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(54) Title: A HIGH TEMPERATURE PIEZOELECTRIC BISCO₃-PBTIO₃ CERAMIC MATERIAL CHEMICALLY ENGINEERED FOR HIGH POWER OPERATION, AND A PROCEDURE FOR OBTAINING SAID CERAMIC MATERIAL

(57) Abstract: The invention relates to a high temperature piezoelectric BiScO₃-PbTiO₃ ceramic material of formula Bi_{0.36}Pb_{0.64}Sc_{0.36-x}MnxTi_{10.6403}, wherein x ranges from 0.02 to 0.05, which includes a point defect engineering for strongly reduced dielectric and mechanical losses. Furthermore, the invention refers to a procedure for obtaining said ceramic material by conventional sintering of nano-crystalline powders synthesized by mechanochemical activation of a stoichiometric mixture of precursors.



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A HIGH TEMPERATURE PIEZOELECTRIC BISCO₃-PBTIO₃ CERAMIC MATERIAL
CHEMICALLY ENGINEERED FOR HIGH POWER OPERATION, 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_{0.36}Pb_{0.64}Sc_{0.36-x}Mn_xTi_{0.64}O₃, wherein x ranges from 0.02 to 0.05, which includes a point defect engineering for strongly reduced dielectric and mechanical losses. 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.

STATE OF ART

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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 applications. This is the case of ultrasound generation and ultrasonic motors that involve high power operation, for the material dielectric and mechanical losses cause

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heating during driving. 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 piezoelectric ceramic material of formula $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$, wherein x ranges from 0.02 to 0.05, which exhibits an enhanced electrochemical response at a perovskite morphotropic phase boundary between polymorphs of rhombohedral $R3m$ and tetragonal $P4mm$ symmetries, high
10 Curie temperature, and a point defect engineering for strongly reduced dielectric and mechanical losses. Furthermore, the high temperature, high sensitivity and low loss 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 1.5 μm up to 9 μm . Specifically, ceramic materials with $x=0.02$ have a Curie temperature of
15 435°C , and a d_{33} coefficient of 250 pC N^{-1} that can be enhanced up to 310 pC N^{-1} by microstructure coarsening, while maintaining the strongly reduced losses.

Moreover, the present invention discloses a process for obtaining said ceramic material that refers to its preparation by conventional sintering of nanocrystalline powders
20 synthesized by mechanochemical activation of precursors in a high energy planetary mill. This procedure based on highly reactive powders allows Bi_2O_3 and PbO volatilization during the high temperature sintering to be suppressed, 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
25 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.

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

- the general formula $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$, wherein x ranges from 0.02 to 0.05;
- perovskite single phase placed at a morphotropic phase boundary between
35 polymorphs of rhombohedral $R3m$ and tetragonal $P4mm$ symmetries; and

- microstructure with average grain size of between 1.5 μm and 9 μm .

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 strongly reduced dielectric and mechanical losses that enables high power operation.

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 Mn^{3+} for Sc^{3+} in the B-site (octahedral coordination) of the ABO_3 perovskite, its partial reduction to Mn^{2+} in the presence of oxygen vacancies, and the association of the two chemical species to form Mn^{2+} -Oxygen vacancy dipolar complexes that effectively decrease the ferroelectric domain wall mobility, and thus, result in the reduced dielectric and mechanical losses. This controlled substitution 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.

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

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 1.5 μm and 3 μm .

In another preferred embodiment of the present invention, the piezoelectric ceramic material mentioned above has the formula $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$, wherein x ranges from 0.02 and 0.03.

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

- a) synthesis of a nanocrystalline powder of formula $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$, wherein x ranges from 0.02 to 0.05, by mechanochemical activation of a stoichiometric mixture of Bi_2O_3 , Sc_2O_3 , PbO , TiO_2 and Mn_2O_3 ; and
- b) air sintering of the nanocrystalline powder obtained in step (a) at a temperature range between 1100 °C and 1150 °C.

In a preferred embodiment, the activation of step (a) is performed, in a planetary mill, at 300 rpm for times between 15 h and 20 h.

- 10 A third aspect of the invention refers to the use of the piezoelectric ceramic material mentioned above, as part, so to say active element in ultrasound generation devices or ultrasonic motors.

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.

25 BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 XRD patterns for $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with x=0, 0.02 and 0.05 ceramic samples, showing the absence of second phases other than perovskite.

- 30 FIG. 2 XRD patterns with improved statistics across the perovskite parent cubic phase 200 diffraction peak for $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with x=0, 0.02 and 0.05 ceramic samples, showing polymorphic phase coexistence and thus, location of materials at the morphotropic phase boundary.

FIG. 3 Scanning electron microscopy (SEM) images for $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with $x=0, 0.02$ and 0.05 ceramic samples, showing the dense and homogenous fine-grained microstructure.

- 5 FIG. 4 SEM image and XRD pattern of a $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with $x=0.02$ ceramic sample with coarsened microstructure.

- FIG. 5 Arrhenius plots for the total dc conductivity for $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with $x=0, 0.02$ and 0.05 A) fine-grained and B) coarsened (EGG) ceramic samples, C) along
10 with its bulk and grain boundary components, demonstrating the correct incorporation of the point defects (by the appearance of the low temperature electronic conduction mechanism with $E_g \approx 0.65$ eV).

- FIG. 6 Relative permittivity $\epsilon_r (\chi\epsilon_0)$ vs Temperature ($^{\circ}\text{C}$) of $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$
15 with $x=0, 0.02$ and 0.05 A) fine-grained and B) coarsened (EGG) ceramic samples, showing the position of the ferroelectric transition (that determines the maximum operation temperature).

- FIG. 7 Ferroelectric hysteresis loops for $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with $x=0, 0.02$ and
20 0.05 fine-grained and coarsened (EGG) ceramic samples, showing the effect of the point defect engineering in increasing coercive field (and thus decreasing the ferroelectric domain wall mobility).

- FIG. 8 Piezoelectric radial resonances for $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with $x=0$ and
25 0.02 fine grained and coarsened (EGG) ceramic samples, showing the effect of the point defect engineering in increasing the mechanical quality factor (and thus decreasing losses).

EXAMPLES

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Preparation of $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with $x=0, 0.02$ and 0.05 piezoelectric ceramic samples

- Perovskite single phase nanocrystalline powders of $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with
35 $x=0, 0.02$ and 0.05 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), TiO_2 (anatase, Cerac, 99% pure) and Mn_2O_3 (Aldrich, 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 (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.

These conditions 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, a soaking time of 1 h and heating/cooling rates of $\pm 3\text{ °C min}^{-1}$ were selected.

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 1.5 and 3 μm were consistently achieved.

Furthermore, a $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ piezoelectric ceramic sample with $x=0.02$ and coarsened microstructure (labeled with EGG in the drawings) was prepared by decreasing the activation time during the mechanosynthesis from 20 h down to 15 h, and increasing the temperature during sintering from 1100 °C up to 1125 °C.

30 **Characterization of the piezoelectric ceramic material**

Samples for phase and microstructural characterizations were prepared by thinning of ceramics to remove one surface ($\sim 100\text{ }\mu\text{m}$), followed by polishing to a mirror finish. A final thermal treatment at 600 °C for 2h with $\pm 0.5\text{ °C min}^{-1}$ 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.

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

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.

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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 .

Electrical characterization started by evaluating the total dc conductivity, along with its bulk and grain boundary components by impedance spectroscopy analysis. Data were recorded in static conditions, from 250°C to 550°C , at 20°C intervals, in the 20 Hz – 1 MHz range with a HP4284A precision LCR meter. The Z-view2 commercial software was used for the analysis.

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Dielectric permittivity and ferroelectric hysteresis loops were characterized in a second stage. 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 $\pm 1.5^\circ\text{C min}^{-1}$ 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 voltage amplifier (TREK model 10/40), while charge was measured with a homebuilt charge to voltage converter and software for loop acquisition and analysis.

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Finally, 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 measured 24 h after the
5 poling step with a Berlincourt type meter. Also, the transverse piezoelectric coefficient was obtained by complex analysis of piezoelectric radial resonances of the discs by the 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 mechanical, electrical and
10 electromechanical losses.

XRD patterns for fine-grained ceramic materials of $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with $x=0, 0.02$ and 0.05 are shown in Figure 1. No second phases in addition to the perovskite one are found in the ceramics with an increasing level of Mn substitution,
15 indicating the targeted incorporation of the new atomic species into the structure.

Patterns 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.
20 Results clearly indicate all materials with increasing amount of Mn to be within the morphotropic phase boundary region.

Indeed, the percentage of rhombohedral and tetragonal phases does not change significantly after substitution with $x=0.02$, the only effect being a small shift of all peaks
25 towards higher angles. This indicates cell shrinkage, which was expected from the ionic radii for sixfold coordination of Sc^{3+} and Mn^{3+} that are $0.745 \text{ \AA}$ and $0.58/0.645 \text{ \AA}$ (low/high spin configurations), respectively.

Larger changes are found after substitution with $x=0.05$, which results in an increase of
30 the rhombohedral percentage, yet still in coexistence with the tetragonal phase, which also shows a decreased tetragonal distortion.

Scanning electron microscopy (SEM) images for the fine-grained ceramics of $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with $x=0, 0.02$ and 0.05 are shown in Figure 3. A
35 homogenous microstructure with average grain size of $2.4, 1.7$ and $2.3 \text{ }\mu\text{m}$ for $x=0,$

0.02 and 0.05 is obtained. No significant microstructural changes are thus induced by the Mn substitution.

SEM images for a ceramic sample of $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with $x=0.02$ and a coarsened microstructure are shown in Figure 4, along with its XRD pattern. No second phases are found in XRD, though a liquid phase is clearly observed at treble points and grain boundaries in SEM. This suggests the occurrence of exaggerated grain growth, and indeed an average grain size of 9 μm resulted.

The effective incorporation of Mn into the perovskite, avoiding the segregation of manganese oxides at the grain boundaries, is clearly indicated by changes in conductivity after Mn substitution. Figure 5a shows the Arrhenius plots for the total dc conductivity of $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with $x=0, 0.02$ and 0.05 samples. All materials show a common high temperature regime characterized by activation energy of 1.1-1.2 eV. This figure is typical of the electromigration of mobile doubly ionized oxygen vacancies $\text{V}_{\text{O}}^{\bullet\bullet}$ and thus, ionic conductivity is assumed to dominate the electrical response above 400°C. A distinctive decrease of conductivity takes place in this regime after Mn substitution. This effect is associated with the partial reduction of the Mn^{3+} to Mn^{2+} , and its association with oxygen vacancies to form dipolar complexes that effectively pin the ionic charge carriers.

In the case of the ceramic materials without Mn substitution ($x=0$), the temperature dependence of conductivity shows a distinctive change of slope at $\sim 450^\circ\text{C}$, below which the activation energy increases up to 1.6 eV. This temperature is that of the ferroelectric transition, at which ferroelectric domains develop. Assuming oxygen vacancies to be still the charge carriers, it is suggested that the increase of activation energy might be associated with domain walls being an obstacle to the movement of the oxygen vacancies.

A very different behavior is found for the materials with Mn substitution ($x=0.02$ and 0.05). A change of slope is also observed, but indicating, in this case, a decrease of activation energy down to 0.65 eV. This figure is rather typical of electronic conduction than of ionic one, and it is associated with hole conduction within the valence band, specifically with electron hopping between Mn^{2+} and Mn^{3+} at the B-site.

Impedance spectroscopy analysis was used to isolate bulk (or grain) and grain boundary contributions to the total electrical response, and to confirm that Mn effects on conductivity were truly bulk effects, and not grain boundary ones. Data were initially analyzed using the electric modulus formalism, which allowed two Debye-like relaxation processes to be readily identified for all materials with increasing content of Mn. This indicates the presence of two electroactive regions that are associated with the bulk (low frequency process) and grain boundary (high frequency process). The contributions of the two regions were separated by using an equivalent electric circuit to model the experimental data. A series connection of two parallel (RQC) and (RQ) elements for the bulk and grain boundary components was used respectively. Results are given in the Figure 5B. Note that the low temperature electronic process that has been associated with hopping between Mn^{2+} - Mn^{3+} species at the B-site of the perovskite is observed in the bulk component. This definitively confirms the correct incorporation of Mn into the perovskite.

Results for the material with a coarsened microstructure are also given in the Figure 5B. The main features of conductivity are reproduced indicating that exaggerated grain growth does not result in Mn segregating at grain boundaries.

Mn incorporation into the bulk perovskite is also indicated by the decrease of the ferroelectric transition temperature with increasing substitution, evaluated from the position of the dielectric anomaly. This shift is illustrated in Figure 6a, where the temperature dependence of permittivity is shown for the three ceramics along a full heating/cooling cycle from RT up to 550°C. The dielectric anomaly associated with the transition is observed at a temperature of 450, 435 and 420 °C for $x=0$, 0.02 and 0.05, respectively. A distinctive decrease of the room temperature dielectric permittivity and losses of the unpoled ceramics is also found with increasing Mn content.

In Figure 6b, the permittivity of the fine-grained material with $x=0.02$ is compared to a ceramic with coarsened microstructure. It is found that exaggerated grain growth does not modify the position of the ferroelectric transition, but results in an increased permittivity, such as the ceramic materials with $x=0.02$ and a grain size of 9 μm has a permittivity larger than the fine grained material with $x=0$.

- The Curie temperature (T_C), dielectric permittivity (ϵ_{33}^σ unpoled) and losses ($\tan \delta$ unpoled) for the unpoled state, and all parameters after poling: longitudinal piezoelectric coefficient (d_{33}), transverse piezoelectric coefficient (d_{31}), longitudinal elastic compliance (s_{11}^E), and transverse elastic compliance (s_{12}^E) for the fine-grained and coarsened (EGG) ceramic samples of $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with $x=0, 0.02$ and 0.05 are given in Table I.

$\text{Bi}_{0.36}$ $\text{Pb}_{0.64}$ $\text{Sc}_{0.36-x}$ Mn_x $\text{Ti}_{0.64}$ O_3 Samples	ϵ_{33}^σ ($x\epsilon_0$) Unpoled	$\tan \delta$ Unpoled	T_C ($^\circ\text{C}$)	d_{33} (pC N^{-1})	d_{31} (pC N^{-1})	ϵ_{33}^σ ($x\epsilon_0$) Poled	s_{11}^E ($\times 10^{-12}$ $\text{m}^2 \text{N}^{-1}$)	s_{12}^E ($\times 10^{-12}$ $\text{m}^2 \text{N}^{-1}$)
$x=0$	835	0.095	450	440	- 144+15i	1486- 143i	13.8-0.7i	-3.6+0.2i
$x=0.02$	820	0.055	435	250	-83+i	1153- 16i	11.3-0.1i	-3.4
$x=0.05$	730	0.025	420	210	-76+i	935-12i	10.6	-3.0
$x=0.02$ EGG	1045	0.050	435	310	-83+3i	978-27i	12.1-0.1i	-4.0

- Ferroelectric hysteresis loops for the fine-grained and coarsened ceramic samples of $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with $x=0, 0.02$ and 0.05 are shown in Figure 7. Note the distinctive increase of coercive field, from 2.5 up to 3.5 kV mm^{-1} , when a Mn content of $x=0.02$ is introduced. This takes place in two materials with very similar grain size and phase coexistence, so it is a direct evidence of domain wall mobility being reduced after Mn substitution.

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- It is surprising the strong depletion of the ferroelectric switching characteristics for the material with $x=0.05$ that has a remnant polarization of $13 \mu\text{C cm}^{-2}$, as compared with 36 and $40 \mu\text{C cm}^{-2}$ for those with $x=0.02$ and 0 . Its lean character is typical of materials with frozen strain or/and compositional gradients, which might be also responsible of the smaller tetragonal distortion found. Besides, this could explain why conductivity

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values hardly change from $x=0.02$ and 0.05 . This material is thus assumed to be inhomogeneous; most probably regarding Mn substitution.

Charge longitudinal coefficient d_{33} values after poling are given in Table I. There is a continuous decrease with x , from 440 down to 250 and 210 pC N⁻¹ for $x=0$, 0.02 and 0.05 , respectively.

Piezoelectric radial resonances are shown in Figure 8 for the materials with $x=0$ and 0.02 . Note the significant narrowing of the resonances after Mn addition (also observed for $x=0.05$ not shown), related to an increase of the mechanical quality factors Q_s and Q_p from 20 and 45 to 235 and 400.

Complex material coefficients obtained from the analysis of these resonances are given in Table I. All the d_{31} piezoelectric coefficient, s_{11}^E and s_{12}^E compliances, and ϵ_{33}^σ permittivity decrease with x , along with all losses, either dielectric, mechanical or electromechanical from values of 0.096, 0.05 and 0.1 down to 0.014, 0.009 and 0.01, respectively when a Mn level of $x=0.02$ is substituted, while microstructure is maintained constant. A slight broadening of the piezoelectric resonance takes place after exaggerated grain growth for $x=0.02$, though the mechanical quality factor does not return to the values of the unmodified material, like do not all coefficient and losses.

CLAIMS

1. A piezoelectric ceramic material characterized in that it has
- the general formula $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$, wherein x ranges from x=0.02 to 0.05;
 - 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 1.5 μm and 9 μm .
2. The ceramic material according to claim 1, characterized in that it as a microstructure with average grain size of between 1.5 μm and 3 μm .
3. The ceramic material according to any of claims 1 and 2, characterized in that it has the formula $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$ with x between 0.02 and 0.03.
4. A process of obtainment of the ceramic material according to any of claim 1 to 3, characterized in that it comprises the following steps:
- a) synthesis of a nanocrystalline powder of formula $\text{Bi}_{0.36}\text{Pb}_{0.64}\text{Sc}_{0.36-x}\text{Mn}_x\text{Ti}_{0.64}\text{O}_3$, wherein x ranges from 0.02 to 0.05, by mechanochemical activation of a stoichiometric mixture of Bi_2O_3 , Sc_2O_3 , PbO , TiO_2 and Mn_2O_3 ; and
 - b) air sintering of the nanocrystalline powder obtained in step (a) at a temperature range between 1100 °C and 1150 °C.
5. The process of obtainment of the ceramic material according to claim 4, characterized in that the activation of step (a) is performed, in a high energy planetary mill, at 300 rpm, for times ranging between 15 h and 20 h.
6. Use of the ceramic material according to any of claim 1 to 3, as part of ultrasound generation devices or ultrasonic motors.

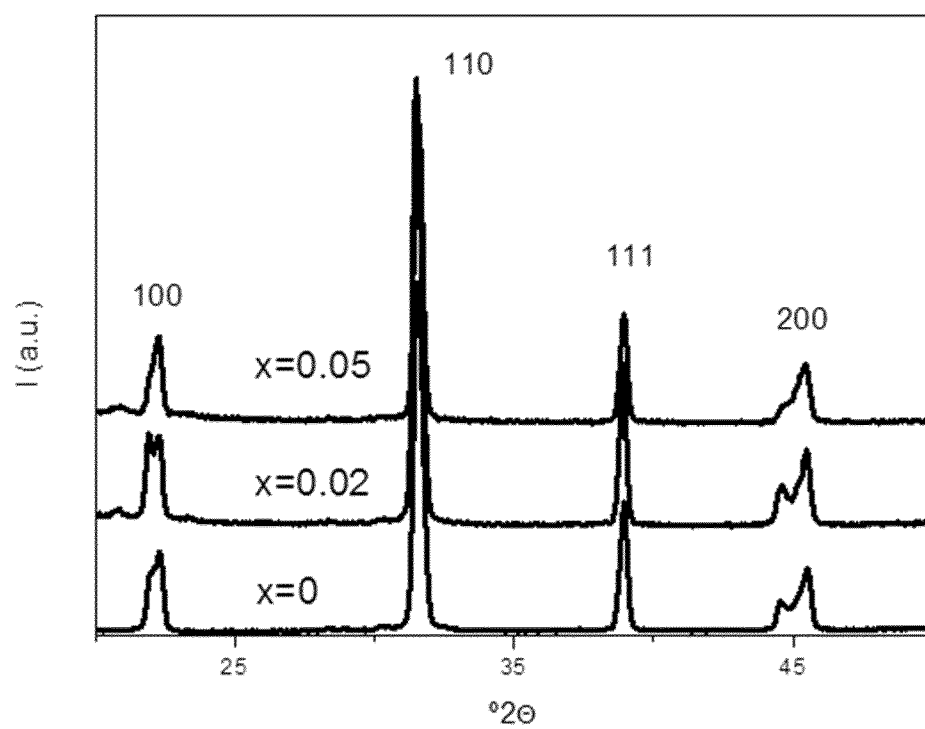


FIG. 1

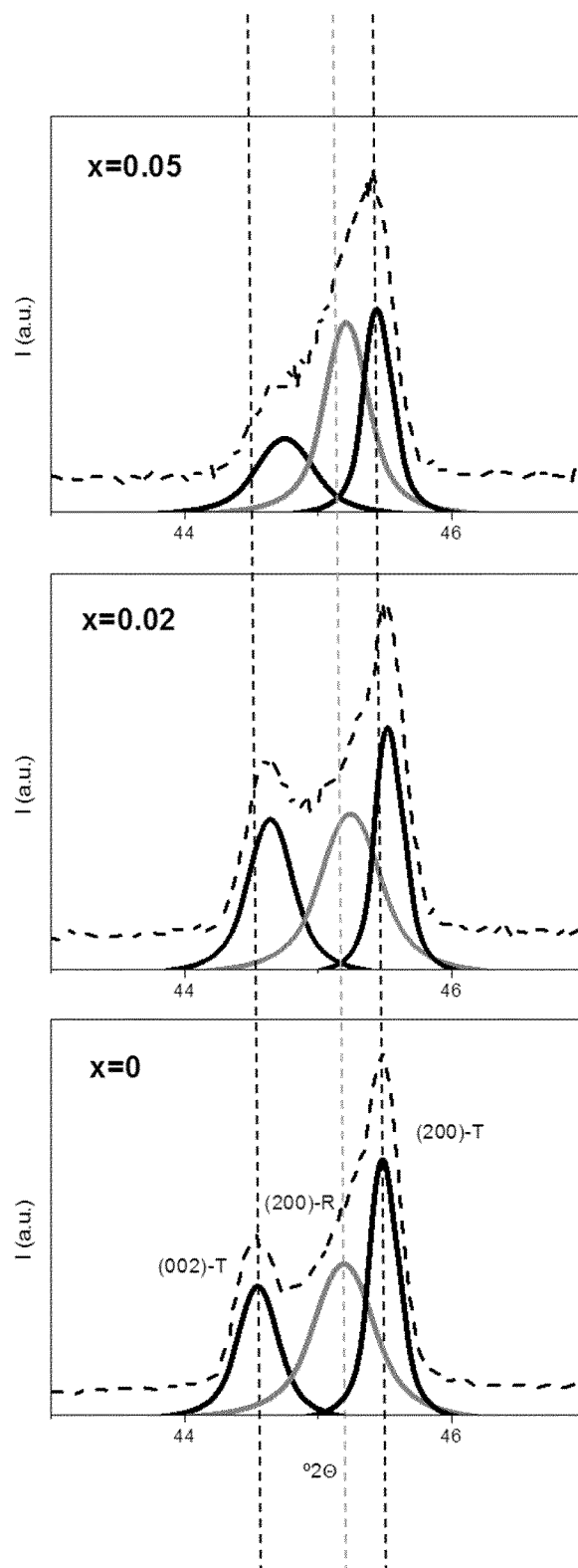


FIG. 2

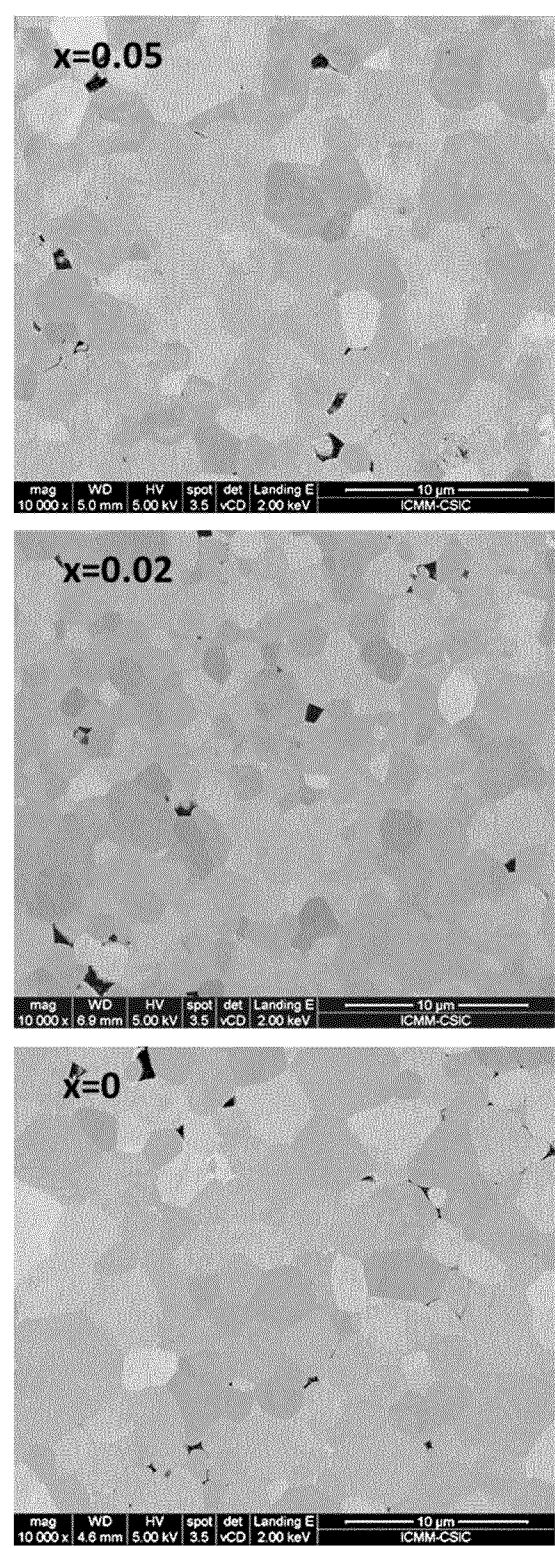
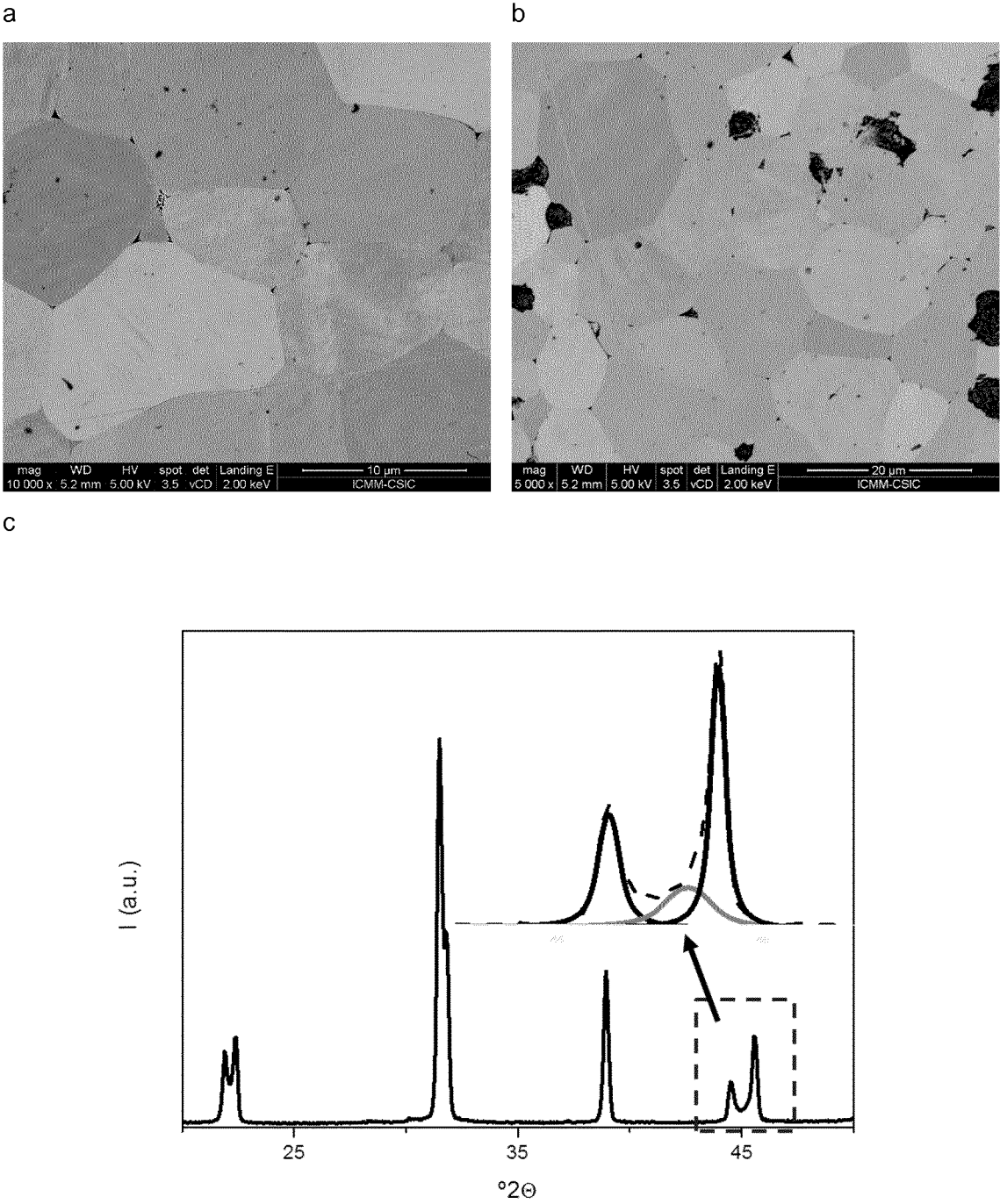


FIG. 3



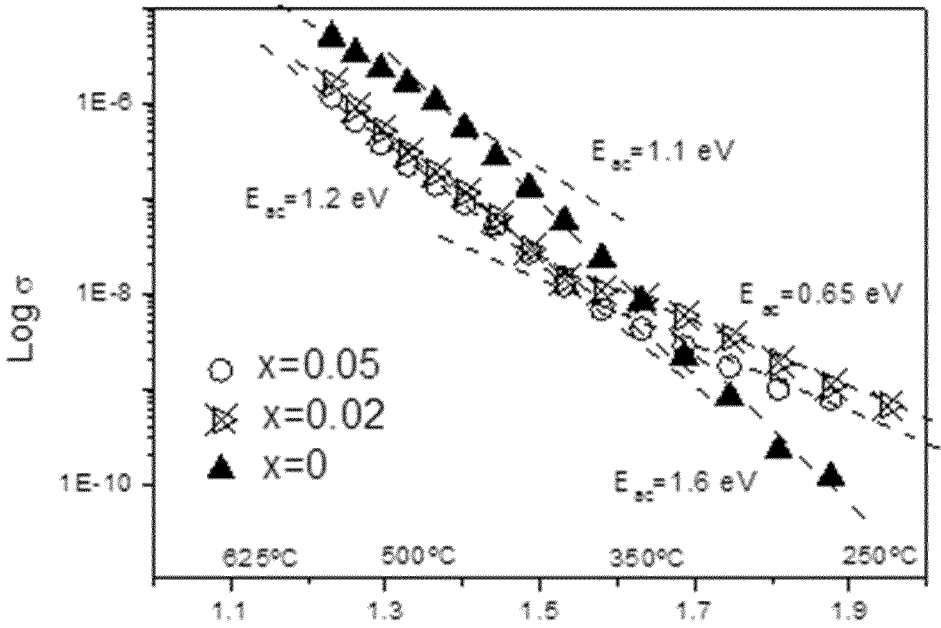


FIG 5A

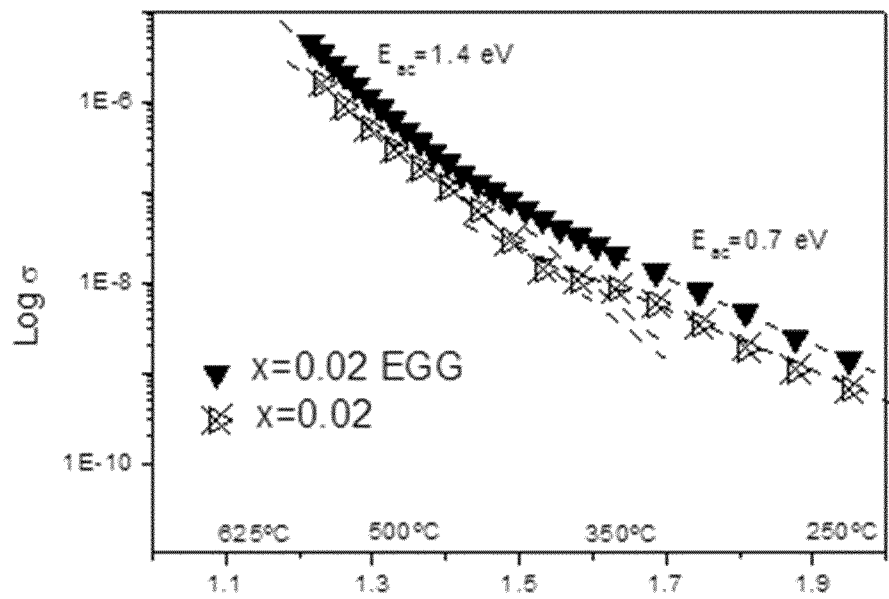


FIG. 5B

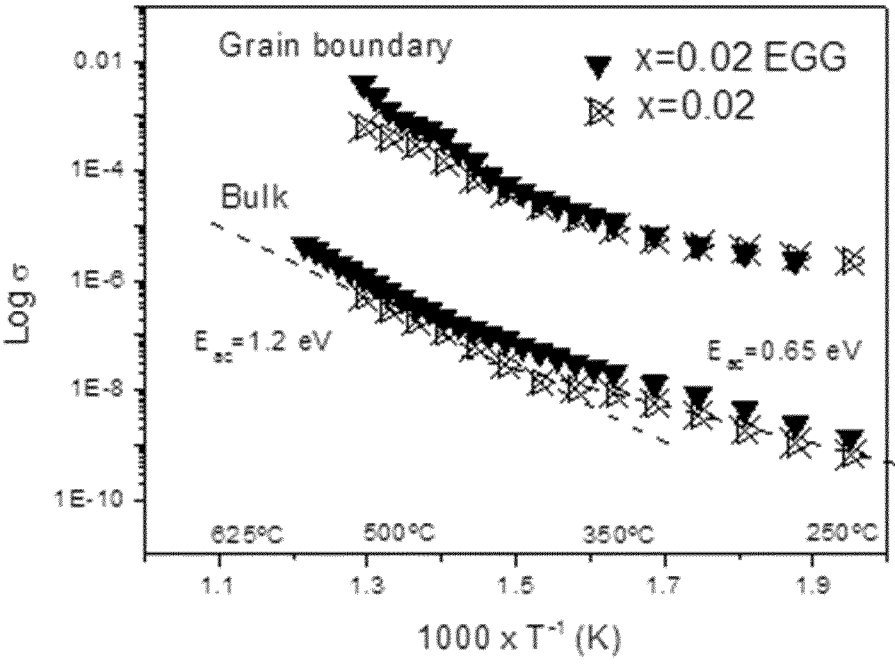
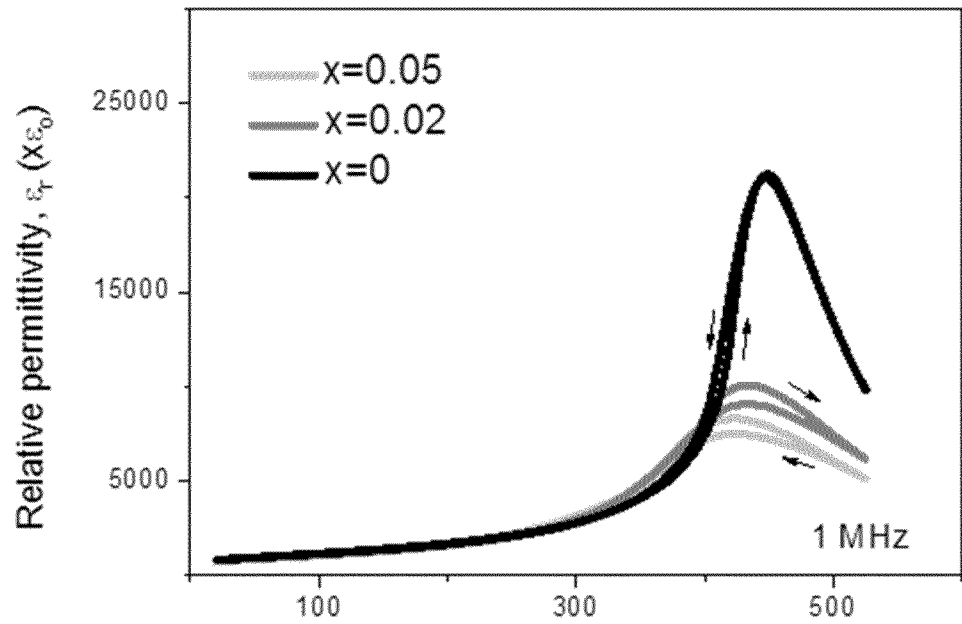


FIG. 5C

a



b

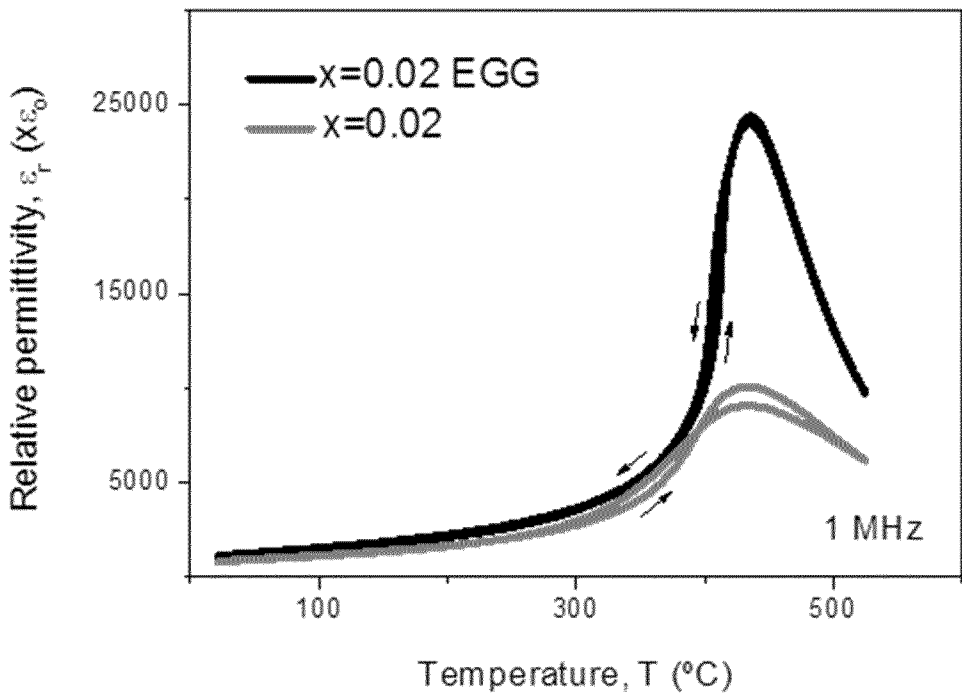


FIG. 6

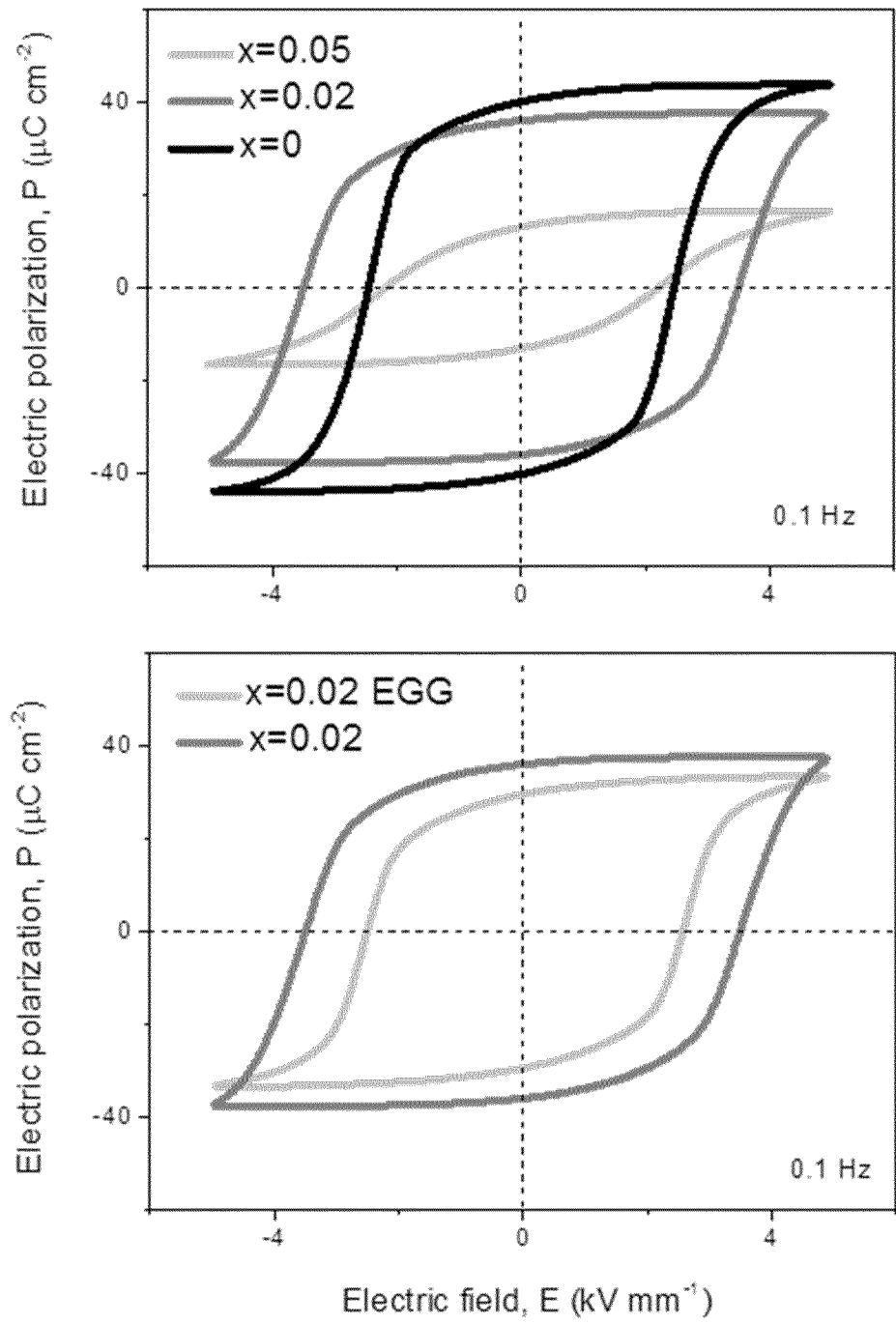


FIG. 7

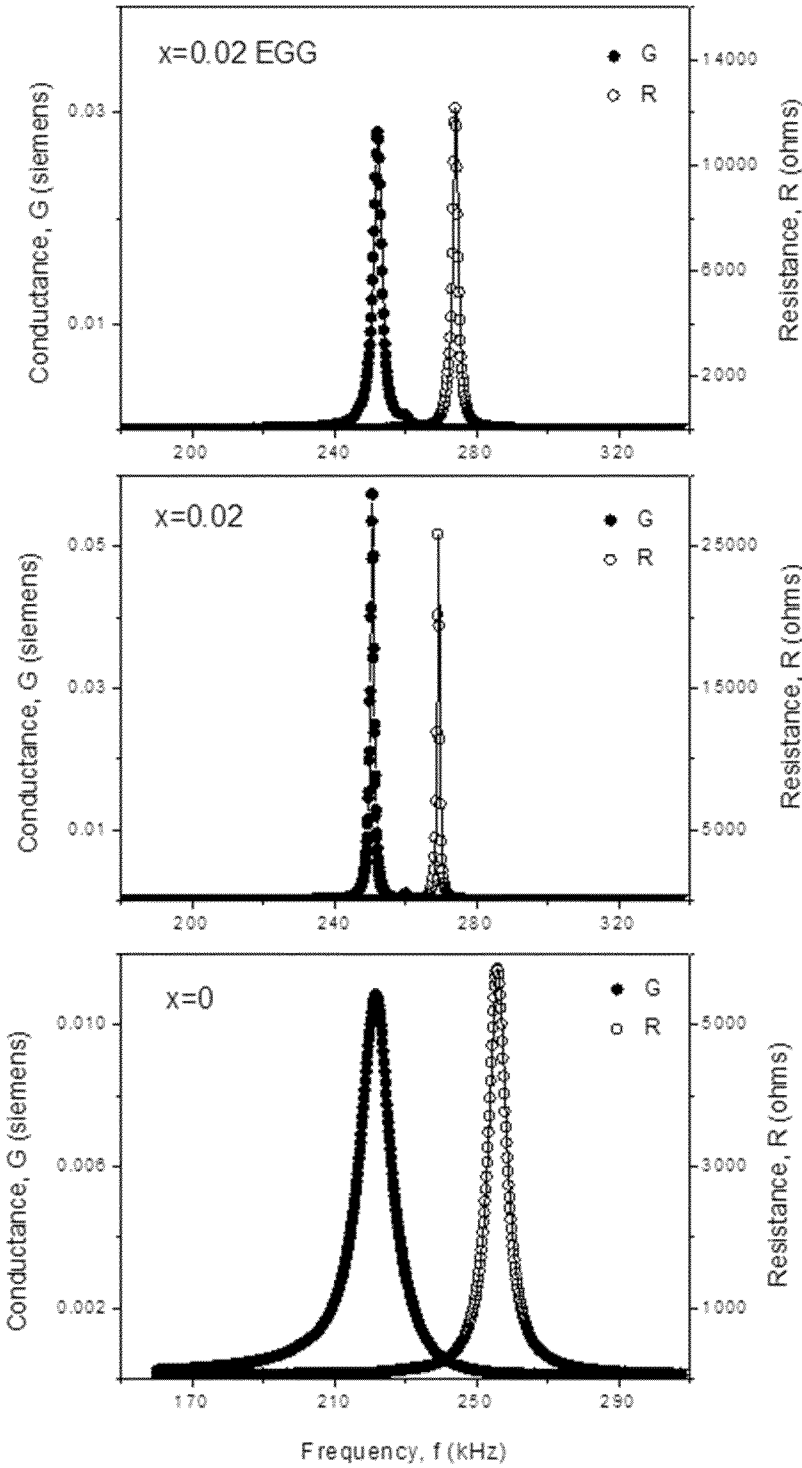


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/082424

A. CLASSIFICATION OF SUBJECT MATTER

INV. C04B35/462 C04B35/472 C04B35/626 C04B35/64 H01G4/12
H01L41/43 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)

C04B H01G 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, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 598 326 A1 (NANOMATERIALS TECH PTE LTD [SG]; UNIV BEIJING CHEMICAL [CN]) 23 November 2005 (2005-11-23) paragraphs [0004], [0005]; claims 1-10; examples 1-9	1-6
X	US 6 835 684 B2 (TIETZ FRANK [DE] ET AL) 28 December 2004 (2004-12-28) claims 1-16; examples 1-3 ----- -/-	1-6



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

17 February 2017

Date of mailing of the international search report

15/03/2017

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Authorized officer

Fortunati, Taddiano

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/082424

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

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International application No

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