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(71) Applicant: CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS (CSIC) [ES/ES]; C/ Serrano, 117, 28006 Madrid (ES).

(72) Inventors: **ALGUERÓ GIMÉNEZ, Miguel**; Instituto De Ciencia De Materiales De Madrid (ICMM), C/ Sor Juana Ines De La Cruz,3, 28049 Madrid (ES). **AMORÍN GONZÁLEZ, Harvey**; Instituto De Ciencia De Materiales De Madrid (ICMM), C/ Sor Juana Ines De La Cruz,3, 28049 Madrid (ES). **CASTRO LOZANO, Alicia**; Instituto De Ciencia De Materiales De Madrid (ICMM), C/ Sor Juana Ines De La Cruz,3, 28049 Madrid (ES).(74) Agent: **PONS ARIÑO, Ángel**; Glorieta Rubén Darío, 4, 28010 Madrid (ES).

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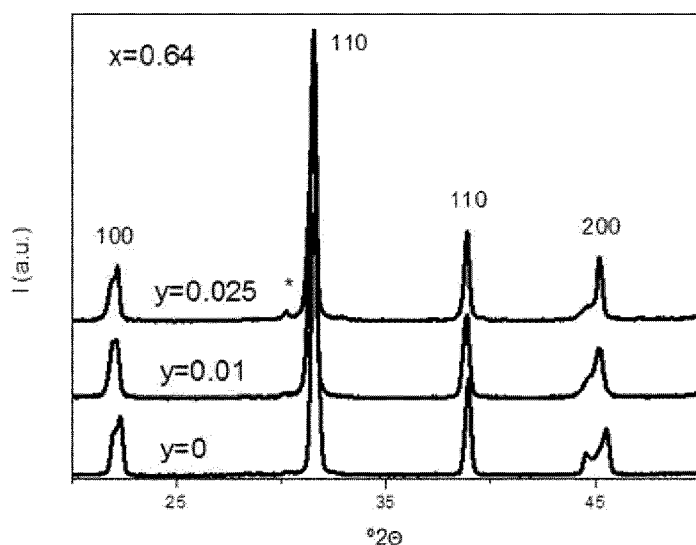
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(54) Title: A HIGH TEMPERATURE PIEZOELECTRIC $\text{BiScO}_3\text{-PbTiO}_3$ CERAMIC MATERIAL CHEMICALLY ENGINEERED FOR ENHANCED VOLTAGE RESPONSE, AND A PROCEDURE FOR OBTAINING SAID CERAMIC MATERIAL

FIG.1

(57) Abstract: The invention relates to a high temperature piezoelectric $\text{BiScO}_3\text{-PbTiO}_3$ ceramic material of formula $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_y\text{O}_3$, wherein x ranges from 0.64 to 0.68 and y ranges from 0.01 to 0.025, which includes a point defect engineering for enhanced voltage response. Furthermore, the invention refers to a procedure for obtaining said ceramic material by conventional sintering of nanocrystalline powders synthesized by mechanochemical activation of a stoichiometric mixture of precursors. Finally, the invention also relates to the use of the chemically engineered $\text{BiScO}_3\text{-PbTiO}_3$ ceramic material as part of sensing devices and magnetic sensing devices.

A HIGH TEMPERATURE PIEZOELECTRIC BISCO₃-PBTIO₃ CERAMIC MATERIAL
CHEMICALLY ENGINEERED FOR ENHANCED VOLTAGE RESPONSE, AND A
PROCEDURE FOR OBTAINING SAID CERAMIC MATERIAL

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DESCRIPTION

The invention relates to a high temperature piezoelectric BiScO₃-PbTiO₃ ceramic material of formula Bi_{1-x+2y}Pb_{x-3y}Sc_{1-x}Ti_xO₃, wherein x ranges from 0.64 to 0.68 and y ranges from 0.01 to 0,025, which includes a point defect engineering for enhanced voltage response. Furthermore, the invention refers to a procedure for obtaining said ceramic material by conventional sintering of nanocrystalline powders synthesized by mechanochemical activation of a stoichiometric mixture of precursors. Finally, the invention also relates to the use of the chemically engineered BiScO₃-PbTiO₃ ceramic material as part of sensing devices and magnetic sensing devices.

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STATE OF ART

BiScO₃-PbTiO₃ is the most promising system among general formula BiMO₃-PbTiO₃, wherein M is a trivalent cation in octahedral coordination, perovskite solid solutions with enhanced electromechanical response at ferroelectric morphotropic phase boundaries (MPB), and high Curie temperature. This material is being extensively investigated as an alternative to state of the art Pb(Zr,Ti)O₃ (PZT) for expanding the operation temperature of high sensitivity piezoelectric ceramics beyond 200°C up to 400°C.

Specifically, the binary system (1-x)BiScO₃-xPbTiO₃ presents a MPB between ferroelectric polymorphic phases of rhombohedral *R3m* and tetragonal *P4mm* symmetry at x~0.64, composition for which the Curie temperature T_C is $\approx 450^\circ\text{C}$, while piezoelectric coefficients d_{33} of $\sim 450 \text{ pC N}^{-1}$ are typically achieved after poling. This T_C is 100°C above that of Pb(Zr,Ti)O₃, likewise d_{33} that also significantly exceeds the figure of $\approx 245 \text{ pC N}^{-1}$ for ceramics of the latter material at its own MPB. Moreover, the charge piezoelectric coefficient is comparable to those of available commercial high sensitivity piezoelectric ceramics of chemically engineered PZT.

However, and in spite of the theoretically expanded operation temperature range enabled by the high Curie temperature, BiScO₃-PbTiO₃ cannot be directly used in most

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applications. This is the case of sensing technologies like accelerometers, vibration monitoring, hydrophones or magnetic field sensors, for which the voltage piezoelectric coefficient g_{33} rather than the charge piezoelectric coefficient d_{33} is the key parameter. This coefficient is equal to d_{33} times the reciprocal permittivity that is very low (or the permittivity very high) in poled $\text{BiScO}_3\text{-PbTiO}_3$. Therefore, and for the reasons stated above, it is needed to develop new $\text{BiScO}_3\text{-PbTiO}_3$ materials, optimized for specific applications.

DESCRIPTION OF THE INVENTION

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The present invention discloses a perovskite piezoelectric $\text{BiScO}_3\text{-PbTiO}_3$ material of formula $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$, wherein x ranges from 0.64 to 0.68 and y ranges from 0.01 to 0.025, which exhibits an enhanced electrochemical response at a perovskite morphotropic phase boundary between polymorphs of rhombohedral $R3m$ and tetragonal $P4mm$ symmetries, high Curie temperature, and a point defect engineering for enhanced voltage response.

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Furthermore, the high temperature, high sensitivity and enhanced voltage response piezoelectric ceramic of the present invention is a dense, and highly homogenous fine grained microstructure with an average grain size that can be tailored from 1.0 μm up to 2.5 μm . Specifically, ceramic materials with $x=0.64$ and $y=0.01$ have a Curie temperature of 395°C, and a g_{33} coefficient of $4.8 \times 10^{-2} \text{ VmN}^{-1}$.

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Moreover, the present invention discloses a procedure for obtaining said ceramic material that refers to its preparation by conventional sintering of nanocrystalline powders synthesized by mechanochemical activation of precursors in a high energy planetary mill. This procedure, based on highly reactive powders, allows the suppression of Bi_2O_3 and PbO volatilization during the high temperature sintering, so that stoichiometric mixtures of the precursors (Bi_2O_3 , Sc_2O_3 , PbO , TiO_2 and Mn_2O_3) can be used, while avoiding the necessity of controlling the atmosphere during the final thermal treatment by burying the green bodies in powder during the sintering. This is very advantageous for an accurate control of composition and phase coexistence while point defects are engineered, which cannot be reproducibly achieved by conventional ceramic technologies such as solid state synthesis by heating of precursors.

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A first aspect of the present invention relates to a piezoelectric ceramic material characterized in that it has

- the general formula $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$, wherein x ranges from 0.64 to 0.68 and y ranges from 0.01 to 0.025;
- 5 • perovskite single phase placed at a morphotropic phase boundary between polymorphs of rhombohedral $R3m$ and tetragonal $P4mm$ symmetries; and
- microstructure with average grain size of between 1.0 μm and 2.5 μm .

10 The piezoelectric ceramic material of the present invention has perovskite single phase placed at a morphotropic phase boundary between polymorphs of rhombohedral $R3m$ and tetragonal $P4mm$ symmetries that is the responsible for the high piezoelectric response and, moreover, it includes an engineered point defect for enhanced voltage response that makes the material suitable to be used in sensing technologies.

15 The term “engineered point defect” refers to a point defect that is introduced at or around a single lattice point of the perovskite, concretely by the controlled substitution of Bi^{3+} for Pb^{2+} in the A-site (cuboctahedral coordination) of the ABO_3 perovskite, along with the formulation of one Pb vacancy per each two substitutions for charge compensation. This controlled substitution that does not require additional chemical
20 species, but the introduction of an A-site non-stoichiometry, results in significant lattice stiffening and thus, a decrease of the dielectric permittivity and elastic compliance. Moreover, this is achieved while the material is maintained at the morphotropic phase boundary between polymorphs of rhombohedral $R3m$ and tetragonal $P4mm$ symmetries, known to be required for high piezoelectric response.

25 Additionally, microstructure is also controlled during the point defect engineering, so that optimized dense, homogenous fine-grained microstructure is obtained for optimal mechanical properties.

30 In a preferred embodiment, the piezoelectric ceramic material of the present invention has a dense and homogeneous fine grained microstructure with average grain size of between 1.0 μm and 1.5 μm .

In another preferred embodiment of the present invention, the piezoelectric ceramic material mentioned above has the formula $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$, wherein $x=0.64$ and $y=0.01$.

5 A second aspect of the present invention relates to a procedure for obtaining the piezoelectric ceramic material mentioned above, characterized in that it comprises the following steps:

- 10 a) synthesis of a nanocrystalline powder of formula $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$, wherein x ranges from 0.64 to 0.68 and y ranges from 0.01 to 0.025 by mechanical activation of a stoichiometric mixture of Bi_2O_3 , Sc_2O_3 , PbO and TiO_2 ; and
- b) sintering of the nanocrystalline powder obtained in step (a) at a temperature range of between 1100 °C and 1150 °C.

Step (a) is preferably performed in a planetary mill at 300 rpm for 20 h.

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In a preferred embodiment, step (a) is performed for the synthesis of a nanocrystalline powder of formula $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$, wherein x is 0.64 and y is 0.01.

A third aspect of the invention refers to a piezoelectric ceramic composite comprising

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 - the piezoelectric ceramic material according to any of claims 1 to 3; and
 - a magnetostrictive material.

The term “magnetostrictive material” refers to a ferromagnetic material that changes its shape or dimensions during the process of magnetization.

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In a preferred embodiment, the magnetostrictive material that forms the piezoelectric ceramic composite is selected from the list consisting of Terfenol-D, Metglass, spinel oxides of formula AFe_2O_4 , wherein A is Ni, Co or a combination thereof, and a combination thereof.

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In another preferred embodiment of the present invention, the piezoelectric ceramic composite mentioned above is of particulate, fiber or laminate type.

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Another aspect of the present invention refers to the use of the piezoelectric ceramic material as described above, as part of a sensing device. Examples of sensing devices

are accelerometers, vibration monitoring or hydrophones. The piezoelectric ceramic material of the present invention is the active element in these sensing technologies.

The last aspect of the invention refers to the use of the piezoelectric ceramic composite described above as part of a magnetic sensing device such as a magnetic transducer. The piezoelectric ceramic composite of the present invention comprising the piezoelectric ceramic material of the present invention and a magnetostrictive material, is the active element in magnetic sensing technologies.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skilled in the art to which this invention belongs. Methods and materials similar or equivalent to those described herein can be used in the practice of the present invention. Throughout the description and claims the word "comprise" and its variations are not intended to exclude other technical features, additives, components, or steps. Additional objects, advantages and features of the invention will become apparent to those skilled in the art upon examination of the description or may be learned by practice of the invention. The following examples and drawings are provided by way of illustration and are not intended to be limiting of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 XRD patterns for $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$ with $x=0.64$ and $y=0, 0.01$ and 0.025 ceramic samples, showing the absence of second phases other than perovskite for low concentration of point defects.

FIG.2 Patterns for $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$ with $x=0.64$ and $y=0, 0.01$ and 0.025 ceramic samples with improved statistics across the perovskite parent cubic phase 200 diffraction peak, showing polymorphic phase coexistence and thus, location of materials at the morphotropic phase boundary for low concentration of point defects.

FIG.3 Scanning electron microscopy (SEM) images for $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$ with $x=0.64$ and $y=0, 0.01$ and 0.025 ceramic samples, showing the dense and homogenous fine-grained microstructure.

FIG.4 Scanning electron microscopy (SEM) images and XRD patterns for $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$ with $x=0.66$ and $y=0.01$ and $x=0.64$ and $y=0.01$ ceramic samples, showing the ability of tailoring phase coexistence, while introducing the point defects.

5 FIG.5 Temperature dependences of the dielectric permittivity for $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$ with a) $x=0.64$ and $y=0, 0.01$ and 0.025 , b) $x=0.64, 0.65$ and 0.66 and $y=0.01$ c) $x=0.64, 0.66$ and 0.68 and $y=0.025$ ceramic samples, showing the position of the ferroelectric transition (that determines the maximum operation temperature).

10 FIG.6 Ferroelectric hysteresis loops for $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$ with a) $x=0.64$ and $y=0, 0.01$ and 0.025 , b) $x=0.64, 0.65$ and 0.66 and $y=0.01$ c) $x=0.64, 0.66$ and 0.68 and $y=0.025$ ceramic samples, showing a limited increase of the domain wall mobility after introducing the point defects.

15 FIG.7 Magnetoelectric voltage coefficient for $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$ with $x=0.64$ and $y=0$ (unmodified) or $y=0.01$ (chemically modified), showing the enhanced voltage response after introducing the point defects.

EXAMPLES

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Preparation of piezoelectric ceramic samples

Perovskite single phase nanocrystalline powders of formula $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$, wherein

x	y
0.64	0, 0.01 and 0.025
0.64 and 0.66	0.01
0.64, 0.66 and 0.68	0.025

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were synthesized by mechanochemical activation of stoichiometric mixtures of analytical grade Bi_2O_3 (Aldrich, 99.9% pure), Sc_2O_3 (Aldrich, 99.9% pure), PbO (Merck, 99% pure), and TiO_2 (anatase, Cerac, 99% pure) with a Pulverisette 6 model Fritsch planetary mill. In all cases, about 10 g of the mixture of the precursor oxides was initially homogenized by hand in an agate mortar, and placed in a tungsten carbide

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(WC) jar of 250 ml with seven, 2 cm diameter, 63 g mass each WC balls for activation at 300 r.p.m., for 20 h.

5 These conditions have been shown to provide perovskite single phase fully crystalline powders with nanometer-scale chemical homogeneity.

About 1 g of nanocrystalline powder was uniaxially pressed into 12 mm diameter pellets, which were then sintered in a closed Al_2O_3 crucible inside a furnace. A temperature of 1100°C, 1125°C and 1150°C, a soaking time of 1 h and heating/cooling rates of $\pm 3^\circ\text{C min}^{-1}$ were selected.

10 Note that significant PbO or Bi_2O_3 losses did not take place under these conditions, which allowed the use of initial precursor excesses or of sacrificial powder; that is, to bury the green bodies in powder during the thermal treatment, to be avoided. This is essential for an accurate composition and phase coexistence control, specially an issue for the problem addressed. Here point defects are engineered while maintaining full control of the structural and microstructural characteristics. Densification values above 95%, and homogenous fine-grained microstructures with average grain sizes between 1.0 and 2.5 μm were consistently achieved.

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Characterization of the piezoelectric ceramic samples

25 Samples for phase and microstructural characterizations were prepared by thinning of ceramics to remove one surface ($\sim 100\ \mu\text{m}$), followed by polishing to a mirror finish. A final thermal treatment at 600°C for 2h with $\pm 0.5^\circ\text{C min}^{-1}$ was carried out to remove the damage introduced, and to restore the equilibrium polymorphic phase coexistence and domain configurations, which are modified by the shear stresses involved in polishing.

30 Perovskite phase stability during sintering was controlled by X-ray diffraction (XRD) with a Siemens D500 powder diffractometer and Cu K_α radiation ($\lambda=1.5418\ \text{\AA}$). Patterns were recorded between 20 and 50° (2 θ) with 0.05° (2 θ) step and 5 s counting rate. Slow scans; 0.02° (2 θ) step and 10 s counting rate, were carried out between 43 and 47° (2 θ) across the perovskite parent cubic phase 200 diffraction peak, for the

analysis of the ferroelectric distortion and the evaluation of the phase percentages within the morphotropic phase boundary region.

5 Microstructure was studied with a FEI NovaTM NanoSEM 230 field emission gun scanning electron microscope equipped with an Oxford INCA 250 electron dispersive X-ray spectrometer for chemical analysis.

10 Ceramic capacitor for electrical and electromechanical characterizations were prepared by thinning discs down 0.5 mm, painting of Ag electrodes on the major faces, and their sintering at 700 °C.

15 Electrical characterization involved the characterization of dielectric permittivity and ferroelectric hysteresis loops. Dependences of the dielectric permittivity and losses on temperature were measured between room temperature (RT) and 550 °C with a HP4284A precision LCR meter. Measurements were dynamically carried out during a heating/cooling cycle with ± 1.5 °C min⁻¹ rate at several frequencies between 100 Hz and 1 MHz. Room temperature ferroelectric hysteresis loops were recorded under voltage sine waves of increasing amplitude up to 10 kV with a 0.1 Hz frequency, obtained by the combination of a synthesizer/function generator (HP 3325B) and a high
20 voltage amplifier (TREK model 10/40), while charge was measured with a homebuilt charge to voltage converter and software for loop acquisition and analysis. Subsequently, the ceramic discs were poled for electromechanical characterization. A field of 4 kV mm⁻¹ was applied at 100 °C for 15 min, and maintained during cooling down to 40 °C. The longitudinal piezoelectric coefficient d_{33} was then
25 measured 24 h after the poling step with a Berlincourt type meter. Also, the transverse piezoelectric coefficient d_{31} was obtained by complex analysis of piezoelectric radial resonances of the discs by an automatic iterative method described in C. Alemany et al J Phys D: Appl Phys 1995; 28:945. This procedure also provides the s_{11}^E and s_{12}^E compliances and ϵ_{33}^σ permittivity of the poled material all in complex form and thus, all
30 mechanical, electrical and electromechanical losses.

Preparation and characterization of a magnetoelectric composite with the piezoelectric ceramic samples

Finally, magnetoelectric composites were fabricated with selected $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$ compositions. Three-layer structures consisting of one piezoelectric ceramic disc, glued between two Terfenol-D metal alloy pieces (ETREMA Products Inc.) by using a silver loaded epoxy adhesive were built, and their magnetoelectric response characterized. A system comprising a combination of two Helmholtz coils, designed to independently provide a static magnetic field up to 1 kOe to magnetize the material, and an alternate magnetic field up to 10 Oe at 10 kHz to play as stimulus (Serviciencia S.L.), was used, while the magnetoelectric voltage response was monitored with a lock-in amplifier. A 31 geometry was chosen to obtain the transverse magnetoelectric coefficient α_{31} as a function of the bias magnetic field H , after normalization to the piezoelectric element thickness (0.5 mm).

Results

XRD patterns for $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$ with $x=0.64$ and $y=0, 0.01$ and 0.025 are shown in **Figure 1**. No second phases in addition to the perovskite one are found in the ceramics with $y=0$ and 0.01 , while an unidentified small diffraction peak appears in the material with $y=0.025$, suggesting the substitution of Bi for Pb to be incomplete at this nominal level.

Patterns for $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$ with $x=0.64$ and $y=0, 0.01$ and 0.025 with improved statistics across the perovskite parent cubic phase 200 diffraction peak, along with their deconvolution by using three pseudovoigt functions are given in **Figure 2**. Coexistence of rhombohedral and tetragonal phases is assumed for simplicity, even though the former polymorph is known to be monoclinic. Results clearly indicate all materials with increasing amount of Bi substitution to be within the morphotropic phase boundary region, yet the percentage of rhombohedral phase clearly increases with y , while the tetragonal distortion decreases.

Scanning electron microscopy (SEM) images for $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$ with $x=0.64$ and $y=0, 0.01$ and 0.025 , this is, the three materials with an increasing amount of Bi substituting for Pb are shown in **Figure 3**. A homogenous microstructure with average grain size of 2.4, 1.2 and 1.3 μm is obtained for $y=0, 0.01$ and 0.025 , respectively. A distinctive decrease in grain size thus results.

In order to obtain a series of ceramic materials with comparable phase coexistence and an increasing concentration of point defects, a new series of ceramics with $x=0.65$ and $y=0.01$, $x=0.66$ and $y=0.01$, $x=0.66$ and $y=0.025$, and $x=0.68$ and $y=0.025$ were processed and characterized.

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Microstructure coarsening was also targeted, so sintering experiments at 1125 and 1150°C were additionally carried out.

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Indeed the material with $x=0.66$ and $y = 0.01$ showed phase coexistence comparable to that of $x=0.64$ and $y=0$ (reference material with no point defect engineering). Its XRD pattern is shown in **Figure 4**, along with that of the ceramic with $x=0.64$ and $y=0.01$. Note the slight increase of tetragonal distortion with x . In this way, a material having an A-site non-stoichiometry, while still being at the core of the MPB has been chemically engineered.

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The temperature dependences of the dielectric permittivity and losses for the different $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$ materials are shown in **Figure 5**, while ferroelectric hysteresis loops are given in **Figure 6**.

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Curves corresponding to the initial series of materials with $x=0.64$ and an increasing level of Bi substitution are given in **Fig. 5(a) and 6(a)**. Note firstly in the former figure (**Fig. 6(a)**) the continuous decrease of the Curie temperature with y . The dielectric anomaly associated with the ferroelectric transition is observed at a temperature of 450, 395 and 375 °C for $y=0$, 0.01 and 0.025, respectively. A distinctive increase of the room temperature dielectric permittivity and losses of the unpoled ceramics with increasing Bi substitution is also found. Specific values are given in Table I, along with T_{CS} .

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This simultaneous increase of permittivity and losses might be interpreted as an enhancement of the domain wall mobility. Indeed ferroelectric hysteresis loops show a distinctive decrease of the coercive field, from 2.5 down to 2.0 kV mm⁻¹, when a Bi substitution of $y=0.01$ is introduced, at the same time that the remnant polarization increases from 40 up to 44 μC cm⁻². Furthermore, this takes place in spite of the decrease of grain size that is known to increase the coercive field. However, this effect might also be caused by the observed shift of the phase coexistence towards the

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rhombohedral polymorph, for its coercive field is lower than that of the tetragonal phase.

Results for the series of ceramics with increasing values of x and $y=0.01$ are presented in **Fig. 5(b) and 6(b)**. Note in the former figure the continuous increase of the Curie temperature with x . The dielectric anomaly associated with the ferroelectric transition is observed at a temperature of 395, 407 and 415 °C for $x=0.64$, 0.65 and 0.66, respectively. Specific values are also given in Table I, along with T_C s. Note also that the coercive field increases, such as the ceramic with $x=0.66$ and $y=0.01$ that has the same phase coexistence of the reference material ($x=0.64$ and $y=0$), has a similar coercive field too. This indicates that the introduced A-site non-stoichiometry does not significantly enhance the domain wall mobility, and actually, a higher remnant polarization is not obtained.

Results for the series of ceramics with increasing x and $y=0.025$ are presented in **Fig. 5(c) and 6(c)**. Note in the former figure the continuous increase of the Curie temperature with x . The dielectric anomaly associated with the ferroelectric transition is observed at a temperature of 375, 388 and 408 °C for $x=0.64$, 0.66 and 0.68, respectively. Generally speaking, materials with $y=0.025$ show a systematic decrease of the room temperature permittivity and losses with x , along with an increase of the coercive field. They also show a strong depletion of the dielectric anomaly, and reduced remnant polarization. All these strongly indicate the presence of a grain boundary phase formed by accumulation of point defects, segregated from the perovskite phase that cannot accommodate them. Results also indicate this phenomenon to become increasingly relevant as x increases, which suggest it to be a characteristic of the tetragonal polymorph.

Charge longitudinal and transverse piezoelectric coefficients after poling are given in Table I.

A first result worth commenting on is the very large enhancement of permittivity experienced by the materials at the core of the MPB after poling. The permittivity of the unmodified high sensitivity $\text{BiScO}_3\text{-PbTiO}_3$ increased from 835 up to 1486, while dielectric losses did not change. Changes in the stress state or/and in the percentage of phases in coexistence at the MPB upon poling could be responsible for the

permittivity increase. This is an issue for voltage response in sensing applications and the reason why the point defect engineering was introduced. Indeed materials with initial phase coexistence shifted towards the rhombohedral side and the A-site non-stoichiometry; those with $x=0.64$ and $y=0.01$ and 0.025 do not show a comparable increase.

A second result worth stressing out is the distinctive decrease of the elastic compliances of the poled ceramics after the introduction of the A-site non-stoichiometry. This takes place for the series of materials with $x=0.64$ and increasing y , and also for the material tailored to remain at the core of the MPB, while incorporating the point defects. This latter material does not only show smaller piezoelectric coefficients and elastic compliances than the unmodified $\text{BiScO}_3\text{-PbTiO}_3$, but also a smaller permittivity after poling, and decreased dielectric, mechanical and electromechanical losses.

Most interesting properties are obtained for the material with $x=0.64$ and $y=0.01$ that shows an enhanced remnant polarization and decreased coercive field, which result in piezoelectric coefficients close to those of the unmodified high sensitivity composition, but a significantly reduced dielectric permittivity (see Table I). As a result, its voltage piezoelectric coefficient is much higher than that of the latter material. Specifically, the g_{33} coefficient increased from 3.3×10^{-2} to $4.8 \times 10^{-2} \text{ V m N}^{-1}$ after the incorporation of the A-site-non stoichiometry. This value is also higher than that of commercially available chemically engineered PZTs with g_{33} values ranging between 2 and $2.8 \times 10^{-2} \text{ V m N}^{-1}$. Note that this enhancement is basically a consequence of the reduced permittivity of the poled material, and it is not caused by a decrease of the domain wall contribution, but of the single crystal one, either as a consequence of the modification of the phase coexistence or a direct effect of the presence of the point defects in polarizability. Moreover, the material has also a strongly decreased elastic compliance; one can assume then that the incorporation of the point defects causes an overall increase of the lattice rigidity with a direct effect on polarizability and deformability.

A new application of high sensitivity piezoelectrics is magnetoelectric composites, in which they are combined with magnetostrictive materials to provide magnetoelectricity as a product property. Magnetoelectric transducers are being considered for a range of technologies like high sensitivity, room temperature operation magnetic field sensors. It

has been shown that the voltage magnetoelectric coefficient of the simplest two-layer piezoelectric-magnetostrictive structure is given by

$$\alpha_{E,31} = \frac{\partial E_3}{\partial H_1} = \frac{-2d_{31}^p q_{11}^m v_m}{\left(s_{11}^m + s_{12}^m\right) \varepsilon_{33}^p v_p + \left(s_{11}^p + s_{12}^p\right) \varepsilon_{33}^p v_m - 2\left(d_{31}^p\right)^2 v_m} \quad (1)$$

Where d and q are the piezoelectric and piezomagnetic coefficients of the respective phases of volume v , s are the elastic compliances, and ε the permittivity, while superindex p and m refer to the piezoelectric and magnetic component, respectively. Note that the voltage response not only increases with the reciprocal permittivity, but also with the reciprocal compliances.

In **Figure 7**, the magnetoelectric voltage coefficient of three-layer structures fabricated with Terfenol-D and either the BiScO₃-PbTiO₃ material incorporating the A-site non-stoichiometry ($x=0.64$ and $y=0.01$), or the reference high sensitivity material ($x=0.64$ and $y=0$), are compared. Indeed, the magnetoelectric coefficient is increased from 0.2 up to 1.05 V cm⁻¹ Oe⁻¹ by the point defect engineering.

Table I.

		ϵ_{33}^{σ} ($x\epsilon_0$)	Tan δ	T_c ($^{\circ}\text{C}$)	d_{33} (pC N $^{-1}$)	d_{31} (pC N $^{-1}$)	ϵ_{33}^{σ} ($x\epsilon_0$)	s_{11}^E ($\times 10^{-12}$ m 2 N $^{-1}$)	s_{12}^E ($\times 10^{-12}$ m 2 N $^{-1}$)
		Unpoled	Unpoled				Poled		
y=0	x=0.64	835	0.095	450	440	-144+15i	1486-143i	13.8-0.7i	-3.6+0.2i
y=0.01	x=0.64	920	0.105	395	412	-115+10i	966-85i	11.7-0.5i	-2.7+0.1i
	x=0.65	890	0.102	407	404				
	x=0.66	1015	0.100	415	366	-105+10i	1368-107i	11.6-0.4i	-3.4+0.1i
y=0.025	x=0.64	1045	0.127	375	312	-70+8i	1012-113i	9.9-0.3i	-2.4+0.1i
	x=0.66	970	0.117	388	320				
	x=0.68	955	0.101	408	274				

CLAIMS

1. A piezoelectric ceramic material characterized in that it has:
 - the general formula $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$, wherein x ranges from 0.64 to 0.68 and y ranges from 0.01 to 0.025;
 - perovskite single phase placed at a morphotropic phase boundary between polymorphs of rhombohedral $R3m$ and tetragonal $P4mm$ symmetries; and
 - microstructure with average grain size of between 1.0 μm and 2.5 μm .
2. The piezoelectric ceramic material according to claim 1, characterized in that it has a microstructure with average grain size of between 1.0 μm and 1.5 μm .
3. The piezoelectric ceramic material according to any of claims 1 to 2, characterized in that it has the formula $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$, wherein $x=0.64$ and $y=0.01$.
4. A procedure for obtaining the ceramic material according to any of claims 1 to 3, characterized in that it comprises the following steps:
 - a) synthesis of a nanocrystalline powder of formula $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$, wherein x ranges from 0.64 to 0.68 and y ranges from 0.01 to 0.025 by mechanical activation of a stoichiometric mixture of Bi_2O_3 , Sc_2O_3 , PbO and TiO_2 ; and
 - b) sintering of the nanocrystalline powder obtained in step (a) at a temperature range of between 1100 $^{\circ}\text{C}$ and 1150 $^{\circ}\text{C}$.
5. The procedure for obtaining according to claim 4, wherein step (a) is performed for the synthesis of a nanocrystalline powder of formula $\text{Bi}_{1-x+2y}\text{Pb}_{x-3y}\text{Sc}_{1-x}\text{Ti}_x\text{O}_3$, wherein x is 0.64 and y is 0.01.
6. A piezoelectric ceramic composite comprising
 - the piezoelectric ceramic material according to any of claims 1 to 3; and
 - a magnetostrictive material.
7. The piezoelectric ceramic composite according to claim 6, wherein the magnetostrictive material is selected from the list consisting of Terfenol-D, Metglass,

spinel oxides of formula AFe_2O_4 , wherein A is Ni, Co or a combination thereof, and a combination thereof.

- 5 8. The piezoelectric ceramic composite according to any of claims 6 or 7, wherein it is of particulate, fiber or laminate type.
9. Use of the piezoelectric ceramic material according to any of claims 1 to 3 as part of a sensing device.
- 10 10. Use of the piezoelectric ceramic composite according to any of claims 6 to 8 as part of a magnetic sensing device.

FIG.1

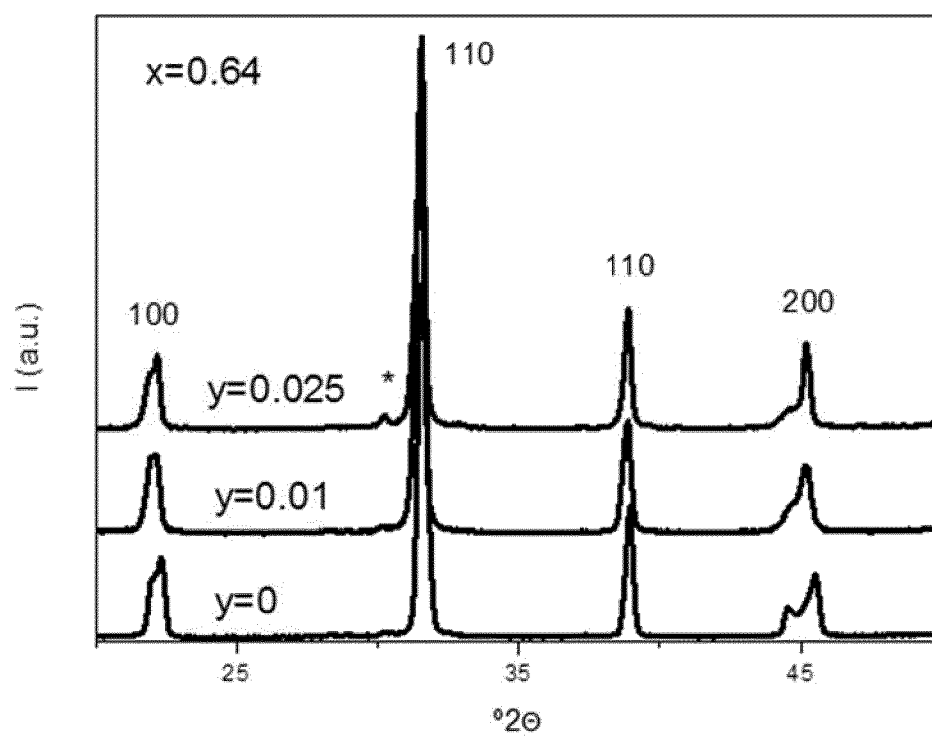


FIG.2

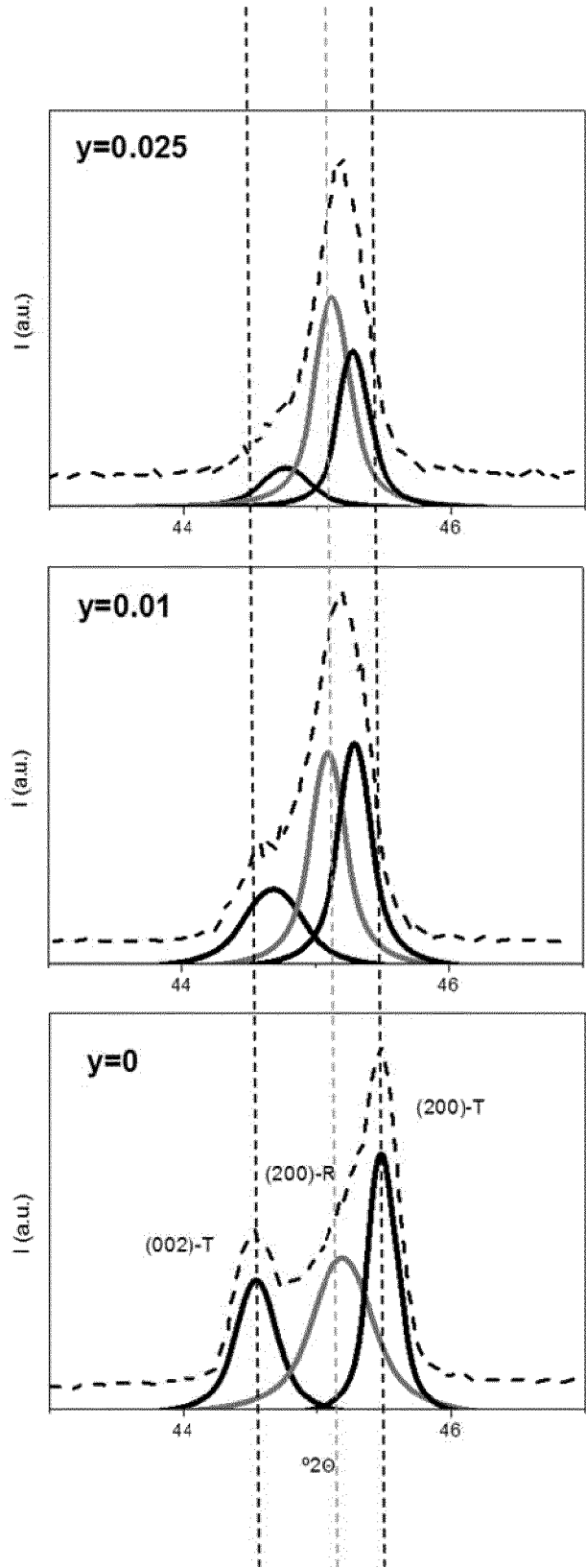


FIG.3

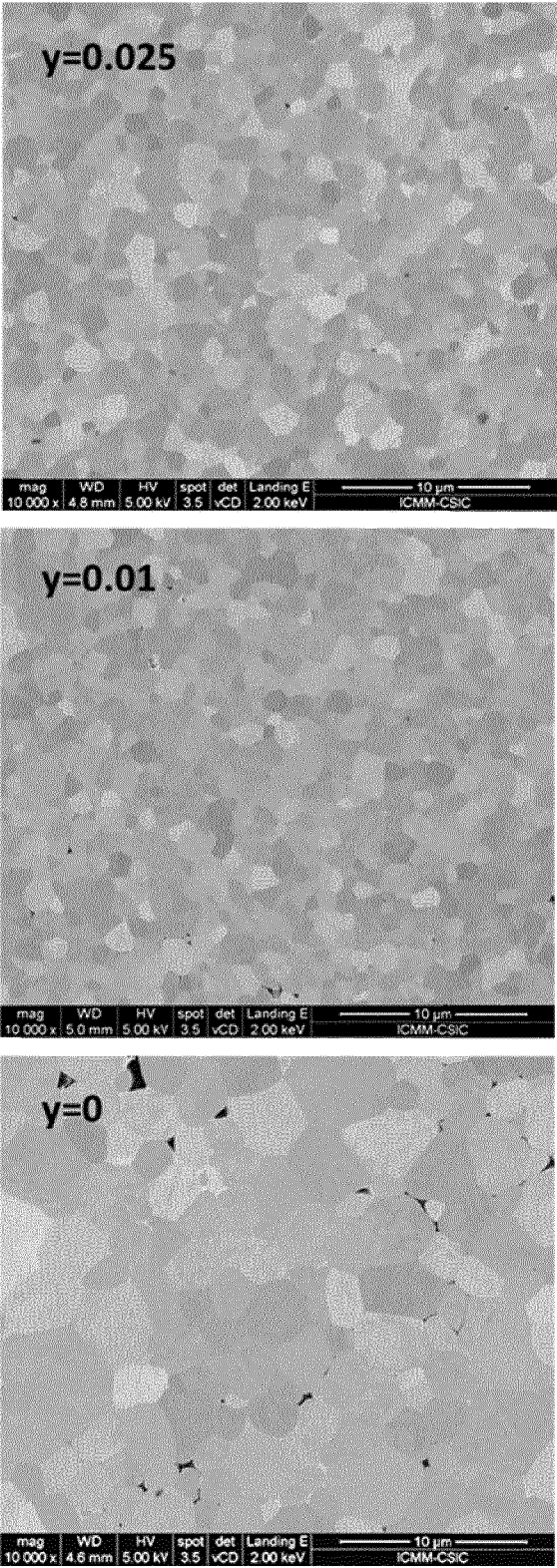


FIG.4

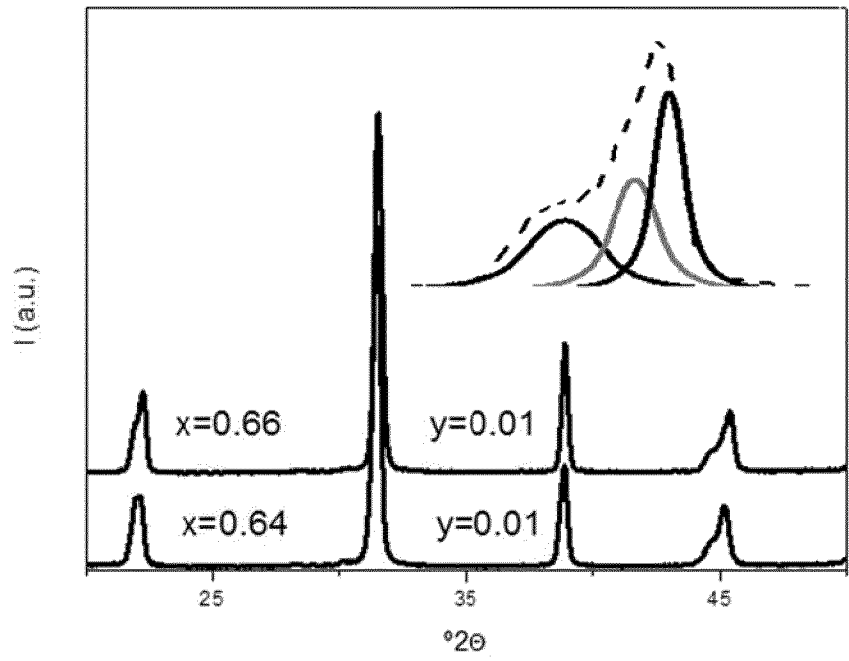
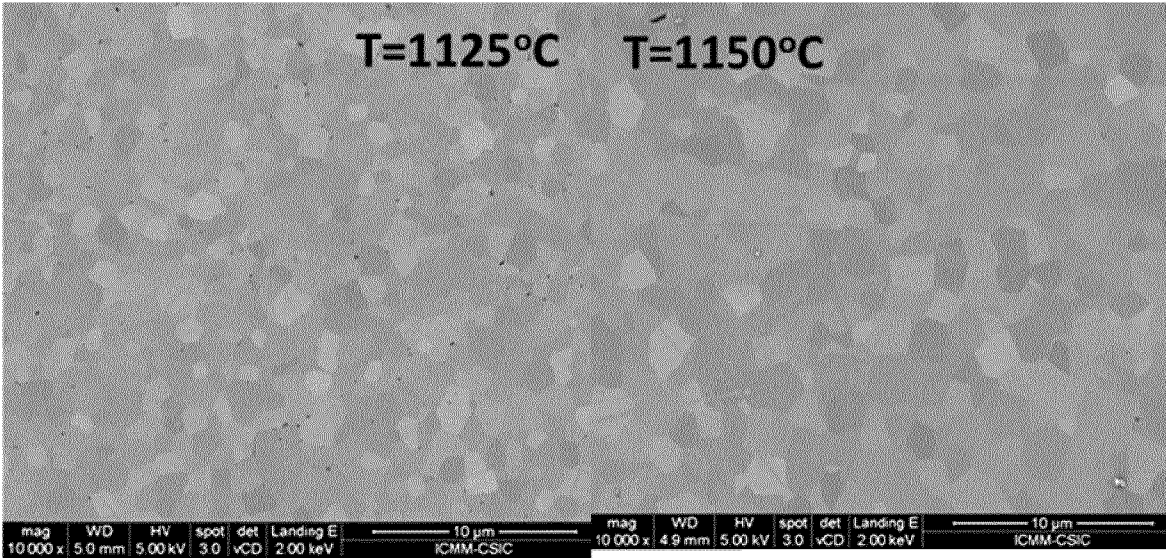
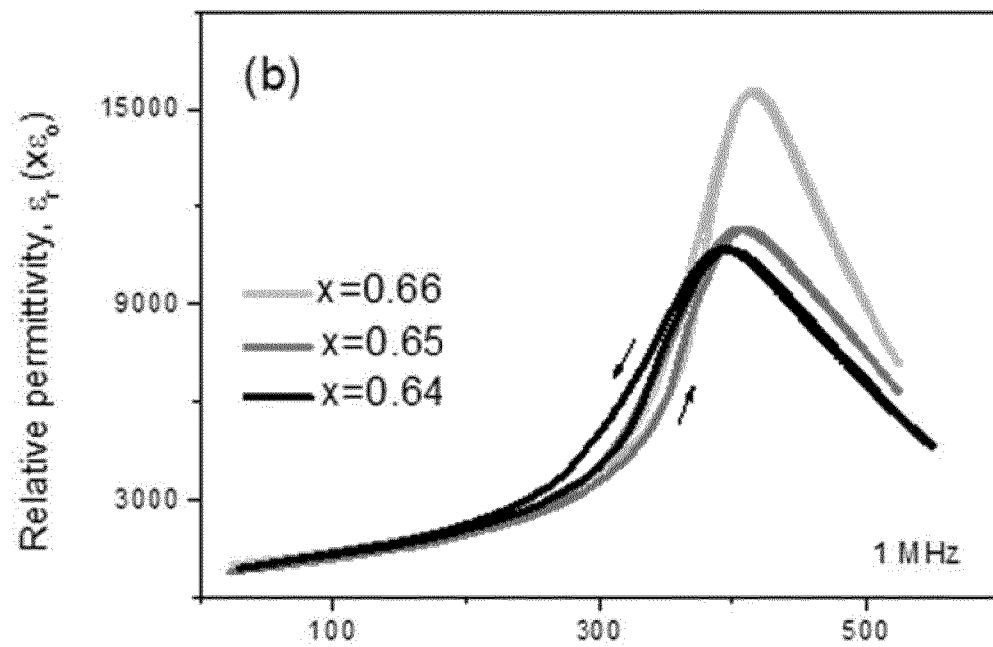
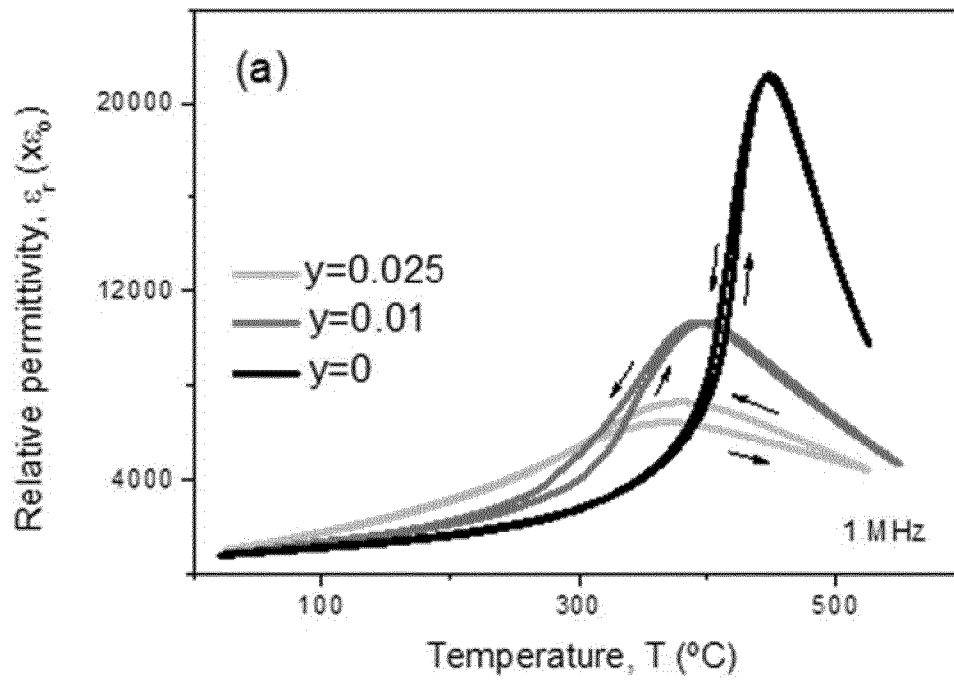


FIG.5



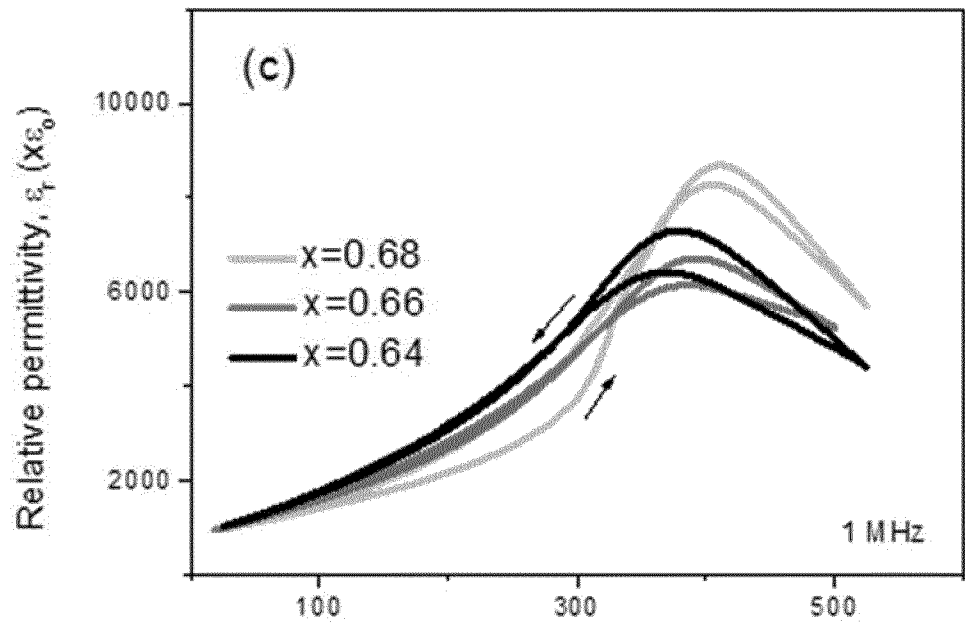
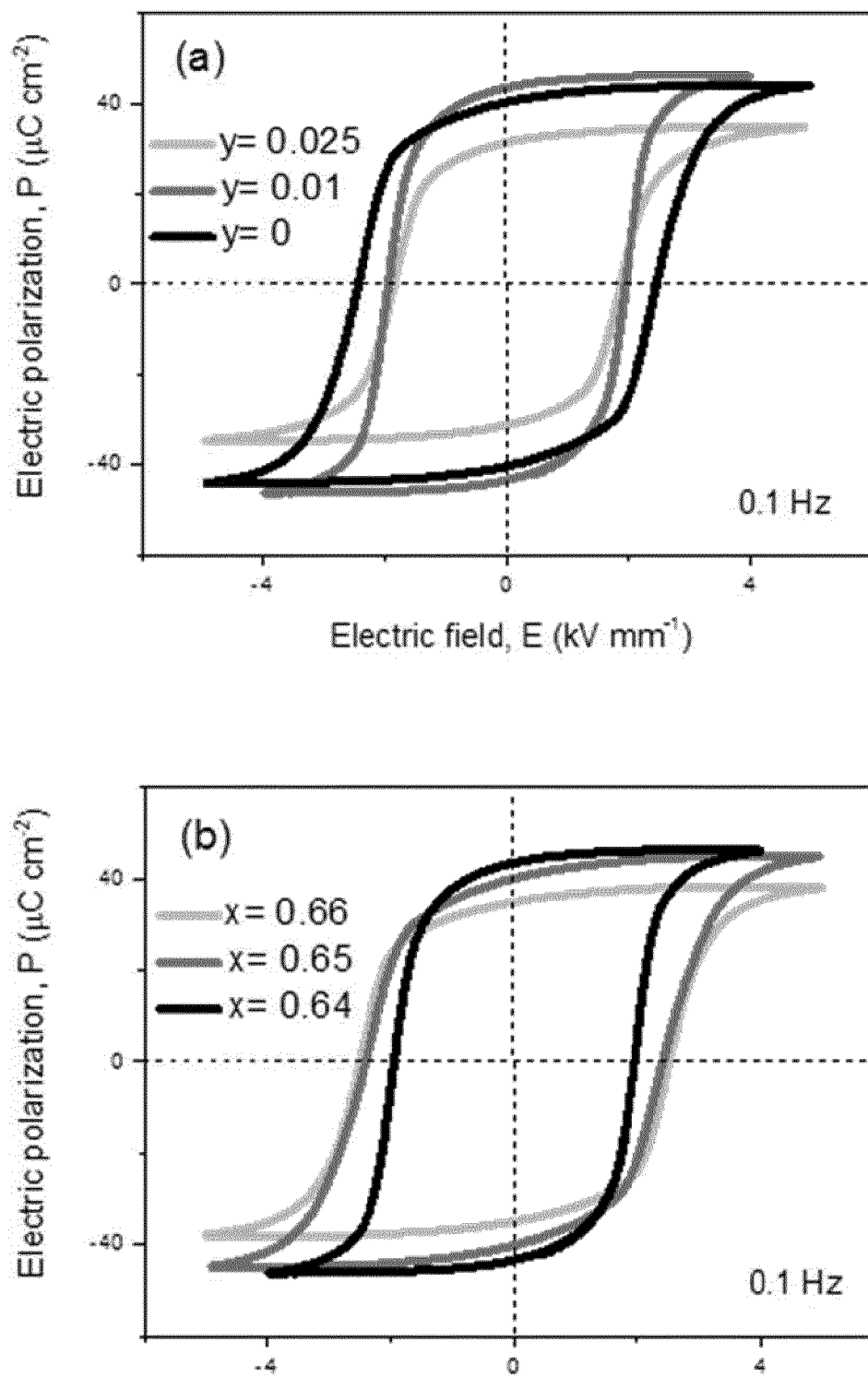


FIG.6



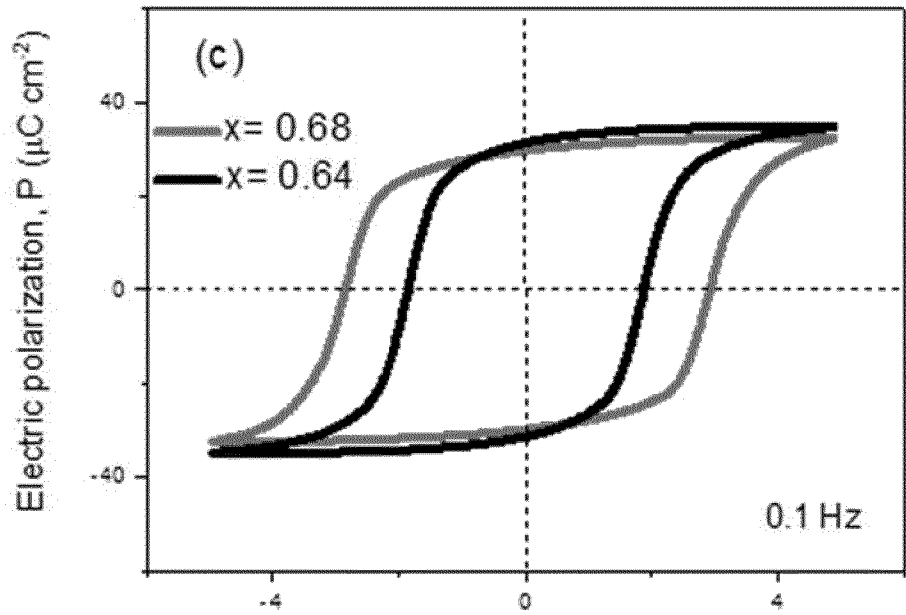
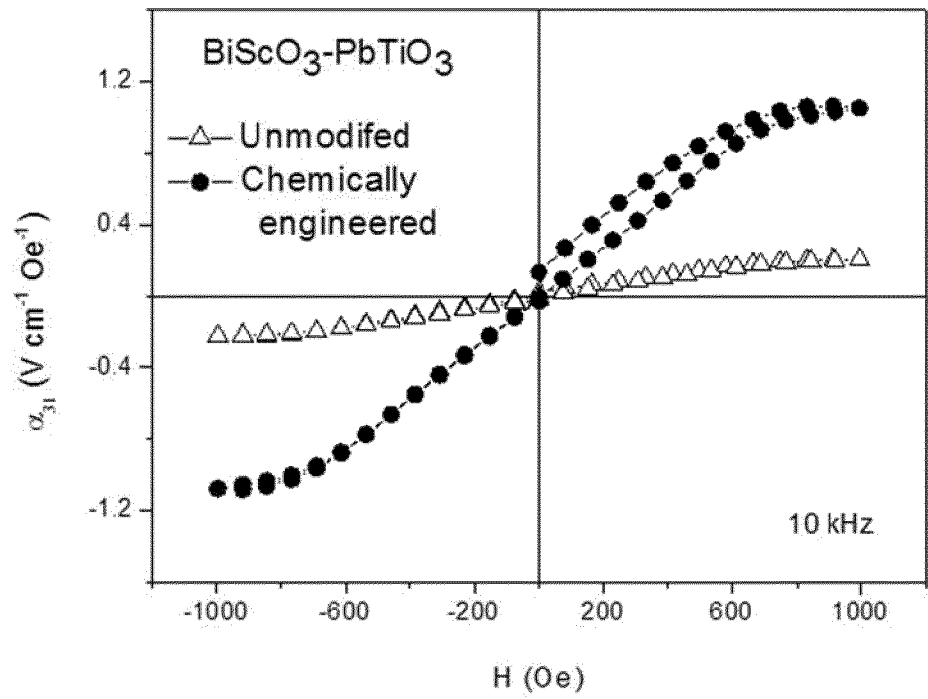


FIG.7



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/082337A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L41/187
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEN JUN ET AL: "Structural evidence for the nonmonotonic trend of TC in tetragonal PbTiO ₃ -BiScO ₃ solid solutions", APPLIED PHYSICS LETTERS, A I P PUBLISHING LLC, US, vol. 96, no. 25, 24 June 2010 (2010-06-24), pages 252908-252908, XP012131685, ISSN: 0003-6951, DOI: 10.1063/1.3456389 ----- -/--	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

31 March 2017

Date of mailing of the international search report

04/05/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Koskinen, Timo

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/082337

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LIN ZHANG ET AL: "Preparation and characterization of high T_c (1-x) BiScO₃-xPbTiO₃ ceramics from high energy ball milling process", JOURNAL OF ELECTROCERAMICS, KLUWER ACADEMIC PUBLISHERS, BO, vol. 21, no. 1-4, 17 August 2007 (2007-08-17), pages 605-608, XP019678792, ISSN: 1573-8663 -----	1-10
A	CHEN Y ET AL: "Bismuth-modified BiScO₃-PbTiO₃ piezoelectric ceramics with high Curie temperature", MATERIALS LETTERS, ELSEVIER, AMSTERDAM, NL, vol. 62, no. 20, 31 July 2008 (2008-07-31), pages 3567-3569, XP022695519, ISSN: 0167-577X, DOI: 10.1016/J.MATLET.2008.03.056 [retrieved on 2008-04-04] -----	1-10