CHARACTERIZATION OF $BaMg_{1/3}(Ta_{1-x}V_x)_{2/3}O_3$ (x = 0.1, 0.2) CERAMICS PREPARED BY MODIFIED PECHINI METHOD

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Pulberile oxidice sintetizate prin metode chimice în soluţie prezintă o omogenitate chimică mai bună şi o dimensiune a particulelor mai redusă decât cele obţinute prin metoda reacţiilor în fază solidă, aceste caracteristici conducând la îmbunătăţirea sinterabilităţii. În această lucrare, prezentăm sinteza şi caracterizarea ceramicilor BaMg1/3(Ta1-xVx)2/3O3 (x = 0.1, 0.2) obţinute prin intermediul metodei Pechini modificate. Pentru caracterizarea compoziţională, structurală şi morfologică au fost utilizate analizele XRD şi SEM. Pulberile preparate prin metoda Pechini, dar şi ceramicile sinterizate obţinute din aceste pulberi prezintă structură cubică. Proprietăţile dielectrice ale ceramicilor BaMg1/3(Ta1-xVx)2/3O3 (x = 0.1, 0.2) obţinute prin această metodă au fost măsurate în intervalul de microunde, cea mai ridicată valoare Qxf fiind 63044 GHz.

Oxide powders synthesized by soft chemistry methods possess better chemical homogeneity and finer particles size than those prepared by the solid-state reaction method, these features leading to the improvement of the sinterability. In this paper, we report the synthesis and characterization of $BaMg_{1/3}(Ta_{1-x}V_x)_{2/3}O_3$ (x = 0.1, 0.2) ceramics obtained via modified Pechini method. XRD and SEM analyses were employed for compositional, structural and morphological characterization. The powders prepared by Pechini method, as well as the sintered ceramics obtained from these powders have cubic structure. The dielectric properties of $BaMg_{1/3}(Ta_{1-x}V_x)_{2/3}O_3$ (x = 0.1, 0.2) ceramics obtained by this method were measured in the microwave range, the highest Qxf value being 63044 GHz.

Keywords: Pechini method, nanopowders, BMT-based ceramics, microwave dielectric ceramics

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1. Introduction

In recent years, the demand for dielectric resonators has been increasing owing to their usage in wireless communications. In this regard, microwave dielectric ceramics are helpful due to their technologically congruent properties, as well as the intrinsic ability of reduced component sizes. There are three important parameters that a dielectric resonator material should have, so that it can meet the desired requirements: a high dielectric constant (ε_r), a low loss at microwave frequencies (usually expressed as a high $Q \times f$ value) and a near-zero value of the temperature coefficient of the resonant frequency (τ_f). These are essential for a stable resonant frequency, possible miniaturization of the device and temperature stabile circuits, respectively. [1, 2]

$BaMg_{1/3}Ta_{2/3}O_3$ (BMT) ceramic has a complex perovskite structure and shows $Q \times f$ values up to 400 THz at frequencies close to 10 GHz [2]. A compromise on the microwave dielectric properties is made by replacing tantalum with less expensive niobium ions. The common method for preparation of BMT-based ceramics is the conventional solid-state reaction method. However, in order to achieve very good dielectric properties, this method requires high sintering temperature (~ 1600 °C) and long annealing time (~ 100 h) [2]. Several authors reported improvement in sinterability by using sintering aids or dopants or by adding glasses [2, 3].

In order to overcome the difficulties of the solid-state reaction method and to synthesize nanocrystalline fine particles at relatively lower temperatures, wet-chemical techniques are being employed to obtain BMT-based nanopowders with high sinterability [4, 5].

In this paper, we report a study regarding the synthesis of $BaMg_{1/3}(Ta_{1-x}V_x)_{2/3}O_3$ (x = 0.1, 0.2) (BMTV) solid solution powders by modified Pechini method and the obtaining of the corresponding ceramics. Pechini method has the advantage of mixing ions on the atomic scale in liquid phase, which yields pure nanopowders. The dielectric properties of BMTV ceramics produced from the Pechini powders have been investigated in detail.

2. Experimental procedure

BMTV powders were prepared by a modified Pechini method that was presented elsewhere [6]. Barium carbonate (Fluka, >99%), tetrahydrated magnesium acetate (Merck, >99%), tantalum butoxide (Aldrich, 98%) and vanadium chloride (Aldrich, >99%) were used as sources of metallic cations.

Briefly, to magnesium acetate, vanadium chloride and citric acid (CA) dissolved in ethylene glycol, tantalum butoxide was added in inert atmosphere, corresponding to a molar ratio (Mg + Ta + V) : (CA), 1:2. Then, barium citrate

obtained by dissolving barium carbonate in 4M aqueous solution of citric acid was added and Ba-Mg-Ta citrate gel was formed. This was polymerized at 135 °C for 10 h. The precursor was burned at 450 °C for 2 h, for organic part removal, resulting a residue powder, which was calcined at 800 °C for 2 h, in air, in order to obtain single phase BMTV crystalline powder. The oxide powder was uniaxial pressed and sintered at 1500 ° or 1600 °C for 4 h, in air.

The oxide powders and the ceramic samples were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). A Rigaku Miniflex II X-ray diffractometer was used to identify the crystalline phases. The morphology of the powders was visualized by a Quanta Inspect F scanning electron microscope. The microstructure of the sintered ceramics was analyzed by a Hitachi S-2600N scanning electron microscope. The relative density was determined by Archimede's method, in alcohol. The crystallites average size values were calculated using Rigaku PDXL software. The dielectric properties were investigated in the microwave domain, at room temperature, by using the Hakki and Coleman dielectric resonator method. A computer aided measurement system containing an HP 8757 C scalar network analyzer and an HP 8350 B sweep oscillator was used.

3. Results and discussion

The XRD patterns of BMTV solid solution powders calcined at 800 °C are shown in Fig. 1. $BaMg_{1/3}(Ta_{0.9}V_{0.1})_{2/3}O_3$ XRD pattern contains only perovskite single phase with a high crystallinity and a cubic symmetry (ICDD 871733).

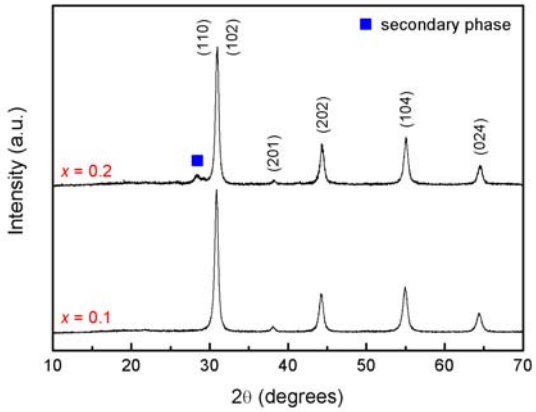

Fig. 1. XRD patterns of BMTV powders

$BaMg_{1/3}(Ta_{0.8}V_{0.2})_{2/3}O_3$ XRD pattern presents, besides the perovskite characteristic peaks, a small amount of secondary phase, most likely VO_2. The behaviour of $BaMg_{1/3}(Ta_{0.8}V_{0.2})_{2/3}O_3$ powder is different from

$BaMg_{1/3}(Ta_{0.8}Nb_{0.2})_{2/3}O_3$ powder obtained by the same method and calcined at the same temperature, for which no secondary phase was identified in the XRD pattern [6].

The SEM images of BMTV powders calcined at 800 °C (Fig. 2) indicate the presence of individual particles that have the tendency to form agglomerates. The particles with spherical shape are nanosized (diameters smaller than 35 nm). It can be noticed that the increasing of vanadium content leads to particles growth and intensifies the particles agglomeration.

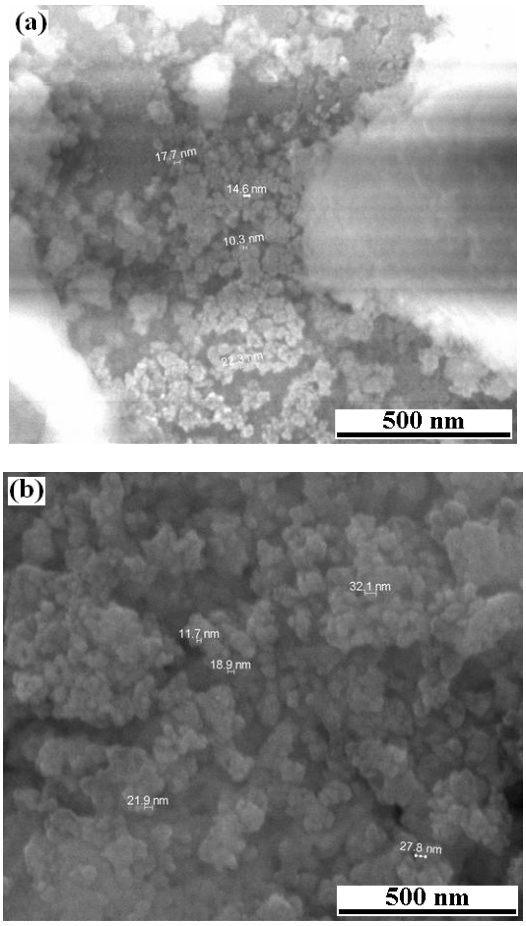

Fig. 2. SEM images of BMTV powders: x = 0.1 (a) and x = 0.2 (b)

Figs. 3 and 4 show the XRD patterns of the sintered ceramics obtained from the powders synthesized by the modified Pechini method. The XRD patterns of the $BaMg_{1/3}(Ta_{0.9}V_{0.1})_{2/3}O_3$ ceramics (Fig. 3) indicate a unique phase with a disordered cubic perovskite structure. It is obvious that the transition from the

disordered cubic perovskite structure to the 1:2 ordered trigonal structure that appears in the case of $BaMg_{1/3}(Ta_{1-x}Nb_x)_{2/3}O_3$ (x = 0, 0.1, 0.2) ceramics [6] does not take place during the sintering process of BMTV solid solution ceramics. $BaMg_{1/3}(Ta_{0.8}V_{0.2})_{2/3}O_3$ ceramic (Fig. 4) has a significant amount of secondary phases, one of these phases being $BaVO_3$, as XRD data confirm.

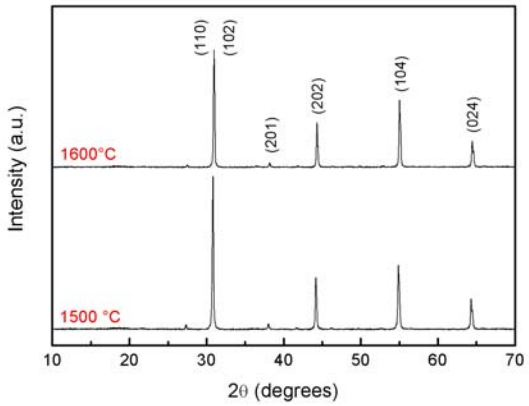

Fig. 3. XRD patterns of $BaMg_{1/3}(Ta_{0.9}V_{0.1})_{2/3}O_3$ ceramics sintered at different temperatures.

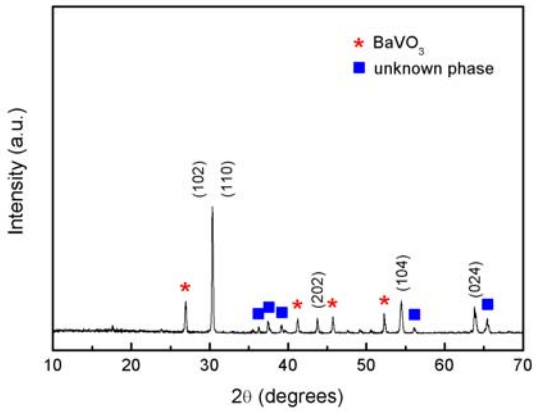

Fig. 4. XRD patterns of $BaMg_{1/3}(Ta_{0.8}V_{0.2})_{2/3}O_3$ ceramics sintered at 1500 °C.

The microstructure of the sintered ceramics is presented in Figs. 5 and 6. $BaMg_{1/3}(Ta_{0.9}V_{0.1})_{2/3}O_3$ powder displayed low sinterability, the ceramic samples consisting of very small grains (Fig. 5); a reason for this behavior has not been yet found. The SEM images of $BaMg_{1/3}(Ta_{0.8}V_{0.2})_{2/3}O_3$ ceramic (Fig. 6) reveal spherical or polyhedral grains with round edges and corners, their size distribution being monomodal, as shown in table 1. The grains are smaller in comparison with $BaMg_{1/3}(Ta_{1-x}Nb_x)_{2/3}O_3$ (x = 0, 0.1, 0.2) ceramics obtained by the same method and in the same processing conditions [6]. The column shape bodies observed in

Fig. 6a could be assigned to the secondary phases. It is supposed that the crystalline second phases indicated by the XRD pattern have appeared after a recrystallization process from the melt that could occur during the sintering treatment.

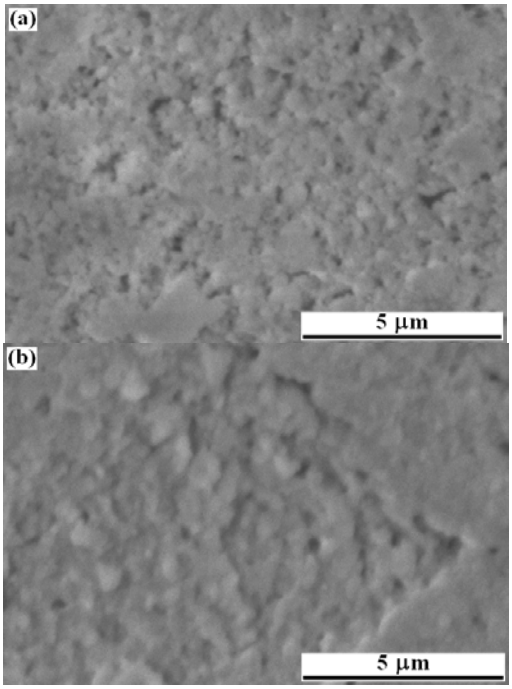

Fig. 5. SEM images of $BaMg_{1/3}(Ta_{0.9}V_{0.1})_{2/3}O_3$ ceramics sintered at: 1500 °C (a) and 1600 °C (b).

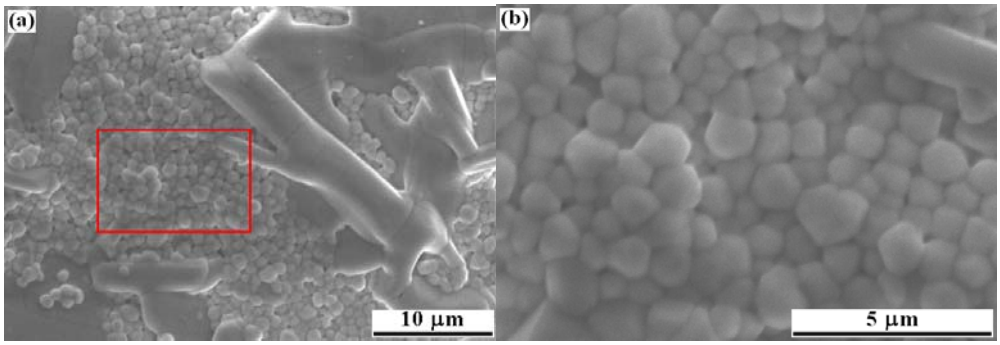

Fig. 6. SEM image of: $BaMg_{1/3}(Ta_{0.8}V_{0.2})_{2/3}O_3$ ceramic sintered at 1500 °C (a) and magnified picture of the marked area (b)

Microwave measurements were performed in the 5 - 12 GHz frequency range. Table 1 presents the grains average size, the values of the relative density

(*d*), the crystallites average size ($\overline{D}$) and the microwave dielectric properties (dielectric constant, ε_r, resonant frequency, *f*, quality factor, $Q \times f$) of the ceramic samples. It can be noticed that the dielectric properties of the $BaMg_{1/3}(Ta_{0.9}V_{0.1})_{2/3}O_3$ ceramic sintered at 1500 °C could not have been determined because of the high porosity. The dielectric properties, as well as the relative density values obtained for BMTV ceramics are poorly than those of $BaMg_{1/3}(Ta_{1-x}Nb_x)_{2/3}O_3$ (x = 0, 0.1, 0.2) ceramics obtained by the same method and in the same processing conditions [6]. The reasons for this could be the pressing defects, the reduced grains size and the secondary phases formation. However, in the case of $BaMg_{1/3}(Ta_{0.9}V_{0.1})_{2/3}O_3$, it is obvious that the increase of sintering temperature from 1500°C to 1600°C promotes the granular growth and improves the value of the relative density.

Tabel 1

Some properties of BMTV ceramics.

x	Calcining / sintering temperature	Grains average size (μm)	d (%)	$\overline{D}$ (nm)	ε_r	f (GHz)	$Q \times f$ (GHz)
0.1	800 °C / 1500 °C	0.13	54.2	57	n.d.	n.d.	n.d.
0.1	800 °C / 1600 °C	0.45	87.1	56	21.7	11.1	13087
0.2	800 °C / 1500 °C	1.16	89.1	60	21.4	10.9	63044

n.d. - not determined

It can be noticed that $BaMg_{1/3}(Ta_{0.8}V_{0.2})_{2/3}O_3$ ceramic sintered at 1500 °C for 4 h displays a high $Q \times f$ value, 63044 GHz, that is higher than the $Q \times f$ values shown by $BaMg_{1/3}(Ta_{1-x}Nb_x)_{2/3}O_3$ (x = 0.1, 0.2) ceramics ($Q \times f$ values smaller than 14100 GHz) and comparable with the $Q \times f$ value displayed by the $BaMg_{1/3}Ta_{2/3}O_3$ ceramic (74393 GHz) [6]. This could be assigned to the presence of the secondary phases. The intrinsic dielectric properties of $BaVO_3$ will be further investigated.

4. Conclusions

$BaMg_{1/3}(Ta_{1-x}V_x)_{2/3}O_3$ (x = 0.1, 0.2) powders with high crystallinity were obtained by modified Pechini method, at low temperature, 800 °C. These powders were uniaxial pressed and sintered at 1500 °C or 1600 °C for 4 h in order to obtain ceramic bodies. $BaMg_{1/3}(Ta_{0.8}V_{0.1})_{2/3}O_3$ powder displays low sinterability. The corresponding ceramic samples present very small grains and exhibit low quality factor. Despite the presence of some secondary phases, $BaMg_{1/3}(Ta_{0.8}V_{0.2})_{2/3}O_3$ ceramic sintered at 1500 °C for 4 h displays a high $Q \times f$ value, 63044 GHz, comparable with $BaMg_{1/3}Ta_{2/3}O_3$ ceramic.

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R E F E R E N C E S

[1] *K.M. Luk, K.W. Leung*; "Dielectric Resonator Antennas"; Research Studies Press Ltd., Baldock, Hertfordshire, England, 2003

[2] *M.T. Sebastian*; "Dielectric Materials for Wireless Communication"; Elsevier Ltd., 2008

[3] *C. Jinga, E. Andronescu, S. Jinga, A. Ioachim, L. Nedelcu, M.I. Toacsan*; "Synthesis and Characterization of Doped $Ba(Mg_{1/3}Ta_{2/3})O_3$ Ceramics"; Journal of Optoelectronics and Advanced Materials, **Vol. 12**, No. 2, February 2010, p. 282–287

[4] *B.S. Vasile, E. Andronescu, D. Florea, C. Ghitulica*; "Structural Investigations of Scandia-Doped Zirconia Nanopowders Obtained by Sol-Gel Method"; U.P.B. Sci. Bull., Series B, **Vol. 72**, Iss. 1, 2010, p. 81–92

[5] *K.P. Surendan, P.C. Rajath Varma, M.R. Varma*; "Solid State and Solution Synthesis of $BaMg_{1/3}Ta_{2/3}O_3$: A Comparative Study"; Materials Research Bulletin, **Vol. 42**, 2007, p. 1831–1844

[6] *C. Jinga, D. Berger, C. Matei, S. Jinga, E. Andronescu*; "Characterization of $BaMg_{1/3}(Ta_{1-x}Nb_x)_{2/3}O_3$ Ceramics Obtained by a Modified Pechini Method"; Journal of Alloys and Compounds, **Vol. 497**, 2010, p. 239–243.