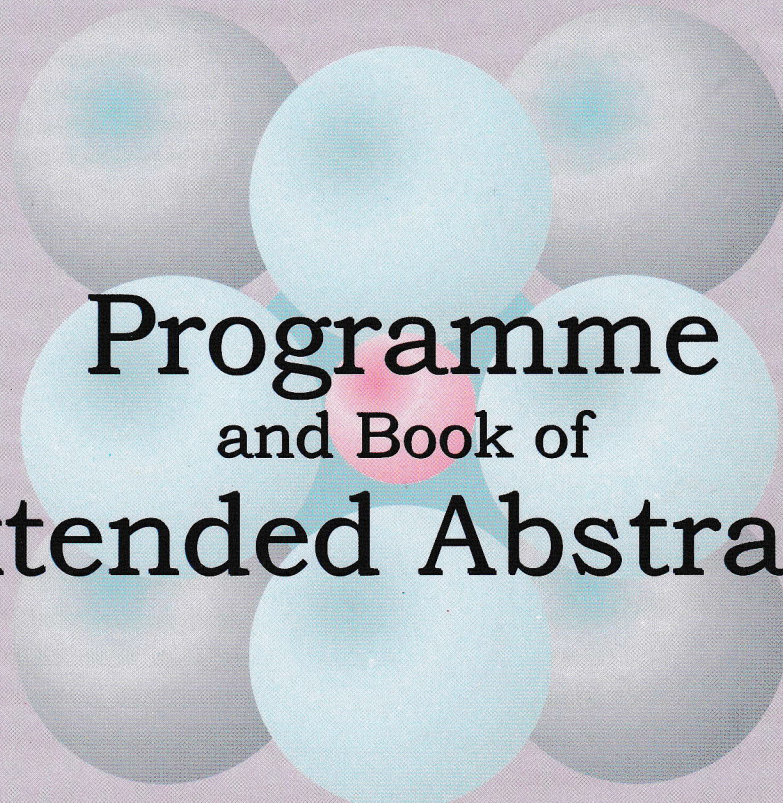


COST 539 Action - ELENA

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Programme
and Book of
Extended Abstracts

2nd Training School and 6th Workshop
*Advanced Functional Characterization
of Nanostructured Materials*

February 23-25, 2009
Madrid, Spain



**Programme and Book of Extended Abstracts
2nd Training School and 6th Workshop COST 539
*Advanced Functional Characterization of Nanostructured
Materials***

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Preface

The co-organizers of this new edition of COST 539 are pleased to begin the beginning of the activities of the COST 539 programme.

The 6th Workshop (on Nanopowders and Films) and covers a wide range of topics within the activities of COST 539. It is devoted to the scientists, devoted to the methods and to their applications. This issue is necessarily competitive in the world market.

Many of the contributions of ferroelectric materials, nanosciences and nanotechnology applications are also covered. Conductors and multiferroics in the design of their properties at the level for specific applications.

This event reflects the cooperation between the action partners and supports the development of methods of nanopowders characterization and control. It also covers advanced aspects of nanotechnology and also on multiferroic materials.

The relationship between the COST 539 programme dates back to the time of the COST 539 programme. It strengthens the numerous benefits of COST cooperation. The organizers of this Workshop are pleased to see the benefit of COST cooperation.

We sincerely wish you good luck in your research interest in Madrid.

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COST-P-3

MICROSTRUCTURE AND DIELECTRIC PROPERTIES OF LANTHANUM DOPED BARIUM TITANATE

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Barium titanate has a special place in the group of ferroelectric perovskites because it can be formulated in a large number of systems and solid solutions that provide a wide range of various applications. The perovskite structure has capability to host ions of different size, so a large number of different dopants can be accommodated in the BaTiO₃ lattice [1]. It was detected that various substitutions of Ba²⁺ and Ti⁴⁺ ions can affect on changing of microstructure and electrical properties of barium titanate ceramics.

In this work, a polymeric precursors method was used to prepare pure and barium titanate doped with different concentration (0.3 and 0.5 mol %) of lanthanum. Obtained powders were nanosized but they were also highly agglomerated. However, obtained powders were pressed in to pellets and sintered at 1300°C for 8h in air atmosphere. Previously analyzed microstructures reveal that the relatively short time of sintering (2h) was not enough for significant grain growth [2].

The formation of phase and crystal structure of BaTiO₃ was carried out by XRD analysis. Microstructural properties such as grain size distribution and morphology of sintered samples were determined using scanning electron microscope (Fig.1.). Average grain size from 0.75-1.0 μm was found in samples with 0.3 mol% La while samples with 0.5 mol % La show average grain size from 0.2-0.4 μm. Therefore, it was detected the influence of lanthanum concentration on grain growth.

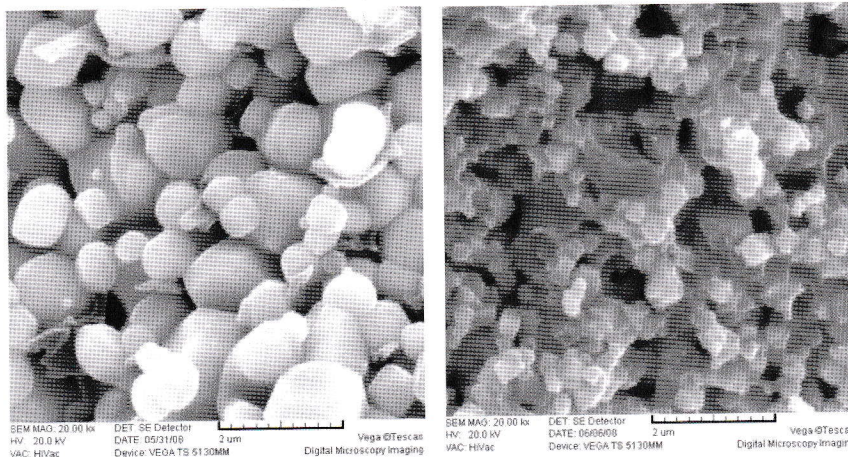


Fig.1. SEM micrographs of BT doped with (a) 0.3 and (b) 0.5 mol% of lanthanum

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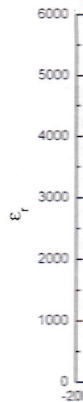


Fig.2. Dielectric constant

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on the crystal structure
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properties of BaTiO₃
September, Manchester
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titanate ceramics with s

Electrical measurement of BT ceramics were carried out and it was observed lanthanum influence on shifting of BT Curie temperature from $T_C = 119^\circ\text{C}$ for pure to 115°C and 89°C for samples doped with 0.3 and 0.5 mol% of La [3]. It was also detected the effect of lanthanum concentration on increasing of dielectric constant (Fig. 2).

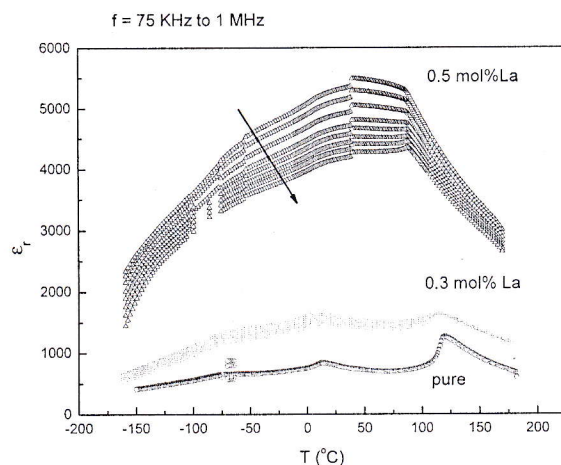


Fig.2. Dielectric constant vs. temperature for pure and doped BT with 0.3 and 0.5 mol% of La for frequency range from 75 KHz to 1 MHz

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COST-P-9

DIELECTRIC INVESTIGATION OF BARIUM TITANATE WITH 0.5% ANTIMONY

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Barium titanate (BaTiO_3) is versatile electroceramic that exhibits high permittivity (ϵ') making it desirable material for capacitor and others widespread applications. On heating, it undergoes a ferroelectric/paraelectric phase transition to the cubic polymorph at a Curie temperature T_c of $\sim 130^\circ\text{C}$, at which ϵ' passes through a maximum ϵ'_{max} and typically reaches values of ~ 10000 in undoped ceramic samples. The phase transition is first order, and the peak in ϵ' is correspondingly sharp [1].

For many years dopants have been used to modify the electrical properties of BaTiO_3 -based ceramics. For example, isovalent dopants are commonly used to alter T_c and the lower temperature orthorhombic/tetragonal and rhombohedral/orthorhombic phase transition temperatures. In this way, the temperature of ϵ'_{max} may be modified and in some cases lead to diffuse phase transition-type behavior.

We prepared 0.5% Sb-doped BaTiO_3 sample. In the present study, the real (ϵ') and imaginary (ϵ'') part and of dielectric permittivity were investigated in the frequency range of 20 Hz to 1.0 MHz at temperature range of 120 K to 460 K.

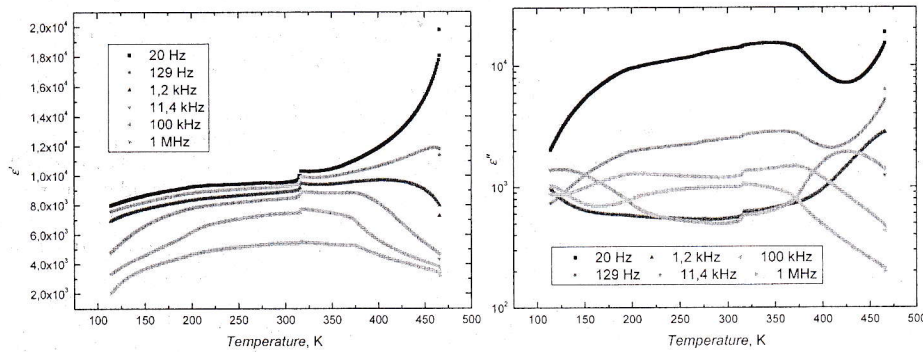


Fig. 1. Temperature dependence of the real and imaginary parts of dielectric permittivity of barium titanate with 0.5% antimony at different frequencies

How we see, the temperature dependence of the dielectric permittivity is not typical for barium titanate. But from Cole-Cole fit parameter relaxation time we see three phase transitions approximately at $T = 207$ K, 298 K and 273 K.

In this study also will be presented barium titanate Sb-doped with different concentration: 0.1% and 0.3%.

Fig. 2. The Cole –

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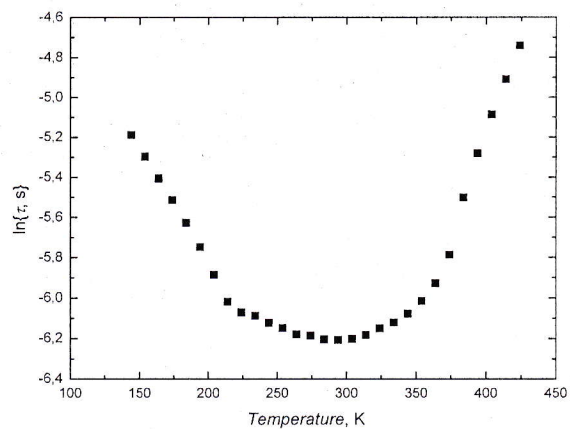


Fig. 2. The Cole – Cole relaxation time temperature dependence of barium titanate with 0.5% antimony

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COST-P-12

RAMAN STUDY OF FERROELECTRIC BARIUM BISMUTH TITANATE

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Barium bismuth titanate, BaBi₄Ti₄O₁₅ has been extensively studied for its ferroelectric and other excellent properties. BaBi₄Ti₄O₁₅ is a candidate material for high temperature piezoelectric applications, memory storage, and optical displays because of its high Curie temperature and electrooptical properties. This family of bismuth oxides, discovered more than 60 years ago by Aurivillius [1]. The structure of the Aurivillius family of compounds consist of (Bi₂O₂)²⁺ layers interleaved with perovskite-like (A_{n-1}B_nO_{3n+3})²⁻ layers. BaBi₄Ti₄O₁₅ as the n = 4 member of the Aurivillius family has Ba ions at the A sites and Ti ions at the B sites of the perovskite (A_{n-1}B_nO_{3n+3})²⁻ block ((Bi₂O₂)²⁺ · ((BaBi₂)Ti₄O₁₃)²⁻) (Fig. 1). It has a high Curie temperature of 417°C [2]. The crystal structure of BaBi₄Ti₄O₁₅ can be described by an orthorhombic or a pseudotetragonal unit cell.

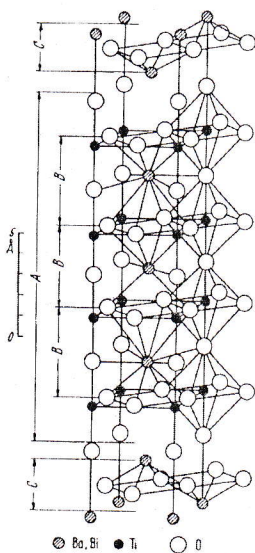


Fig.1 The lattice structure of BBT ceramics

provide indications for this compound to take a disordered structure, i.e. Ba-ions are likely to be randomly configured on Bi-ion sites in the BaBi₄Ti₄O₁₅ crystal lattice. The noticed mode at 160 cm⁻¹ is ascribed to the vibration of rigid-layer modes that are typical in these layered structures where a layer makes vibrations as a whole. The mode at 280 cm⁻¹ arises

BaBi₄Ti₄O₁₅ was prepared by homogenization and sintering of mixture of stoichiometric quantities of barium titanate and bismuth titanate obtained via mechanochemical synthesis. Barium titanate, BaTiO₃ has been synthesised from mixture of oxides BaO and TiO₂ and bismuth titanate, Bi₄Ti₃O₁₂ was prepared starting from mixture of Bi₂O₃ and TiO₂, commercially available. The reaction mechanism of BaBi₄Ti₄O₁₅ formation and the characteristics of BBT powders and ceramics were studied using XRD, Raman spectroscopy, particle size analysis and SEM. The Bi-layered perovskite structure of BaBi₄Ti₄O₁₅ forms by solid state reaction and sintering at 1100°C. Microstructure of bismuth perovskite – layered materials exhibit plate-like grains. The Ba²⁺ addition leads to the change in the microstructure development, particularly in the change of the average grain size.

The Raman spectra of BaBi₄Ti₄O₁₅ have three modes at around 160, 280 and 880 cm⁻¹ at room temperature (Fig. 2). The low-frequency modes are considerably damped, whereas the basic modes are wider in comparison to Raman modes originated from a pure Bi₄Ti₃O₁₂. Such damped frequencies

from TiO₆ octahedral vibrations. The two modes of ABi₄Ti₄O₁₅ (A = Ba) are two modes caused by the vibrations whose frequency amount corresponds to the sort of ions which vibrations are closely related

Intensity (a.u.)

Fig. 2. Raman

The obtained results symmetry was confirmed. addition leads to the crystallinity was formed structure typical for layered

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- [3] Kojima S., Imaizumi R.,

from TiO_6 octahedral vibrations and represents a combination made of bending-stretching vibrations. The two modes of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ around 537 cm^{-1} and 615 cm^{-1} change into a band in $\text{ABi}_4\text{Ti}_4\text{O}_{15}$ ($A = \text{Ba}$) around 558 cm^{-1} . This fact can be due to the line-broadening of the two modes caused by the structural disorder in $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ [3]. Hence this mode corresponds to the vibration in a pseudo-perovskite layer. Also, the mode at 880 cm^{-1} , whose frequency amounts 851 cm^{-1} in the case of a pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compound, depends on the sort of ions which are embedded in the lattice instead of Bi. The most probably, these vibrations are closely related to the vibrations of the Ba-O bond.

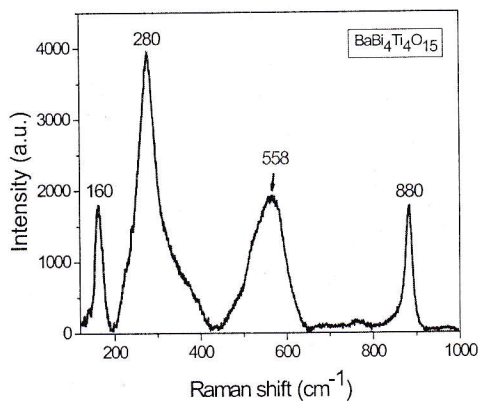


Fig. 2. Raman spectra at room temperature of the $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ceramic sintered at $1100\text{ }^\circ\text{C}$ for 4 h

The obtained results indicate that the formation of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ with tetragonal symmetry was confirmed. Only 4 Raman bands are clearly observed. It is evident that Ba^{2+} addition leads to the change in microstructure development. $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ with good crystallinity was formed after sintering without pre-calcinations step with the plate-like structure typical for layered structure materials was obtained.

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COST-P-14

ELECTRICAL PROPERTIES OF BARIUM BISMUTH TITANATE

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Family of bismuth oxides was discovered more than 50 years ago by Aurivillius [1]. Recently, there has been renewed interest in the properties of the Aurivillius phases as temperature-stable ferro-piezoelectrics [2]. Several bismuth-layered crystal structures and their properties have been investigated in detail. However, a lot of aspects of the preparation and properties of barium bismuth titanate, $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ [BBiT] remain unexplored, whereas being promising candidate for high-temperature piezoelectric applications, memory application and ferroelectric nonvolatile memories (Fe-RAM). The lattice structure of the Aurivillius family of compounds is composed of n number of like perovskite $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+3})^{2-}$ unit cells sandwiched between $(\text{Bi}_2\text{O}_2)^{2+}$ slabs along pseudo tetragonal c -axis. The 12 coordinate perovskite-like A-site is typically occupied by a large cation such as Na^+ , K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Bi^{3+} or Ln^{3+} and the 6-coordinate perovskite-like B-site by smaller cations such as Fe^{3+} , Cr^{3+} , Ti^{4+} , Nb^{5+} or W^{6+} [2]. BBiT, as the $n=4$ member of the Aurivillius family has Ba and Bi ions at the A sites and Ti ions at the B sites of the perovskite block $[(\text{Bi}_2\text{O}_2)^{2+} \cdot ((\text{BaBi}_2)\text{Ti}_4\text{O}_{13})^{2-}]$ [3].

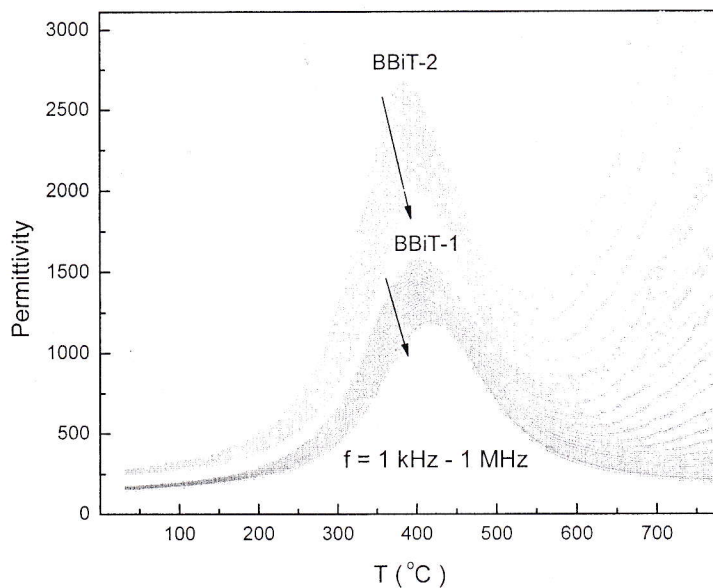


Fig. 1. The real part of dielectric permittivity as a function of temperature determined on cooling in BBiT ceramics measured in frequency interval from 1 kHz to 1 MHz. The arrow shows the direction of increase of frequency f

In present work oxides. The first route obtained via mechanical synthesis from mixture of BaO , TiO_2 and Bi_2O_3 was 4 h. Ceramic samples (MPa) pellets at 1130°C

Figure 1. display determined during cooling from 1 kHz to 1 MHz accompanied by a relaxation permittivity (ϵ_m) is shifted BBiT-2 as the frequency relaxor ferroelectric. Such Aurivillius compounds [

The value of dielectric loss kHz to 1 MHz is approx

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In present work, BBiT was prepared by solid state reaction from different starting oxides. The *first rout (BBiT-1)* is from stoichiometric quantities of $\text{BaTi}_3\text{O}_{12}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ obtained via mechanically assisted synthesis in planetary ball mill. $\text{BaTi}_3\text{O}_{12}$ has been synthesised from mixture of BaO and TiO_2 and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was prepared starting from Bi_2O_3 and TiO_2 , commercially available. The *second rout (BBiT-2)* is from mixture of oxide: BaO , TiO_2 and Bi_2O_3 which was milled for 6 h. The both 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.

Figure 1. displays the real part of dielectric permittivity as a function of temperature determined during cooling in BBiT-1 and BBiT-2 ceramics measured in frequency interval from 1 kHz to 1 MHz. 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 for BBiT-1 and from 385°C to 406°C for BBiT-2 as the frequency increases from 1 kHz to 1 MHz. This behavior is typical for relaxor ferroelectric. Such a phenomenon has already been observed in several Ba-bearing Aurivillius compounds [4].

The value of dielectric constant for BBiT-1 ceramic in frequency interval from 1 kHz to 1 MHz is approximately 1300 and for BBiT-2 approximately 2300.

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