The jump-like PTCR effect in a Ni-BaTiO$_3$ magnetic composite

Igor Zajc$^{1,*}$ and Mihael Drofenik$^{1,2}$

$^1$Department for Materials Synthesis, Jožef Stefan Institute, 1000 Ljubljana, Slovenia
$^2$Faculty of Chemistry and Chemical Engineering, University of Maribor, 2000 Maribor, Slovenia

Received: 25 February 2021  
Accepted: 6 February 2022  
Published online: 22 February 2022

© The Author(s) 2022

ABSTRACT

The ceramic composites BaTiO$_3$@Ni, composed of a conducting nickel and a highly resistive ferroelectric BaTiO$_3$ phase, exhibiting a positive temperature coefficient of electrical resistivity (PTCR), are prepared using a conventional ceramic method at less than 1000 °C. The BaTiO$_3$@Ni composites show a jump-like PTCR effect in electrical resistivity by about eight orders of magnitude ($\rho_{\text{max}}/\rho_{\text{min}} \approx 10^8$) with $\rho_{\text{min}} < 1 \Omega\text{cm}$. This is the first example of a standard PTCR element with a relatively high magnetization. The grain relocations (a microstructural rearrangement) on a microscopic scale in the composite are filmed using a transmission electron microscope while heating through the ferroelectric phase transition (Curie temperature), which induces the PTCR anomaly. The resistivity anomaly of the composite is explained in terms of the ferroelectric phase transition-assisted anomaly in the electrical resistivity.

1 Introduction

Materials with a PTCR effect are important components in electronic and electrical engineering. Many devices exploiting the PTCR effect, such as self-regulating heaters, starter motors, over-current limiters, and sensors use PTCR ceramics in the form of bulk ceramics or films [1, 2]. Currently, the best-known example is a PTCR ceramic based on the semi-conducting donor-doped BaTiO$_3$ [3, 4]. There are, however, other PTCR materials. Some are based on pure ceramics, while others are based on composites composed of at least two constituent phases: a conductive phase and an isolating phase. This isolating phase is crucial and must exhibit, at a distinct temperature, an irregularity, i.e., a significant change in the temperature coefficient of expansion [5], a crystal transformation, and/or change in its crystal morphology [6]. Recently, a new type of PTCR composite based on the phenomenon known as the “ferroelectric phase-transition-assisted anomaly in the electrical resistivity” (FPTAA) was reported [7, 8]. Here, the BaTiO$_3$@Ni composite was considered in the context of the recently reported FPTAA phenomenon.

In the open literature we can find reports on ceramic composites where the additions of metals improve the PTCR and/or dielectric properties of composites. Ni metal was added to BaTiO$_3$-based PTCR samples to lower the room-temperature resistivity of the PTCR ceramics; however, nickel is not...
used to modify the PTCR effect at the Curie temperature [9]. The addition of Ni and graphite to BaTiO$_3$-calcined powder induces a low room-temperature resistivity and a better PTCR effect, which were explained by the decrease of the potential height on the grain boundaries of the BaTiO$_3$ ceramics [10]. Furthermore, chromium was added to (Ba, Pb)TiO$_3$ ceramics and a composite with a high-temperature PTCR effect (180 °C) was obtained. However, the mechanism of the resistivity anomaly is different from the FPTAA principle [11]. In addition, materials with a higher BaTiO$_3$ concentration in the Ni/BaTiO$_3$ mixtures have been reported. By sintering these materials at above 1300 °C higher dielectric constants were achieved due to the dispersion of the conductive Ni particles in the dielectric matrix (BaTiO$_3$) [12, 13].

This contribution reports on a composite material BaTiO$_3$@Ni exhibiting a jump-like increase in electrical resistivity of a few orders of magnitude inside a relatively narrow temperature interval at the Curie temperature of BaTiO$_3$. This material, with outstanding electrical properties, is new and belongs to the family of materials with a positive temperature coefficient of electrical resistivity (PTCR).

2 Experimental

Two constituent phases were used for the sample preparation: barium titanate (BaTiO$_3$ = BT) from the Ferro Company (219–9, Ba/Ti = 0.995, surface area 2.3 m$^2$/g, 0.06 wt% impurities) and nickel powder (Ventron, particle size < 1 µm). High-resistivity BT particles were prepared by calcination of the BT powder at 1350 °C for 15 min. After the calcination the powder was milled in ethanol using a ball mill for 1 h. The composite was prepared using a conventional ceramic fabrication method. Weighed amounts of high-resistivity BT with an average particle size of 1 µm and conductive nickel particles were admixed in ethanol using a ball mill for 1 h, dried, and pressed at 10 MPa into pellets with a diameter of 6 mm, a height of 2 mm, and a green density of 50% of the theoretical density (determined geometrically).

The samples were annealed at up to 1000 °C for 2 h in nitrogen. The density of the annealed samples was about 80% of the theoretical density, measured using Archimedes’ method. The microstructures of the samples were inspected with a scanning electron microscope (model Ultra plus, Zeiss, Germany). The constituent composite phases were analyzed using an EDX analyser (model Inca, Oxford Instruments, UK). The calcined products were examined with X-ray diffraction (model X’Pert, PRO analytical, the Netherlands). The dilatation vs. temperature of the composite was measured with a dilatometer (model Misura 3 ODHT 1600–5, TA Instruments, DE, USA). The electrical contacts were made on the annealed samples with a Ga/In alloy. The electrical resistivity of the composite samples was measured with a multimeter (model HP 3457A, Hewlett Packard, CA, USA), under a heating rate of 3 K/min in a furnace. A d. c. voltage < 1.5 V was employed for the resistivity measurements. In order to optimize the samples’ properties regarding the extent of the resistivity anomaly and the room-temperature electrical resistivity, several samples were prepared with various amounts of BT phase (20, 30, 40, and 50 wt%) annealed at 400 °C, 800 °C, and 1000 °C. The 20 wt% BT mixture was found to exhibit the best electrical properties and was subjected to further examinations. The annealing temperatures (max. 1000 °C) were adjusted in order to obtain a low-resistivity PTC thermistor with a room-temperature resistivity of less than 1 Ωcm and with a high-resistivity anomaly (up to 7 orders of magnitude).

For the bulk sample preparation with the TEM heating experiment the sample was cut into a 3-mm disc. This was then ground to a thickness of 100 µm (Disc Grinder, Gatan Inc., PA, USA) and dimpled down to 15 µm at the disc’s center (Dimple grinder, Gatan Inc., PA, USA). The TEM specimen was finally ion milled (PIPS, Precision Ion Polishing System, Gatan Inc., PA, USA) using 3-kV Ar$^+$ ions at an incidence angle of 8° until perforation. Detailed structural investigations of the samples were performed with transmission electron microscopy (TEM) using a 200-kV microscope (TEM; JEM-2100, Jeol, Japan). The heating experiment was performed using a Double Tilt Heating Holder (Model 652.F, Gatan Inc., PA, USA) in the range from 25 to 400 °C and was filmed using an TEM-adapted furnace between 100 and 140 °C, which covers the Curie temperature of the BT at 120 °C.

Room-temperature magnetization curves of the samples were measured with a vibrating-sample magnetometer (VSM) LakeShore 7307 VSM. The measurements were made on powdered samples in
the external magnetic field from $-1 \, \text{T}$ to $1 \, \text{T}$ at room temperature in an air atmosphere.

3 Results and discussion

The X-ray diffraction of the composite in Fig. 1 shows only the constituent phases, i.e., BaTiO$_3$ (BT) and the nickel phase, as confirmed by the JCPDS card data for BT (005-0626) and nickel (088-2326). Due to the relatively low firing temperatures, no reactions between the constitutive phases during annealing of the composite were detected. Owing to the relatively low firing temperature the composite grains were not subjected to any significant grain growth and mostly retain their initial morphology. The SEM images show the composite microstructure, Fig. 2a, and provide an overall visualization of the distribution of the conductive nickel phase in Fig. 2d and of the high-resistivity BT ferroelectric phase Fig. 2b and c by inspecting the maps of barium and titanium, respectively.

The composite samples exhibit a magnetization related to the magnetic phase of nickel, Fig. 3. In this composite one phase (BT) shows ferroelectricity, while the other, the nickel phase, demonstrates a high electrical conductivity and magnetization. Here, the magnetic properties of the Ni phase have an additional effect, which works in the composite as a soft magnetic component that has a relatively high magnetization. The primary property of this new type of PTC thermistor is its low electrical resistivity and a jump-like resistivity increase, while the magnetization is an accompanying property. This is the first example of a standard PTCR element with a relatively high magnetization—a magnetic PTCR composite. Regarding the applicability, it is too early to predict the advantage of this magnetic property with respect to other conventional PTC thermistors, with the exception that it might be handled as a soft magnet for the whole working temperature range of the PTC thermistor. The magnetization of the composite is $45 \, \text{emu/g}$, compared to the pure metal nickel’s $58 \, \text{emu/g}$, which shows that the composite comprises about 20% of non-magnetic phase.
The diagrams in Fig. 4 show how the composition modifies the course of the resistivity anomaly. A large change in the composite’s phase ratio in the range from 20 to 50 wt% BT shows a resistivity anomaly at the same temperature, which is consistent with a $T_C$ at around 120 °C for the high-resistivity constitutive ferroelectric phase BaTiO$_3$ in the composite.

The room-temperature resistivity of the samples is very low. This is in agreement with the metallic Ni conductive phase in the composite. On the other hand, the PTCR curves, Fig. 4, indicate that the resistivity anomaly is like a jump in resistivity, i.e., a metal–insulator transition, near the Curie temperature of the BT. Here, the PTCR curves show small resistivity jumps below $T_C$ in the sample sintered at 400 °C. At this time, when sintering proceeds at relatively low temperatures the inhomogeneities remained after the sample preparation, which might cause grain relaxations on heating and can cause such small resistivity jumps.

Such courses of R(T) are not known among ceramic PTC thermistors. The mechanism of the PTCR anomaly can be treated of the “ferroelectric phase transition-assisted anomaly in the electrical resistivity” (FPTAA) [8]. Here, the BT ferroelectric constitutive phase, which exhibits the transition between the tetragonal and cubic BaTiO$_3$ at the Curie temperature, induces a noticeable shrinkage of the composite at the $T_C$, Fig. 5b, due to notable shrinkage of the BT crystallite in the c-axis direction, i.e., a BT grain shape change at $T_C$. Here, the anomaly in the resistivity of $10^8$ Ωcm at 120 °C coincides with the shrinkage in the c-axis from 4.035 to 4.009 Å in the range from 0 to 130 °C [14].

In Fig. 5a, a typical electrical resistivity anomaly of the BaTiO$_3$@Ni composite, with 20 wt% BT annealed in nitrogen for 1 h, during heating and cooling, is shown besides the corresponding dilatation curve, Fig. 5b. These two diagrams, the anomaly in the resistivity and the dilatation curve exhibiting a shrinkage of the composite at the Curie temperature, show the crucial effects responsible for the PTCR anomaly in this composite. The explanation of the PTCR anomaly in the resistivity in BT@Ni is based on

![Fig. 4](image_url) Temperature dependences of the electrical resistivity of the BaTiO$_3$@Ni composites with different additions of highly resistive BaTiO$_3$ phase, 20 wt%, 30 wt%, 40 wt%, and 50 wt% of BT annealed at different temperatures, as shown in diagram

![Fig. 5](image_url) a Hysteresis in the temperature dependence of the electric resistivity of BaTiO$_3$@Ni composite with 20 wt% of highly resistive BaTiO$_3$ phase and b the thermal expansion curve of the same sample.
the two above-documented effects, i.e., that the composite exhibits a shrinkage at the Curie temperature, Fig. 5b and a resistivity anomaly that coincides with the shrinkage, Fig. 5a.

At this time the resistivity of the BT@Ni metal/ceramic composite sees a rapid increase of the resistivity in a relatively narrow temperature interval at the phase transition of the ferroelectric barium titanate (BT). This jump-like increase in the resistivity must be caused by the disconnection of the conducting Ni grains. These novel ceramic–metal thermistors are still under consideration; however, they also demonstrate the possibility of preparing PTC thermistors without any lead content.

The anomaly in the resistivity for this novel class of PTC thermistor will occur at temperatures close to the \( T_C \) and might also occur at temperatures of the ferroelectric phases with a \( T_C \) higher than that of BT, as shown in our previous contribution [8]. Here, the explanation of the PTCR effect of the thermistor at the Curie temperature of the BT constitutive phase is based on the abrupt crystallite shape change at \( T_C \), where the c-axis shrinks to a relatively large degree.

When we consider the composite shrinkage at \( T_C \), Fig. 5b, and adjust it with the change of the crystallite shape, we are justified in concluding that the comprehensive shrinkage of the composite (negative CTE) at the Curie temperature must be related to the relocations between the crystallites of both constituent phases. This was established using TEM, see Fig. 6, where a microstructural location was filmed using a TEM-adapted furnace between 100 °C and 140 °C, covering the Curie temperature at 120 °C. In the images Fig. 6a and b the microstructure at the initial and final temperatures can be seen, where a distinct relocation of the microstructure can be observed from the marker diagonal. The entire course of the microstructure reordering is in the film clip as shown in Fig. 6c.

The marker diagonal is drawn in the figures, indicating the relocation/displacement of the grains during the phase transition. However, these relocations/displacements occurred without inducing cracks, which were noted when we investigated the thermistor material ZnO-NiO [5]. There were cracks formed immediately after the first heating cycle. Here, there is an indication that this PTC thermistor composite can be applied as an electronic element.

The driving force of this process is the shrinkage of the BT crystallite in the c-axis direction (from 4.035 to 4.009 Å, from 0 to 130 °C, respectively). This must be the reason for inducing a jump-like anomaly in resistivity at the Curie temperature. Namely, a relatively large absolute shrinkage of the c-axis of BT ferroelectric grains, when connected with the Ni grains, can shift the Ni grain and disconnect the Ni conduction path, which was established at room temperature, as can be seen from the low resistivity of the composites. Here, the connection between the grains is a junction and/or a neck developed during annealing of the composite. There are three types of connections between the grains present in the

![Fig. 6](https://example.com/fig6.png)

**Fig. 6 a, b** TEM images showing the BT@Ni microstructure details during heating: **a** the microstructure at 30 °C (initial temperature) and **b** the microstructure at 140 °C (final temperature). The inserted diagonal is a guide for the eye when watching the grain displacement in the images. **c** The film clip showing the microstructure reordering in the examined temperature interval, available in the supplementary material.
composite material: the connections between the BT-Ni grains, between the Ni–Ni grains, and between the BT–BT grains.

The strength of the first connection is the most important because it pulls the grain in the direction of the BT grain c-axis contraction and disconnects the Ni–Ni grains when passing through the Curie temperature. The BT-Ni connection in the metal–ceramic system is subjected to the diffusion of metal ions into the ceramics, forming a firm junction between the grains [11]. On the other hand, the relatively large Ni grains are not prone to neck formation and present no hindrance to the disconnection of the Ni–Ni contacts. In addition, the connections of the BT grains are less important, as they do not directly participate in the process and are also limited to form firm connections as the powders have been previously inactivated by heating to 1330 °C.

It is assumed that the direction of the BT grain in Fig. 7, denoted by C, is correctly randomly oriented. Figure 7 shows a schematic model of the microstructure of a BT@Ni composite focused on conductive Ni–Ni chains, while Fig. 8 shows the microstructure of the BT-Ni grain connections.

4 Conclusion

A magnetic composite BaTiO₃@Ni composed of a magnetic conducting network based on nickel and a highly resistive ferroelectric phase BaTiO₃ exhibiting a jump-like anomaly in electrical resistivity at the Curie point of BaTiO₃ was prepared and the resistivity anomaly examined. Here, the magnetic properties of the constitutive phase (Ni) have a supplementary property and offer a synergetic effect during its manipulation. The driving force for this process is the shrinkage of the BaTiO₃ crystallite in the c-axis direction, i.e., a BaTiO₃ grain shape change at $T_C$. This must be the reason for inducing the jump-like anomaly in the resistivity. Namely, the relatively large absolute shrinkage of the c-axes (c/a = 1.011 for the tetragonal BT at room temperature) [14] of the ferroelectric BaTiO₃ grains when in line with the BaTiO₃-Ni connection might shift the Ni grain and disconnect the Ni network and/or the Ni conducting path.

This study has revealed the idea of preparing PTC thermistors with an anomaly of resistivity at elevated temperatures above the $T_C$ of BaTiO₃ without the use of toxic lead oxide when using ferroelectrics without lead having a higher $T_C$ than BT.
Acknowledgements

The authors thank Dr. Sandra Drev for her help with the TEM investigations and Dr. Srečo Škapin for his help with the SEM investigations. The authors acknowledge the financial support from the Slovenian Research Agency (research core funding No. P2-0089). We acknowledge the CENN Nanocenter for the use of Vibrating Sample Magnetometer LakeShore 7400 Series VSM.

Author contributions

IZ performed conceptualization, validation, investigation, resources, data curation, writing (reviewing and editing), visualization, and project administration. MD performed writing the original draft (reviewing and editing) and visualization.

Funding

The work was supported by Grant No. P2-0089 (research core funding) from the Slovenian Research Agency.

Data availability

Data available on reasonable request from the corresponding author.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

Supplementary Information: The online version contains supplementary material available at http://doi.org/10.1007/s10854-022-07913-7.

References

1. B. Huybrechts, K. Ishizaka, M. Takata, J. Mater. Sci. 30, 2463 (1995)
2. O. Saburi, K. Wakino, IEEE Trans. Compon. Parts 10, 53 (1963)
3. W. Heywang, J. Am. Ceram. Soc. 47, 484 (1964)
4. G.H. Jonker, in Advances in Ceramics, vol. 1, ed. by L.M. Levinson (American Ceramic Society, Westerville, 1981), p. 155
5. M. Drofenik, D. Lisjak, I. Zajc, J. Am. Ceram. Soc. 80, 1741 (1997)
6. D. Wei-Fang, T. Xu, D. Hai-Ging, J. Mater. Sci. 29, 1097 (1994)
7. I. Zajc, M. Drofenik, Ceram. Int. 40, 8033 (2014)
8. I. Zajc, M. Drofenik, J. Mater. Sci.: Mater. Electron. 29, 2868 (2018)
9. F. Lui, Y. Qu, J. Phys. Chem. Solids 68, 41 (2007)
10. J. Du, Y. Qu, W. Ma, J. Electroceram. 12, 163 (2004)
11. Z. He, J. Ma, Y. Gu, C. Wang, J. Mater. Sci.: Mater. Electron. 11, 235 (2000)
12. H. Emoto, J. Hojo, J. Ceram. Soc. Jpn. 100, 555 (1992)
13. C. Pecharromán, F. Esteban-Betegón, J.F. Bartolomé, S. López-Esteban, J.S. Moya, Adv. Mater. 13, 1523 (2001)
14. S. Pradhan, G.S. Roy, Researcher 5, 63 (2013)

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.