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KRZYSZTOF STANUCH*

INFLUENCE OF VANADIUM DOPPING ON DIELECTRIC PROPERTIES OF BARIUM TITANATE CERAMICS

WPŁYW DOMIESZKOWANIA VANADEM NA WŁAŚCIWOŚCI DIELEKTRYCZNE CERAMIK TYTANIANU BARU

Abstract

The purpose of this article is to present the impact of vanadium substitution on the dielectric properties of barium titanate. Doping barium titanate ($BaTiO_3$) by different ions such as vanadium V^{5+} provides the possibility of changing its dielectric properties. SEM images indicate the differences between pure $BaTiO_3$ (BT) and $Ba(Ti_{0.98}V_{0.02})O_3$ (BTV2).
Using dielectric measurements, the Curie temperatures (T_c) were calculated – they were found to be equal to 403 K and 396 K, respectively. Moreover, for BTV2 the Curie - Weiss temperature and the Curie constant (C) were determined (T_0 = 368 K and C = 1.46 ×10^5 K, respectively).

Keywords: *Ferroelectric ceramics*, *perovskite*, *barium titanate*, *phase transition*

Streszczenie

Domieszkowanie tytanianu baru $BaTiO_3$ (BT) jonami innych pierwiastków, jak wanad V^{5+}, umożliwia zmiany jego właściwości dielektrycznych. Obserwacje z wykorzystaniem SEM wskazują na różnice w strukturze mikrokrystalicznej między $BaTiO_3$ (BT) a $Ba(Ti_{0.98}V_{0.02})O_3$ (BTV2). Z pomiarów dielektrycznych wyznaczono temperaturę Curie (T_c). Dla BT wynosi ona 403 K, a dla BTV2 396 K. Dla BTV2 określono również temperaturę Curie-Weissa oraz stałą Curie (T_0 = 368 i C = 1.46 × 10^5 K).

Słowa kluczowe: *ceramika ferroelektryczna*, *perowskit*, *tytanian baru*, *przemiana fazowa*

* M.Sc. Eng. Krzysztof Stanuch, Institute of Physics, Pedagogical University, Cracow.

1. Introduction

Some of the most important ferroelectric materials are solid solutions based on barium titanate $BaTiO_3$. They are characterized by a relatively high dielectric constant value that can reach the order of 10^4. The Curie temperature of $BaTiO_3$ is around 403 K [1, 2]. Barium titanate belongs to the group of compounds of an oxygen octahedral perovskite crystal structure, the unit cell of *a* perovskite cubic is shown in Fig. 1. The name is derived from the mineral called perovskite with the chemical formula $CaTiO_3$. Compounds which adopt a structure similar to $CaTiO_3$ belong to a group of perovskites and are described by the general formula ABO_3, where A and B are cations of different sizes, and O is an oxygen anion [1, 3]. Due to its excellent dielectric, piezoelectric and ferroelectric properties, barium titanate began to be used in the end of the 1950s [4, 5]. Nowadays, $BaTiO_3$-based compounds are used for different electroceramical applications such as: multi-layer ceramic capacitors MLCC; ferroelectric random access memory FRAM; piezoelectric sensors; pyroelectric sensors; optoelectronic devices; actuators [1, 5–7]. Long-term studies of $BaTiO_3$ have shown that it is possible to change the dielectric and ferroelectric properties by appropriate substitution or the addition of ions of other elements in addition to or instead of Ba^{2+} in sublattice A and/or Ti^{4+} in *sublattice* B [8–17]. These substitutions can be isovalent when atoms are doped with the same valence or heterovalent, when they have a different valence [5]. Solid solutions based on barium titanate can be obtained through various methods, e.g. using the thermal synthesis of oxides, sol-gel, microwave and mechanochemical methods [18, 19]. Doping by vanadium can change the value of the Curie temperature and dielectric losses in barium titanate [5, 20].

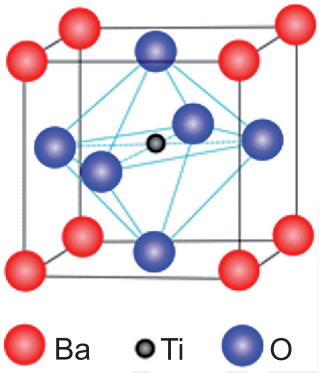

Fig. 1. Unit cell of $BaTiO_3$

2. Experimental

The samples BTV2 and BT were prepared using barium oxalate BaC_2O_4, titanate dioxide TiO_2, and vanadium pentoxide V_2O_5 with a purity of 99.99%. The modification was based on the substitution of V^{5+} (an amount of 2%) in sublattice B (Ti^{4+}). The process of the preparation of BTV2 and of BT in terms of technology, was identical. Pressing was performed at a 0.2 GPa. Samples were synthesized at a temperature of 1373 K for 2 hours. Subsequently, the samples were milled and pressed under a 0.3 GPa and sintered at 1543 K for 2 hours. The last stage of the samples' preparation before dielectric measurements were taken was the application of silver electrodes. Dimensions of the samples were as follows – a diameter of 7 mm and a thickness of 1.5–2.0 mm. A study of the structure and chemical composition of polycrystalline samples BTV2 and BT was made by scanning electron

microscopy (SEM) using a JSM-6610 apparatus coupled with an X-ray energy-dispersive spectrometer (EDS). Dielectric measurements were performed using broadband dielectric spectroscopy. Instrumentation consisted of a dielectric analyzer with high resolution Alpha – AN together with cryogenic temperature control system Quatro Cryosystem and WinDETA Novocontrol software. The samples were measured at the temperature range 148 K to 500 K in steps of 5 K, and from 1 Hz to 10 MHz, respectively. The amplitude of the test voltage was 1 V. Nitrogen gas was used as a cooling and heating medium.

3. Results and discussion

SEM photomicrographs of the microstructure and EDS spectra for BT and BTV2 are presented in Fig. 2–4. Fig. 2a shows the structure of barium titanate with highly visible grains and their boundaries. The proportions in the elements analysis presented in Fig. 2b correspond to the chemical composition of $BaTiO_3$.

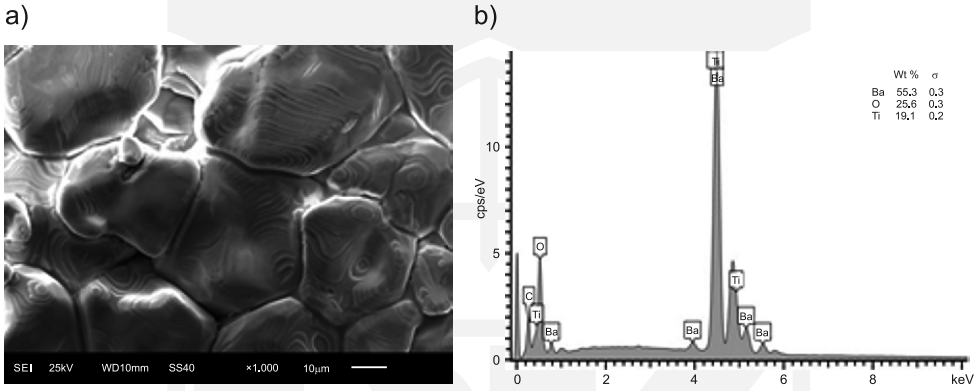

Fig. 2. SEM photomicrograph of the microstructure (a) and the spectrum of the elemental composition of BT ceramics (b)

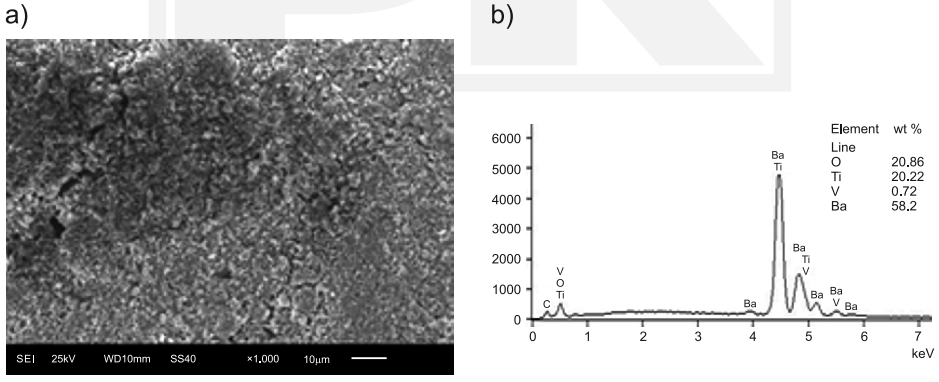

Fig. 3. SEM image of the microstructure (a) and EDS spectrum of the chemical composition of BTV2 ceramics (b)

The SEM photomicrograph of the barium titanate doped by vanadium in Fig. 3a shows a significant difference in the microstructure in comparison to $BaTiO_3$ (Fig. 2a).

An analysis of the chemical composition of BTV2 ceramics is shown in Fig. 3b. The addition of vanadium ions has a destructive influence causing the formation of much smaller crystallite grains. The larger magnification of the SEM image in Fig. 4 reveals the structure of smooth crystallites.

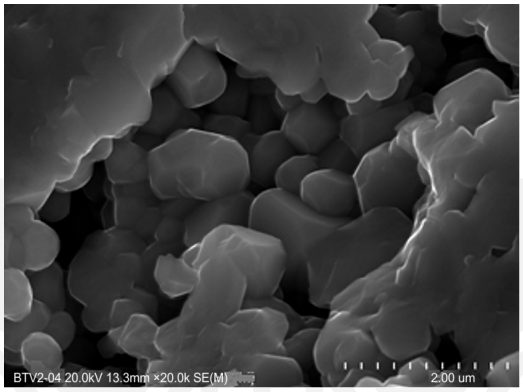

Fig. 4. SEM image of the microstructure of $Ba(Ti_{0.98}V_{0.02})O_3$ ceramics

The results of the dielectric measurements of the polycrystalline samples of BT and BTV2 are presented in Fig. 5a and b. They show the dependence of the real part of the dielectric permittivity $\varepsilon'(T)$ in the temperature range 148 K to 500 K.

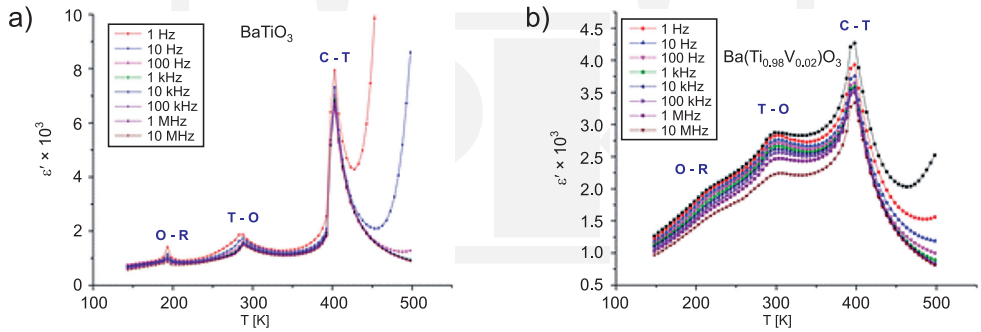

Fig. 5. The temperature dependence of the dielectric permittivity (ε') for: a) BT, b) BTV2

For BT (Fig. 5a), one can see three structural changes: from the cubic to tetragonal (C–T); tetragonal to orthorhombic (T–O); orthorhombic to rhombohedral (O–R) [5, 21]. In the case of BTV2 (Fig. 5b), there are three diffused phase transitions.

Temperature of the paraelectric – ferroelectric phase transition is about 403 K for BT. This value is consistent with the literature data [22]. In the case of the BTV2 sample, T_m = 396 K. It can be seen that 2% vanadium doping, decreased maximum value of the dielectric permittivity, from about 8×10^3 for BT to about 4×10^3 for BTV2.

The reciprocal of the real part of the electric permittivity BTV2 for 1kHz frequency is presented in Fig. 6. For the paraelectric phase ε^{-1} (T) function obeys the rule of Curie--Weiss [5]. The Curie-Weiss temperature T_0 was determined as being 368 K.

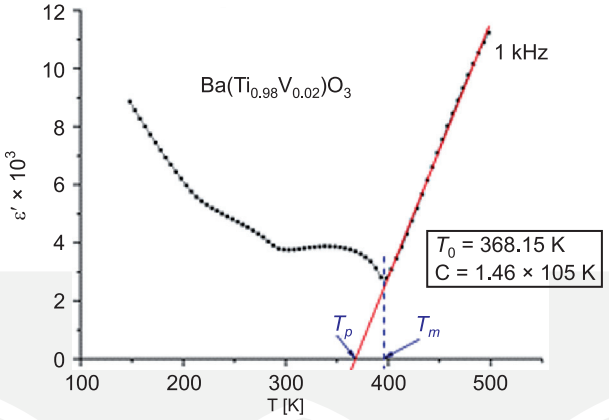

Fig. 6. The temperature dependence of the reciprocal dielectric permittivity (ε^{-1} (T)) for 1 kHz

Using the Curie-Weiss law in the following form:

$$\frac{1}{\varepsilon} = \frac{1}{c}(T - T_0) \tag{1}$$

determined the Curie constant, which is C = 1.46 × 10^5 K at 1 kHz.

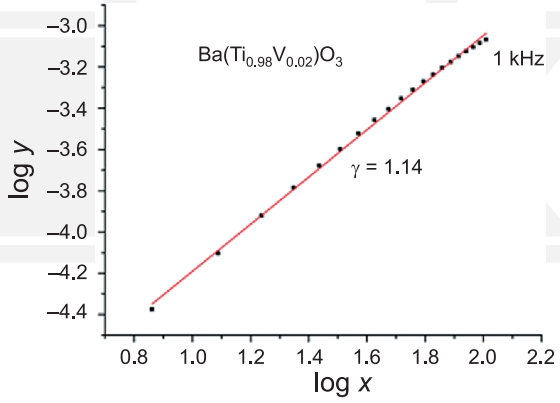

Fig. 7. Dependence log(y) from log(x) by 1 kHz for polycrystalline sample BTV2

Fig. 7 shows the geometrical interpretation of the Curie-Weiss law as the relationship $\log(y) = f(\log(x))$.

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + A(T - T_m)^{\gamma} \tag{2}$$

where:

ε_m – the maximum value of the electric permittivity,
T_m – the temperature corresponding to the maximum value ε_m, A,
γ – a constant for the selected frequency

$$x = T - T_m \tag{3}$$

$$y = \varepsilon^{-1} - \varepsilon_m^{-1}$$

For the diffused phase transition value $\gamma \approx 2$, when $\gamma \approx 1$, the transition is a sharp [23–25]. Using linear regression determined that $\gamma = 1.14$ for BTV2. This value indicates a weak *diffusion* of the phase transition.

4. Conclusions

Modifications of $BaTiO_3$ by vanadium ions introduced in sublattice B allows for the changing of its dielectric properties. This is very important in the design of materials used in electroceramics.

In this case, the addition of vanadium ions to the BT causes significant changes in the dielectric permittivity. It was also found that vanadium doping has a destructive influence on the microstructure of ceramics. In the result aggregation of the crystallites in the sintering process for the BTV2 sample creates a structure with a much smaller grains than in the case of BT sample (Fig. 2–4). Using the dielectric spectroscopy method, the Curie temperature T_c for BT was identified as 403 K. However, for BTV2, besides T_c = 396 K, the Curie-Weiss temperature T_0 = 368 K and the Curie constant $C = 1.46 \times 10^5$ K were determined by graphical methods. Using the Curie-Weiss law (2) for the diffuse phase transition a parameter of $\gamma = 1.14$ was obtained. This value indicates that the phase transition is minimally diffused.

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