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Synthesis, characterization and application aspects of barium titanate-based ceramic samples with graphene nanostructures introduced

A. A. Georgieva*, F. S. Yovkova, K. Z. Panayotova

Burgas State University "Prof. Dr. Assen Zlatarov", Department of Chemical Technology, 1, Prof. Yakimov Blvd., Burgas 8000, Bulgaria

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The share of research work aimed at finding innovative approaches to the synthesis of new porous ceramic products to be applied as filters for purification of waste waters, as adsorbents, heat-insulation materials and other components with high thermal resistance, as well as biomedical and catalytic substrates has recently increased. The present paper reports for the preparation of barium titanate-based ceramic samples containing up to 2 mass % of graphene nanostructures (graphene nanoplatelets GnP), synthesized by the method of solid-state sintering. The methods of X-ray diffraction, FT-IR spectroscopy, scanning electron microscopy and light microscopy were used for the characterization of the initial blends and the titanate ceramic samples obtained from them. The results of the analyses showed that the introduced nano-additive initiated the formation of fine-grain porous structure with grain sizes from 0.5 to 1 μm. Some basic physicomechanical properties of the samples synthesized were determined, e.g., water absorption ($WA,\%$), apparent density ($\rho_{app,}, g/cm^3$) and apparent (open) porosity ($P_{app},\%$). The apparent density was close to the theoretical one - 5.51 g/cm^3, the open porosity was 2.04 % and the minimal water absorption - 0.37 %. Some aspects of application are proposed.

Keywords: Ceramic samples, Barium titanate, Graphene nanostructures, Porous ceramic materials, Physicomechanical properties

INTRODUCTION

Ceramic materials based on titanium dioxide, titanates, zirconates and compounds with similar properties form a class of technical ceramics widely used in radio-engineering, electronics, ultrasonic and other application fields for preparation of capacitors and piezoceramic components. Many ceramic materials, obtained from titanates, zirconates and stannates, which are characterized by higher, very high and ultrahigh dielectric permeability, are used to manufacture high-frequency and low-frequency capacitors with linear (induced) or non-linear (spontaneous) polarization [1]. $BaTiO_3$, as a very important dielectric ceramic material, was widely used for large-scale production of capacitors due to its superior dielectric properties and low cost [2]. Capacitors made from insulating ceramics provide outstanding power density and fast charge-discharge features, making them ideal devices for pulse power applications [3]. Despite the proven benefits, the exploration of $BaTiO_3$-based high-entropy ceramics is lacking. There's still much potential to uncover in this area.

The literature review revealed that numerous research teams are concentrating on developing approaches for synthesizing new porous ceramic components. These components have potential applications as wastewater filtration materials, adsorbents, heat insulation materials, and high thermal resistance parts for use in biomedical and catalytic substrates. Besides, the introduction of graphene and its derivatives in the ceramics provides new possibilities for enhancing existing materials and imparting new versatile properties, such as crack propagation resistance, bending strength, electric conductivity, electromagnetic and heat-conductive properties [1, 4-8].

In this regard, the aim of the present work is to obtain and characterize barium titanate-based ceramic samples containing graphene nanostructures, to determine their main physicomechanical properties and propose areas of their possible application.

MATERIALS AND METHODS

Materials

Barium titanate ceramic samples containing up to 2 mass % of graphene nanostructures were prepared by the method of solid-state sintering of predominantly diffusion nature. In most cases, this approach is used for the preparation of special ceramics and it is considered to be completed to sufficient degree when the initial materials are in the form of highly disperse powders.

* To whom all correspondence should be sent:
E-mail: *adriana_georgieva79@yahoo.com*

- *Initial materials and blend compositions.* The following initial materials were used for the preparation of the barium titanate-based ceramic samples with composition D0: highly dispersed $BaTiO_3$ powder - 98 mass % (Sigma Aldrich, purity > 99%) and graphene nanoplatelets GnP - 2 mass % (graphene nanoplatelets, Sigma Aldrich).
- *Formation and sintering of the ceramic samples.* The preparation of the ceramic blends and the synthesis of the samples were carried out as follows: the initial highly dispersed materials were weighed and dry homogenized. The plasticizer used was 4% polyvinyl alcohol. The samples were formed by a semi-dry method on a hydraulic press under pressure of 40 MPa. The samples were then dried at 120°C for 70 min and at 180°C for 50 min. The temperature regime of the sintering process was: at 200°C - isothermal period of 20 min, at 300°C - 20 min, at 400°C - 20 min, at 500°C - 30 min, at 800°C - 30 min, at 1100°C - 30 min, and 1 h isothermal period at the highest temperature of 1300ºC. After the end of the second isothermal period, the furnace was switched off and the samples were left to cool freely. The aim of this method was to achieve maximum densification of diffusion nature and obtain porous materials with good physicomechanical properties.

Methods

The initial powders and the barium titanate-based ceramic obtained from them were characterized by X-ray powder diffraction, FT-IR spectroscopy, scanning electron microscopy and light microscopy.

- *Infrared spectroscopy*. FT-IR spectra were taken using Tensor 27 FT-IR spectrophotometer (Bruker, Germany) in the interval 400 - 4000 cm^{-1} at a resolution of 1 cm^{-1}. The studies were carried out at room temperature. The sample (0.3 mg) was pressed into KBr (100 mg) pellet at a pressure of 2-4 atm.
- *X-ray powder analysis.* The XRD pattern was recorded using automated computer-controlled XRD system D500 Siemens (Germany) under the following regime: 40 kV, 30 mA, monochromatic copper radiation.
- *Scanning electron microscopy.* The SEM analysis of the ceramic materials obtained was carried out on a scanning electron microscope Tabletop SEM HIROX SH-4000M, 30× - 60 000×, SE&BSE detector, voltage 5 kV - 30 kV, resolution 15 nm. The samples were preliminarily wired with gold.
- *Light microscopy.* The Celestron 5 MP LCD Deluxe digital light microscope was used.

RESULTS AND DISCUSSION

The initial blends and the sintered samples were studied by IR spectroscopy. The IR spectra obtained were analyzed and interpreted and the main functional groups present in the compositions of the samples containing 2% of GnP were established. The results of the FT-IR analysis of blend D0 are presented in tabular form in Table 1 and graphically in Fig. 1.

Table 1. Absorption bands and functional groups present in the composition of sintered ceramic samples containing 2 mass % of graphene nanostructures

Wave numbers, cm^{-1}	Samples from blend D0 sintered at 1300°C	Bond
	3447.49	C-H
	533.35	Ba-Ti-O
	407.57	Ti-O

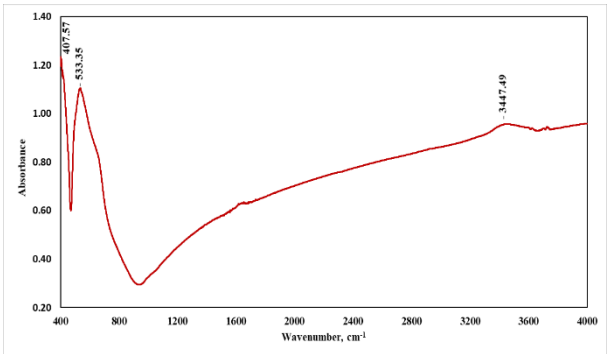

Figure 1. FT-IR spectrum of barium titanate-based sample prepared from blend D0 and sintered at 1300ºC

In the spectra of the samples studied, absorption bands were observed at ~3447.49 cm^{-1} (Fig. 1) which are characteristic of the C–H bond [5] and indicate the presence of carbon containing structures. Most probably, part of the specially introduced graphene structures was burnt during the high-temperature sintering, thus imparting certain porosity within the ceramics obtained.

XRD proved the synthesis of barium titanate ceramics with main phase $BaTiO_3$ (Fig. 2). Its existence was confirmed by FT-IR analysis.

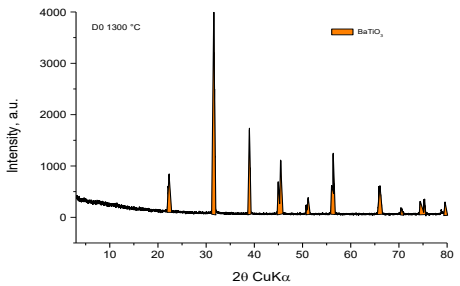

Figure 2. Powder X-ray diffraction pattern of blend D0

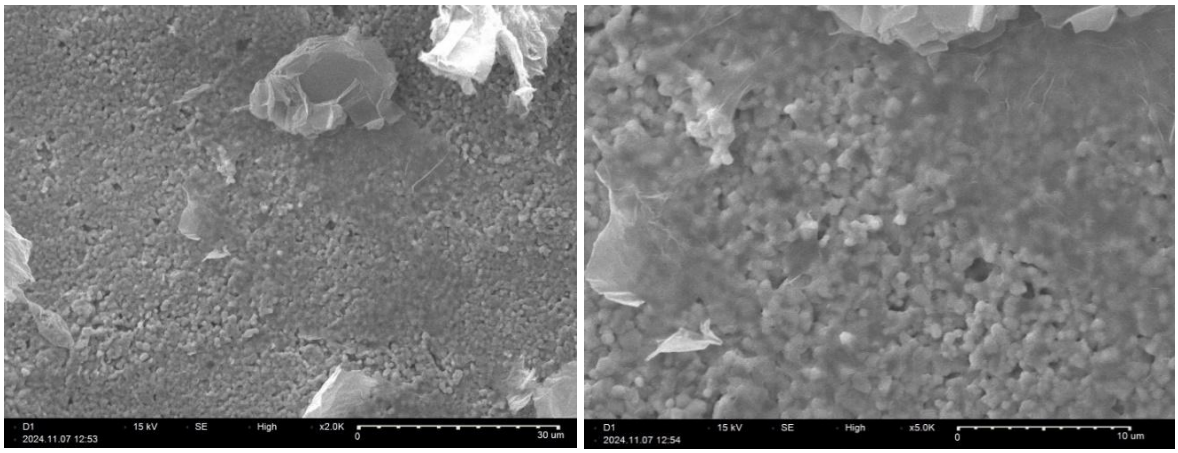

Figure 3. SEM microphotographs of barium titanate-based ceramic samples synthesized from blend D0 at 1300ºC

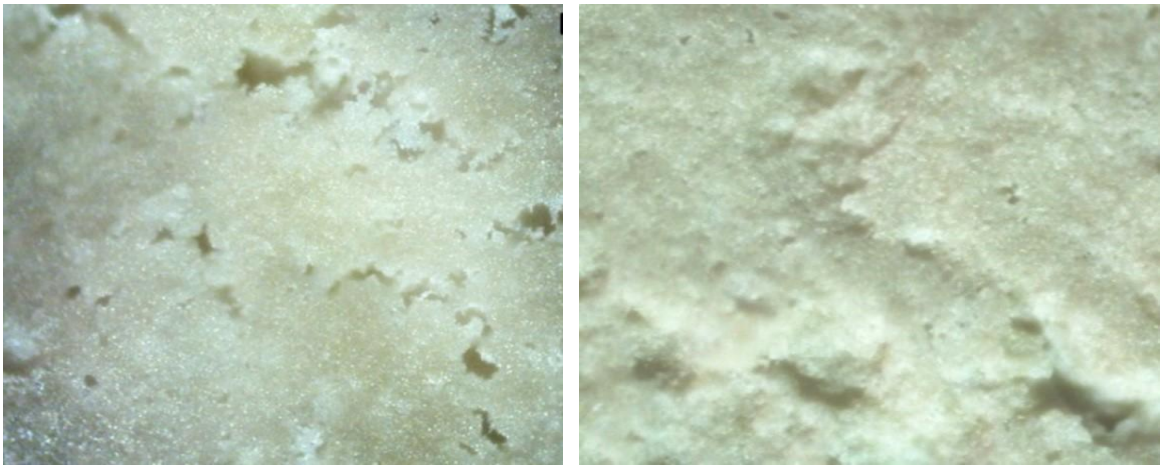

Figure 4. Photographs of the surface of the ceramic materials synthesized

Table 2. Basic physicomechanical properties of the ceramic samples synthesized

Sample № with composition	WA, %	ρ_{app}, g/cm^3	P_{app}, %
D0	0.37	5.51	2.04

The SEM analysis of the ceramic samples obtained revealed finely grained porous structure with grain sizes from 0.5 to 1 μm. SEM images of titanate ceramics with added 2% of graphene nanoplatelets GnP taken at different magnifications are shown in Fig. 3.

The surface of the ceramic samples synthesized with added 2% of graphene GnP was studied by light microscopy. The photographs shown in Figure 4 reveal a relatively homogeneous and finely grained structure. It can be seen that open pores had been formed in some places. Obviously, part of the carbon containing material burned with the increase of the temperature and this resulted in formation of certain porosity in the ceramic.

Some basic physicomechanical properties of the barium titanate-based ceramics with added graphene nanoplatelets were determined: water absorption (WA, %), apparent density (ρ_{app},, g/cm^3) and apparent (open) porosity (P_{app}, %).). The results obtained are presented in Table 2. The apparent density is the ratio between the mass of the material and the volume it occupies including the pores $\rho_{app} = \frac{m}{V}, \frac{kg}{m^3}, \frac{g}{m^3}$. The volume of the pores is usually determined by hydrostatic weighing of water-soaked samples. The apparent density of the samples synthesized was calculated by the expression:

$$\rho_{app} = \frac{m_0 . \rho_m}{V} = \frac{m_0 . \rho_m}{m_1 - m_2}, \frac{kg}{m^3}$$

where: m_0 – mass of the dry sample, kg; m_1 – mass of the water-soaked sample, kg; m_2 – mass of the water-soaked sample weighed under water, kg; V – sample volume, m^3; ρ_m – density of the liquid used, kg/m^3.

The apparent porosity is the ratio between the volumes of the open pores to the volume of the material including all the pores it contains, in %. The apparent porosity is determined by the expression:

$P_{app} = WA.\rho_{app}, \%$ and the water absorption - $WA = (m_1 - m_0).\frac{100}{m_0}$, where - m_0 is the mass of the dry material, g; m_1– mass of the material water soaked at high temperature, g [1].

According to literature data, the density of $BaTiO_3$ is $5.3 \div 5.8\ g/cm^3$ [1].

The data in Table 2 show that the introduction of a small quantity of graphene in the initial blends (2 mass %) followed by solid-state sintering gave barium titanate-based ceramics with sufficient density (close to the theoretical one), minimal water absorption and some open porosity. Therefore, the graphene structures introduced even in small quantities play the role of pore-forming agents in the ceramics. This observation was confirmed by the results obtained from the analyses carried out (infrared spectroscopy, scanning electron microscopy and light microscopy), as discussed above.

CONCLUSIONS

As a result of the research carried out, samples of barium titanate ceramics were synthesized using the diffusion-type solid-state sintering method. The samples were prepared from initial blends where a small amount of graphene nanostructures (2 mass %) was introduced. For the characterization of the initial blends and the ceramics obtained from them, the methods of X-ray phase analysis, infrared spectroscopy, scanning electron microscopy and light microscopy were used. The main crystalline phases present in the ceramics synthesized were determined by XRD. The analysis proved the synthesis of ceramic with main phase $BaTiO_3$. The main functional groups present in the compositions of the ceramic samples synthesized were identified by FT-IR while the morphology and structure were studied by SEM. The results of the analyses showed that the introduced nano-additive initiated the formation of a finely grained porous structure with grain sizes from 0.5 to 1 μm. The surface of the $BaTiO_3$ ceramics prepared by sintering at 1300ºC was investigated by light microscopy to find that the samples prepared from blend D0 had relatively homogeneous and finely grained surface. Some physicomechanical properties of the barium titanate ceramics synthesized were also determined. It had sufficient density, close to the theoretical one – 5.51 g/cm^3, certain open porosity – 2.04 % and minimal water absorption – 0.37 %. The results of the studies carried out indicate that, most probably, the introduction of small quantities of graphene in the initial blends, followed by high temperature sintering resulted in burning of part of the graphene structures and imparted some porosity to the ceramic samples obtained.

The porous ceramic materials can be used as heat insulation materials, filtering components, catalytic substrates and dielectric materials in capacitors. Given the characteristics of the synthesized barium titanate ceramics, its dielectric permeability needs to be determined to evaluate its potential application in capacitor devices.

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REFERENCES

1. A. Gerasimov, A. Atanasov, V. Toshev, D. Petkov, D. Ivanov, L. Georgieva, L. Pavlova, H. Drenska, P. Vinarov, P. Petrov, S. Bachvarov, S. Panova, S. Bagarov, S. Serbezov, S. Stefanov, S. Dzhambazov, T. Stojkova, T. Datskova, H. Berlinov, Technology of Ceramic Products and Materials, S. Bachvarov (ed.), Saraswati press, Sofia, Bulgaria, 2003, p. 889.
2. Zh. Bi, Sh. Zhou, J. Ye, N. Wang, F. Shang, J. Xu, H. Wang, *Ceramics International*, **51 (12)**, Part A, 16052 (2025).
3. J. Zhou, Z. Xu, H. Yang, L. Chu, L. Chen, H. Li, J. Ding, S. Ran, Zh. Sun, X. Hao, *Chem. Eng. J.,* **487**, 150476 (2024).
4. H. Porwal, S. Grasso, MJ. Reece, *Adv. Appl. Ceram.,* **112**, 443 (2013).
5. M. Georgieva, A. Georgieva, K. Panayotova, F. Yovkova, I. Markovska, *Bulg. Chem. Commun.*, **55 (3),** 344 (2023).
6. Y. Huang, Ch. Wan, *J. of Adv. Ceram*., **9 (3),** 271 (2020).
7. I. Ali, X. Mbianda, A. Burakov, E. Galunin, I. Burakova, E. Mkrtchyan, A. Tkachev, V. Grachev, *Environ. Int*., **127**, 160 (2019).
8. M. Li, X. Yin, L. Chen, M. Han, L. Cheng, L. Zhang, *Ceram. Int*, **42 (6)**, 7099 (2016).