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Synthesis and structural characterization of three different tantalum-based ceramics

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In this work, I have studied three different tantalum-based compositions: $Ba(Y_{1/2}Ta_{1/2})O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$. The ceramic bodies were obtained by the solid-state reaction method or via a modified Pechini method. The Pechini powders, as well as the final ceramics were compositional, structural and morphological characterized by thermal analysis, X-ray diffraction, transmission electron microscopy and scanning electron microscopy. Single-phase powders with cubic structure, containing spherical nanosized particles, with average diameters between 13 and 25 nm, were obtained by modified Pechini method. In the case of $Ba(Mg_{1/3}Ta_{2/3})O_3$, the sintering process makes possible the transition from a disordered cubic perovskite structure to a 1:2 ordered trigonal structure, specific to this type of ceramics. The ceramics synthesized via modified Pechini method exhibit intensive grain growth, resulting in higher grains sizes relatively to the conventional ceramics.

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1. Introduction

The recent progress of microwave communication systems has led to the increasing demand for ceramic resonators. There are three important parameters that a dielectric resonator 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 $Q\times f$ product) and a near-zero value of the temperature coefficient of the resonant frequency (τ_f). These are essential for the miniaturization of the microwave devices, with increased frequency selectivity and thermal stability. The microwave applications include filters and antennas [1].

$A(B'_{1/2}B''_{1/2})O_3$ and $A(B'_{1/3}B''_{2/3})O_3$ complex perovskite-type materials are two of the most widely studied families of ceramics for microwave applications. Usually, their structures have ordered arrangements of B' and B'' cations, 1:1 or 1:2 cation ordering, being derived from the simple perovskite structure by substituting with a pair of two cations (B' and B'') on the octahedral B site [2]. A large number of compounds with niobium or tantalum as B'' cations was reported, about 39 % of the resonator materials being based on tantalates or niobates. Their properties are directly influenced by the starting materials purity, cation ordering, grains size and second phases formation [3, 4].

The common method for preparation of this type of ceramics is the conventional solid-state reaction method. However, for achieving good dielectric properties, this method needs high sintering temperature (~ 1600 °C) and long annealing times (~ 100 h) [2, 5-7]. Synthesis of oxide powders by soft-chemistry methods has certain advantages over the solid-state reaction route in terms of homogeneity and morphology, leading to a better sinterability of the ceramics [8-10]. On the other hand, wet-chemical synthesis of this type of powders, usually, includes complex and inconvenient processes and, in most cases, the researchers had to compromise on the microwave dielectric properties, which is still a matter of much scientific debate [8].

In this paper, I report a comparative study regarding $Ba(Y_{1/2}Ta_{1/2})O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics obtained by two different methods: the conventional solid-state reaction technique and a soft-chemistry technique that supposes a modified Pechini procedure. The last method has the advantage of mixing ions on atomic scale in liquid phase, which yields single-phase precursor nanopowders. Since now, this unconventional method has not been used for $Ba(Y_{1/2}Ta_{1/2})O_3$ ceramic synthesis.

2. Experimental procedure

In the case of the conventional technique, starting materials consisting of carbonate ($BaCO_3$) and oxides (MgO, ZnO, Y_2O_3 and Ta_2O_5) were weighted, wet homogenised and ball milled, dried, calcined, granulated with PVA and uniaxial pressed into pellets. In the case of modified Pechini technique, carbonate ($BaCO_3$), acetates ($Mg(Ac)_2\cdot 4H_2O$ and $Zn(Ac)_2\cdot 2H_2O$), chloride ($YCl_3\cdot 6H_2O$) and butoxide ($Ta(OBu)_5$) were used as sources of metallic cations. This method is suitable for preparing complex oxides from resin-type precursors, being presented in detail elsewhere [10]. Briefly, to $Mg(Ac)_2\cdot 4H_2O$ / $Zn(Ac)_2\cdot 2H_2O$ / $YCl_3\cdot 6H_2O$ and citric acid (CA) dissolved in ethylene glycol, $Ta(OBu)_5$ was added, corresponding to a molar ratio (Mg / Zn / Y + Ta) : (CA) of 1:2. Then, barium citrate, obtained by dissolving $BaCO_3$ in aqueous solution of CA, was added and a citrate gel was formed. This was polymerized at 135 °C for 10 h, burned at 450 °C for 2 h (resulting in a residue powder) and calcined at 750 °C for 2 h, in order to obtain single-phase $Ba(Y_{1/2}Ta_{1/2})O_3$ (BYT) / $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) / $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) crystalline powder. The oxide powders were uniaxial pressed into pellets. For both techniques, the pellets were sintered at different temperatures, 1400, 1500 or 1600 °C, depending on composition, for 4 h.

The precursors were analyzed by thermal analysis (DSC or DTA-TG), which was performed on a Shimadzu DTG-60 equipment, in the 20 - 1000 °C temperature range, or a Shimadzu DTA-TA-51H analyzer, in the 20 - 1500 °C temperature range. The Pechini oxide powders were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). A Rigaku MiniFlex II X-ray diffractometer was used to identify the crystalline phases and the structure of the resulting powders. The unit cell parameter values were calculated using the PANalytical X'Pert HighScore Plus software. The powders morphology was visualized by a Tecnai G^2 F-30 S-Twin transmission electron microscope. The ceramic samples were characterized by XRD and scanning electron microscopy (SEM). Compositional and structural analysis was performed by using a Shimadzu XRD 6000 diffractometer. The microstructure of the sintered ceramics was analyzed by a Hitachi S-2600N scanning electron microscope. The bulk relative density values were determined by Archimede's method, in alcohol.

3. Results and discussion

Fig. 1a presents the thermal analyses of all precursor mixtures in the case of the conventional method. BZT precursor mixture was granulated with PVA before this analysis step, as a consequence, the exothermic effect that takes place below 500 °C can be attributed to PVA and other organic compounds combustion. The small endothermic effects, with maxima at 820 - 830 °C, that appear for all compositions, represents $BaCO_3$ decomposition, but also $BaCO_3$ partial reaction with the other oxides, leading to binary or ternary intermediate compounds. The large endothermic dips, with maximum at about 1250 °C for BMT and approximately 1190 °C for BZT, indicate the main stage in the perovskite compounds formation. After this process, an increase of the crystallinity degree can be noticed. In the case of BYT, DSC curve is different, the small endothermic effect being followed by a large one, which ends at about 1060 °C, this meaning that the formation stage takes place at lower temperatures, while above 1060 °C, the crystallization process occurs.

The thermal analysis of BYT resin-type precursor is displayed in Fig. 1b. The thermogravimetric data show three weight loss steps in the 30 - 740 °C temperature range. The first endothermic effect represents the solvents loss. The strong complex exothermic effect in the 250 - 540 °C temperature range could be attributed to the organic part decomposition, with oxycarbonate intermediates formation [10]. The third endothermic effect could be assigned to the carbonate-type intermediates decomposition and perovskite structure formation. Above 710 °C, no other weight loss is noticed. The behaviour of BMT and BZT resin-type precursors is similar to the previous one, with three thermal effects, the temperature ranges varying with no more than 10 °C [10].

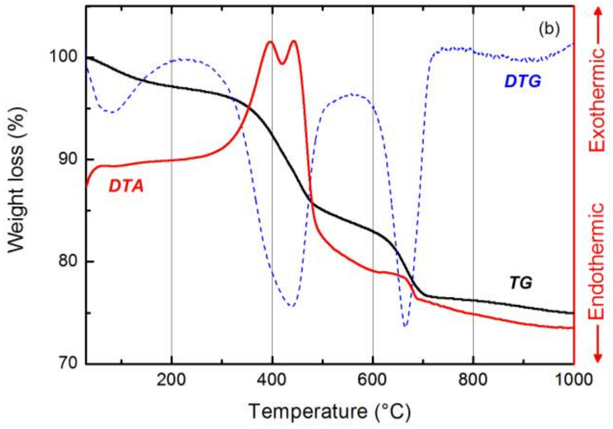

Fig. 1. Thermal analyses of: (a) the precursor mixtures in the case of the conventional method and (b) BYT resin-type precursor in the case of modified Pechini method.

Fig. 2a shows the XRD patterns of BYT residue and powders calcined at three different temperatures. The XRD data of the residue present no perovskite characteristic peaks, while the XRD pattern of BYT powder calcined at 550 °C exhibits the incipient perovskite phase formation. The powders calcined at 650 or 750 °C, respectively, contain only BYT perovskite single-phase with a high crystallinity and a cubic symmetry (JCPDS 01-089-2970). The calculated values of the lattice parameter are: a = 4.1913 Å for 650 °C and a = 4.1898 Å for 750 °C. In the case of BMT and BZT, the incipient perovskite phase formation appears from the residue stage [10].

The XRD patterns of BMT and BZT powders calcined at 750 °C are shown in Fig. 2b. These patterns contain only the characteristic peaks of the disordered cubic perovskite structure (JCPDS 01-070-9200). The calculated values of the lattice parameter are: a = 4.0848 Å for BMT and a = 4.0907 Å for BZT.

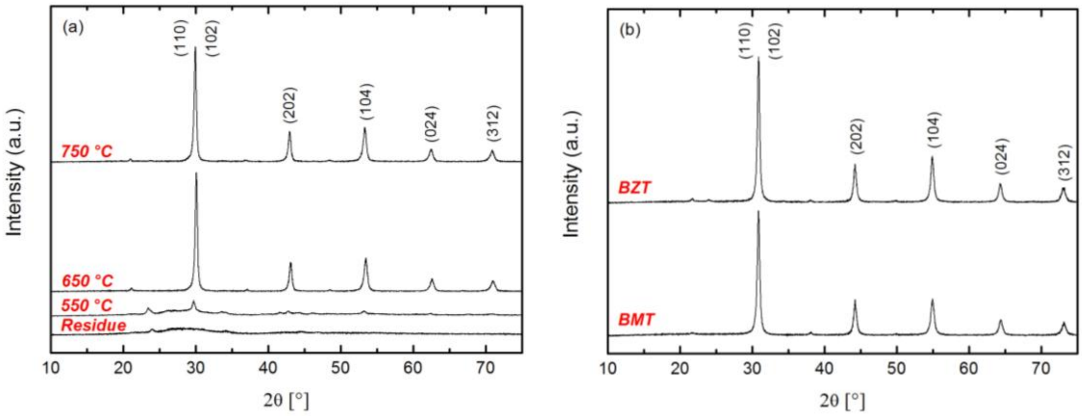

Fig. 2. XRD patterns of: (a) BYT powders calcined at different temperatures and (b) BMT and BZT powders calcined at 750 °C.

The TEM investigation of the Pechini powders calcined at 750 °C (Fig. 3) reveals the shape, size, as well as the crystallinity. The particles have quasi-spherical shapes and the particles size distributions are relatively narrow, with average sizes of 25 nm for BYT, 13 nm for BMT and 14 nm for BZT. The value determined for BMT powder is lower than the values obtained in the case of other soft-chemistry methods [8], while the value for BZT powder is comparable or lower [9]. It can be noticed that the 1:2 molar ratio between Mg / Zn and Ta cations promotes smaller particles diameters than the 1:1 molar ratio between Y and Ta cations, in this case, approximately two times smaller. In the HRTEM micrographs, particles boundaries, as well as crystalline planes can be observed for all compositions. Moreover, the SAED patterns (Fig. 4) indicate a polycrystalline character.

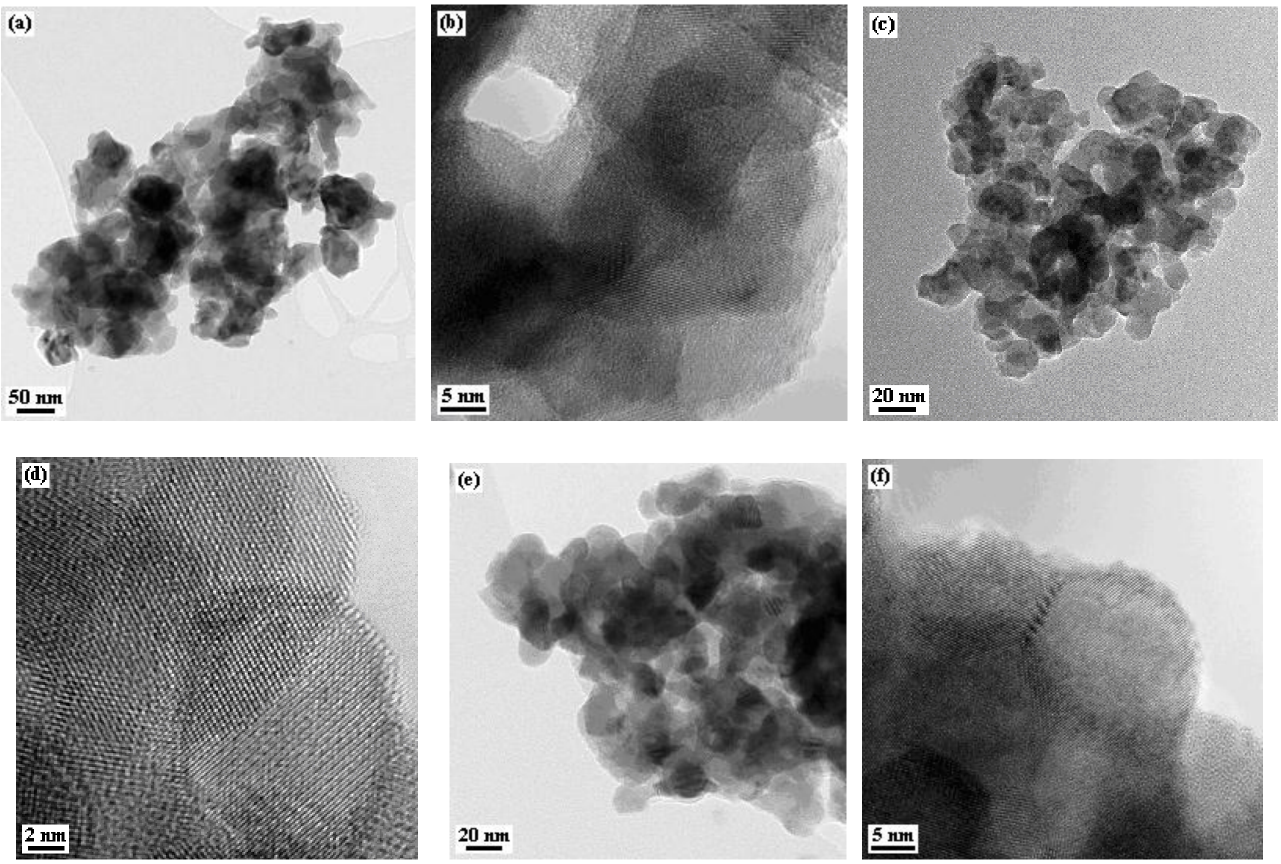

Fig. 3. TEM and HRTEM images of: (a) and (b) BYT, (c) and (d) BMT, (e) and (f) BZT powders calcined at 750 °C.

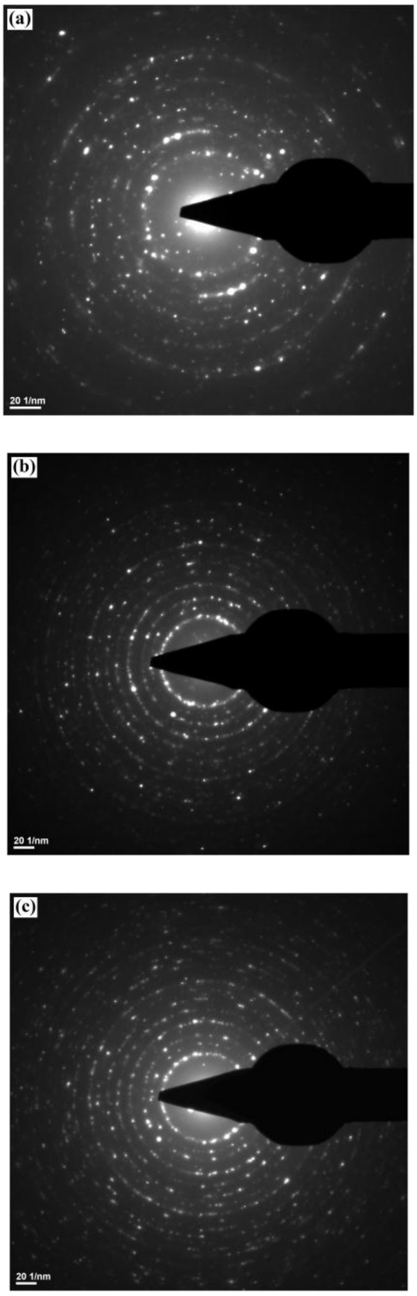

Fig. 4. SAED patterns of: (a) BYT, (b) BMT and (c) BZT powders calcined at 750 °C.

Fig. 5 shows the XRD patterns of the sintered ceramics obtained by both methods (SS = solid-state, P = Pechini). BYT ceramics present single-phase composition when sintered at 1500 °C, as XRD patterns confirm (Fig. 5a). In this case, no structure transition is expected, since BYT is a 1:1 ordered perovskite.

In the case of BMT (Fig. 5b), the XRD patterns show single-phase ceramics for all sintering temperatures. For BMT ceramics obtained via modified Pechini method, the sintering process makes possible the transition from a disordered cubic perovskite structure to a 1:2 ordered trigonal structure (JCPDS 01-070-9201). For the conventional BMT ceramics, the literature sets long annealing times in order to obtain the 1:2 ordered perovskite structure [2].

Unexpected, BZT ceramics contain secondary phases even for a sintering temperature of 1400 °C (Fig. 5c). It is obvious that the secondary phases formation is correlated with zinc volatilization [11], for both methods. It was expected to reduce this volatilization process by the preliminary obtaining of BZT compound at low temperature, by modified Pechini method. On the contrary, BZT ceramic synthesized by the soft-chemistry method contains an appreciable quantity of secondary phases. It is believed that the nanoparticles high surface area accelerates the volatilization process during sintering [9], resulting in binary compounds as secondary phases [2, 9, 11]. This behaviour could be improved by muffling the samples with BZT powder during the sintering process.

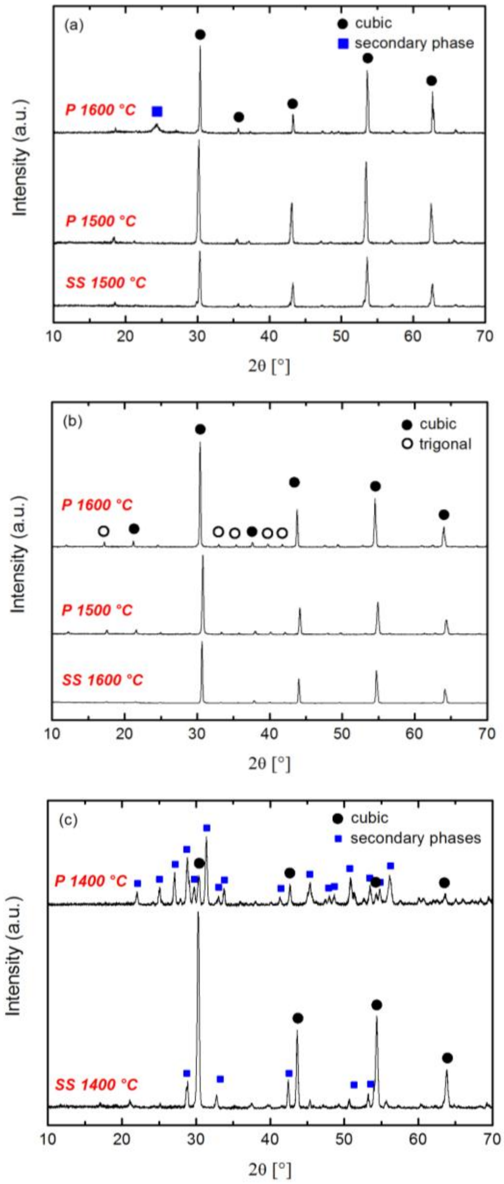

Fig. 5. XRD patterns of: (a) BYT and (b) BMT ceramics sintered at different temperatures and (c) BZT ceramics sintered at 1400 °C.

The microstructure of some ceramics sintered at different temperatures is shown in Fig. 6. The SEM images reveal polyhedral grains with round edges and corners and monomodal grains size distributions. For all compositions, it is obvious that the grains are larger for the ceramics obtained via modified Pechini method. BZT sample sintered at 1400 °C (Fig. 6e), followed by BYT sample sintered at 1500 °C (Fig. 6a), both obtained by the solid-state reaction method, present the higher porosity. BYT ceramic synthesized by the soft-chemistry method (Fig. 6b) shows pronounced growth steps on the surface, these being a result of an intense grains surface diffusion; the grains average size is with an order of magnitude higher towards the corresponding conventional ceramic (2 μm versus 20 μm); BYT ceramic reported by Khalam *et al.* [12], obtained by the conventional method and sintered at 1575 °C for 4 h, also contains grains with dimensions of 1 - 2 μm, as well as huge grains of 6 - 7 μm, due to the use of 0.5 wt% Nb_2O_5 as sintering aid. In the case of BMT, the grains average size is two times higher for the Pechini ceramic (Fig. 6d) in relation to the conventional ceramic (Fig. 6c), 1.5 μm versus 3 μm, while for BZT ceramics there are not significant differences (1 μm versus 1.2 μm). BZT powder sinterability is poor due to the volatile nature of zinc and its depletion. The values of the bulk relative density are in good agreement with the SEM investigation: in the case of BYT, it increases from 73.4 % for the conventional method to 97.5 and 98.3 % for modified Pechini method, in the case of BMT, it increases from 81.7 % for the solid state reaction method to 92.1 and 92.3 % for the soft-chemistry method, while for BZT, both values are relatively low, 54.1 % for the conventional method and 68.1 % for modified Pechini method. As a conclusion, it can be stated that a molar ratio of 1:1 between B' and B'' cations (BYT) promotes a more intense granular growth than a molar ratio of 1:2 (BMT and BZT); furthermore, considering the same molar ratio (1:2), B' cations kind influences the diffusion processes that take place during sintering, in this case, by zinc volatilization.

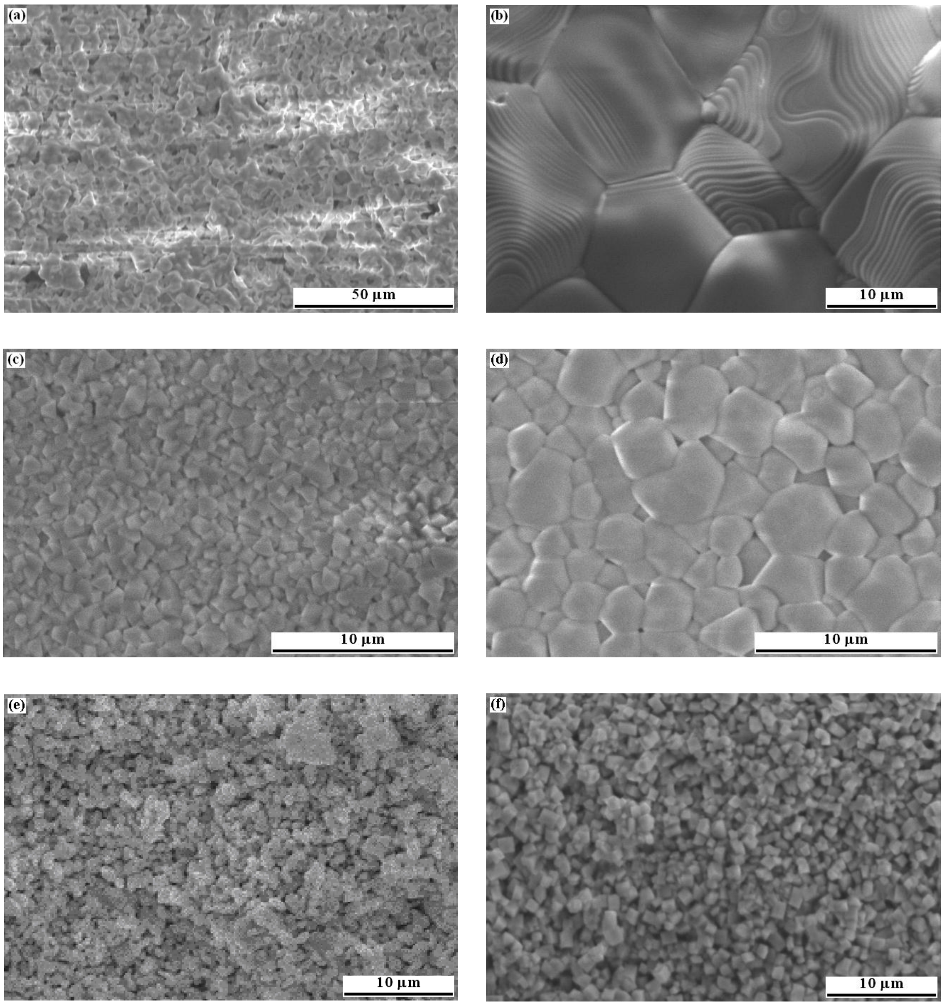

Fig. 6. SEM images of: (a) BYT-SS and (b) BYT-P ceramics sintered at 1500 °C, (c) BMT-SS and (d) BMT-P ceramics sintered at 1600 °C, (e) BZT-SS and (f) BZT-P ceramics sintered at 1400 °C.

4. Conclusions

$Ba(Y_{1/2}Ta_{1/2})O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics were synthesized by two different methods: the conventional solid-state reaction technique and via a modified Pechini technique. Single-phase tantalum-based powders with a high crystallinity degree and quasi-spherical nanosized particles were obtained by modified Pechini method, at low temperature (750 °C). The 1:2 molar ratio between B' and B'' cations from $AB'B''O_3$ compounds promotes smaller particles sizes than the 1:1 molar ratio. All powders exhibit cubic structure. In the case of $Ba(Mg_{1/3}Ta_{2/3})O_3$, the sintering process makes possible the transition from a disordered cubic perovskite structure specific to the powder to a 1:2 ordered trigonal structure typical of this type of ceramics. The granular growth is directly influenced by the type and molar concentration of B' cations from $AB'B''O_3$ compounds. The SEM images evidence higher grains sizes for those ceramics obtained by modified Pechini method, this being a consequence of the diffusion mechanisms. $Ba(Y_{1/2}Ta_{1/2})O_3$ ceramic prepared by the soft-chemistry method and sintered at 1600 °C exhibits the largest grains, with dimensions up to 20 μm.

The advantage of modified Pechini method over the conventional solid-state reaction technique is the achievement of low porosity and high grains average sizes by processing the ceramics for short period of time at high temperatures. As a conclusion, it is a promising route for obtaining high quality microwave ceramics or composites.

Acknowledgments

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