A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 58 2013 Issue 4
DOI: 10.2478/amm-2013-0182

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# FABRICATION OF $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ CERAMICS BY CONVENTIONAL SOLID STATE REACTION METHOD

# OTRZYMYWANIE CERAMIKI 0,95$BaTiO_3$-0,05 $Pb(Mg_{1/3}Nb_{2/3})O_3$ METODĄ KONWENCJONALNĄ

The possibility to obtain of ceramic solid solution between barium titanate and lead magnesium niobate by two-step sintering technique through conventional solid-state reaction method has been investigated. In the first step $MgNb_2O_6$ has been synthesized. In the second step $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ has been obtained using $MgNb_2O_6$, PbO and $BaTiO_3$. The two-step sintering technique is effective for the synthesized of $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics. Single-phase (pyrochlore-free) ceramics with perovskite phase were obtained.

*Keywords*: $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$, barium titanate, $BaTiO_3$, lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$

Badano możliwość otrzymania ceramicznego roztworu stałego tytanianu baru i niobianu ołowiu magnezu metodą reakcji w fazie stałej. Ceramikę otrzymano dwuetapowo. W pierwszym etapie zsyntezowano $MgNb_2O_6$. W drugim etapie z $MgNb_2O_6$, PbO i $BaTiO_3$ otrzymano 0,95$BaTiO_3$-0,05$Pb(Mg_{1/3}Nb_{2/3})O_3$. Użyta metoda dwuetapowa okazała się skuteczna dla otrzymania ceramiki 0,95$BaTiO_3$-0,05$Pb(Mg_{1/3}Nb_{2/3})O_3$. Otrzymano jednofazową ceramikę o strukturze typu perowskitu, bez niepożądanej fazy pirochloru.

## 1. Introduction

The following article describes obtention of ceramic solid solution between barium titanate $BaTiO_3$ and lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ with the composition: $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$. Barium titanate (BT) and lead magnesium niobate (PMN) ceramics have been investigated extensively, both from academic and commercial viewpoints. $BaTiO_3$ is a ferroelectric, whereas lead magnesium niobate is a lead-based relaxor material. Barium titanate is one of the most widely used ceramic materials in industry due to its excellent dielectric properties [1, 2, 3]. Also lead magnesium niobate is most widely studied because of its excellent dielectric and electrostrictive properties, which makes it very promising candidate for applications such as multilayer capacitors, sensors and actuators [4]. The ceramics solid solutions between $BaTiO_3$ and PMN are expected to be interesting materials. However there are scarce literature reports concerning its preparation. Such a ceramics is difficult to obtain.

## 2. Experimental procedure

Barium titanate-lead magnesium niobate ceramics $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ were prepared by two-step sintering technique through conventional solid-state reaction method. The major technological issue is the fact, that both ceramics $BaTiO_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$ require completely different synthesis and densification conditions. Traditionally, barium titanate is prepared by a solid-state reaction between $BaCO_3$ and $TiO_2$. Calcination requires high temperatures between 1350°C and 1400°C [5, 6]. Due to lead evaporation, ceramic $Pb(Mg_{1/3}Nb_{2/3})O_3$ is obtained in temperatures not higher than 1250°C, for a short time (up to two hours), with high speed of heating and cooling [7]. In such conditions it is not possibile to prepare a dense $BaTiO_3$. Commercially $BaTiO_3$ (Inframat Advanced Materials) was used. The flowchart for the fabrication of $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics is shown in Fig. 1.

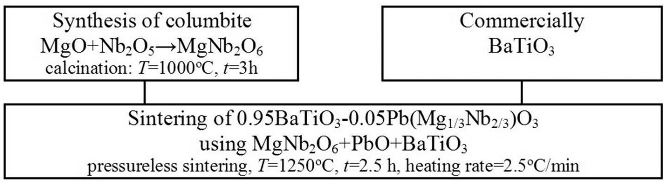


Fig. 1. Flowchart for the preparation of $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics

The main problem in fabrication of pure perovskite PMN ceramics is formation of the unwanted pyrochlore phase with low dielectric constant which decreases the dielectric and electromechanical performances of the resulting material. Swartz et al. [8] minimized the amount of the pyrochlore

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phase using the so-called "columbite precursor method". This route consists in the precalcining of a stoichiometric mixture of MgO and $Nb_2O_5$ in order to form $MgNb_2O_6$ (which has a columbite structure), which subsequently reacts with PbO. First magnesium oxide MgO (Fluka) and niobium pentoxide $Nb_2O_5$ (Aldrich) with 5% excess MgO were ball-milled in ethanol using zirconia balls for 12 h by Pulverisette 6 Planetary Mono Ball Mill (Fritsch). Rotational speed of milling chamber was 300 rpm. Dried powders were calcined at 1000°C for 3 h in an alumina crucible to form magnesium niobate $MgNb_2O_6$ (columbite). In the second step, the appropriate amount of barium titanate $BaTiO_3$ (Inframat Advanced Materials) and lead oxide PbO (Chempur) were weighed and mixed with magnesium niobate $MgNb_2O_6$ by ball milling in ethanol using zirconia balls for 24 h by Pulverisette 6 Planetary Mono Ball Mill (Fritsch). Rotational speed of milling chamber was 300 rpm. 3 mol% excess of PbO was added. The obtained powders are uniaxially pressed into disk samples with a diameter of 10 mm and a thickness of 1 mm. Polyvinyl alcohol was used as binder.

The samples were pressureless sintered in sealed alumina crucibles at 1250°C for 2.5 h with a heating rate of 2.5°C/min, and then furnace cooled. PbO volatilization during sintering was minimized by surrounding each pellet with "atmosphere powder" of chemical composition 80vol% $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ and 20vol% PbO.

## 3. Results and discussion

The morphology of fresh fracture surfaces were studied by scanning electron microscopy HITACHI S-4700. The microstructure is fine-grained with polyhedral grains (Fig. 2). An energy dispersive X-ray spectroscopy (EDS) attached to the SEM was used to analyze chemical compositions. Five areas of 60 $\mu$m× 45 $\mu$m were EDS-analyzed. The small deviations from theoretical composition of $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ have occurred but they do not exceed a value of ±3% what is consistent with resolution of the utilized method of investigation.

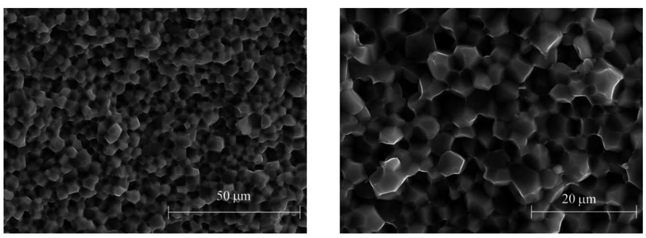


Fig. 2. Microstructure of fresh fracture surfaces of $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics sintered at 1250°C for 2.5 h

The bulk density was measured using the Archimedes' method. Bulk density of sintered $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ pellets was 5560 kg/m$^3$. Density of used $BaTiO_3$ (Inframat Advanced Materials) is 5850 kg/m$^3$, according to literature density of PMN is 6670 to 7610 kg/m$^3$ [7].

The sintered $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics were examined by XRD using Philips X'Pert APD diffractometer with CuK$\alpha$ radiation. Because this is a new material it don't own a template. The ICSD-67520 card for $BaTiO_3$ have been used. The major peak (222) of $Pb_3Nb_4O_{13}$ pyrochlore phase at 2Θ =29.2° is not found. Single-phase ceramics with tetragonal *P4mm* structure were obtained (Fig. 3). Lattice parameters are: $a$ =0.40074 nm, $b$ =0.40074, $c$ =0.40122 nm.

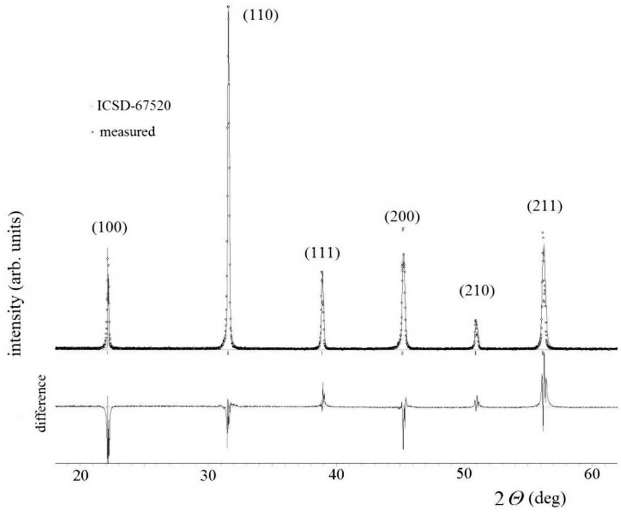


Fig. 3. The XRD profile of $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics sintered at 1250°C for 2.5 h

The dielectric properties were investigated as functions of temperature (from 40°C to 150°C) and frequency (from $f$ =0.1 kHz to 200 kHz). Results of investigations of dielectric permittivity vs. temperature are presented in Fig.4. The temperature of maximum of dielectric permittivity amount to 85°C (for $f$ =1 kHz). The Curie point of $BaTiO_3$ is 120°C [2]. An 5% amount of $Pb(Mg_{1/3}Nb_{2/3})O_3$ leads to the decrease of temperature of maximum of dielectric permittivity at 35°C.

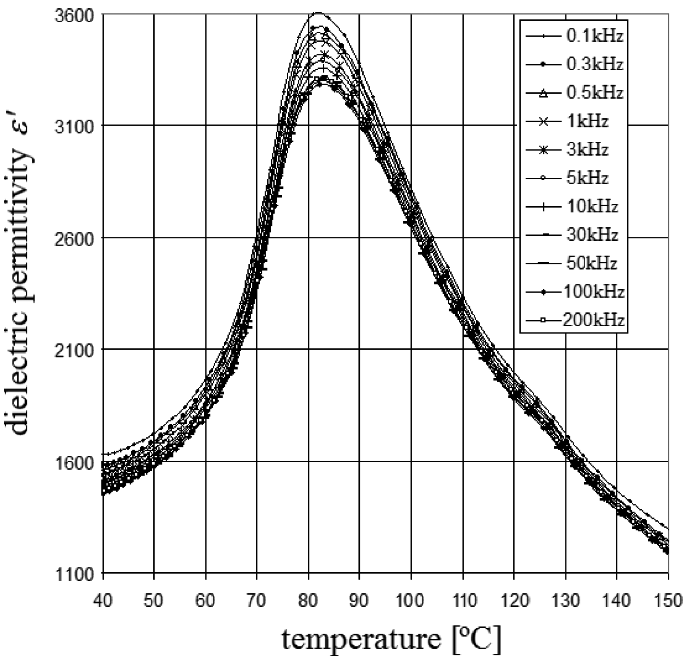


Fig. 4. Temperature dependences of dielectric permittivity of $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics sintered at 1250°C for 2.5 h (on cooling)

## 4. Conclusion

This paper reports the successful synthesis of a single-phase (pyrochlore-free) $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics. The ceramics solid solutions between barium titanate and lead magnesium niobate were prepared by two-steps sintering technique through conventional solid-state reaction method. In the first step $MgNb_2O_6$ (which has a columbite structure) has been synthesized. In the second step $BaTiO_3$, PbO and $MgNb_2O_6$ powders are used to obtain $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$. Tests of chemical composition confirmed the qualitative and quantitative chemical composition of ceramics. Single-phase ceramics with perovskite phase were obtained. It has been found that the two-step sintering technique is effective for the synthesized of $0.95BaTiO_3$-$0.05Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics.

**Acknowledgements**

This work has been supported by the Ministry of Science and Higher Education of Poland (Grant No. 2012/05/B/ST5/00371).

*Received: 20 September 2013.*

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