JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 5, May 2007, p. 1576 - 1581

Dielectric and morphological studies of BST ferroelectric ceramics

A. IOACHIM*, F. VASILIU, M. I. TOACSĂN, L. NEDELCU, M. G. BANCIU, H. V. ALEXANDRU[a], G. STOICA[b]
National Institute of Materials Physics, P.O. Box MG-7, RO 077125, Bucharest-Magurele, Romania
[a]*University of Bucharest, Faculty of Physics, Romania*
[b]*S.C. Armtech S.A., Curtea de Argeş, Romania*

Barium strontium titanate with molar formula $Ba_{0.75}Sr_{0.25}$ TiO_3 (BST) was prepared from raw materials by solid-state reaction. Samples were sintered at 1230 °C and 1260 °C for 2 h. In order to improve the sintering process, 1 wt. % MgO and 1 wt. % MnO_2 were used as sintering additives. The sinterability, structural, morphological and dielectric properties of pure and doped BST samples were investigated. Perovskite structure of polycrystalline BST ceramics was determined by X-ray diffraction. SEM investigations revealed a grain and pore size distribution, which is shifted to higher values by a slight increase of the sintering temperature from 1230 °C to 1260 °C. In the presence of additives, a better sintering and grain refining could be observed, whereas their lack induce a strong effect of exaggerated grain growth, by forming of large faceted grains. The presence of Mn ions in the doped BST ceramics was revealed by the EDX analysis. On the other hand, Mg ions are not evidenced. Temperature dependence of dielectric constant measured at 1 kHz shows a diffuse ferroelectric-paraelectric transition, which can be attributed to the large size dispersion of grains. The increase of sintering temperature leads to a shift of the Curie temperature to higher values.

(Received November 14, 2006; accepted April 12, 2007)

Keywords: Barium strontium titanate, Ceramics, Ferroelectric-paraelectric transition

1. Introduction

Ferroelectric materials have been intensively investigated in the last years for applications in informatics (storage medium in dynamic random access memories, DRAM) [1], as well as in microwaves (dielectric resonators, substrates for microwaves hybrid integrates, planar antennas, tunable capacitors, phase shifters, filters controlled oscillators, etc.) [2-3]. In paraelectric phase, these materials have considerably high dielectric constant and low losses at microwave frequencies. BST ferroelectric ceramics are very attractive for tunable microwave devices. The dielectric constant of these ceramic compounds can be modified using a bias electric field [2-5] with possible applications based on this property as varactors, phase shifters or tunable filters.

BaO-SrO-TiO_2 (BST) compounds with the molar formula $Ba_{0.75}Sr_{0.25}TiO_3$ were prepared from raw materials by solid-state reaction. Samples were sintered at 1230 °C and 1260 °C for 2 h. In order to improve the sintering process, 1 wt. % MgO and 1 wt. % MnO_2 were used as sintering additives. Structural parameters were measured by X-ray diffraction, which confirmed the perovskite crystalline structure. Bulk densities were measured using the Archimedes method. Structural parameters, the grains morphology, crystallite sizes, porous structure and the compositions homogeneity were investigated by using SEM and EDX methods. Low frequency (1 kHz) dielectric characterization of ceramics was performed on a large range of temperatures (-200 to 200 °C). The effect of additives and sintering temperature upon the structural and dielectric properties was studied in order to select the optimum BST material for the development of microwave devices.

2. Experimental

The $Ba_{0.75}Sr_{0.25}TiO_3$ samples were prepared by standard ceramic technology. Two BST compositions, with and without additives (1 wt. % MgO and 1 wt. % MnO_2), were realised. The starting materials were $BaCO_3$, $SrCO_3$, TiO_2, MgO and MnO_2, powders with purity higher than 99.9%. The raw materials were weighed out in stoichiometric proportions, ball-milled in water for two hours, dried and then calcined at 1150 °C for 2 hours. The synthetised powder was crushed and then milled again for 2 hours. Mixing was carried out in an agate mortar containing agate balls, for 2 hours. The mixture was pressed into pellets of 11 mm diameter and 12 mm thickness, before the sintering for 2 hours at temperatures (T_s) of 1230 °C and 1260 °C .The relative densities of sintered samples were measured using water immersion technique.

The crystalline structure of BST compositions, with and without additives (1 wt. % MgO and 1 wt. % MnO_2) was performed on a Seifert Debye-Flex 2002 diffractometer using Ni-filtered Cu K_α radiation and a counter scan speed of 7°/min.in a 2θ range from 20° to 60°. In order to obtain the unit cell parameters, a speed of 5°/min was used.

SEM and EDX measurements were performed by using a ZEISS DSM 960 A scanning electron microscope equipped with an X-ray energy dispersive EDX

spectrometer. The grain and pore size histograms were calculated from SEM data.

Low frequency dielectric measurements were performed on 1 mm thick samples by using a self-acting RCL bridge at 1 kHz. The BST samples were cut, cleaned and then treated at 150 ^{o}C for 15 hours in order to eliminate residual water from the porous ceramics. Then silver paste was painted on the polished samples. Low frequency dielectric characterization of ceramics was performed on a large interval of temperatures (-200 to 200 ^{o}C).

3. Results and discussion

3.1 X-ray and density data

Following the sintering process at two different sintering temperatures (T_s) 1230 ^{o}C and 1260 ^{o}C, with and without additives, samples with good compactness were obtained as shown Table 1. Reported to the theoretical density, ρ_t=5.39 × 10^{-3}kg/m^3, BST samples sintered at higher T_s with additives exhibit higher porosity. For all the treatments, the data reveals a slow decrease of the densities in the presence of additives. That indicates that the T_s= 1230 ^{o}C is the necesary temperature in order to obtain well-sintered $Ba_{0.75}Sr_{0.25}TiO_3$ ceramic samples.

Table 1. Bulk density and porosity of the BST samples as function of technological parameters (sintering temperature and additives presence).

Samples	Additives (Mg+Mn)	Sintering temperature (^{o}C)	Bulk density (kg/m^3) ×10^{-3}	Porosity (%)
BST 1	No	1230	5.34	7.9
BST 2	Yes	1230	5.35	7.8
BST 3	No	1260	5.24	9.6
BST 4	Yes	1260	5.21	10.2

The X-Ray diffraction (XRD) patterns confirmed the perovskite structure of BST ceramics. Fig. 1 presents the XRD patterns of investigated samples without additives. The XRD patterns of BST samples sintered at 1230 ^{o}C and 1260 ^{o}C are similar and no differences appear in the additives presence. The differences in the tetragonal ratio c_o/a_o are very small as indicate the data calculated in Table 2. However, for doped samples, a little decrease of tetragonal character with the increase in sintering temperature can be observed.

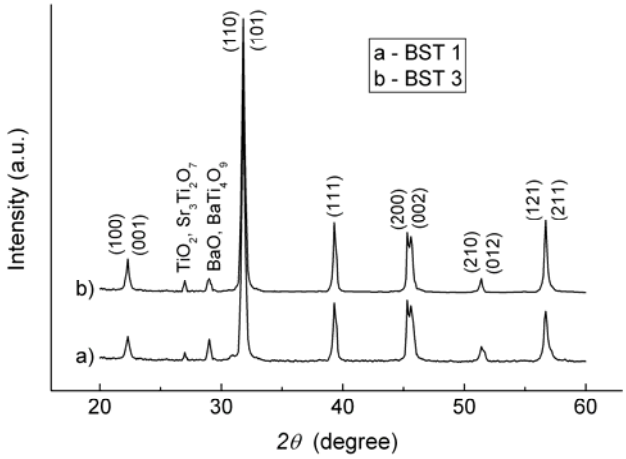


Fig. 1. XRD patterns of BST samples without additives Sintered at 1230 ^{o}C(a) and 1260 ^{o}C(b).

Table 2.Calculated unit cell parameters for BST samples with and without additives sintered at 1230 ^{o}C and 1260 ^{o}C.

Sample	Unit cell parameters		Unit cell volume	Tetragonal ratio
	a_o (Å)	c_o (Å)	V_o (Å^3)	c_o/a_o
BST 1	3.967	3.985	62.71	1.004
BST 2	3.966	3.984	62.66	1.005
BST 3	3.969	3.985	62.77	1.004
BST 4	3.971	3.985	62.84	1.003

At high sintering temperature, the diffraction peaks are higher and narrower, which indicates the better structural order of the BST ceramics. In addition, a slow increase of a_o and V_o unit cell parameters with the temperature increase was noticed.

3.2. SEM and EDX results

SEM images (Fig. 2a) show that in BST 1, the grain size is in a range between 0.2÷1.5 μm, whereas in the specimens BST 2 and BST 4 a broadening of grain size distributions was found. Thus, in the first case a major fraction of small grains is identified but also large grains (2÷3 μm) are present. The additives (Mg and Mn oxides) lead to a better sintering and grain refining (Fig. 2 b,c,d) whereas their lack induce a strong effect of exaggerated grain growth, by forming of large faceted grains, many of them having a cuboidal morphology. On the other hand, in the presence of the additives, an increase of grain size and a tendency to grain homogenization is observed for a small increase of the sintering temperature, which reduces the volume ratio of the grain boundary region / bulk grain region.

SEM images are in agreement with the mean crystalline size estimation obtained for BST samples from X-ray diffraction spectra.

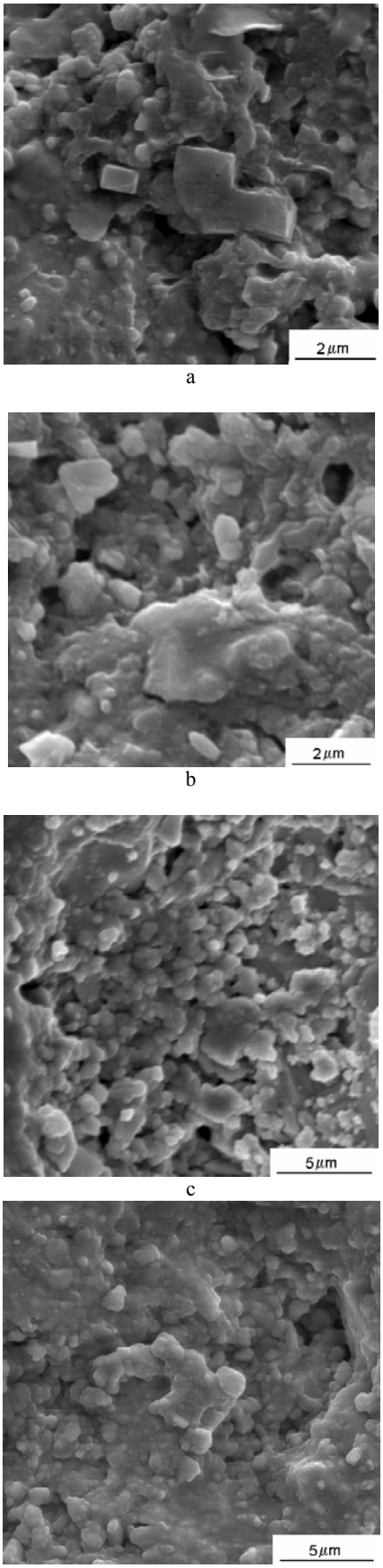


Fig. 2. SEM images of BST samples: a) BST 1; b) BST 2; c), d) different regions of BST 4.

The qualitative EDX spectra (Fig. 3) show the presence of main elements (Ba, Sr, Ti) and addition elements (Mn) but also an artefact related to the presence of Au used for the specimen preparation. The addition element Mg cannot be detected by EDAX technique. X-ray maps (Fig. 4) show generally relatively homogeneous Ti distributions for all specimens whereas there are many grains with a small Sr amount.

The grain boundary regions are Ba deficient, whereas the Ti content remained approximately the same, according to previous results related to BST thin films [6-8]. This Ba deficiency is relatively enhanced in the specimen sintered at higher temperature.

The ratio Ti/(Ba+Sr) $\geq$ 1 found in the specimens is accommodated by the creation of Ba and Sr cation vacancies, which segregate to the grain boundary regions. Segregation of the Ba and Sr vacancies to grain boundaries creates negative space-charge regions which are expected to be compensated by an excess of Ti ions or by oxygen vacancies [9].

The compositional heterogeneity and grain size could explain the different dielectric behavior as a function of temperature in ferroelectric phase.

SEM images of BST samples show a structure consisting of fine matrix grains and some abnormally growing grains. The size distributions of the fine matrix grains and small pores calculated from SEM data for samples sintered at 1230 ^{o}C and 1260 ^{o}C, with and without additives, are shown in Figs. 5-7.

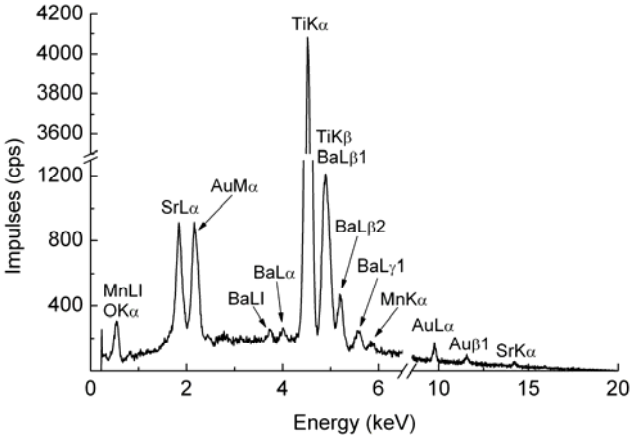
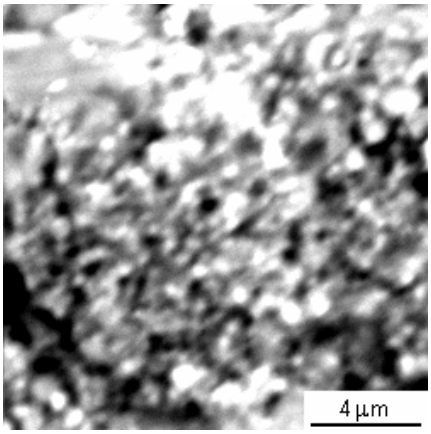
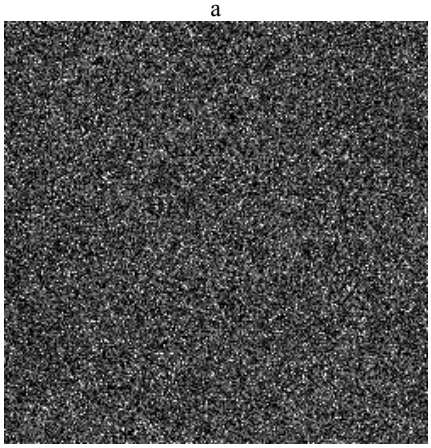


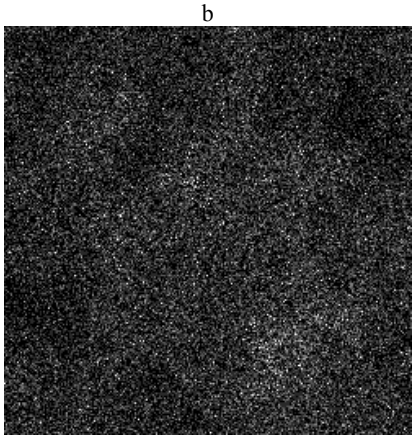
Fig. 3. EDX spectrum of the BST 2 specimen sintered at 1230 ^{o}C for 2h, with additions of 1%MgO and 1% MnO_2.



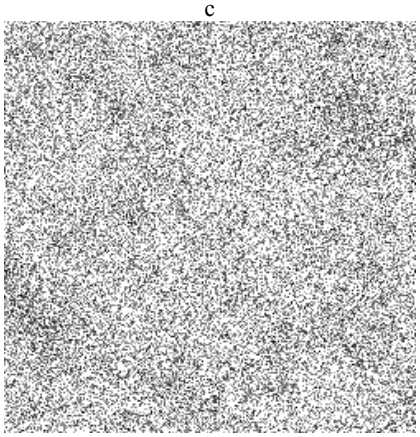
a



b

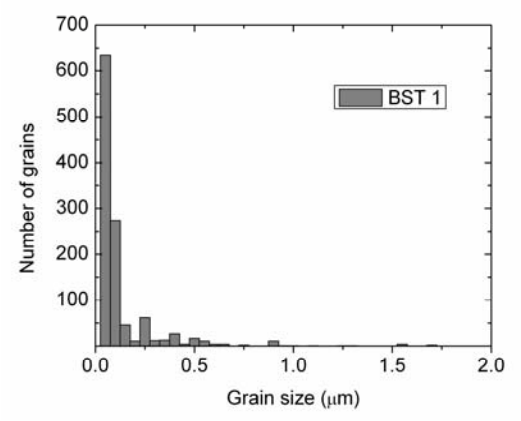


c

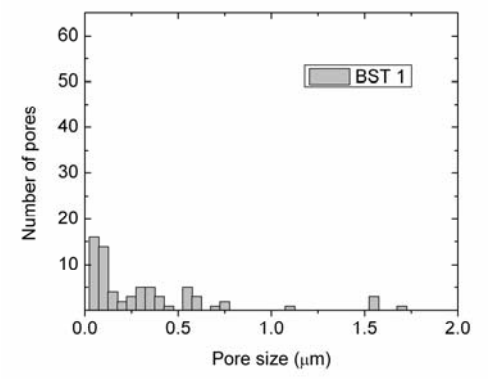


d

Fig. 4. SEM image (a) and X-ray maps for Ba (b), Sr (c) and Ti (d) in a BST 2 specimen.

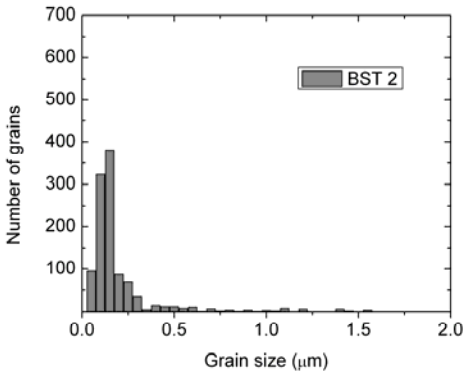


a

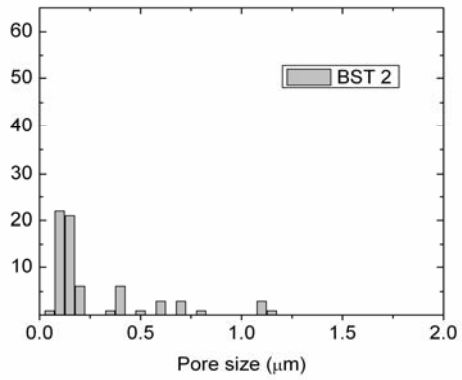


b

Fig. 5. Histograms for grains (a) and pores (b) of BST 1 sample.

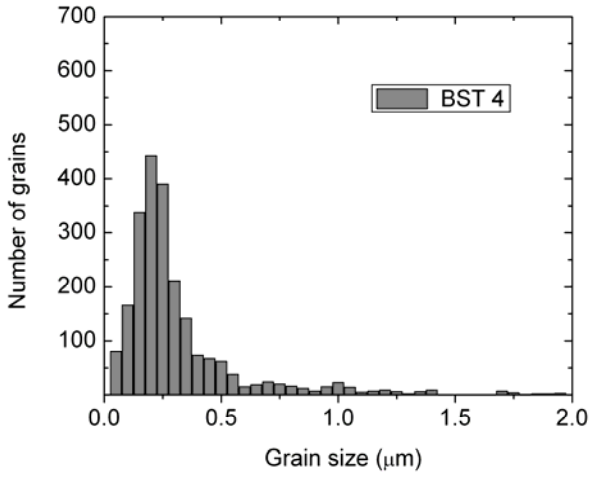


A

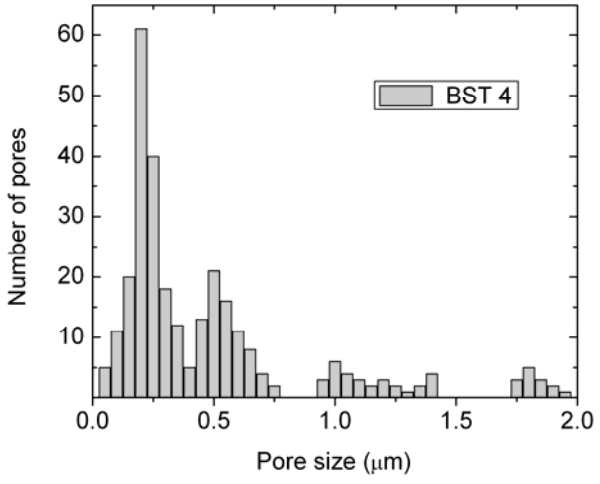


b

Fig. 6. Histograms for grains (a) and pores (b) of BST 2 sample.



a



b

Fig. 7. Histograms for grains (a) and pores (b) of BST 4 sample.

As can be observed from Figs. 5-6, at T_s=1230 °C, the presence of additives induces an increase of both grain and pore sizes. The increase of sintering temperature in the presence of additives (Fig. 7), leads to an increase of both grain and pore sizes. The grain size increase with the increase of sintering temperature is enhanced in the presence of the additives.

3.3 Dielectric measurements

The temperature dependence of permittivity of the analyzed samples is presented in Fig. 8.

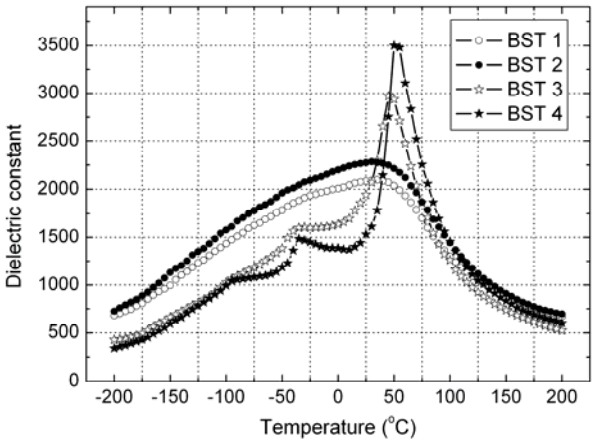


Fig. 8. Temperature dependence of the dielectric constant for BST ceramics sintered at 1230 °C and 1260 °C, with and without additives at 1kHz.

Dielectric measurements at 1 kHz show a slightly increase of the Curie temperature with the increase of sintering temperature and the presence of additives. BST 1 and BST 2 samples sintered at 1230 °C exhibit a diffuse phase transition. The additives presence strongly increases the permittivity maximum values. Moreover, well-defined ferroelectric-paraelectric transitions can be seen for BST 3 and BST 4 samples sintered at 1260 °C. The additives have a benefic effect on dielectric properties. This effect is clearer for high sintering temperatures. For the samples with additives, well-defined transitions can be observed: around 50 °C ferroelectric-paraelectric transition, but also at –40 °C a second transition (tetragonal – orthorhombic) and a third transition around –90 °C (orthorhombic – rhombohedral).

4. Conclusions

BST materials with formula $Ba_{0.75}Sr_{0.25}TiO_3$, prepared from raw materials by solid-state reaction, are in ferroelectric state at room temperatures.

Perovskite structure with tetragonal distortion was evidenced by XRD analysis. 1 wt. % MgO and 1 wt. % MnO_2 additives have a strong influence on morphological and dielectric properties of BST material. The additives presence changes the character of the transitions. A grain refining is observed in the presence of Mg and Mn additions.

For a small increase of the sintering temperature, in the presence of additives, an increase of grain size and a tendency to grain homogenization is observed.

Low frequency dielectric measurements show a slightly increase of the Curie temperature with the increase of sintering temperature and the presence of additives. The additives presence strongly increases the permittivity maximum values.

Acknowledgements

This work was partially supported from the CEEX project 2-Cex 06-11-44 (DINAFER).

References

[1] D. Roy, S. D. Krupandihi, Appl. Phys .Lett. **62**, 1056 (1993).
[2] S. J. Fiedziuszko, I. C. Hunter, T. Itoh, Y. Kaobayashi, T. Nishikawa, K. Wakino, S. N. Stitzer, IEEE Trans. Microw. Theory Techn. **MTT-50**, 706 (2002).
[3] Yukio Higuchi, Hiroshi Tamura, J. Eur. Ceram. Soc. **23**, 2683 (2003).
[4] D. Kim, Y. Choi, M. G. Allen, J. S. Kenney, D. Kiesling, IEEE Trans. Microw. Theory Techn. **MTT-50**, 2903 (2002).
[5] W. Chang, S. W. Kirchoefer, J. M. Pond, J. S. Horwitz, L. Sengupta, J. Appl. Phys. **92**, 1528 (2002).
[6] M. Jain, S. B. Majumder,R. S. Katiyar, S. B. Desu, Appl. Phys. A **77**, 789 (2003)
[7] I. Levin, R. D. Leapman, D. L. Kaiser, P. C. Van Buskirk, S. Bilodeau, R. Carl, Appl. Phys. Lett. **75**, 1299 (1999).
[8] I. Levin, R. D. Leapman, D. L. Kaiser, J. Mater. Res. **15**, 1433 (2000).
[9] Y-M. Chiang, T. Takagi, J. Am. Ceram. Soc. **73**, 3278 (1990).

*Corresponding author: ioachim@infim.ro