## Supplementary Information

# UV-absorber bismuth(III)-N-methyldiethanolamine complex as low-temperature precursor for bismuthbased oxide thin films

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1. Synthesis of bismuth-based oxides precursor solutions



Figure S1. Preparation of Bi(III) and Bi(III)-mdea liquid precursors.



Figure S2. Synthesis of BiFeO3 and BiFeO3-mdea precursor solutions



Figure S3. Synthesis of (Bi<sub>0.5</sub>Na<sub>0.5</sub>)<sub>0.945</sub>Ba<sub>0.055</sub>TiO<sub>3</sub> and (Bi<sub>0.5</sub>Na<sub>0.5</sub>)<sub>0.945</sub>Ba<sub>0.055</sub>TiO<sub>3</sub>-mdea precursor sols



#### 2. Infrared spectra of the Bi(III) and Bi(III)-mdea gels

**Figure S4.** FTIR spectra of the Bi(III) and Bi(III)-*mdea* gels. The precursor solutions were dried overnight at 120°C. Shaded areas indicate the most relevant bands for discussion and comparison of both Bi(III) and Bi(III)-*mdea* gel samples

Fourier transform infrared (FTIR) spectra of gel powders were recorded in the region of 4000-400 cm<sup>-1</sup> using a Nicolet FTIR 20SXC spectrophotometer. These spectra were collected at room temperature with a scanning speed of 30cm<sup>-1</sup>·min<sup>-1</sup>.

The FTIR spectra acquired from the Bi(III) and Bi(III)-*mdea* precursor gels dried at 120°C is shown in Figure S4. The band at ~1730 cm<sup>-1</sup>, present in both systems, is assigned to the  $v_{as}$  (C=O) stretching of a carboxylic acid. This band is accompanied by the  $v_s$  (C=O) stretching mode at ~1238 cm<sup>-1</sup>. The large splitting of the asymmetric/symmetric vibration modes is characteristic for organic carbonates.

Therefore, the occurrence of these bands proves the presence of carbonate groups in the gels, coming from the acetic acid added for solution preparation.

The asymmetric stretching modes ascribed to the NO<sub>3</sub><sup>-</sup> and the CO<sub>3</sub><sup>2-</sup> ions are recorded between ~1700 cm<sup>-1</sup> and ~1300 cm<sup>-1</sup>. The symmetric stretching modes of these ions are detected between ~1300 cm<sup>-1</sup> and ~1000 cm<sup>-1</sup>. The large number of bands detected in these ranges is explained from the splitting of the stretching modes into non-degenerate vibrations, as a consequence of measuring solid samples.

For the Bi(III) gel, the bands at ~1475 cm<sup>-1</sup> and ~1426 cm<sup>-1</sup> are identified as the asymmetric stretching modes,  $v_{as}$ (CO), ascribed to the carbonate groups present in the Bi(III) system. Note the absence of these bands in the FTIR spectrum of the Bi(III)-*mdea* gel and the presence of a new band at ~1567 cm<sup>-1</sup>, which may be ascribed to bridging *mdea* ligands.

A large number of bands is present in the bond-stretching region (1000-500 cm<sup>-1</sup>) for both the Bi(III) and Bi(III)-*mdea* system. These bands could be ascribed to the out-of-plane bending and in-planebending of the nitrate and carbonate groups. Finally, the band presented at ~600 cm<sup>-1</sup> in both systems could be due to the stretching mode (Bi-O).<sup>1</sup>

### 3. Additional results from the <sup>1</sup>H and <sup>13</sup>C NMR spectra



**Figure S5.** a) 1,3-propanodiol conformers and the multiplets associated to them in the <sup>1</sup>H and <sup>13</sup>C spectra at  $\sim$ 3.00-4.50 ppm and  $\sim$ 58.00-64.00 ppm, respectively. b) Signals detected in the <sup>1</sup>H and <sup>13</sup>C spectra associated to acetate esters

**Table SI.** Chemical shifts associated to acetic acid and 1,3-propanediol before and after the reaction that

 leads to the formation of the Bi(III)-*mdea* complex

Compounds	Bonds	Chemical shift before reaction		Chemical shift after reaction	
		(Figure 1 in the manuscript)		(Figure 2 in the manuscript)	
		In <sup>1</sup> H NMR	In <sup>13</sup> C NMR	In <sup>1</sup> H NMR	In <sup>13</sup> C NMR
		spectrum	spectrum (ppm)	spectrum	spectrum (ppm)
		(ppm)		(ppm)	
1,3-	<b>HO-</b> CH <sub>2</sub> -	δ~ 1.85		δ~ 1.60	
propanediol	CH <sub>2</sub> -OH				
	HO-CH <sub>2</sub> -	δ~ 1.78	δ~ 27.87/31.15	δ~ 1.47	$\delta \sim 31.65$ (multiplets)
	CH <sub>2</sub> -				
	CH <sub>2</sub> -OH				
	HO-CH <sub>2</sub> -	δ~ 3.54/3.96	δ~ 58.98/61.59	δ~3.74	$\delta \sim 61.00$ (multiplets)
	CH <sub>2</sub> -OH				
Acetic acid	CH <sub>3</sub> -	δ~ 1.87	δ~ 20.61	δ~ 1.67	δ~20.57/21.60/27.92
	СООН				
	CH <sub>3</sub> -	δ~ 8.58	δ~172.29/173.82	δ~ 7.12	δ~ 170.29/175.82
	СООН				

The <sup>1</sup>H-NMR and <sup>1</sup>C-NMR spectra (Figures 1 and 2 in the manuscript) indicate towards the formation of a metal complex between bismuth and *mdea* in the Bi(III)-*mdea* solution, as described in this work. Apart from that, NMR spectra demonstrate that secondary reactions (Figure S5) are produced under the synthesis conditions used to form the Bi(III)-*mdea* complex. Acetic acid is reacting with 1,3propanodiol, producing acetate esters (mono- and di-esters) as byproducts of the reaction. This is proven by the change of the intensity heights of the C<sub>a</sub> and C<sub>b</sub> carbons (Figure 2) and the decrease of the shifts of the hydrogen bonds (Figure 1). Note that the amounts of reagents used to prepare both solutions, Bi(III) and Bi(III)-*mdea* are the same, so the lower signal intensity of the H<sub>b</sub> protons in Figure 1b indicates a real decrease of the amount of hydrogen bonds, which is joined to the formation of acetate esters as byproducts of the reaction.

As the used metal starting reagents is bismuth nitrate, the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra obtained for the Bi(III) solution is a sum of the spectra of the solvents themselves: 1,3-propanediol and acetic acid. The multiplicity of the chemical shifts for C<sub>c</sub> (~ 58.98 ppm and ~ 61.59 ppm) and C<sub>d</sub> (~ 27.87 ppm and ~ 31.15 ppm) in the <sup>13</sup>C-NMR spectrum of the Bi(III) solution are due to non-degenerated conformers of 1,3-propanodiol (Figure 1b). The most stable conformer is ascribed to the signals with the highest intensity (Figure S5). This fact is also observed in the signals corresponding to H<sub>e</sub> (multiplets at ~ 1.78 ppm) and to H<sub>d</sub> (at ~ 3.54ppm/ 3.96 ppm). The chemical shifts attributed to the *mdea* ligands in the <sup>13</sup>C-NMR of the Bi(III)-*mdea* solution (at ~61.00 ppm) prevents the assignment of those associated to diol conformers.<sup>2</sup>

#### 4. Electrospray Ionization Mass Spectrometry of the Bi(III)-mdea sol



**Figure S6.** ESI-MS spectrum of the Bi(III)-*mdea* sol diluted in acetonitrile ( $C_2H_3N$ ). Insets show the molecular ions related to the fragmentation of the Bi(III)-*mdea* complex.

The Bi(III)-*mdea* complex synthesized in this work was studied by ESI in positive ion mode<sup>3</sup>, to obtain additional information to the NMR results that supports the molecular structure indicated in Figure 2. The ESI-MS spectrum shows the molecular  $[M/2]^+$  ion (m/z= 445.15) and the  $[M/2+CH_3CN]^+$  ion (m/z= 484.29) resulted from the fragmentation of the Bi(III)-*mdea* specie during the analysis (Figure S6). This fragmentation is due to the high voltage applied (+5.5 kV), needed for dispersing the sample into a highly charged aerosol (electrospray). Polymerization among 1,3-propanediol and acetic acid solvents, amine excess and byproducts (esters) produces the m/z fragments of 239.20, 302.20, 326.0 also observed. Moreover, the presence in the synthesized sol of free acetic acid and a ternary amine enhances the ionization mechanisms of the chemical system that finally results in a large number of m/z fragments detected in the spectrum<sup>4</sup>.



5. TGA/DSC profiles and UV-spectrum of N-methyldiethanolamine (NCH<sub>3</sub>(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>)

**Figure S7.** (a) TGA/DSC profile for reference of pure N-methyldiethanolamine (*mdea*) (5.5390 mg, Aldrich, 99%) in dried air (100 mL·min<sup>-1</sup>). (b) UV absorption spectrum for reference of N-methyldiethanolamine (*mdea*)

The thermal decomposition pathway of pure N-methyldiethanolamine (*mdea*) is studied by means of thermogravimetric analysis and differential scanning calorimetry (TGA/DSC). In the TGA curve, a weight loss of ~99% is recorded between 50°C and 183°C, which is accompanied by an endothermic peak in the DSC curve at ~183°C. This temperature is in good agreement with the value reported for the thermal degradation of *mdea*.<sup>4</sup> This decomposition has been widely studied since aqueous alkanolamines solutions are used to trap CO<sub>2</sub> from the flue gas in industrial processes.<sup>6</sup> At temperatures

over 200°C, others energetic anomalies are not detected in the profiles in Figure S7, for this tertiary amine. Therefore, the total degradation of *mdea* occurs at temperatures between ~50-185°C. It has been published that this decomposition leads to a primary amine (monoethanolamine, MEA) and secondary amines (methyl-aminoethanol, MAE, and diethanolamine, DEA).<sup>7</sup>

The UV-absorption spectrum of pure N-methyldiethanolamine (*mdea*) shows three absorption maxima in the UV-range at ~ 207 nm and ~ 270 nm. None of these maxima are detected in the UV-spectrum of the Bi(III)-*mdea* sol (Figure 5 of the manuscript), where a single maximum at ~ 250 nm is observed. This fact is a proof for the formation of a new chemical photosensitive compound in the Bi(III)-*mdea* solution.

#### 6. UV-Vis spectra of metal precursor solutions



Figure S8. UV spectra of Ba(II)-mdea and Zr(IV)-mdea precursor solutions

The N-methyldiethanolamine (*mdea*) should be considerate a potential amine-polyalcohol ligand which is able to accommodate a large number of d- or f- elements. The coordination occurs through the N-donor and the -O and -OH arms, forming the so-called butterfly complex <sup>*cf.* ref. 16</sup>. The electron cloud of the ligand interacts with d or f- orbitals of the metal, which are energetically accessible. The figure S8 include the UV-Vis spectra of a Zr(IV)-*mdea* and Ba(II)-*mdea* solutions. The Zr(IV)-*mdea* sol exhibits an absorption band at ~300 nm, which is ascribed to a LMCT transition. In the case of the Ba(II)-*mdea* solution bands are not detected from 200 to 400 nm.

The Zr(IV) is a d<sup>0</sup> element, therefore a ligand to metal transfer complex (LMCT) is formed between the *mdea* and the metal. In the case of the Bi(III)-*mdea*, described in the manuscript, the complex expected is a metal to ligand transfer complex (MLCT), (Figure 5 and Figure 6b) where the *mdea* acts as a bridge between the two metal centers. The bismuth-metal sites are each six-coordinated, with the central metal bonded to -O/-OH arms and N-donor of the amine group <sup>cf. ref.13(a)</sup>. The key of the method to prepared bismuth- based oxides films at low temperature is the presence of the photosensitive Bi(III)-*mdea* complex. A considerable weakening of the bonds may take place by UV-irradiation through MLCT transition. This process involves the promotion of a M-L bonding electron to a antibonding  $\pi^*$  orbital which may be sufficient to induce the photolysis of the metal complex. An analogous process could be expected for the Zr(IV)-*mdea* complex. In this case, the photo-dissociation should be initiated by LMCT excited states, where the complex is rather reactive.

#### 7. UV-Vis spectra of the Bi(III)-mdea film onto fused silica



Figure S9. UV spectra of Bi(III)-*mdea* films onto fused silica treated at 250°C and 350°C in oxygen with UV-irradiation

The UV-Vis spectrum of a UV-irradiated film at 250° C (for 60 minutes in  $O_2$ ) was recorded (Figure S9). Then, the film was transferred to the UV-furnace and irradiated at 250° C to accumulative 120 minutes of treatment and collected its spectrum. Ultimately, the film was treated at 350°C, which is the temperature used to crystallize the  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> film. As observed, a decrease in intensity is recorded after heating at 350 °C but the UV-Vis spectrum shows the same region of absorbance that those presented in the spectra of the films UV-irradiated at 250 °C. This result indicates that the UV-irradiation does not produce important changes in the film after 60 minute and the capacity of absorption of the film could be considered close to that exhibited for the crystalline film obtained after heating at 350 °C.



**Figure S10.** DTA/TGA-MS profiles of (a) BNBT and (b) BNBT-*mdea* gels carried out in dry air  $(10^{\circ}\text{C}\cdot\text{min}^{-1})$ . Only relevant fragments in the m/z=5-80 region are shown (ion current)

Results from the thermogravimetric coupled to mass spectrometric and differential thermal analysis (TGA-MS and DTA) of the BNBT and BNBT-*mdea* gels are shown in Figure S10. The decomposition process for the BNBT and BNBT-*mdea* gels show a first weight loss at ~50°C, similar to that found for Bi(III) and Bi(III)-*mdea* (Figure 4 in the manuscript), related to the evaporation of solvents. The recorded weight loss is ~5% for BNBT and ~6% for BNBT-*mdea*. In the 200-400°C region, a large exothermic peak, ascribed to a weight loss of ~20%, is observed for both gels. The mass fragments

detected in this step, (m/z=12, 17, 18, 22, 44, 45) are associated with the decomposition of the organic matrix, which forms the gels. In addition to these fragments, a m/z=43 ( $C_2H_3O^+$ ) fragment ascribed to methylacetones is recorded at ~ 293°C for BNBT.

There are significant differences between the BNBT and the BNBT-*mdea* systems in the range of 400-600°C. For the BNBT gel, a small weight loss of ~1.3% is detected at ~575°C associated with a m/z=44 fragment. In the case of BNBT-*mdea*, a large weight loss (~19%) is observed from 400°C to 600°C ascribed to the decomposition of the former metal complexes. The complexity of the BNBT-*mdea* system prevents the identification of the m/z fragments associated with the decomposition of the *mdea* ligands. In addition to these fragments, others related to the decomposition of the organic chains are recorded (m/z=12, 17, 18, 22, 44, 45). Over 600°C, others exo or endothermic processes are not detected for these gels.

9. Grazing Angle Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (GATR-FTIR) of (Bi<sub>0.5</sub>Na<sub>0.5</sub>)<sub>0.945</sub>Ba<sub>0.055</sub>TiO<sub>3</sub> gel layers, prepared from solutions with and without the Bi(III)-*mdea* complex



**Figure S11.** Grazing Angle Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (GATR-FTIR) of the  $(Bi_{0.5}Na_{0.5})_{0.945}Ba_{0.055}TiO_3$  gel layers on Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(100)Si substrates, recorded in the 4000-500 cm<sup>-1</sup> wavelength. (a) BNBT films derived from a solution without *mdea* and (b) BNBT-

*mdea* films derived from a solution with *mdea*. The solution derived films were heated with/without UV-irradiation at 150°C and 350°C [brackets indicate UV-irradiated thin films]. Shaded areas show the wavenumber interval where the COO<sup>-</sup> vibrations appear for both the Bi(III) and Bi(III)-*mdea* systems

Grazing angle attenuated total reflectance Fourier transform infrared spectroscopy (GATR-FTIR) was performed using a 65° single reflection Ge-ATR (Harrick) placed inside the sample compartment of a FTIR spectrometer (Bruker, Vertex 70, 256 scans) in the spectral region of 4000-200 cm<sup>-1</sup>. For these measurements, one layer of the BNBT and BNBT-*mdea* diluted sols (~0.20 mol·L<sup>-1</sup>) was deposited onto Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(100)Si substrates by spin coating (2000 rpm, 45s) and dried at 150°C for 600s on a hotplate. After that, films were heated at 150°C or 350°C, in oxygen, for 1h. Others films were prepared as described, but heated and UV-irradiated at the same time, at 150°C or 350°C, using an excimer UV lamp (Heraeus, 222 nm).

The efficiency of UV-irradiation to get a prompt elimination of the organic compounds enhanced by the UV-absorption of the Bi(III)-*mdea* complex, and thus an advance in the crystallization of the oxide, is demonstrated in the most intricate system here studied; that of the (Bi<sub>0.5</sub>Na<sub>0.5</sub>)<sub>0.945</sub>Ba<sub>0.055</sub>TiO<sub>3</sub> (BNBT). Grazing Angle Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (GATR-FTIR) was carried out directly on the BNBT gel layers on Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(100)Si substrates, derived from the Bi(III) and Bi(III)-*mdea* solutions. The films were treated at 150°C and 350°C with/without UV-irradiation [brackets indicate UV-irradiated layers].

Differences are observed between the BNBT and BNBT-mdea films (Figures S11(a) and (b)).

(i) Let us analyze first the GATR-FTIR spectra of the BNBT films. The spectrum of the BNBT film just deposited and dried at 150°C shows the band at ~1540 cm<sup>-1</sup> and the very small one at ~1340 cm<sup>-1</sup> assigned to the asymmetric,  $v_a(COO^-)$ , and symmetric,  $v_s(COO^-)$ , respectively, stretching vibrations of carboxylate groups <sup>cf. ref. 18(a)</sup>. In addition, two bands at ~3000 cm<sup>-1</sup> and ~1410 cm<sup>-1</sup>, associated with the v(C-H) and  $\delta$ (C-H) vibrations, respectively, are also recorded. After irradiation at [150°C] or [350°C], the symmetric mode of the carboxylate groups

 $v_s(\text{COO}^-)$  at ~1340 cm<sup>-1</sup> is now clearly observed; the presence of this band is probably due to the formation of an intermediate carbonate resulting from an advanced decomposition of the organic compounds promoted by UV irradiation. In all of the spectra, a broad band between 3600 cm<sup>-1</sup> and 3100 cm<sup>-1</sup>, associated with the v(O-H) vibration, and the absorption band at ~1720 cm<sup>-1</sup> due to a carbonyl groups, are recorded. At wavelengths below 900 cm<sup>-1</sup>, bands corresponding to v(M<sup>n+</sup>-O) vibrational modes are observed.

(ii) The spectrum of the BNBT-mdea film just deposited at 150°C shows an appreciable decrease in the v(O-H) stretching vibration between 3600 cm<sup>-1</sup> and 3100 cm<sup>-1</sup>, and the v(C=O) at ~1720 cm<sup>-1</sup> associated to carbonyl groups of acidic groups is not recorded in it. The  $v_s(COO^-)$ and  $v_a$  (COO<sup>-</sup>) at ~1500 cm<sup>-1</sup> and 1540 cm<sup>-1</sup> of the coordinated acetate groups are observed. In addition, a new band at  $\sim 1080 \text{ cm}^{-1}$ , related with the v(C-N) stretching vibrations, is detected in this spectrum, indicating the presence of *mdea* in the the Bi(III)-*mdea* system, probably due to the formation of the metal complex in this film. After irradiation at [150°C] and [350°C], the intensity of the described IR bands for the 150°C film has a considerable decrease, and the bands assigned to carboxylate groups are now recorded at different wavenumbers, ~1430 cm<sup>-1</sup> and  $\sim 1362$  cm<sup>-1</sup>. This can indicate that the UV-irradiation is producing the cleavage of the Bi(III)-mdea bonds of the metal complex, forming new species in the irradiated films where  $COO^{-}/M^{n+}$  bonds are probably formed, as an intermediate step to the formation of the metaloxygen-metal (M-O-M) bonds of the oxide. This effect of the UV-light on these BNBT-mdea films demonstrates the photoreactivity of this precursor, whose efficiency is clearly shown in the Figure 6, 7 and 8 of the manuscript. Here the ferroelectric perovskite is formed at a low temperature (400°C).

10. Crystalline bismuth oxide films derived from the Bi(III) and Bi(III)-*mdea* solutions and deposited on Pt-coated (100)Si substrates



**Figure S12.** X-ray diffraction patterns of bismuth oxide thin films a) and b) on Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(100)Si, c) on SiO<sub>2</sub>/(100)Si and d) on borosilicate glass substrates. The films were deposited from the Bi(III) and Bi(III)-*mdea* solutions and annealed at 250°C and 350°C with or without irradiation of UV-light of  $\lambda$ =222 nm in an oxygen atmosphere

The temperatures at which the different polymorphs of Bi<sub>2</sub>O<sub>3</sub> are stable can be found in the work reported by M. Mehring: <sup>cf. ref. 1</sup> (i) a metastable orthorhombic  $\epsilon$ -Bi<sub>2</sub>O<sub>3</sub> that appears below 400°C, (ii) a low temperature monoclinic  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> that transforms into  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> at 729°C, (iii) a cubic  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> that is stable between 729°C and 825°C; however upon cooling, a melt of bismuth forms the  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> at 639°C-650°C, which transforms into one of two metastable phases; (iv) body centred cubic (b.c.c.)  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> or (v) tetragonal  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>. It is reported that the high-temperature  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> phase can be stabilized by addition of trace amounts of metal impurities, texturing of the sample or using nanocrystalline grain sizes. <sup>cf. ref. 6</sup> Over 825°C, melting of Bi<sub>2</sub>O<sub>3</sub> occurs. Non-stoichiometric bismuth oxides are also reported in the literature. In the case of the Bi(III) solution layers on Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/(100)Si substrates, UVirradiated at 250°C (Figure S12(b)), the high peak recorded at ~28° is close to non-stoichimetric bismuth oxides. JCPDS-ICDD files used for the indexation of peaks associated to different bismuth oxide phases in the X-ray diffraction patterns of Figure S12 are the following: Bi<sub>2</sub>O<sub>3</sub> silenite JCPDS-ICDD-74-2351,  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> JCPDS-ICDD-41-1449,  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> JCPDS-ICDD-06-0294,  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> JCPDS-ICDD-27-0052,  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> JCPDS-ICDD-27-0050,  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> Harwig et al.<sup>8</sup> and  $\epsilon$ -Bi<sub>2</sub>O<sub>3</sub> Locherer et al.<sup>9</sup>

#### 11. Ferroelectric behavior of BiFeO<sub>3</sub> and (Bi<sub>0.5</sub>Na<sub>0.5</sub>)<sub>0.945</sub>Ba<sub>0.055</sub>TiO<sub>3</sub> thin films

An important obstacle for the integration of multifunctional thin films into the existing semiconductor processes is the high annealing temperature necessary to prepare optimum perovskite phases. Temperatures required to transform the as-deposited amorphous layers into crystalline thin films are typically situated over 600°C. UV-irradiation on deposited solution layers containing a metal complex Bi(III)-*mdea* has been used in this work to test the possibility of obtaining multifunctional (ferroelectric) thin films for electronic devices at lower temperatures. Bismuth ferrite (BiFeO<sub>3</sub>, a multiferroic compound) and solid solution of bismuth sodium barium а titanate \_ titanate. ((Bi<sub>0.5</sub>Na<sub>0.5</sub>)<sub>0.945</sub>Ba<sub>0.055</sub>TiO<sub>3</sub>, a lead-free ferroelectric material) have been used to demonstrate the efficiency of the chemical system shown in this paper for reducing the temperature of formation of crystalline complex oxides films. An important key-point of both ferroelectric compositions here tested, is that are lead-free ferroelectric oxides, potential candidates to substitute the lead-based piezoferroelectrics compounds, thus following the European directive on the restriction of hazardous substances in electric/electronic equipments.<sup>cf. ref. 9</sup> Bismuth ferrite, BiFeO<sub>3</sub> (BFO), is a perovskite compound with a ferroelectric and antiferromagnetic behavior at room temperature, which had attracted a large interest in the last years in the field of the multiferroic materials. This perovskite has high Curie (Tc ~830°C) and Néel (T<sub>N</sub> ~370°C) temperatures. The spontaneous polarization of BFO is the biggest switchable polarization (100  $\mu$ C·cm<sup>-2</sup> along the [111] polar direction) found in any ferroelectric compound, larger than that reported for the most widely used ferroelectric material, the lead zirconate titanate, Pb(Zr, Ti)O<sub>3</sub> (PZT). These properties are indications for the potential applications of films of BFO in ferroelectric memories, piezoelectric devices and spintronics.

In the case of  $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$  (BNBT), an enhanced piezoelectric response is obtained for compositions close to the morphotropic phase boundary (MPB), which is located at x $\approx$ 0.055 of BaTiO<sub>3</sub>. The high piezoelectric properties are a result of a large polarizability, arising from the coupling between two different equivalent energetic states, rhombohedral and tetragonal phases. Bulk ceramics of MPB-

BNBT exhibit a strong ferroelectric polarization (Pr ~40  $\mu$ C·cm<sup>-2</sup>) and a large piezoelectric coefficient (d<sub>33</sub>~125 pC·N<sup>-1</sup>) at room temperature. P<sub>r</sub> ~12  $\mu$ C·cm<sup>-2</sup> and d<sub>33</sub>~19 pm·V<sup>-1</sup> have been reported<sup>12</sup> for BNBT solution derived films with compositions close to the MPB region and annealed at temperatures over 600°C. *cf.* ref 8, 10(a), 10(b)

Both BFO and BNBT perovskites are crystallized at high temperatures<sup>*cf.* ref. 17</sup>, especially for BNBT, where ferroelectric response cannot be obtained in films prepared at temperatures below 650°C.

#### 12. Energy Dispersive X-Ray Spectroscopy (EDX) of BiFeO<sub>3</sub> and (Bi<sub>0.5</sub>Na<sub>0.5</sub>)<sub>0.945</sub>Ba<sub>0.055</sub>TiO<sub>3</sub> thin

films



**Figure S13**. Energy Dispersive X-ray spectra of the (a)  $BiFeO_3$  and (b)  $(Bi_{0.5}Na_{0.5})_{0.945}Ba_{0.055}TiO_3$  thin films. Insets show the atomic percent for the elements detected on the films.

For the multiferroic  $BiFeO_3$  thin film, energy-dispersive X-ray spectrum shows signals corresponding to O, Bi and Fe of the film and Pt and Si signals ascribed to the substrate. The average measured Bi/Fe atomic ratio is  $1.10\pm0.10$ , which is close to the theoretical Bi/Fe atomic ratio (Figure S13(a)).

In the case of the ferroelectric-relaxor  $(Bi_{0.5}Na_{0.5})_{0.945}Ba_{0.055}TiO_3$  thin film, the EDX analysis shows peaks related to Na, Bi, Ti, O of the perovskite layer and other peaks associated with Si and Pt from the substrate. The signal of the barium is not detected due to its low concentration in the film. The average measured Bi/Ti atomic ratio is of  $0.49\pm0.10$ . This is close to the theoretical atomic ratio of 0.47 $((Bi_{0.5}Na_{0.5})_{0.945}Ba_{0.055}TiO_3 \text{ solid solution})$  (Figure S13(b)).

In both samples, measurements were carried out on different zones of the film surface with an area of  $10^3 \ \mu m^2$ , showing all of them close values. This is an indication of compositional homogeneity of the films.

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