. In the first step, TiCl<sub>4</sub>, BaCl<sub>2</sub>, and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solutions are reacted to form barium titanyl oxalate (BTO), BaTiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> · 4H<sub>2</sub>O, as a reaction intermediate. In the second step, the BTO is calcined at temperatures above 700°C to give barium titanate (BaTiO<sub>3</sub>) powder.

BTO can be precipitated by several techniques, which differ in mixing sequence, process temperature, and Ba/Ti and Ba/C<sub>2</sub>O<sub>4</sub> molar ratios in the starting mixture. The Clabaugh and Merker processes are used most widely. In the Clabaugh process [7], a mixture of BaCl<sub>2</sub> and TiCl<sub>4</sub> solutions is added to a hot oxalic acid solution. In the Merker process [8], an aqueous TiCl<sub>4</sub> solution is added to oxalic acid to give titanyl oxalic acid, H<sub>2</sub>TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>. Next, barium chloride is added to a heated titanyl oxalic acid solution, and the resultant BTO precipitate is separated. The precipitation procedure and BTO calcination conditions have a significant effect on the characteristics (yield and particle size) of barium titanate powders [9].

Earlier, we studied the electrical properties of PTCR ceramics fabricated from oxalate-derived barium titanate powders synthesized by the Clabaugh method [10–12]. The use of reactive, fine-particle (100–200 nm) powders allowed us to lower the sintering temperature by  $50-60^{\circ}$ C relative to materials produced from submicron- and micron-sized particles and to improve the performance parameters of thermistors (electric strength and resistance jump).

The purpose of this work was to study the microstructure and properties of PTCR ceramics produced from barium titanate powders prepared through the Merker process.

#### **EXPERIMENTAL**

The starting material used was BTO, BaTiO( $C_2O_4$ )<sub>2</sub> · 4H<sub>2</sub>O, precipitated by the Merker method. To obtain barium titanate powders differing in crystallinity, BTO was calcined in air for 1 h at temperatures from 800 to 1200°C.

Figure 1 plots the average crystallite size of the barium titanate powders and the percentage of residual phases against BTO calcination temperature. The characteristics of the barium titanate powders were described in greater detail elsewhere [9]. Calcium titanate was prepared by solid-state reaction between calcium carbonate and titanium dioxide in air at 1000°C. Ground barium titanate and calcium titanate powders were mixed with  $TiO_2$ ,  $SiO_2$ , and PbO by grinding with polyamide media in deionized water to give the overall composition

$$100(Ba_{0.89}Ca_{0.08}Pb_{0.03})TiO_3$$
  
+ 0.8TiO<sub>2</sub> + 0.7Y + 0.1Mn + 2.5SiO<sub>2</sub>.

Yttrium (donor dopant) and manganese (acceptor) were introduced in the form of aqueous YCl<sub>3</sub> and MnSO<sub>4</sub> solutions. To precipitate yttrium and manganese carbonates,  $(NH_4)_2CO_3$  was added to the starting mixture. The mixture was pressed into compacts with a green density of 3.0 g/cm<sup>3</sup>. The compacts were fired in air at temperatures of up to 1320°C. The heating rate was 350°C/h. Cooling to 800°C was performed at a rate of 110 to 300°C/h, depending on the required resistivity of the ceramics.

The complex impedance was measured at room temperature with a Hewlett-Packard 4285A LCR bridge at frequencies from 75 kHz to 10 MHz and with a BM538 impedance meter at frequencies from 5 to 110 MHz. In impedance measurements, we used ceramic samples  $5.6 \times 5.6 \times 2.6$  mm in dimensions.

## **RESULTS AND DISCUSSION**

Figure 2 illustrates the microstructure of the PTCR ceramics prepared using the Merker process followed by calcination at different temperatures. Figure 3 plots the average grain size of barium titanate  $(d_{BT})$  against synthesis temperature  $(t_{synth})$ . The average grain size of the ceramics is seen to decrease monotonically with increasing  $t_{synth}$ . The average grain size varies from 6.8 µm at  $t_{synth} = 800^{\circ}$ C to 4.7 µm at  $t_{synth} = 1200^{\circ}$ C. The microstructure ranges widely in grain size, with an increased content of a glass phase, which is encountered on the surface of the samples. These features are related to the morphology of the parent barium titanate powder and the diffusion of ionic additives during sintering [13].

There is a strong correlation between the donor concentration, the surface composition of the grains, and the microstructure and electrical properties of the ceramics. Rare-earth enrichment at grain boundaries inhibits the recrystallization process. This effect has been demonstrated in a number of studies concerned with both semiconducting [14–16] and dielectric (capacitor) barium titanate ceramics [17–20]. As the overall rare-earth content increases, the grain-boundary rare-earth concentration increases more rapidly than the bulk concentration because of segregation processes [21]. As a result, the rare-earth elements form a zonal shell on the outer layers of the grains. This considerably reduces the mobility of the grain boundaries, because of the slow diffusion of the donors.

Below the sintering temperature, the surface and grain-boundary diffusion coefficients exceed the volume diffusion coefficient by more than two orders of magnitude [22]. During sintering, the Y dopant is first relatively uniformly distributed over the surface of pri-

**Fig. 2.** Microstructure of PTCR ceramics produced from barium titanate synthesized at (a) 800, (b) 1000, and (c)  $1200^{\circ}$ C (firing at  $1320^{\circ}$ C for 40 min).





Fig. 1. (1) Percentage of residual phases and (2) average



**Fig. 3.** Average grain size of PTCR ceramics as a function of barium titanate synthesis temperature.





**Fig. 4.** 25°C resistivity of PTCR ceramics as a function of barium titanate synthesis temperature.

mary barium titanate grains. Subsequent recrystallization and diffusion processes bring the donor to the bulk of the grains.

In our experiments, the percentage of yttrium in the starting mixture was the same for all of the samples. As a result, when microcrystalline barium titanate powder, with a large grain-boundary area, was used  $(t_{synth} = 800-900^{\circ}C)$ , the initial donor concentration on the surface of primary crystallites was lower. The volume diffusion path was thus shorter, and the recrystallization process was more active. This led to the formation of PTCR ceramics with a uniform yttrium distribution over the grains and a relatively coarsegrained microstructure. Because macrocrystalline barium titanate powders have a smaller specific surface area, the yttrium content on the surface of primary crystallites will be higher. When such powders are



Fig. 5. Equivalent circuit of PTCR ceramics.

used, it is reasonable to assume the presence of excess yttrium on the grain boundaries of the ceramic because rare-earth ions have a small volume diffusion coefficient [23]. As a result, the recrystallization process slows down.

Note that, in ceramics prepared from powders synthesized using the Clabaugh process [10, 11],  $d_{\text{BT}}$ (8.5–4.5 µm) is a stronger function of  $t_{\text{synth}}$  (800– 1200°C). This correlates well with the observed morphology of the as-prepared barium titanate powders: when the Clabaugh process was used, the increase in the size of primary crystallites with increasing  $t_{\text{synth}}$  was more pronounced.

Figure 4 shows the 25°C resistivity of the PTCR ceramics produced from barium titanate synthesized at various temperatures. All of the samples were sintered at a maximum temperature of 1320°C for 40 min and then cooled at a rate of 215°C/h. The  $\rho_{25}(t_{synth})$  curve has a minimum at  $t_{synth} = 950$ °C, which is due to a competitive effect of two factors. On the one hand, raising the BTO calcination temperature leads to a reduction in the residual barium carbonate content of the synthesized barium titanate. This would be expected to reduce the resistivity of the PTCR ceramic through a reduction in the volume of intergranular glass phases in the sintered samples because this rules out reaction between BaCO<sub>3</sub> and SiO<sub>2</sub>. On the other hand, as mentioned above, the use of macrocrystalline starting powders (at increased  $t_{synth}$ ) leads to yttrium enrichment at grain boundaries. It is well known that, at low donor concentrations, the charge of the donor ions is compensated by free electrons, which results in semiconducting properties. With increasing donor concentration, the charge of the donors is compensated by negatively charged cation vacancies, which leads to a rise in the resistance of grain-boundary regions (to the point of formation of a dielectric layer) [24].

PTCR behavior is a grain-boundary effect and is best described in terms of the Heywang–Jonker model. According to this model, the PTCR effect is due to a grain-boundary double Schottky barrier formed by electron traps. Actually, the grain-boundary barrier has a more complex structure. It comprises a Schottky barrier and an adjacent diffusion layer with a reduced conductance, due to a nonuniform distribution of defects and impurities (donors and acceptors) [25–27]. To analyze such structure, it is necessary to examine an equivalent circuit (Fig. 5) whose impedance is the sum of three components, related to the grain boundaries ( $Z_1^*$ ), diffusion layers ( $Z_2^*$ ), and grain bulk ( $Z_b^*$ ). The three components are given by

$$Z_i^* = R_i / (1 + j \omega R_i C_i) (i = 1, 2, b),$$

where  $R_i$  and  $C_i$  are the equivalent resistances and capacitances, which are adjustable parameters of the model.

In this approach, the contribution of each layer can be estimated by analyzing Cole–Cole diagrams. In par-

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ticular, the diagrams of samples prepared from barium titanate synthesized using the Clabaugh process were similar in shape to a semicircle, with high-frequency distortions [10]. This attests to a nearly single relaxation and homogeneity of potential barriers, and the distortions are well represented by the contribution of the diffusion layer to the total resistance of the samples.

Figure 6 presents impedance spectroscopy data for the ceramics produced from barium titanate powders prepared using the Merker process. The three diagrams are seen to be severely distorted  $(Z''_{max}/Z'_{max} < 0.38)$ . This means that the potential barrier height varies markedly from grain to grain. It is then necessary to introduce a so-called arc depression factor,  $\alpha_i$  [25]. The complex impedance is then given by

$$Z_i^* = R_i / [1 + (j \omega \tau_i)^{\alpha i}] (i = 1, 2, b).$$

The  $\alpha_i$  value characterizes the relaxation time distribution of grains and ranges from 0 to 1. At higher  $\alpha_i$  values, the grain boundaries are more uniform and the shape of the Cole–Cole diagram approaches a semicircle.

According to analysis in this model (Fig. 6), the right-hand semicircle corresponds to the complex impedance  $Z_1^*$  (boundary layer), and the left-hand semicircle, to  $Z_2^*$  (adjacent diffusion layer). It can be seen that the depression of the Cole–Cole diagram increases with an increase in the calcination temperature of barium titanate. The diffusion layer makes an appreciable contribution to the total resistance of the samples. This contribution increases with increasing barium titanate crystallinity.

The Schottky barrier height can be effectively controlled by varying the cooling rate, which influences the density of grain-boundary acceptor states [12, 28]. Reducing the cooling rate increases the density of grain-boundary electron traps and vice versa. This allows one to achieve a constant resistance  $R_{25}$  of samples prepared from barium titanate powders differing in  $d_{\rm BT}$ . This approach is of importance for the ability to produce PTC thermistors with a predetermined resistance.

Adjusting the cooling rate in the range from 1320 to 800°C, we achieved the same room-temperature resistance ( $R_{25} = 31 \Omega$ ) in ceramics produced from barium titanate powders of different particle sizes. Figure 7 plots the electric strength and resistance ratio against BTO calcination temperature for thermistors with  $R_{25} = 31 \Omega$ . Also given in Fig. 7 are the cooling rates of samples prepared from various barium titanate powders with  $R_{25} = const$ . The electric strength of PTCR ceramics is known to increase with increasing resistance ratio and decreasing voltage sensitivity of  $\rho$  (varistor effect) [29, 30]. The varistor effect is, in turn, weaker at a smaller grain size and a more uniform microstructure of ceramics because the grain-boundary voltage drop is then smaller [31].

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**Fig. 6.** Cole–Cole diagrams for samples prepared from barium titanate synthesized at (a) 800, (b) 1000, and (c) 1200°C (firing at 1320°C for 40 min, cooling at 215°C/h). The large semicircle corresponds to the calculated complex impedance  $Z_1^*$  (Schottky barrier), and the small semicircle, to  $Z_2^*$  (diffusion layer). The dots represent the measured total impedance.



**Fig. 7.** (1) Electric strength and (2) resistance ratio as functions of barium titanate synthesis temperature for samples with the same  $\rho_{25}$ ; (3) cooling rate that ensures  $\rho_{25}$  = const (sintering at 1320°C for 40 min).



**Fig. 8.** (1) Electric strength and (2) resistance ratio as functions of barium titanate synthesis temperature for samples with the same  $\rho_{25}$ ; (3) cooling rate that ensures  $\rho_{25}$  = const (sintering at 1320°C for 15 min).

The  $R_{\text{max}}/R_{\text{min}}$  ratio of the thermistors produced from BTO powders calcined in the range 800–1000°C increases with increasing  $t_{\text{synth}}$ , which is due to the increase in the density of acceptor states and the drop in grain size. This is accompanied by an increase in breakdown voltage. The use of coarser powders reduces the breakdown voltage, even though the ceramic has a small grain size and rather large PTCR. This points to an increase in the magnitude of the varistor effect in such materials. The increase in the magnitude of the varistor effect may be due to the severe inhomogeneity of grain-boundary barriers, as evidenced by the above impedance spectroscopy data. The optimal  $t_{\text{synth}}$  is 950°C. The size of primary barium titanate crystallites is then 250–300 nm.

To improve the performance of thermistors, we studied samples sintered at 1320°C for a short time (15 min). Reducing the sintering time (or sintering temperature) reduces the room-temperature resistance of manganese-containing ceramics [12]. During synthesis,  $Mn^{2+}$  ions occupy Ti<sup>4+</sup> sites, and the excess charge is compensated by oxygen vacancies ( $V_0^{\circ}$ ), which form various  $(Mn)_n - V_0$  complexes, for example,  $Mn_{Ti}^n - V_0^{\circ}$  [32]. During cooling, the grain boundaries oxidize, and the  $V_0^{\circ}$  concentration drops. As a result, the oxidation state of the manganese ions changes from 2+ to 3+ or 4+ and they act as electron traps, increasing the electron trap density  $N_s$ .

The increase in  $N_S$  is accompanied by an increase in resistance ratio. However, at high  $N_S$  values, the resistivity  $\rho_{\min}$  also rises because the grain-boundary states cannot be compensated by spontaneous polarization in the ferroelectric phase. It is worth pointing out that, when barium titanate is codoped with donors (Y) and acceptors (Mn), the latter may not only prevent rare-earth accumulation at grain boundaries but also segregate [33–35]. This process may also play an important part not only during cooling of ceramics but also during high-temperature synthesis [12, 32, 36]. For this reason, in the case of prolonged high-temperature synthesis, manganese-containing ceramics degrade rather rapidly.

The microstructure of the ceramics produced by sintering at the highest temperature for 15 min was essentially identical to that of the samples prepared by heat treatment for 40 min. At the same time, their room-temperature resistance was lower in comparison with the materials prepared by prolonged sintering (provided the cooling rate was 215°C/h in all cases). Therefore, to obtain thermistors with  $R_{25} = 31 \Omega$ , this regime allows one to reduce the cooling rate and, accordingly, to raise the density of grain-boundary acceptor states.

The electrical properties of thermistors held at the highest temperature for 15 min are presented in Fig. 8. It can be seen that the above trends persist and that the breakdown voltage and resistance ratio are higher when microcrystalline active powders are used.

## CONCLUSIONS

Increasing the calcination temperature of BTO precipitated by the Merker method increases the average crystallite size of the barium titanate powder from 110 ( $t_{synth} = 800^{\circ}$ C) to 740 nm ( $t_{synth} = 1200^{\circ}$ C) and reduces the percentage of residual phases. The synthesized barium titanate powders were used to produce PTCR ceramics with the composition

$$100(Ba_{0.89}Ca_{0.08}Pb_{0.03})TiO_3 + 0.8TiO_2 + 0.7Y + 0.1Mn + 2.5SiO_2.$$

The average grain size of the ceramics decreases with increasing barium titanate synthesis temperature owing to the donor impurity enrichment at grain boundaries.

The PTCR ceramics produced from the powders synthesized at 900–1000°C has the lowest resistivity (250–300  $\Omega$  cm), and the grain-boundary barriers are less uniform at higher BTO calcination temperatures.

Adjusting the cooling rate, we obtained PTC thermistors with a room-temperature resistance of 31  $\Omega$ . The samples prepared from the barium titanate powders synthesized at 950–1000°C offer the highest electric strength: 350 V/mm. The average crystallite size of the parent barium titanate powder is 250–320 nm.

Our results demonstrate that the use of active microcrystalline materials with a small percentage of residual phases helps to optimize the dopant distribution, to raise the density of grain-boundary acceptor states, and to improve the electrical performance of the thermistors.

#### REFERENCES

- 1. Chen, Y.L. and Yang, S.F., PTCR Effect in Donor Doped Barium Titanate: Review of Compositions, Microstructures, Processing and Properties, Adv. Appl. Ceram., 2011, vol. 110, no. 5, pp. 257-269.
- 2. Al-Allak, H.M., Anomalous Increase in the Resistivity of n-Doped BaTiO<sub>3</sub>-Based Ceramics with Pressure Observed at Room Temperature, J. Am. Ceram. Soc., 2011, vol. 94, no. 9, pp. 2757–2760.
- 3. Syrtsov, S.R., Shut, V.N., Kashevich, I.F., et al., Positive Temperature Coefficient of Resistivity in Thin Films of Barium Titanate, Mater. Sci. Semicond. Process., 2002, vol. 5, nos. 2-3, pp. 223-225.
- 4. Blamey, J.M. and Parry, T.V., The Effect of Processing Variables on the Mechanical and Electrical Properties of Barium-Titanate Positive-Temperature-Coefficient-Of-Resistance Ceramics: I. Additives and Processing Prior to Sintering, J. Mater. Sci., 1993, vol. 28, no. 16, pp. 4311–4316.
- 5. Park, K., Ha, J.-G., Kim, C.-W., and Kim, J.-G., PTCR Characteristics of Semiconducting Barium Titanate Ceramics Produced by High-Energy Ball-Milling, J. Mater. Sci., 2008, vol. 19, no. 4, pp. 357-362.
- 6. Pithan, C., Hennings, D., and Waser, R., Progress in the Synthesis of Nanocrystalline BaTiO<sub>3</sub> Powders for MLCC, Int. J. Appl. Ceram. Technol., 2005, vol. 2, no. 1, pp. 1–14.
- 7. Clabaugh, W.S., Swiggard, E.M., and Gilchrist, R., Preparation of Barium Titanyl Oxalate Tetrahydrate for Conversion to Barium Titanate of High Purity, J. Res. Natl. Bur. Stand., 1956, vol. 56, no. 5, pp. 289-291.
- 8. Vakhmenina, O.N., Bokman, G.Yu., Kharash, M.Sh., et al., RF Patent 2 224 718, 2004.
- 9. Shut, V.N. and Kostomarov, S.V., Properties of Barium Titanate Powders in Relation to the Heat Treatment of the Barium Titanyl Oxalate Precursor, Inorg. Mater., 2012, vol. 48, no. 6, pp. 613–618.
- 10. Shut, V., Kostomarov, S., and Gavrilov, A., PTCR Barium Titanate Ceramics Obtained from Oxalate-Derived Powders with Varying Crystallinity, J. Mater. Sci., 2008, vol. 43, no. 15, pp. 5251-5257.
- 11. Shut, V.N., Kostomarov, S.V., and Gavrilov, A.V., PTCR Ceramics Produced from Oxalate-Derived Barium Titanate, Inorg. Mater., 2008, vol. 44, no. 8, pp. 905-910.
- 12. Shut, V.N. and Kostomarov, S.V., Semiconducting Ceramics Produced Using Nanocrystalline Barium Titanate Powder, Inorg. Mater., 2009, vol. 45, no. 12, pp. 1417-1422.
- 13. Huybrechts, B., Ishizaki, K., and Takata, M., The Positive Temperature Coefficient of Resistivity in Barium Titanate, J. Mater. Sci., 1995, vol. 30, no. 10, pp. 2463-2474.
- 14. Peng, C.J. and Lu, H.Y., Compensation Effect in Semiconducting Barium Titanate, J. Am. Ceram. Soc., 1988, vol. 71, no. 1, pp. 44-46.

- 15. Urek, S. and Drofenik, M., PTCR Behavior of Highly Donor Doped BaTiO<sub>3</sub>, J. Eur. Ceram. Soc., 1999, vol. 19, nos. 6–7, pp. 913–916.
- 16. Buscaglia, M.T., Viviani, M., Buscaglia, V., et al., Incorporation of Er<sup>3+</sup> into BaTiO<sub>3</sub>, J. Am. Ceram. Soc., 2002, vol. 85, no. 6, pp. 1569–1575.
- 17. Wang, S.F. and Dayton, G.O., Dielectric Properties of Fine-Grained Barium Titanate Based X7R Materials, J. Am. Ceram. Soc., 1999, vol. 82, no. 10, pp. 2677-2682
- 18. Yoon, S.H., Lee, J.-H., Kim, D.-Y., and Hwang, N.M., Effect of the Liquid-Phase Characteristic on the Microstructures and Dielectric Properties of Donor-(Niobium) and Acceptor-(Magnesium) Doped Barium Titanate, J. Am. Ceram. Soc., 2003, vol. 86, no. 1, pp. 88–92.
- 19. Brzozowski, E. and Castro, M.S., Influence of Nb<sup>5+</sup> and Sb<sup>3+</sup> Dopants on the Defect Profile, PTCR Effect and GBBL Characteristics of BaTiO<sub>3</sub> Ceramics, J. Eur. Ceram. Soc., 2004, vol. 24, no. 8, pp. 2499–2507.
- 20. Mitic, V.V., Nikolic, Z.S., Pavlovic, V.B., et al., Influence of Rare-Earth Dopants on Barium Titanate Ceramics Microstructure and Corresponding Electrical Properties, J. Am. Ceram. Soc., 2010, vol. 93, no. 1, pp. 132–137.
- 21. Desu, S.B. and Payne, D.A., Interfacial Segregation in Perovskites. II. Experimental Evidence, J. Am. Ceram. Soc., 1990, vol. 73, no. 11, pp. 3398–3406.
- 22. Boltaks, B.I., Diffuziva i tochechnve defekty v poluprovodnikakh (Diffusion and Point Defects in Semiconductors), Leningrad: Nauka, 1972.
- 23. Liu, G., Wang, X., Lin, Y., et al., Growth Kinetics of Core-Shell-Structured Grains and Dielectric Constant in Rare-Earth-Doped BaTiO<sub>3</sub> Ceramics, J. Appl. *Phys.*, 2005, vol. 98, no. 4, pp. 044 105–044 111.
- 24. Glinchuk, M.D., Bykov, I.P., Kornienko, S.M., et al., Influence of Impurities on the Properties of Rare-Earth-Doped Barium-Titanate Ceramics, J. Mater. Chem., 2000, vol. 10, no. 4, pp. 941-947.
- 25. Hari, N.S., Padmini, P., and Kutty, T.R.N., Complex Impedance Analyses of *n*-BaTiO<sub>3</sub> Ceramics Showing Positive Temperature Coefficient of Resistance, J. Mater. Sci.: Mater. Electron., 1997, vol. 8, no. 1, pp. 15-22.
- 26. Morrison, F.D., Sinclair, D.C., and West, A.R., Characterization of Lanthanum-Doped Barium Titanate Ceramics Using Impedance Spectroscopy, J. Am. Ceram. Soc., 2001, vol. 84, no. 3, pp. 531-538.
- 27. Kirstein, K., Reichmann, K., Preis, W., and Mitsche, S., Effect of Commercial Anatase-TiO<sub>2</sub> Raw Materials on the Electrical Characteristics of Ceramics with Positive Temperature Coefficient of Resistivity, J. Eur. Ceram. Soc., 2011, vol. 31, no. 13, pp. 2339–2349.
- 28. Koschek, G. and Kubalek, E., Grain-Boundary Characteristics and Their Influence on the Electrical Resistance of Barium Titanate Ceramics, J. Am. Ceram. Soc., 1985, vol. 68, no. 11, pp. 582–586.
- 29. Pavlov, A.N. and Raevskii, I.P., Varistor Effect in Semiconducting Ferroelectric Ceramics, Zh. Tekh. Fiz., 1997, vol. 67, no. 12, pp. 21–25.
- 30. Shut, V.N. and Gavrilov, A.V., Thermal Stresses in Layered Barium Titanate-Based Semiconductor Ceramics, Tech. Phys., 2008, vol. 53, no. 11, pp. 1508–1512.

- Roseman, R.D. and Mukherjee, N., PTCR Effect in BaTiO<sub>3</sub>: Structural Aspects and Grain Boundary Potentials, *J. Electroceram.*, 2003, vol. 10, no. 2, pp. 117–135.
- 32. Miki, T., Fujimoto, A., and Jida, S., An Evidence of Trap Activation for Positive Temperature Coefficient of Resistivity in BaTiO<sub>3</sub> Ceramics with Substitutional Nb and Mn As Impurities, *J. Appl. Phys.*, 1998, vol. 83, no. 3, pp. 1592–1603.
- 33. Chiang, Y.-M. and Takagi, T., Grain-Boundary Chemistry of Barium Titanate and Strontium Titanate: I. High-Temperature Equilibrium Space Charge, *J. Am. Ceram. Soc.*, 1990, vol. 73, no. 11, pp. 3278–3285.
- 34. Yoon, S.H., Lee, K.H., and Kim, H., Effect of Acceptors on the Segregation of Donors in Niobium-Doped

Barium Titanate Positive Temperature Coefficient Resistors, *J. Am. Ceram. Soc.*, 2000, vol. 83, no. 10, pp. 2463–2472.

- 35. Vyunov, O.I., Kovalenco, L.L., and Belous, A.G., The Effect of Isovalent Substitutions and Dopants of 3*d*-Metals on the Properties of Ferroelectrics–Semi-conductors, *Condens. Matter Phys.*, 2003, vol. 6, no. 2, pp. 213–220.
- 36. Gallego, M.M. and West, A.R., Effect of Annealing Treatments on Positive Temperature Coefficient of Resistance Properties of Barium Titanate Ceramics and a New Model for the Positive Temperature Coefficient of Resistance Effect, *J. Appl. Phys.*, 2001, vol. 90, no. 1, pp. 394–403.