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THE TECHNOLOGY AND STRUCTURAL PROPERTIES OF SPECIAL GLASS MODIFIED $(Ba0.6Pb0.4)TiO_3$ CERAMICS

The present paper widely describes the details of technology of $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics modified with PbO-B_2O_3-Al_2O_3-WO_3 special glass, as well as the influence of admixture on the microstructure and crystal structure of basic material. The microstructure investigations reveal the significant increase of grain size and a decrease of pores participation in volume of modified samples, whereas the X-Ray Diffraction (XRD) measurements show a decrease of the volume of unit cell. The obtained results are discussed due to processes occurring during the sintering process at high temperature.

Keywords: $(Ba_xPb_{1-x})TiO_3$ ceramics, special glass, SEM microstructure, XRD measurements

1. Introduction

Although the materials possessing the perovskite structure have been known for decades, they still attract attention of scientists due to their interesting properties. These properties makes them very useful in the modern technology, for example in applications such as corrosion resistant coating for a positive battery electrode [1] and capacitor barrier layers [2, 3].

Barium titanate and lead titanate are the most popular members of perovskite materials. Both ceramics are the model, fundamental ferroelectric materials, which, at room temperature, show spontaneous polarization. As it is commonly known the appearance of spontaneous polarization in the $BaTiO_3$ and $PbTiO_3$ is a consequence of displacement of the ions within the tetragonal unit cell. Namely bivalent barium or lead ions occupy each corner position, with the tetravalent titanium ion near, but just above, the center of the cell. The oxygen ions are moved below center of the (001) plane and just below the centers of the (100) and (010). Such location of ions in unit cell caused that the centers of positive and negative charge do not coincide, which lead, in consequence, to appearing of spontaneous polarization [4]. Connection of barium titanate and lead titanate gives a solid solution, with the excellent piezoelectric and ferroelectric properties. The increase of lead titanate molar fraction in $(Ba_xPb_{1-x})TiO_3$ system causes the Curie temperature shift to high values and decrease of maximum permittivity values [5].

For few decades it has been known, that the proper modification of materials belonging to $(Ba_xPb_{1-x})TiO_3$ system results in appearance of semiconductive properties with strong positive temperature coefficient of resistivity (PTCR) [6, 7, 8]. The dopants often, but not only, are the rare-earth elements [8]. In literature, numerous references related to modify the BPT system with special glass appear. The special glass is a source of ions, which allow to achieve the semiconductive properties with positive resistivity temperature coefficient. The choice of glass is never accidental and is based on the following conditions:

a) ability to interact with the crystalline phase of PBT,
b) low viscosity at the temperature of ceramics sintering,
c) propensity to crystallize.

An example of glass fulfilling these conditions is PbO-B_2O_3-Al_2O_3-WO_3 system, with chemical composition as given in Table 1.

TABLE 1

Composition of the special glass

Glass composition [wt. %]			
PbO	B_2O_3	Al_2O_3	WO_3
73.4	18.4	5.2	3.0

The properties of the glass are widely discussed in the papers [9, 10], so they will not be described in the following papier. The investigations confirm the amorphous character of glass and presence of BO_3 and BO_4 groups.

The mentioned glass was introduced as a dopant to the synthesis powder of $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics. The main aim of hereby article is to present the details of technology as well as the admixture influence on crystal structure and microstructure.

2. Experimental

The technological process of receiving of $(Ba_{0.6}Pb_{0.4})TiO_3$ (BPTO) ceramics modified with special glass comprised

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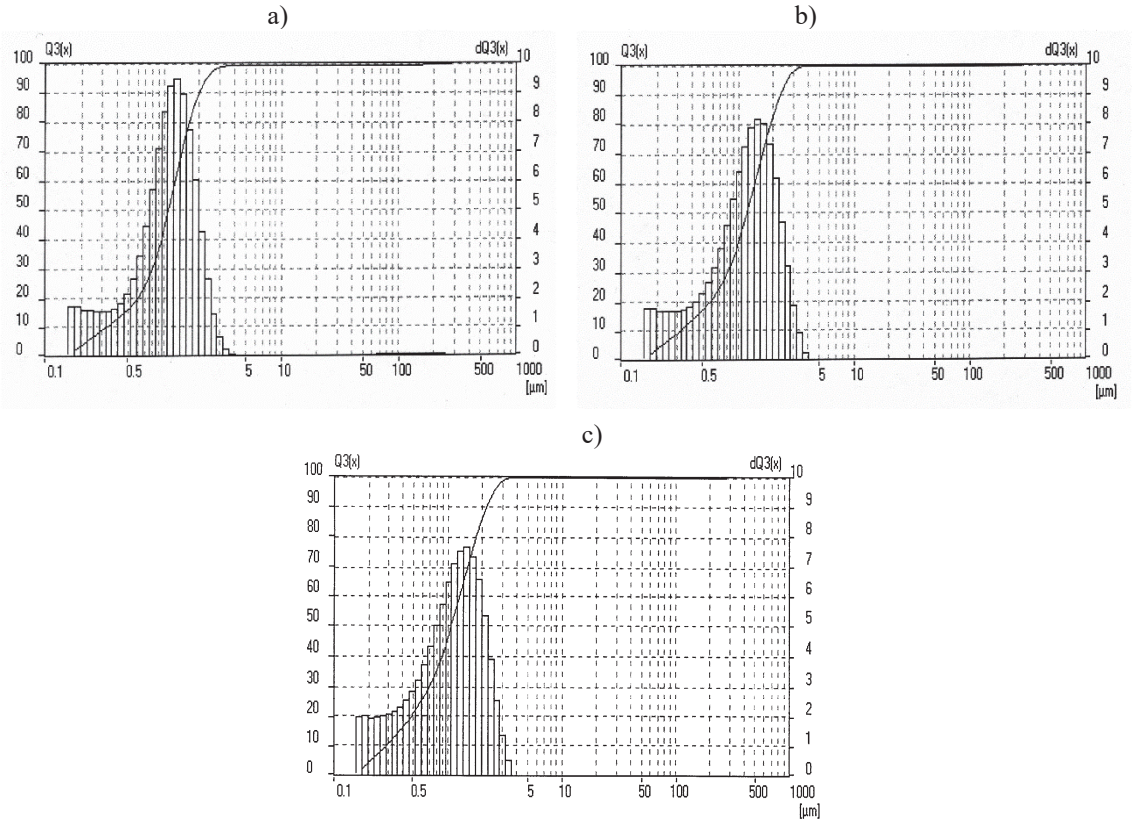

Fig. 1. The particle size distribution of the ceramic powder $(Ba_{0.6}Pb_{0.4})TiO_3$ without dopant (a), containing 1.5 wt.% of glass (b) and 6.0 wt.% glass (c)

three basic steps. The first stage was associated with obtaining special glass containing W^{6+} cations. The appropriate amounts of lead oxide, boron oxide, aluminum oxide, tungsten oxide were prepared, then substrates were mixed together in an agate ball mill for 2h. The process of melting of oxides mixture was carried out at 900°C. After melting the liquid mixture of oxides was rapidly solidified by pouring on a steel surface. The second stage of technology was connected with the preparation and synthesis of the $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics powder. A stoichiometric mixture of oxides $BaCO_3$, PbO, TiO_2 was thoroughly prepared, corresponding to the chemical solid-phase reaction (1):

$$3\,BaCO_3 + 2\,PbO + 5\,TiO_2 \rightarrow 5\,(Ba_{0.6}Pb_{0.4})\,TiO_3 + 3\,CO_2\uparrow \quad (1)$$

The synthesis was carried out at $T = 950$°C for 4h. After the thermal treatment the moldings were crushed and milled. The third stage concerned the introduction of special glass dopant in an amount of 1.5; 4.0; 6.0 and 8.0 wt.% of the basic ceramic powder. Then the modified powders were milled in a planetary mill. After the process an analysis of particle size distribution of the ceramic powder $(Ba_{0.6}Pb_{0.4})TiO_3$ was conducted using a laser particle meter – Analysette 22 . The distribution of particle sizes for pure BPTO as well as the ones containing glass in an amount of 1.5 wt.% and 6.0 wt.% is shown in Fig. 1.

As can be seen above the presented distribution curves are homogeneous and their shape is close to Gaussian. The grain size does not exceed 5 µm, and the largest percentage of the powdery material have a grain size between 1-2 µm. With increase of dopant distribution curve becomes more diffuse, and the participation of particles with the size 1-2 µm in whole amount of particles decreases from 95% to 75%. After the process of milling the obtained powders were pressed into pellets (discs) with a diameter of 0.01 meter. The first sintering was carried out at T = 1050°C for t = 4h. Then, the procedure of crushing, grinding, pressing was repeated. The final sintering was conducted at T = 1200°C for t = 4h. Scheme of manufacturing technology of $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics modified with special glass is shown in Fig. 2.

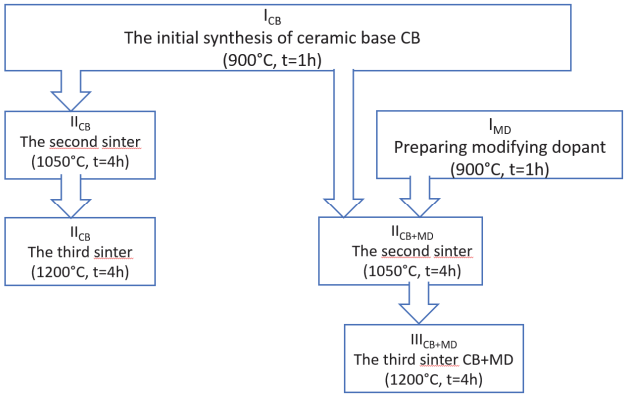

Fig. 2. Scheme of manufacturing technology of $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics modified with special glass

The crystalline structure of obtained ceramic samples was investigated using XRD diffraction method. XRD measurements were carried out on powdered samples using a high resolution INEL diffractometer with filtered Cu Kα1

radiation (40 kV, 30 mA). The powder diffraction spectrum was measured at room temperature from 5 to 120° in 2θ.

Stereological analysis of these materials was carried out using optical metallographic microscope Olympus BX-60 M. The microscopic observation is the simplest method allowing an initial assessment of the quality of the obtained ceramics. Such an assessment, although subjective, however, is the fastest and cheapest way to pre-select samples.

3. Results and discussion

In order to determine the effect of the dopant on the crystal structure of the glass ceramics XRD studies were carried out. The X-ray diffraction patterns of discussed materials are shown in Fig. 3.

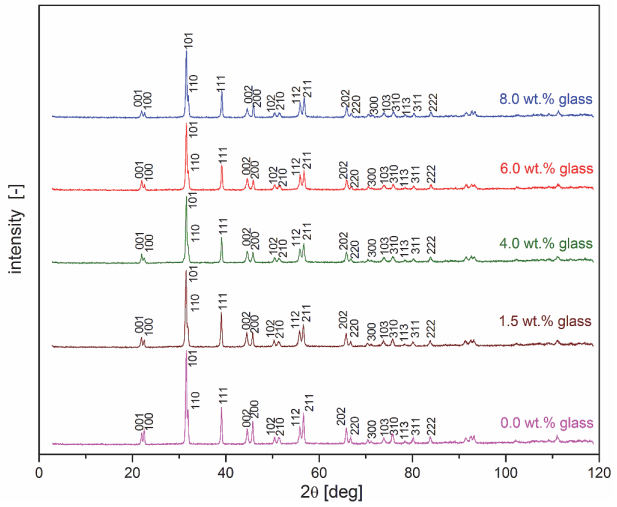

Fig. 3. The evolution of the X-ray diffraction peaks of $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics with increased concentration of glass PbO - B_2O_3 - Al_2O_3 - WO_3

Comparison of diffraction patterns indicates that with the increase of glass modifier the intensity of diffraction maxima decreased. The location and intensity of all diffraction lines in the range of measured angle were compared with the reference patterns from JPCDS-ICDD. The results of analysis indicated, that at room temperature, discussed material are monophasic and show tetragonal structure ($a_0=b_0\neq c_0$, $\alpha=\beta=\gamma=90°$). The symmetry of the crystal lattice may be described by space group (*P4mm*) belonging to the class of tetragonal bipyramids and have four planes of symmetry intersect in a fourfold symmetry axis of the pole.

The Rietveld method was used to determinate the unit cell parameters, volume (V) and a uniform deformation of the tetragonal parameter ($\delta_T = |1-c_0/a_0|$). The value of δT coefficient is equal to $2.47x10^{-2}$ for pour BPTO ceramics and increase with the increasing of modifier content. For ceramics containing 8.0 wt.% of dopant the $\delta_T = 2.80x10^{-2}$. The observed change of δ_T indicate, that the admixture of lead-boron glass is connected with simultaneous decrease of a_0 parameter and increase of the c_0 parameter of tetragonal unit cell (Table. 2). Described changes resulted in a change of unit cell volume. For low concentration of glass dopant the changes in volume are not significant, but a sharp decrease in volume is observed for 6wt.% modifier concentration (Fig. 4).

TABLE 2
The value of lattice parameter of special glass modified $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics

The dopant glass [wt.%]	a_0 [nm]	c_0 [nm]
0.0	0.3959	0.4057
1.5	0.3959	0.4061
4.0	0.3959	0.4062
6.0	0.3955	0.4063
8.0	0.3955	0.4065

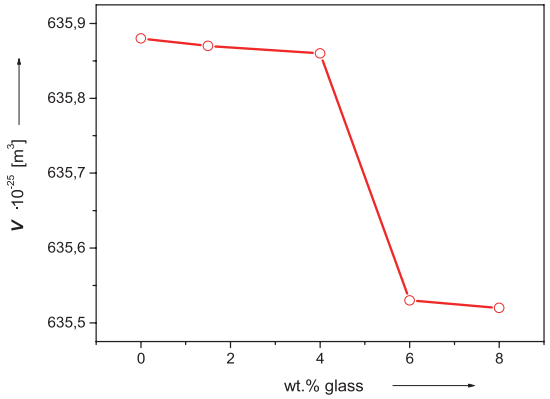

Fig. 4. The dependence of the volume of the $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics unit cell versus the quantity of glass introduced

The observed reduction of the unit cell volume with increase of doped glass amounts, can be due to the partial replacement of the Ti^{4+} ions by W^{6+} ions. The process may be described by the chemical reaction (2):

$$(Ba^{2+}_{(1-x)}\,Pb^{2+}_{x})Ti^{4+}\,O^{2-}_{3} + yW^{6+}\,O^{2-}_{3} \rightarrow (Ba^{2+}_{(1-x)}\,Pb^{2+}_{x})(Ti^{4+}_{1-y}\,W^{6+}_{y})O^{2-}_{3} + ye^{-} \quad (2)$$

The tungsten ions are smaller than the titanium ones – the atomic radius of tungsten is 0.137 nm, and the ionic radius for W^{+2} is 0.042 nm, whereas the titanium atomic radius and ionic radius are respectively 0.1460 nm and 0.0605 nm. The increase of dopant concentration is connected with the increase of tungsten ions content in the volume of sample, and shrinkages of the $(Ba_{0.6}Pb_{0.4})TiO_3$ unit cell (Table 3). The observed decrease of unit cell volume is the direct confirmation of assumed substitution.

TABLE 3
The glass dopant in weight and molar percent and the concentration of tungsten in the ceramic atomic percentage

glass		W^{6+} [at.%]
[wt.%]	[mol.%]	
1.5	2.5	0.02
4.0	6.8	0.05
6.0	9.7	0.08
8.0	13	0.1

Knowing the unit cell volume and its weight allowed to determine the theoretical density of discussed ceramic materials. The density of each sample was compared with the experimental one, obtained by the Archimedes displacement

method (Table 4). The relative density is smallest for a sample without admixture and increase almost linearly with the increasing glass content (Fig. 5), indicating the gradual improvement of ceramics quality. That fact could be explained basing on the phenomena which occurred during the sintering processes. Namely the glass dopant, at high sintering temperature, forms a liquid phase, which not only fills the empty places, but also favors grains shift – in effect the grains occupy the less volume and the content of pores is drastically reduced. Liquid phase also prevents the evaporation of volatile components (PbO) from ceramics material, which helps to reduce the amount of pores even more.

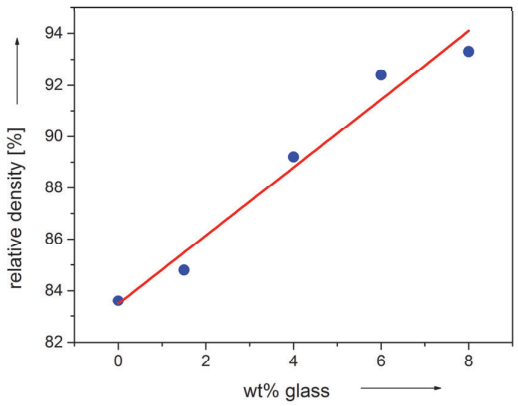

Fig. 5. The dependence of relative density of ceramics $(Ba_{0.6}Pb_{0.4})TiO_3$ versus the amount of glass doped

TABLE 4
The density of the ceramic samples $(Ba_{0.6}Pb_{0.4})TiO_3$ with different content of dopant

The dopant glass [wt.%]	ρ_{rtg} [kg/m^3]	ρ_{exp} [kg/m^3]	ρ_{exp}/ρ_{rtg}
0.0	6869.7	5743	83.6
1.5	6869.8	5826	84.8
4.0	6869.9	6131	89.2
6.0	6873.5	6348	92.4
8.0	6873.6	6411	93.3

The effects described above found the confirmation in the results of microstructure investigation (Fig. 6 and Fig. 7).

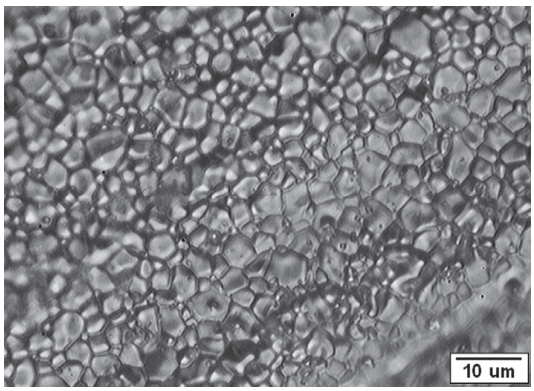

Fig. 6. The microstructure of $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics

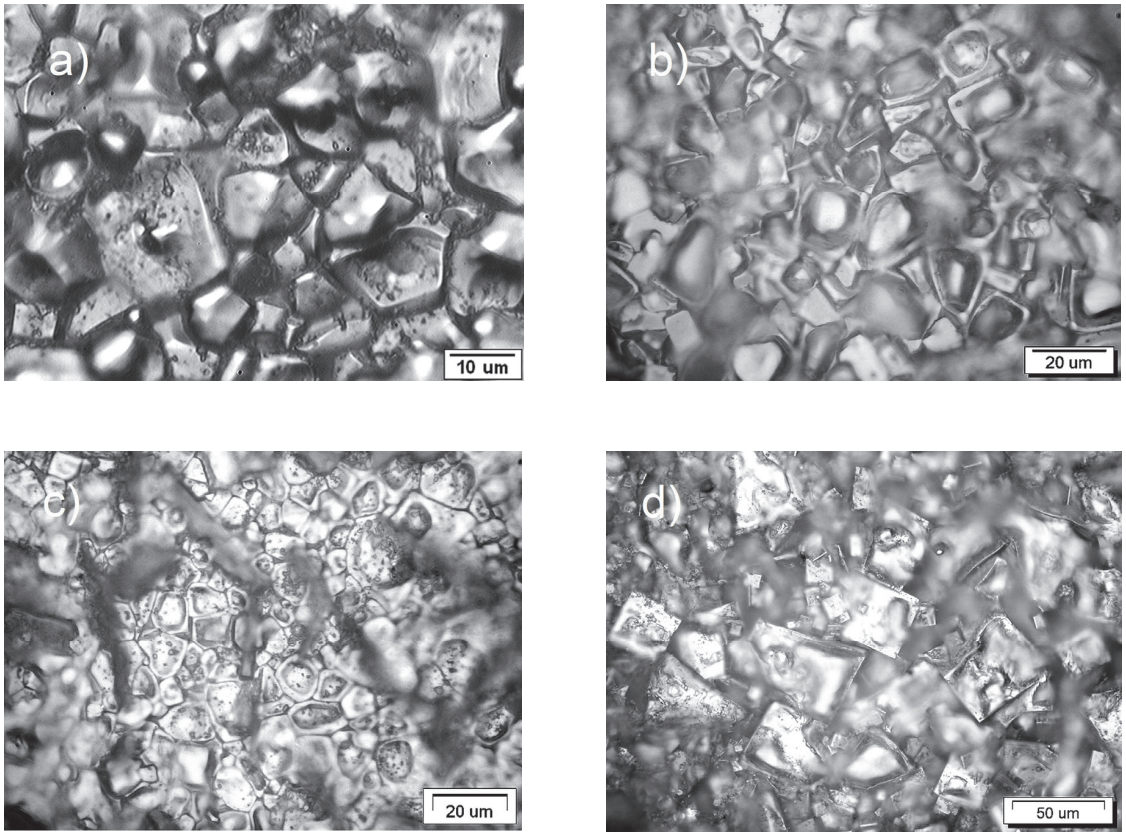

Fig. 7. The microstructure of $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics with different content of glass, $(Ba_{0.6}Pb_{0.4})TiO_3$ + 1.5 wt.% glass (a), $(Ba_{0.6}Pb_{0.4})TiO_3$ + 4.0 wt.% glass (b), $(Ba_{0.6}Pb_{0.4})TiO_3$ + 6.0 wt.% glass (c) and $(Ba_{0.6}Pb_{0.4})TiO_3$ + 8.0 wt.% glass (d)

The surface of BPTO ceramics consists of single, well-developed grains separated by clear boundaries. The structure is not homogenous, it includes areas of fine and coarse-grained regions. The glass admixture coats the grains. For materials with the glass content of 1.5, 4.0 and 6.0 wt.% the grain structure is build by the grains with sharp edges and of high heterogeneity of size, but their size is comparable regardless of the dopant. When the concentration of admixture is 8.0 wt.% the significant increase of grains is observed. Generally the grains size changes from $\overline{d}$=3.20 μm for undoped ceramics, up to $\overline{d}$ =50 μm for ceramics containing 8.0 wt.% of glass.

4. Conclusions

The investigations presented above clearly show that the admixture of special glass to base $(Ba_{0.6}Pb_{0.4})TiO_3$ ceramics favors the formation of microstructure with largely-sized grains and low contribution of pores. The volume of crystal unit cell decreases with the dopant concentration due to the phenomena, which occurred during the sintering process. At high sintering temperature the admixture is liquid and in such form the shifting of grains is much easier and leads to filling the empty spaces. In result the density of samples increases and their quality significantly improves.

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