

Journal of Physics and Chemistry of Solids 61 (2000) 1423-1431

JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS

www.elsevier.nl/locate/jpcs

# Preparation, structural characterization and ferroelectric properties of compensated Te-doped n = 2 Aurivillius oxides ceramics

P. Durán-Martín<sup>a,\*</sup>, B. Jiménez<sup>b</sup>, P. Millán<sup>b</sup>, A. Castro<sup>b</sup>

<sup>a</sup>Ceramics Laboratory, Materials Department, EPFL Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland <sup>b</sup>Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain

Received 10 August 1999; accepted 7 January 2000

## Abstract

New solid solutions  $\text{Bi}_{2-x}\text{Te}_x\text{SrNb}_{2-x}\text{B}_xO_9$  (B = Zr, Hf;  $0 \le x \le 0.5$ ) and  $\text{Bi}_{2-y}\text{Te}_y\text{Sr}_{1-y}A_y\text{Nb}_2O_9$  (A = K;  $0 \le y \le 0.25$ ) have been synthesized and characterized by powder X-ray diffraction methods, thermal analysis and dielectric measurements. Evolution of the unit-cell parameters at room temperature shows that doping the A or B perovskite sites dominates the size of (001) plane in the structure, whereas the *c* value is largely influenced by the cations which occupy the bismuth position in its layer. Thermogravimetric studies show that these materials are stable up to 800°C for *x*, *y* = 0.25 and 750°C for *x* = 0.5. Differential thermal analysis curves of *x* = 0.25 compounds exhibit one exothermic peak at 400 and 500°C for zirconium and hafnium phases, respectively. This effect is related to the expansion of their network, without changing the symmetry or space group. All compositions are ferroelectric at room temperature, and exhibit a non-zero  $d_{33}$  value after poling. Measurements of the dielectric permittivity as a function of the temperature reveal signs of at least two possible phase transitions. The disappearance of the induced spontaneous polarization when heating samples above the lower temperature anomaly in the dielectric permittivity clarifies the  $T_c$  value of the compounds. Assuming they are displacive-type ferroelectrics, it can be shown that the variation of  $T_c$  with the composition is an effect of the change of the unit cell size. This result offers the possibility of tailoring a ferroelectric material with the desired thermal working range. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: A. Oxides; D. Ferroelectricity; D. Phase transitions

# 1. Introduction

In recent years there has been an increasing interest in the family of bismuth layered Aurivillius oxides because of their exciting electrical properties and promise as ferropiezoelectric materials for high temperature applications [1-4].

The structure of these compounds consist of a stacking of n perovskite-like units of nominal composition  $[A_{n-1}B_nO_{3n+1}]$  between  $[Bi_2O_2]$  layers. The A-site of the perovskite slab can be occupied by several cations accepting a cubooctahedral coordination, such as Bi, Ba, Sr, K, Ca, Na, Pb or a combination of them, while smaller ions, such as Ti, Nb, Ta, Fe, W, Mo and Ga, can occupy the octahedral B-site.

The double-sided Bi<sub>2</sub>O<sub>2</sub> sheets are composed of square

In view of the relationship between composition and properties observed in these Aurivillius-substituted materials, we have undertaken the study of new  $Bi_{2-x}Te_xSrNb_{2-x}B_xO_9$  (B = Zr, Hf) and  $Bi_{2-y}Te_yS-r_{1-y}A_yNb_2O_9$  (A = K) bismuth layered solid solutions, in

<sup>\*</sup> Corresponding author. Tel.: +41-21-693-4952; fax: +41-21-693-5810.

E-mail address: pedro.duran@epfl.ch (P. Durán-Martín).

pyramidal BiO<sub>4</sub> groups sharing their basal edges. Studies carried out in our laboratory have demonstrated that Bi<sup>3+</sup> in this layer can be replaced by other p-cations which posses a stereoactive lone pair of electrons, allowing preservation of the basal network [5–7]. Moreover, it was shown that it is possible to modify the charge balance compensation between layers, i.e.  $[Bi_2O_2]^{2+}$  [SrNb<sub>2</sub>O<sub>7</sub>]<sup>2-</sup>, by means of different cationic doping into both the perovskite and bismuth layers [8–11]. Electrical characterization of these materials, carried out on highly dense ceramics sintered using uniaxial hot-pressing technique, has shown that increasing the amount of Bi<sup>3+</sup> substitution results in higher ferroelectric transition temperature values [12–14].

<sup>0022-3697/00/\$ -</sup> see front matter 2000 Elsevier Science Ltd. All rights reserved. PII: S0022-3697(00)00017-2

order to attempt the improvement of their ferroelectric characteristics. The structural characterization by X-ray diffraction methods, thermal behavior and electrical properties of these new materials are reported, and the results are compared with those previously reported of B = Ti and A = Na substituted phases.

## 2. Experimental procedure

series of polycrystalline Three samples of  $Bi_{2-x}Te_xSrNb_{2-x}B_xO_9$  (B = Zr, Hf) with  $0 \le 0.5$ and  $Bi_{2-v}Te_vSr_{1-v}K_vNb_2O_9$  with  $0 \le y \le 0.25$ , were prepared by solid state reaction from appropriate amounts of stoichiometric mixtures of Bi2O3, TeO2, SrCO3, Nb2O5, ZrO2, HfO2 and  $K_2CO_3$ . The reactants were thoroughly mixed in an agate mortar. These mixtures were processed in alumina crucibles, with the temperature sequences: 600, 700, 750, 800, 810 and 820°C for 24 h and 820°C for 12 h. After each thermal treatment, the samples were quenched in air, and then weighed, reground and examined by X-ray powder diffraction methods.

Ceramics of these compositions were obtained from the synthesized powders by uniaxial hot-pressing techniques. Sintering was performed at temperatures between 800 and 850°C, depending upon the composition, and with applied pressures of 270 Pa, during one hour. Resultant ceramic materials presented a bulk density of 98% compared to theoretical.

Room temperature X-ray diffraction data were collected on a Siemens Kristalloflex 810 generator, a D-501 goniometer, with a graphite monochromator, between 5 and  $110^{\circ} (2\theta)$  with increments of  $0.05^{\circ} (2\theta)$  and counting time of 4 s per step. A Phillips PW 1310 diffractometer was employed to record the XRD patterns at increasing temperatures, between 5 and 66° (2 $\theta$ ) with increments of 0.02° (2 $\theta$ ) and counting time of 2 s per step. In both experiments, Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) was employed. The X-ray diffraction profiles were analyzed by a pattern matching procedure using the Fullprof program [15]. The line shape of the diffraction peaks was generated with a pseudo-Voigt function. Fifteen different parameters were refined, including six background coefficients, zero-point, half-width, pseudo-Voigt and asymmetry parameters for the peak shape, as well as the unit-cell parameters. This refinement was performed for a variety of symmetries and space groups and the best agreement was obtained for the B2cb (No. 41), as it was previously reported for other similar compounds [8]. Standard X-ray diffraction patterns at room temperature were also collected for the ceramics and no differences between those and the powder ones were observed. That rules out the possibility of any second phase appearances during the sintering process, and insures that this process keeps the integrity of the synthesized phase.

Possible phase transition and stability of selected samples were studied using a thermal analysis instrument Stanton Redcroft STA-781. Approximately 50 mg of the sample was employed in each measurement with standard platinum crucibles, using  $Al_2O_3$  as the reference material. DTA and TG curves were collected simultaneously at a heating rate of  $10^{\circ}/min$  in air.

Dielectric measurements as a function of the temperature from 20 up to 800°C were performed on the different samples, previously electroded on their largest faces with platinum paint, mounted in a alumina holder and then placed into a high temperature furnace. A Hewlett Packard Impedance Analyzer 4194A was used for AC measurements, in the frequency range from 100 Hz to 15 MHz.

The ferroelectric character of these compositions at room temperature was confirmed by poling the samples. The poling process consisted of introducing the samples into a silicone oil bath and heating them up to 200°C. Then a 100 kV/cm DC electric field was applied to the sample at this temperature and keeping it applied during cooling to room temperature. The resultant polarization yield was followed by measuring the piezoelectric coefficient,  $d_{33}$ , with a Berlicourt-meter, at room temperature.

#### 3. Results and discussion

As reported elsewhere [8,16], the increase of the positive charge generated by the substitution of Te<sup>4+</sup> by Bi<sup>3+</sup>, into its layer, must be balanced by increasing the negative charge of the perovskite sheets by means of the simultaneous substitution of A or B cations with appropriate oxidation state and ionic radius [17]. In this way, single phases  $[Bi_{2-x}Te_xO_2]^{(2+x)+}$  [SrNb<sub>2-x</sub>B<sub>x</sub>O<sub>7</sub>]<sup>(2+x)-</sup> (B = Zr, Hf),  $0 \le$  $x \le 0.5$ , and  $[Bi_{2-y}Te_{y}O_{2}]^{(2+y)+}$   $[Sr_{1-y}K_{y}Nb_{2}O_{7}]^{(2+y)-}$ ,  $0 \le 0.5$  $x \le 0.25$ , have been isolated. In contrast with the results obtained for the equivalent Na doped compounds [8], for y > 0.25 not single phases can be isolated but a mixture of two different n = 2 Aurivillius-type phases, probably due to the presence of the not substituted Bi2SrNb2O9 compound and the lower substituted y = 0.25 one. This fact can be understood taking into account the ionic radii of the different A-cations [17]  $(r(Sr^{2+}) = 1.44 \text{ Å}, r(Na^{+}) = 1.39 \text{ Å},$  $>r(K^+) = 1.64$  Å), because the higher doping of K<sup>+</sup> involves the increase of the averaged A radius and then the tolerance factor for the perovskite layer [18], giving rise to the instability of the phase.

Fig. 1 shows, for example, the X-ray diffraction pattern and the pattern matching agreement of the representative  $Bi_{1.75}Te_{0.25}SrNb_{1.75}Hf_{0.25}O_9$  oxide. Table 1 reports the lattice parameters for all the known single phases  $Bi_{2-x}Te_xSrNb_{2-x}B_xO_9$  (B = Ti, Zr, Hf) and  $Bi_{2-y}Te_yS$  $r_{1-y}A_yNb_2O_9$  (A = Na, K) together with the averaged A and B ionic radii for these compounds, according to the following expressions:

$$\bar{r}_{\rm B} = \frac{1}{2}((2-x)r_{\rm Nb} + xr_{\rm B})$$
 (1)

$$\bar{r}_{\rm A} = (1 - y)r_{\rm Sr} + yr_{\rm A} \tag{2}$$



Theta - 2Theta (°)

Fig. 1. X-ray powder diffraction profile of  $Bi_{1.75}Te_{0.25}SrNb_{1.75}Hf_{0.25}O_9$ . Crosses are the raw data points, the solid line is the best calculated profile and the difference plot appears at the bottom. Thin marks indicate the position of the allowed Bragg reflections.

where  $r_A$  and  $r_B$  correspond to the ionic radii of the substituting cations, and *x* and *y* are the doping amounts for each case.

In general, the *a* and *b* unit-cell parameters show a continuos evolution as a function of the averaged ionic radii of both A and B cations ( $\bar{r}_A$  and  $\bar{r}_B$ ), whereas *c* parameter is more affected by the degree of substitution, *x* or *y*. In fact, since [001] direction is perpendicular to perovskite and bismuth layers building up such structures, the doping in the perovskite sites only can have a slightly influence in the *c* value, which is particularly governed by the different behavior between  $\text{Bi}^{3+}$  and  $\text{Te}^{4+}$  ns<sup>2</sup> lone pair of electrons [19] and their size. Therefore it seems that the character of cations forming the perovskite layer dominates the size of (001) plane in the structure whereas the *c* value largely influences from the occurrence of different cations in the bismuth slab.

This fact could be related with the recent discovery from the electronic structure of another n = 2 Aurivillius phase, that the Bi–O layer controls the electronic response of these materials and the ferroelectric response originates mainly from the perovskite block [20].

Table 1

Lattice constants and ionic radii of A and B cations in the  $Bi_{2-x}Te_xSrNb_{2-x}B_xO_9$  (B = Ti, Zr, Hf) and  $Bi_{2-y}Te_ySr_{1-y}A_yNb_2O_9$  (A = Na, K) solid solutions

x	у	А	В	$r_{\rm A}$ (Å)	r <sub>B</sub> (Å)	a (Å)	b (Å)	c (Å)	$V(\text{\AA}^3)$	Reference
0	0	Sr	Nb	1.44	0.64	5.5147(3)	5.5122(3)	25.0775(8)	762.3(2)	[5]
0.25	_	Sr	Nb/Ti	1.44	0.636	5.5112(6)	5.5008(3)	25.066(1)	759.9(3)	[8]
0.5	_	Sr	Nb/Ti	1.44	0.631	5.5017(6)	5.4832(4)	25.078(2)	756.5(4)	[8]
0.25	_	Sr	Nb/Zr	1.44	0.650	5.512(1)	5.5132(9)	25.034(4)	760.8(8)	Present work
0.5	_	Sr	Nb/Zr	1.44	0.660	5.514(2)	5.517(2)	25.038(3)	762(1)	Present work
0.25	_	Sr	Nb/Hf	1.44	0.649	5.512(1)	5.5153(8)	25.047(3)	761.4(7)	Present work
0.5	_	Sr	Nb/Hf	1.44	0.658	5.513(1)	5.516(1)	25.047(4)	761.7(8)	Present work
_	0.25	Sr/Na	Nb	1.428	0.64	5.4926(6)	5.4911(3)	24.974(2)	753.2(4)	[8]
_	0.5	Sr/Na	Nb	1.415	0.64	5.4386(8)	5.4916(7)	24.972(3)	752.0(6)	[8]
-	0.25	Sr/K	Nb	1.490	0.64	5.510(2)	5.5086(8)	25.047(4)	760(1)	Present work



Fig. 2. Thermogravimetric (TG) and differential thermal analysis (DTA) curves for Bi1.75Te0.25SrNb1.75Zr0.25O9.

The differential thermal analysis (DTA) data from  $Bi_{2-x}Te_xSrNb_{2-x}B_xO_9$  (B = Zr, Hf,  $0 \le x \le 0.5$ ) samples show a very wide effect at the temperature range between 100 and 750°C. Furthermore, the x = 0.25 oxides exhibit one well defined exothermic peak at 400 and 500°C for zirconium and hafnium compounds, respectively. Fig. 2 shows the thermogravimetric (TG) and DTA curves for the representative Bi1.75Te0.25SrNb1.75Zr0.25O9 phase. The DTA curve behavior for Bi1.75Te0.25Sr0.75K0.25Nb2O9 exhibit, like the above phases, only the very large effect between 100 and 800°C. On the other hand, the TG curves, performed in air conditions, show that these materials are stables up to 800°C for x, y = 0.25 and 750°C for x = 0.5. At those temperatures the decomposition of the compounds take place with the volatilization of tellurium as TeO<sub>2</sub> and the formation of several oxides, like Bi2SrNb2O9 and BO2 (B = Zr, Hf) or  $K_2O$ , as it has been verify by X-ray diffraction methods. It is interesting to point out as the decomposition temperatures decrease with increasing tellurium doping, while the occurrence of the exothermic peak in B-doped phases is rather independent of tellurium content.

X-ray diffraction patterns at higher temperatures have been recorded for the representative compound  $Bi_{1.75}Te_{0.25}SrNb_{1.75}Zr_{0.25}O_9$  in order to study the possible structural transformation joined to the observed exothermic effect. In this case, as it has been previously reported for Ti and Na doped materials [8], the viewed evolution involves only a displacement of diffraction lines to small angles, together with some intensity variations. The X-ray diffraction profiles always must be analyzed retaining the symmetry and space group. The *a*, *b* and *c* parameters have been calculated for seven increasing temperatures in the range between room temperature and 700°C. Fig. 3 shows the evolution of the unit-cell parameters versus temperature for this oxide (B = Zr, x = 0.25). Only an expansion of the network is observed and any important structural transition has been detected.

From the dielectric measurements, the real part of the permittivity,  $\epsilon'_r$ , has been represented as a function of the temperature for the different compositions, Figs. 4 and 5, grouped as a function of the cationic substitution amount, y = 0.25, 0.5. As shown, for all samples there are three anomalies during the heating run. The first of them is reversible, which indicates that it should be related to a structural ferro-ferro or ferro-paraelectric type phase transition. The character of this anomaly indicates a diffuse phase transition occurs at this temperature, because of the thermal hysteresis between heating and cooling runs, the fat and broad instead of narrow shape, and also its frequency dependence. The other two anomalies that appear while heating become only one anomaly in the cooling run, taking place at an intermediate temperature between the above two. This suggests that indeed they are not associated to a real phase transition. All these temperatures are listed in Table 2.

To find out the  $T_c$  of the materials, samples were poled. All of them presented a non-zero  $d_{33}$  value after poling (Table 2) which confirms them as ferroelectric materials at room temperature. Then, each sample was heated up to the different temperatures of the  $\epsilon'_r$  anomalies above mentioned, and cooling down to the room temperature to measure again the  $d_{33}$  value. All samples showed a  $d_{33}$  value equal to zero, which means the disappearance of the ferroelectric polarization induced during the poling process, after heating them above the temperature of their first anomaly. This strategy provided us the information of the character of



Fig. 3. Evolution of the unit-cell parameters ( $\blacksquare -a$  (Å),  $\bullet -b$  (Å),  $\blacktriangle -c$  (Å) and  $\Box -V$  (Å<sup>3</sup>)) as a function of temperature in Bi<sub>1.75</sub>Te<sub>0.25</sub>SrNb<sub>1.75</sub>Zr<sub>0.25</sub>O<sub>9</sub>. Represented error bars are the double of the real values, to make them visible.

these anomalies, indicating that this is the first one that is related to a ferro-paraelectric phase transition.

The other higher temperature peaks of the dielectric constant as a function of the temperature could be due to changes in the electric conductivity paths that take place during the heating and the cooling runs. It is shown in literature that it is possible to obtain very frequency dependent maximum of the dielectric constant as a function of the temperature, by applying a mean field theory to heterogeneous materials [21,22]. In this case, the anisotropic conductivity of the material would be the parameter to be considered, and this possibility is under study now.

From the previously reported works of Subbarao [23,24], it is well-known that, for n = 2 structure compounds with different A-sites cations, the lower  $\bar{r}_A$  value, the higher is  $T_c$ of the resulting material. The authors of the present work have already reported elsewhere [25] that the compounds with cationic substitutions in the perovskite A-sites that is  $Bi_{2-y}Te_ySr_{1-y}A_yNb_2O_9$  (A = Na, K) are in agreement with the above-mentioned dependence of  $T_c$  versus the averaged ionic radii,  $\bar{r}_A$ . However, if we represent the evolution of  $T_c$ as a function of the averaged ionic radii,  $\bar{r}_B$ , for the samples under study in the present work with cationic substitutions in the B-sites of the perovskite, we will not observe a clear dependence between both of them.  $T_c$  does not decrease with decreasing value but changes randomly. This is also in agreement with results shown in above mentioned Subbarao's studies. The same family of compounds has a lower  $T_c$ when B-site is occupied by Tantalum ( $r_B = r_{Ta} = 0.64 \text{ Å}$ ) than when is occupied by Niobium ( $r_B = r_{Nb} = 0.64 \text{ Å}$ ). In these case, only two groups of compounds with two different values for the ionic radius  $r_B$  were studied. Now we come with a more extended study that confirms that  $r_B$  is not the parameter that explains the change of  $T_c$ . One characteristic that changes among the B-cations typically used in Aurivillius's compounds is their electronegativity. Subbarao [23] already commented the possible influence of this parameter. Let us calculate an averaged electronegativity value for cations in B-sites as:

$$\bar{e}_{\rm B} = \frac{1}{2}((2-x)e_{\rm Nb} + xe_{\rm B}) \tag{3}$$

where  $e_{Nb} = 1.6$  and  $e_B(e_{Ti} = 1.5, e_{Zr} = 1.4, e_{Hf} = 1.3)$  are the Pauling's electronegativity values for former, Nb, and doping B-site cations, and x represents the substitution amount. In Fig. 6,  $T_c$  as a function of this  $\bar{e}_B$ , is represented for those phases doped in B-sites. We can effectively see a continuous increase of  $T_c$  with  $\bar{e}_B$ , almost linear for  $T_c$  values measured during cooling. Moreover, there are two samples with very different chemical composition,  $Bi_{1.5}Te_{0.5}SrNb_{1.5}$ .  $Ti_{0.5}O_9$ , and  $Bi_{1.75}Te_{0.25}SrNb_{1.75}Zr_{0.25}O_9$  that have the same  $\bar{e}_B = 1.575$ , and, as shown, the same  $T_c$  measured during the cooling run. This confirms the hypothesis to consider the



Fig. 4. Relative dielectric constant as a function of temperature for samples with cationic substitution amount of x = 0.25 ( $\Box$ —Bi<sub>1.75</sub>Te<sub>0.25</sub>SrNb<sub>1.75</sub>Ti<sub>0.25</sub>O<sub>9</sub>, O—Bi<sub>1.75</sub>Te<sub>0.25</sub>SrNb<sub>1.75</sub>Zr<sub>0.25</sub>O<sub>9</sub> and  $\triangle$ —Bi<sub>1.75</sub>Te<sub>0.25</sub>SrNb<sub>1.75</sub>Hf<sub>0.25</sub>O<sub>9</sub>).

electronegativity of the B-site cation as the main parameter that justifies changes in  $T_c$  when doping in that crystallographic position.

Nevertheless, it is curious that two different parameters are needed to explain changes in  $T_c$  promoted when doping or when making cationic substitutions. In deed, if we regard structural parameters like *axb* or the unit-cell volume, the  $\bar{r}_B$ parameter becomes no longer necessary. Reordering the samples as a function of  $T_c$  (Table 2), we can realize that the greater the volume the lower the  $T_c$  of the compound,



Fig. 5. Relative dielectric constant as a function of temperature for samples with cationic substitution amount of x = 0.5 ( $\Box$ — Bi<sub>1.5</sub>Te<sub>0.5</sub>SrNb<sub>1.5</sub>Ti<sub>0.5</sub>O<sub>9</sub>, O—Bi<sub>1.75</sub>Te<sub>0.5</sub>SrNb<sub>1.5</sub>Zr<sub>0.5</sub>O<sub>9</sub> and  $\triangle$ — Bi<sub>1.5</sub>Te<sub>0.5</sub>SrNb<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>9</sub>).

including the composition with A-site substitution, mentioned above.

Most of the perovskite-type ferroelectric oxides have a large Curie–Weiss constant and present a displacive type ferroelectric phase transition [26]. In these materials occurrence of spontaneous polarization can be explained as a problem of electrostatic equilibrium, and the phase transition can be associated to structural distortion which promotes the relative cationic displacement, allowing the appearance of spontaneous polarization,  $P_s$  [27]. Thus, this

Table 2

Several ferroelectric parameters of the compounds under study, ordered as a function of its  $T_c$ 

Composition	$T_{\rm c}$ (up/down) $f = 10$ kHz	$\gamma$ (Å)	<i>d</i> <sub>33</sub> (pC/N)	
Bi1.5Te0.5SrNb1.5Hf0.5O9	230/222	9.1326	5	
$Bi_{1.5}Te_{0.5}SrNb_{1.5}Zr_{0.5}O_9$	250/250	9.1338	5	
Bi <sub>1.75</sub> Te <sub>0.25</sub> SrNb <sub>1.75</sub> Hf <sub>0.25</sub> O <sub>9</sub>	285/275	9.1314	9	
Bi <sub>1.75</sub> Te <sub>0.25</sub> SrNb <sub>1.75</sub> Zr <sub>0.25</sub> O <sub>9</sub>	300/290	9.1290	9	
$Bi_{1.75}Te_{0.25}SrNb_{1.75}Ti_{0.25}O_9$	300/295	9.1254	9	
$Bi_{1.75}Te_{0.25}Sr_{0.75}K_{0.25}Nb_2O_9$	310/300	9.1258	13	
$Bi_{1.5}Te_{0.5}SrNb_{1.5}Ti_{0.5}O_{9}$	330/325	9.1118	7	
$Bi_{1.75}Te_{0.25}Sr_{0.75}Na_{0.25}Nb_2O_9$	366/346	9.0985	11	
$Bi_{1.5}Te_{0.5}Sr_{0.5}Na_{0.5}Nb_2O_9$	460/390	9.0937	8	



Fig. 6. Variation of the  $T_c$  ( $\bullet$ —heating,  $\blacksquare$ —cooling) with the averaged electronegativity value of cations in B-crystallographic sites,  $\bar{e}_B$ , for the different compounds under study.

 $P_{\rm s}$  is usually estimated as a vectorial sum of the different dipoles contributions inside the unit cell that can be expressed as:

$$P = \frac{1}{V} \sum_{i} q_i r_i \tag{4}$$

where V is unit cell volume,  $r_i$  the displacement of the *i*-cation from its position in the network at the paraelectric state, and  $q_i$  the electric charge of the *i*-cation.

One of the best-studied compounds belonging to this group is BaTiO<sub>3</sub>. In BaTiO<sub>3</sub>, the hydrostatic pressure effect on the  $T_c$  of the compound is extensively studied [28,29], which decreases linearly with increasing pressures [30]. Also its solid solutions present a monotonic decrease with increasing lattice parameters. Finally, it has been recently shown that change of  $T_c$  can be attributed to a volume effect of the unit cell whether the change is produced by a change in pressure or a change in the composition [31]. In such systems, it is usual to select  $\gamma$  as structural parameter, being  $\gamma = \sqrt[3]{(a * b * c)}$ .

The Aurivillius-type structure is also defined as an alternating stacking of perovskite unit blocks, interconnected by  $[Bi_2O_2]^{2+}$  layers. They posses a high *c* value [32], and many studies present in the literature intend to explain the *P*<sub>s</sub> existence by different structural shifts taking place across the phase transformation [33,34], and estimate its value by using expression (4). Then, assuming our materials as displacive-type ferroelectric compounds, we have calculated  $\gamma$  for them as it is shown in Fig. 7. From this graph, it is clear that *T<sub>c</sub>* increases with decreasing lattice parameter  $\gamma$ , for all the compounds under study. In other words, it is confirmed that the cationic substitutions promote a change in the volume of the unit cells that provides a reciprocal change in the  $T_c$  of the compound.

In conclusion, we would remark first that a new solid solution starting from the well-known n = 2 Bi<sub>2</sub>SrNb<sub>2</sub>O<sub>9</sub> have been successfully synthesized and characterized by different analytical techniques. It has also demonstrated that all of them are ferroelectric compounds at room temperature.

From the DTA, TG and dielectric analysis data we have induced that these phases do not show a first order, or even close to, ferroelectric to paraelectric phase transition, but a diffuse one. By means of depoling experiences we found out the  $T_c$  of these materials vary between 230°C (Bi<sub>1.5</sub>Te<sub>0.5</sub>SrNb<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>9</sub>) and 460°C (Bi<sub>1.5</sub>Te<sub>0.5</sub>Sr<sub>0.5</sub>Na<sub>0.5</sub>Nb<sub>2</sub>O<sub>9</sub>), which corresponds to temperature of the first dielectric constant anomalies.

Probably, the most outstanding fact of the present work is that we have shown that changes in the volume of the unit cell in these structures, by means of cationic substitutions, are responsible for the change of its  $T_c$ . There are two parameters that mainly affect this change: for A-site substitutions, the bigger  $\bar{r}_A$  the higher  $T_c$ . For B-sites substitutions,  $T_c$  increases when increasing the  $\bar{e}_B$  value. The interesting point of this result is that it offers the feasibility to tailor by applying the suitable partial substitution. Those substitutions should take into account that, first, the evolution of the unit-cell parameters at room temperature shows that doping in A or B perovskite sites dominates the size of



Fig. 7. Evolution of  $T_c$  ( $\bullet$ —heating,  $\blacksquare$ —cooling) as a function of the  $\gamma$  parameter, for the different compounds under study.

(110) plane in the structure, while the *c* value is mostly influenced by the cations occupying the bismuth position in its  $[Bi_2O_2]^{2+}$  layer, and second, the limits of the Goldschmidt's tolerance factor as well. The comparative study of the ferroelectric properties of these phases and the role of the cationic substitutions on their improvement still remains, and will be the focus of future works.

## Acknowledgements

The authors express their warmly gratitude to Dr A. Ramirez for the preparation of the powdered samples. The present work has been supported by the CICYT project, Mat97-0711.

#### References

- S. Ikegami, I. Ueda, Pieyoelectricity in ceramics of ferroelectric bismuth compound with layer structure, Jpn. J. Appl. Phys. 13 (1974) 1572–1577.
- [2] J.P. Mercurio, A. Souirti, M. Manier, B. Frit, Phase transition and dielectric properties in some compounds with bismuth oxide structure, Mater. Res. Bull. 27 (1992) 123–128.
- [3] O. Auciello, A.R. Krauss, J. Im, D.M. Gruen, E.A. Irene, R.P.H. Chang, G.E. McGuire, Studies of film growth processes and surface structural characterization of ferroelectric memory-compatible SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> layered perovskites via in situ, real-time ion-beam analysis, Appl. Phys. Lett. 69 (18) (1996) 2671–2673.
- [4] H.N. Al-Shareef, D. Dimas, T.J. Boyle, W.L. Warren, B.A.

Tuttle, Qualitative model for the fatigue free behaviour of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>, Appl. Phys. Lett. 68 (1996) 690–692.

- [5] P. Millan, A. Castro, J.B. Torrance, The first doping of lead2 + into the bismuth oxide layers of the Aurivillius oxides, Mater. Res. Bull. 28 (1993) 117.
- [6] A. Castro, P. Millan, R. Enjalbert, Structural evolution of the Aurivillius framework in the solid solutions Bi<sub>2</sub>WO<sub>6</sub>– Sb<sub>2</sub>WO<sub>6</sub>, Mater. Res. Bull. 30 (1995) 871–882.
- [7] P. Millan, A. Ramirez, A. Castro, Substitutions of smaller Sb<sup>3+</sup> and Sn<sup>2+</sup> cations for Bi<sup>3+</sup> in Aurivillius-like phases, J. Mater. Sci. Lett. 14 (1995) 1657–1660.
- [8] A. Ramirez, P. Millan, A. Castro, J.B. Torrance, Compensated doping between layers ub-Aurivillius oxides, Eur. J. Solid State Inorg. Chem. 31 (1994) 173–185.
- [9] T. Rentschler, M. Karus, A. Wellm, A. Reller, Synthesis and characterization of the Aurivillius phases Bi<sub>(2-x)</sub>Pb<sub>x</sub>Sr<sub>(1-x)</sub>Nd<sub>x</sub>Nb<sub>2</sub>O<sub>9</sub>, Solid State Ionics 90 (1996) 49– 55.
- [10] T. Rentschler, Substitution of lead into the bismuth oxide layers of the n = 2 and n = 3 Aurivillius phases, Mater. Res. Bull. 32 (1997) 351–369.
- [11] P. Millan, M.T. Montero, P. Duran-Martin, B. Jimenez, A. Castro, Material solid solutions of lead-doped bismuth layer of Aurivillius n = 2 and 3 oxides: structural and dielectric characterization, Res. Bull. 33 (7) (1998) 1103–1115.
- [12] B. Jimenez, P. Duran-Martin, A. Castro, P. Millan, Obtention and caracterization of modified Bi<sub>2</sub>SrNb<sub>2</sub>O<sub>9</sub> Aurivillius-type ceramics, Ferroelectrics 186 (1996) 93–96.
- [13] P. Duran-Martin, B. Jimenez, A. Castro, P. Millan, Influence of cationic substitutions on the ferroelectric properties of new aurivillius-type ceramics, Proc. Electroceramics V 1 (1996) 535–538.
- [14] P. Duran-Martin, A. Castro, P. Millan, B. Jimenez, submitted for publication.

- [15] J. Rodriguez-Carvajal, Fullprof program for Rietveld refinement and pattern matching analysis, XV Congress International Union Cryst, Toulouse, France, 1990.
- [16] A. Castro, P. Millan, M.J. Martinez-Lope, J.B. Torrance, Substitution for  $Bi^{3+}$  into  $(Bi_2O_2)^{2+}$  layers of the Aurivillius  $(Bi_2O_2)$   $(A_{n-1}B_nO_{3n+1})$  oxides, Solid State Ionics 63–65 (1993) 897–903.
- [17] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Cryst. A32 (1976) 751–767.
- [18] V.M. Goldschmidt, Geochemische verteilungsgesetze der elemente, VII, Skirft Norske Vidensk. Akad. Ns. (2 and 8) (1926).
- [19] J. Galy, G. Meunier, S. Andersson, A. Strom, Stéréochimie des Eléments Comportant des Paires Non Liées: Ge(II), As(III), Se(IV), Br(V), Sn(II), Sb(III), Te(IV), I(V), Xe(VI), Tl(I), Pb(II) et Bi(III) (Oxides, Fluorures et Oxyfluorures), J. Solid State Chem. 13 (1975) 142–159.
- [20] J. Robertson, C.W. Chen, W.L. Warren, C.D. Gutleben, Electronic structure of the ferroelectric layered perovskite SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub>, Appl. Phys. Lett. 69 (1996) 1704–1706.
- [21] R. Jimenez, Application of the P.E.M. theory to solid electrolyte pressed powder pellets: electrically isotropic solid electrolyte particles, Solid State Ionics 90 (1996) 230–244.
- [22] R. Jimenez, Application of the Percolation Effective Medium Theory (PEMT) to solid electrolyte pressed powder pellets. II, Solid State Ionics 92 (1996) 225–241.
- [23] E.C. Subbarao, Ferroelectricity in mixed bismuth oxides with layer-type structure, J. Chem. Phys. 34 (1961) 695–696.
- [24] E.C. Subbarao, family of ferroelectric bismuth compounds, J. Phys. Chem. Solids 23 (1962) 665–676.

- [25] P. Duran-Martin, A. Castro, P. Millan, B. Jimenez, Influence of Bi-site substitution on the ferroelectricity of the Aurivillius compound Bi<sub>2</sub>SrNb<sub>2</sub>O<sub>9</sub>, J. Mater. Res. 13 (9) (1998) 2565– 2571.
- [26] T. Mitsui, I. Tatsuzaki, E. Nakamura, An introduction to the physics of ferroelectrics, Gordon and Breach, New York, 1976.
- [27] B.A. Strukov, A.P. Levanyuk, Ferroelectric phenomena in crystals, Springer, Berlin, 1998.
- [28] W.J. Merz, The effect of hydrostatic pressure of the Curie point of barium titanate single crystals, Phys. Rev. 78 (1950) 52–54.
- [29] G.A. Smolenskii, K.I. Rozgachev, Seignettoelectric properties of solid solutions in the system barium titanate–strontium titanate, Zh. Tekhn. Fiz. 24 (1954) 1751–1760.
- [30] G.A. Samara, Pressure and temperature dependences of the dielectric properties of the perovskites BaTiO<sub>3</sub> and SrTiO<sub>3</sub>, Phys. Rev. 151 (1966) 378–386.
- [31] L. Zhang, W.L. Zhong, Y.G. Wang, P.L. Zhang, The cell volume effect in barium strontium titanate, Solid State Commun. 104 (5) (1997) 263–266.
- [32] Landolt-Börnstein. Vol 16, Ferroelectric and Related Substances, Subvol. A: "Oxides", 1981.
- [33] A.D. Rae, J.G. Thompson, R.L. Withers, A.C. Willis, Structure refinement of commensurated modulated bismuth titanate, Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, Acta Cryst. B46 (1990) 474–487.
- [34] A.D. Rae, J.G. Thompson, R.L. Withers, Structure refinement of commensurately modulated bismuth strontium tantalate, Bi<sub>2</sub>SrTa<sub>2</sub>O<sub>9</sub>, Acta Cryst. B48 (1992) 418–428.