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Final Workshop

Electroceramics from Nanopowders
Produced by Innovative Methods

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Final Workshop COST 539
Electroceramics from Nanopowders Produced by Innovative Methods

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RELAXOR BEHAVIOR OF $BaBi_4Ti_4O_{15}$ CERAMICS

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Family of bismuth oxides was discovered more than 50 years ago by Aurivillius [1]. The lattice structure of the Aurivillius family of compounds is composed of *n* number of like perovskite $(A_{n-1}B_nO_{3n+3})^{2-}$ unit cells sandwiched between $(Bi_2O_2)^{2+}$ slabs along pseudo tetragonal c-axis. Majority of Aurivillius oxides are normal ferroelectrics with fairly high Curie temperature, while only a few of them such as $BaBi_4Ti_4O_{15}$, $BaBi_2Nb_2O_9$, $BaBi_2Ta_2O_9$, etc. exhibit relaxor behaviour. Relaxor materials are characterized by frequency dispersion having broad dielectric anomaly in their dielectric behavior near the dielectric maximum. The latter properties are very useful for wide range of applications owing to their excellent high dielectric and piezoelectric responses over a wide range of temperatures [2].

In present work, $BaBi_4Ti_4O_{15}$ - BBiT was prepared by noncoventional solid state reaction from mixture of oxide: BaO, TiO_2 and Bi_2O_3 which was milled for 6 h. The powders were heated at 750°C for 4 h. Ceramic samples were prepared by conventional sintering of isostatic pressed (298 MPa) pellets at 1130°C for 1 h. Dielectric properties were investigated in a wide range of temperatures (20-800°C) and frequencies (1 kHz-1 MHz).

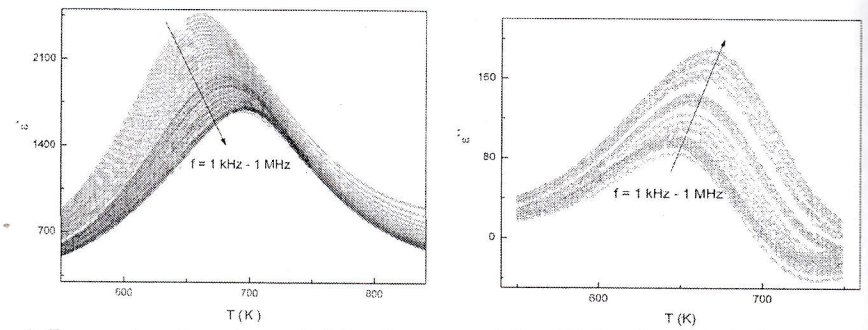

Fig. 1. Temperature dependence a) dielectric constant (ε') and b) loss factor (ε'') of BBiT ceramics

Fig. 1a. displays temperature dependence of dielectric constant (ε') of BBiT ceramics determined during cooling in BBiT ceramics. The results give an evidence of a diffuse phase transition accompanied by a relaxation of the permittivity. The temperature T_m of the maximum permittivity (ε_m) is shifted from 402°C to 417°C as the frequency increases from 1 kHz to 1 MHz. The temperature corresponding to ε''_m also increases with the increase of frequency (Fig. 1b). The associated imaginary permittivity (ε'') exibits a maximum at temperature close to the low temperature inflexion point of ε' and this maximum is also shiftes towards the high temperature side as the frequency increases This behavior is typical for relaxor ferroelectric.

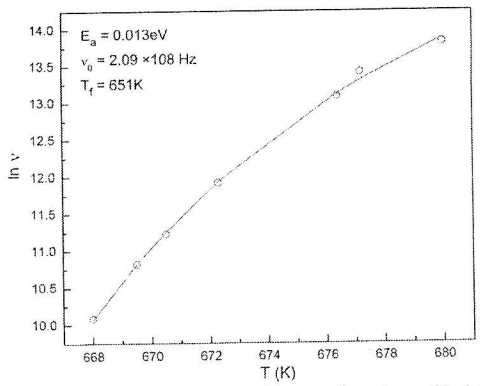

Fig. 2. Temperature of the dielectric maximum T_m as a function of ln(ν) for the BBiT ceramics (The square dots represent the experimental data and the solid line is the fit to the Vogel-Fulcher relation).

The broad dielectric constant peaks at temperature T_m was frequently dependent. A modified Curie-Weiss relationship is used to study the diffuseness behavior of a ferroelectric phase transition where value of γ indicates the degree of diffuseness of BBiT material. The value of γ calculated from the slot of the curve is found to be 1.88 which reveals the near-relaxor nature of BBiT ceramics.

The variation of temperature of the dielectric maximum T_m as a function of ln(ν) is presented on Fig. 2. The dielectric relaxation rate follows the Vogel-Fulcher relation with E_a = 0.013 eV, $\nu_0 = 2.09 \times 10^8$ Hz, and T_f = 651 K. All these parameters indicate that $BaBi_4Ti_4O_{15}$ is a relaxor ferroelectric.

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COST-P-15

INFRARED SPECTROSCOPY OF UNDOPED AND La AND Sb DOPED $BaTiO_3$ PREPARED BY POLYMERIC PRECURSORS METHOD

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The infrared spectra of ABO_3 perovskites have been studied extensively. Factor group analysis for $BaTiO_3$ with cubic symmetry (space group $Pm3m = O_h^1$) predicts only infrared bands (three triply degenerate infrared active modes of F_{1u} symmetry) and one optically silent (neither infrared nor Raman active) mode of F_{2u} symmetry [1]. The three infrared active modes are commonly called the stretching modes (B-O bond-length modulation), and the external mode in which the BO_6 octahedron vibrates against the A atoms. In tetragonal symmetry (space group $P4mm = C_{4v}^1$), 12 fundamental optical modes with the following irreducible representation are expected: $3A_1$, $4E$ and B_1 [2,3]. The perovskite structure has capability to host ions of different size, so a large number of different dopants can be accommodated in the $BaTiO_3$ lattice that makes $BaTiO_3$ semiconductive. Doping of BT ceramics is very important for obtaining very interesting characteristics for potential applications.

The aim of this study is to investigate the influence of La- and Sb- doping on the $BaTiO_3$ synthesized through the Pechini method. Infrared spectroscopy was used in addition to the XRD, Raman spectroscopy and SEM investigations in order to find evidence of the structural phase in undoped and doped $BaTiO_3$ ceramics.

$BaTiO_3$ powders were prepared by the polymeric organometallic precursors method (Pechini process) using barium and titanium citrates and for doping were used lanthanum nitrate and antimony acetate. The powders were isostatically pressed into pellets 8 mm in diameter and average thickness of about 2.5 mm at pressure of 98.1 MPa. Sintering was performed at 1300°C for 8 h and the heating rate was 10 °C/min with nature cooling in an air atmosphere. Far-infrared reflectivity measurements were made in spectral range (50-700 cm^{-1}) at room temperature with BOMEM DA8 spectrometer.

Figure 1 show the IR spectrum of the $BaTiO_3$ and La- and Sb-doped $BaTiO_3$ ceramics sintered at 1300°C for 8 h. The bands in the lower wave number range (50-700 cm^{-1}) are due to Ti-O vibrations. The characteristic peak is found for all samples. The modes at 180 and 470 cm^{-1} belong to the A_1 representation to which the soft phonon mode associated with the ferroelectric phase transition at Tc = 395 K belongs. The broad band over 50-180 cm^{-1} is due to soft phonon. Because of the overdamped character of the soft phonon, it is difficult to determine the frequency. The intensity of three peaks of the doped BT 0.5 mol% Sb, undoped barium titanate and BT doped 0.5 mol% La appear on 183, 184 and 185 cm^{-1}, respectively. The intensities of the modes at 180, 250 and 470 cm^{-1} decrease for $BaTiO_3$ and La- and Sb-doped $BaTiO_3$, respectively. The modes at 382, 439 and 612 cm^{-1} can be observed in case Sb- doped $BaTiO_3$. This suggests a change of crystal structure. These results are in agreement with our previous investigations [4]. All observations related to IR indicate the formation of pure single phase of BT and La and Sb doped BT.

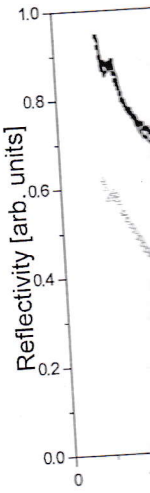

Fig. 1. IR spectra

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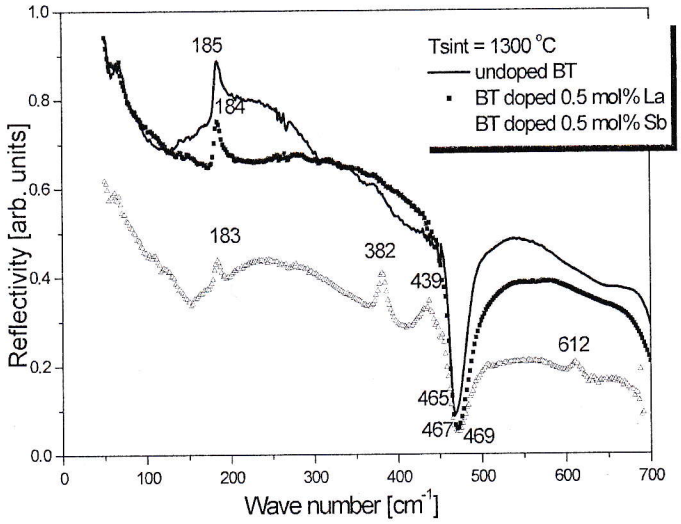

Fig. 1. IR spectra of the $BaTiO_3$, La- and Sb-doped $BaTiO_3$ ceramic obtained by Pechini method and sintered at 1300°C for 8 h.

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COST-P-18

EFFECT OF ANTIMONY DOPING ON PROPERTIES OF BARIUM TITANATE CERAMICS

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Doping of $BaTiO_3$ (BT) ceramics is very important to obtain required characteristics for different applications.

In this work, pure and Sb- doped barium titanate powders were prepared by polymeric precursors method (0.1 mol% Sb -BTS1, 0.3 mol% Sb -BTS3 and 0.5 mol% Sb - BTS5). Obtained powders were pressed and sintered at 1300°C for 8h in air atmosphere [1].

XRD results indicated only the presence of $BaTiO_3$. In all sintered samples was detected well crystallized tetragonal phase. Fig. 1 depicts SEM micrographs of sintered samples and it can be observed that antimony has significant effect on grain growth as well as on densification of obtained ceramics (higher then 90% TD) [2].

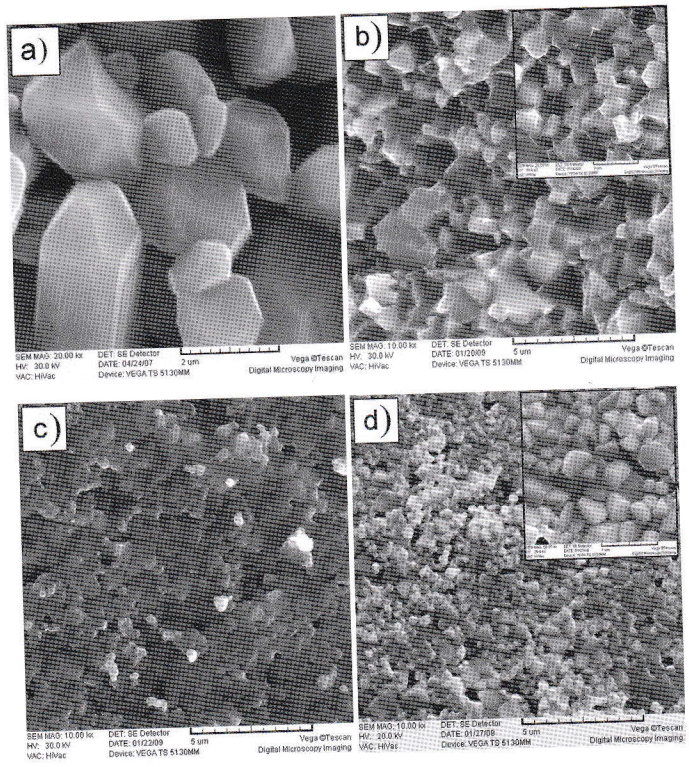

Fig. 1. SEM micrographs of (a) pure-BT, (b) BTS1, (c) BTS3 and (d) BTS5

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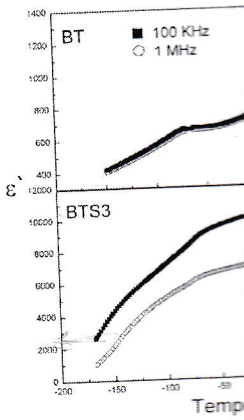

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Temperature dependence of dielectric permittivity was established in the temperature range -200 to 175°C and at frequencies of 100 KHz and 1 MHz (Fig. 2).

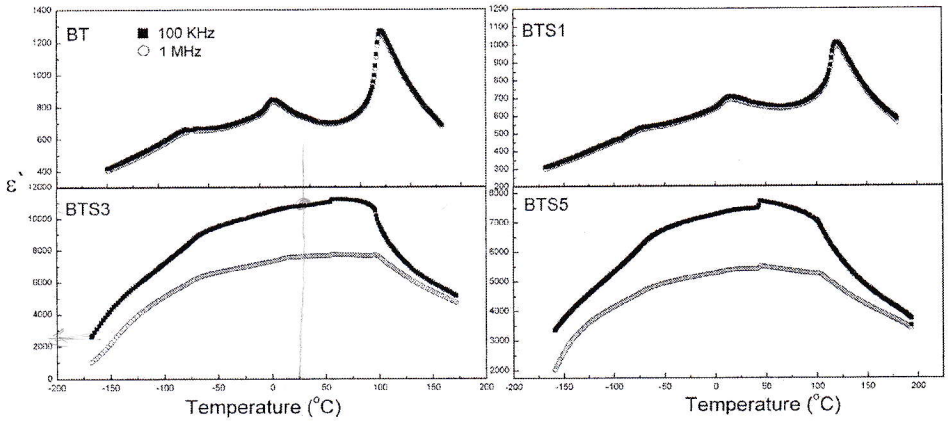

Fig. 2. Dielectric permittivity vs. temperature for pure and Sb-doped BT ceramics

The positions of all structural transitions are shifted to lower temperatures. In doped samples lower temperature transitions can not be clearly detected. Peaks become more broaden as the concentration of Sb increases. Barium titanate ceramic doped with 0.3 mol% Sb has the highest dielectric constant value and with further increase in dopant concentration dielectric constant become lower. Observed Curie temperatures and dielectric constant value at 100 KHz are given in the table.

SAMPLE	T_{C-T} (°C)	$\varepsilon`(T_{room})$	$\varepsilon`(T_C)$
BT	120	730	1336
BTS1	119	698	1016
BTS3	100	10825	11088
BTS5	98	7090	7475

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COST-P-27

DIELECTRIC INVESTIGATIONS OF BARIUM TITANATE DOPED WITH DEFERENT CONCENTRATION OF LANTHANUM OR ANTIMONY

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The dielectric properties of barium titanate doped with different concentration lanthanum or antimony are investigated. There are samples with 0.3 mol%, 0.5 mol% lanthanum and 0.1 mol%, 0.3 mol%, 0.5 mol% antimony concentrations. All samples were prepared by Pechini procedure. Dielectric measurements in the temperature range of 170 K to 420 K and frequency range of 1 kHz to 1 MHz show three phase transitions, which temperatures matches those of bulk barium titanate.

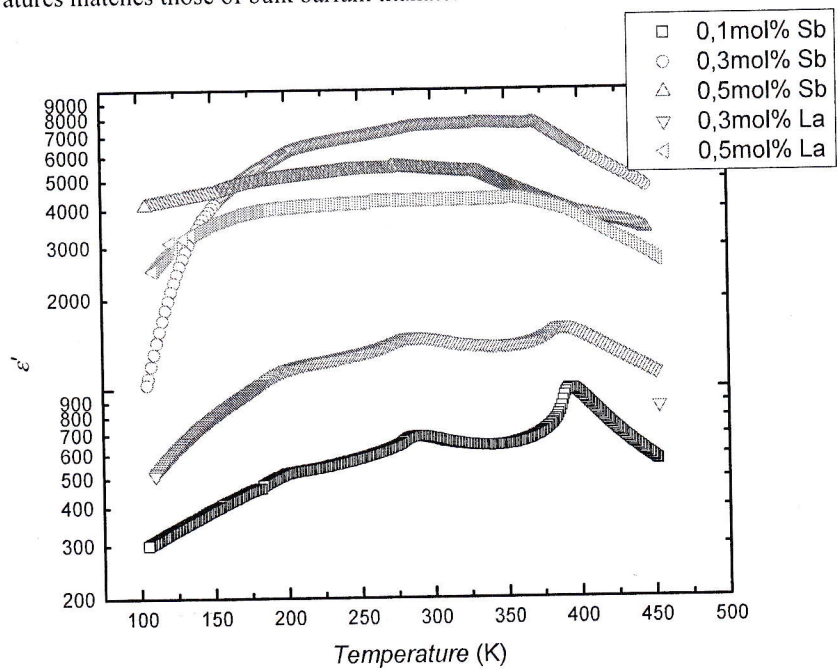

Fig. 1. Real part of dielectric constant dependency of barium titanate doped with different concentration of lanthanum or antimony at the temperature range of 120 K to 450 K at frequency 1 MHz

Curie temperature shifts to the lower temperature when lanthanum or antimony concentration grows. At low frequencies, the samples present conductivity. Conduction-

free loss spectra are calculated using a compact solution of the Kramers–Kronig transformation and an approximation based [1]:

$$\varepsilon''_{\mathrm{der}} = -\frac{\pi}{2}\frac{\partial \varepsilon'(\omega)}{\partial \ln \omega} \approx \varepsilon''_{\mathrm{rel}}$$

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