CRYSTALLINE STRUCTURE, DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF BISMUTH-LAYER $Ca_xBi_4Ti_{3+x}O_{12+3x}$, (x=1,2) COMPOUNDS

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ABSTRACT

Bismuth titanates are of great technological interest because of their applications as non-volatile ferroelectric memories, and high-temperature piezoelectric materials. All of them belong to the Aurivillius bismuth layer-structure. Some compounds belonging to that family show high-conduction behaviour, which difficult the poling process. On the contrary, the Calcium Bismuth Titanates have shown very high resistivity values, which make suitable the poling process at relatively high temperatures, necessary for a correct polarization step. Compounds of the following composition: $Ca_xBi_4Ti_{3+x}O_{12+3x}$, (x=1,2), has been synthesized by solid-state reaction between the corresponding oxides and carbonates. Lattice parameters, Structure crystalline, and Space Group have been established by XRD techniques. Sintering of isopressed compacts has been studied by Dilatometer tests. High-density bodies have been obtained at relatively low temperature. Curie temperature, T_C, Room Temperature permittivity, conductivity as a function of temperature and piezoelectric parameters have been measured on sintered, well-densified samples. The results seem to indicate that these compounds are very promising piezoelectric materials for high-temperature applications.

Keywords: : Bismuth titanates, crystalline structure, piezoelectricity

1. INTRODUCTION

Bismuth titanates are compounds of great technological interest because of their applications as non-volatile ferroelectric memories, (1) and high-temperature piezoelectric materials, (2-3). All of them belong to the Aurivillius bismuth layer-structure, with a general chemical formula $A_{m-1}Bi_2B_mO_{3m+3}$, where A is a large ionic-radius cation, such as K^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Pb^{2+}, Bi^{3+}, and B is a small ionic-radius cation, such as Fe^{3+}, Ti^{4+}, Nb^{5+}, W^{6+}, ...The general formula can be developed as follows:

$$A_{m-1}Bi_2B_mO_{3m+3}=(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-} \qquad [1]$$

where $(Bi_2O_2)^{2+}$ is a bismuth oxide layer and $(A_{m-1}B_mO_{3m+1})^{2-}$ is a pseudo-perovskite layer; and m can vary between 1 and 5 (4). Most of them show ferroelectric transitions, while some associated families such as $Bi_2Sr_2Ca_xCu_{1+x}O_y$ (x=0,1,2), are high-temperature superconducting materials (5).

The compounds with m=4,5, A=Ba, Sr, Ca, Pb, or Bi^{3+} and B=Ti^{4+}, or Fe^{3+} are two subgroups of that compound family. All of them are ferroelectric and have Curie temperatures that ranging from 395ºC for A=Ba to 785ºC for A=Ca (6-8). Besides that, all show high-resistivity behaviour, except the $Bi_5FeTi_3O_{15}$ compound that shows a higher conductivity (6). In this compound the Bi^{3+} cation combines with a trivalent cation, Fe^{3+}, to maintain the valence state equilibrium. Those compounds can be described as derived of the three-perovskite-layer $Bi_4Ti_3O_{12}$ compound by the incorporation of a fourth perovskite layer, $ATiO_3$, or $BiFeO_3$. The bismuth titanate, $Bi_4Ti_3O_{12}$, compound has good ferroelectric properties, and a relatively high Curie temperature, T_c. Nevertheless, it shows a relatively high, anisotropic, electrical conductivity, which makes very difficult to polarise the ceramic bodies based on this composition (9). Doping with donors, such as W^{6+} substituting Ti^{4+} leads to a strong increase of the resistivity, allowing a better poling procedure (10). The $ABi_4Ti_4O_{15}$ compounds, A=Ba,

Sr, Ca, show very high resistivity values, which allows a good poling process. Between them, the $CaBi_4Ti_4O_{15}$ shows the higher permittivity value and the lower electrical conductivity (11). Its solid solution with the $Bi_5FeTi_3O_{15}$ compound increases strongly the electrical resistivity of this last compound (12) allowing an adequate poling procedure. Although it seems to crystallise with a similar structure that the others m=4 compounds, there is not a precise parameter determination. On the other hand, precise crystalline data of the $Ca_2Bi_4Ti_5O_{18}$ compound are not disposable in the revised literature (13).

The present work is devoted to an approach to the precise determination of the crystalline structure of the $Ca_xBi_4Ti_{3+x}O_{12+3x}$ compounds, (x=1,2), and to the measure of their dielectric and piezoelectric properties.

2. EXPERIMENTAL PROCEDURES

Submicronic powders of $Ti(OH)_4$, $Bi(OH)_3$, and $CaCO_3$ were weighted at stoichiometric proportions, mixed and homogenised by planetary ball milling, using isopropanol as liquid medium. The dried mixture was then calcined at 1050ºC for 2h. The obtained powders were milled again by planetary ball and attrition milling, sieved by 63 μm mesh for granulating and isopressed at 200 MPa. The isopressed pellets were sintered between 1050 and 1200ºC for 2h in air atmosphere. Apparent density was measured by Archimedes method. XRD analysis were performed both on the calcined powder and on the sintered samples using a D-5000 Siemens Diffractometer and CuK_α radiation. The powder was identified by scanning at a rate of 2º 2θ/min, and the lattice parameters were calculated from the spectra obtained on the sintered samples at a scanning rate of 1/8º 2θ/min. Si powder was employed as an internal standard. The microstructure of the powder and the sintered ceramics was observed by Scanning Electron Microscopy (SEM), (Zeiss DSM 950, Oberkochem, Germany) on polished

and thermally etched surfaces. Discs were sliced from the sintered samples. Silver electrodes were applied by painting with paste and firing at 700ºC. T_c was evaluated from permittivity-temperature curves taken during heating and cooling, using an impedance meter, model HP4291A, (Hewlett-Packard, CA, USA), controlled by a desktop PC computer. Poling procedure was carried out at 200ºC, in a silicone oil bath, under poling field up to 40 kV/cm; during cooling the applied field was maintained. Piezoelectric constants were evaluated according the IRE Standard using the same impedance meter, model HP4291A. D_{33} values were measured by means of a Berlincourt Piezometer, (model CADT, Channel Inc. OH, USA).

3. RESULTS

Figure 1 shows the XRD patterns of the synthesised powders. Both patterns have been indexed according to an orthorhombic unit cell. Tables 1 and 2 resume the observed crystalline data and the calculated lattice parameters for the two compounds.

Samples were isothermally sintered at temperatures taken according to the shrinkage rate curves, (not represented here). Apparent density values of ~95 % D_{th} have been measured for sintering at 1150ºC (n=1) and 1100ºC, (n=2). Figure 2a and b shows the microstructure of the polished and thermally etched surface of both samples. As it can be seen, the microstructure is very typical of the well-known Aurivillius-type bismuth-layered compounds. Large plate like grains have growth, and straight grain boundaries separate the different platelets. The asymmetric platelets may form small colonies of oriented grains, but the whole microstructure showed a randomly distributed grain orientation. Figure 3a and b displays the ε vs. T of the samples. According to these curves, the sample n=1 has a Curie temperature T_c=785ºc, whereas the n=2 composition has it at T_c=774ºC.

Table 3 summarises the electrical resistivity parameters of the ceramic samples. The electrical resistivity is very high for both compositions, being somewhat lower in the n=2 sample. These high values of electrical resistivity have allowed carrying out the poling of the ceramic samples. The measured piezoelectric parameters are summarised in the same table. The n=1 composition has shown higher piezoelectric values than the n=2 composition, being in both cases small values.

4 DISCUSSION

Several authors have previously studied solid solutions of $CaBi_4Ti_4O_{15}$ with another Aurivillius phases. Incorporation of highly resistive $CaBi_4Ti_4O_{15}$ as solid solution to highly conductive $Bi_5Ti_3FeO_{15}$ compound allowed to low the electrical conductivity and thus to perform a poling process, which led to obtain acceptable piezoelectric parameters in several solid solution compositions (12). Takenaka measured the lattice parameters of pure $CaBi_4Ti_4O_{15}$ and established a Curie temperature of 785ºC. Nevertheless, more crystalline data and piezoelectric parameters are lacking in its work (14). In a previous work (11), some ceramic and piezoelectric features of the $CaBi_4Ti_4O_{15}$ compound were established, but a more detailed study of the crystalline features was not carried out. Besides these considerations, information about the crystalline properties and electrical behaviour of another calcium bismuth titanium oxides, such as $Ca_2Bi_4Ti_5O_{18}$, is not found in the revised literature, being so that similar compounds, such as $Me_nBi_4Ti_{3+n}O_{12+3n}$, n=1,2, Me=Ba,Sr,Pb are well known.

According to the XRD patterns and Tables 1 and 2, compositions with $Ca_nBi_4Ti_{3+n}O_{12+3n}$, n=1,2 form single phases, which seems to crystallise with a Space Group, SG, Bb21m. The XRD patterns have been indexed according to that orthorhombic S.G. Adjust has been carried out by a minimum square values program. The correlation factor has been >0.999 in both

cases. The lattice parameters of both crystalline structures have been calculated. The results are some different from one to another. The orthorhombicity factor for n=1 is very near to unity, b/a=1.0016, whereas that of the n=2 is somewhat higher, b/a=1.0017. The crystalline structure of both compositions above the Curie temperature is unknown, and complementary analyses of high-temperature are needed to establish them. Nevertheless, the high-temperature crystalline structure is, probably, of higher symmetry of that of lower temperature. This behaviour differs of that shown by others families, in which the increase of n leads to an increase of the symmetry, with a and b parameters which trend to match their values.

If the ionic radius of the different families are compared, it can be seen that the Ca^{2+} is the smaller cation. Corresponding to this fact, the perovskite layer $CaTiO_3$ shows a very low symmetry degree. Table 4 shows that different degree of symmetry for several perovskite structures associated to the different Aurivillius families, parent to those here studied. This fact can be the cause of the increase of anisotropy degree of the compounds when the n value increases.

The correlation factor seems to be sufficiently high to assess the correctness of the Space Group that we have supposed. Nevertheless, further analyses are needed to attain a correct determination of lattice structure and parameters.

The Curie temperature of both compositions is very similar. At difference of that found in other families, in which the increase of n led to a strong decrease of the T_C values, with a good correlation with the increase of the crystalline symmetry, in this case the symmetry has been decreased with n, and therefore, the Curie temperature only shows a small variation.

The conductivity values are lower than those measured on compounds of the Aurivillius ferroelectric family, such as $Bi_4Ti_3O_{12}$, and others. According to the tentative model exposed elsewhere, (12), the presence of very low conductive perovskite layers, such as $CaTiO_3$

intercalated between the more conductive layers "$BiTiO_3$" leads to a significative decrease of the electrical conductivity.

5. CONCLUSIONS

Crystalline parameters of the $Ca_xBi_4Ti_{3+x}O_{12+3x}$ compounds, (x=1,2), have been established. Incorporation of $CaTiO_3$ led to a slight increase of the orthorhombicity. Existence of a compound with n=3 can't be established for equivalent conditions of synthesis. Compounds with $CaTiO_3$ showed high resistivity values and could be polarised under very high electrical fields.

Curie temperatures were very high. Good piezoelectric properties of bulk materials have been measured.

6. REFERENCES

1. S.B. Desu, P.C. Joshi, X. Zhang S.O. Ryu, Thin films of layered-structure (1-x)$SrBi_2Ta_2O_9$-x$Bi_3Ti(Ta_{1-y}Nb_y)O_9$ solid solutions for ferroelectric random access memory devices, Appl. Phys. Lett. 1997,. **71**, 1041.

2. R.C. Turner, P.A. Fuierer, R.E. Newnham, T.R. Srout, Materials for high temperature acoustic and vibration sensors: a review. Applied Acoustics, 1994, **41**, 299.

3. M. Villegas, C. Moure, P. Duran, J.F. Fernandez, Nuevas perspectivas en piezoeléctricos de alta temperatura basados en compuestos laminares de bismuto. Bol. Soc: Esp. Ceram. Vidr. 1997, **36**, 179.

4. E.C, Subbarao, Systematic of bismuth layer compounds, Int. Ferroelectrics, 1996, **12**, 33.

5. M. Boekholt, D. Götz, et al., Structural and superconducting properties of $Bi_{2-x}Pb_xSr_2CaCu_2O_{8+\delta}$. Physica C, , 1991, **176,** 420,

6. E.C. Subbarao, Crystal chemistry of mixed bismuth oxides with layer-type structure, J. Amer. Ceram. Soc, 1962, **45** ,**166**.

7. I.G. Ismailzade, V.I. Sterenko, F.A. Mirishli, P.G. Rustamov, X-Ray and electrical studies of the system $Bi_4Ti_3O_{12}$-$BiFeO_3$, Soviet Phys.-Crystallography, 1967, **12**, 400.

8. L. Lascano, A.C. Caballero, M. Villegas, C. Moure, P. Duran, J.F. Fernandez, Materiales ceramicos texturados $Pb_xBi_4Ti_{3+x}O_{12+3x}$ (x=1,2,3). Parte II propiedades eléctricas, Bol. Soc: Esp. Ceram. Vidr. , 1999, **38**, 573.

9. A. Fouskova, L.E. Cross, Dielectric properties of bismuth titanate, J. Appl. Phys., (1970, **41**, 2834

10. M. Villegas, A.C. Caballero, C. Moure, P. Duran, J.F. Fernandez, Low temperature sintering and electrical properties of chemically W-doped $Bi_4Ti_3O_{12}$ ceramics, J. European Ceram. Soc., 1999, **19**, 1183,

11. C. Moure, J.F. Fernandez, M. Villegas, P. Duran, Processing and sintering of $CaBi_4Ti_4O_{15}$ powders for high temperature piezoelectric materials, in E. Gusmano, E. Traversa Ed, Euroceramics IV Vol 5, Faenza, 1995, pp 139-144

12. C. Moure, L. Lascano, J. Tartaj, P. Durán, Electrical behaviour of $Bi_5FeTi_3O_{15}$ and their solid solutions with $CaBi_4Ti_4O_{15}$. Ceram. International, 2003, **29**, 91

13. K. Kato, K. Suzuky, D. Fu, K. Nishizawa, T. Miki, Structure and ferroelectric properties of alkoxy-derived $Ca_2Bi_4Ti_5O_{18}$ thin films on Pt(111)/TiO_x/SiO_2/Si(100) Jpn J. Appl Phys. 2002, **41**, 2110.

14. T. Takenaka, K. Sakata, Grain-Oriented and Mn-doped $(NaBi)_{(1-x)/2}Ca_xBi_4Ti_4O_{15}$ Ceramics for Piezo- and Pyrosensor materials, Sensors and Materials, , 1988, **1**, 35

FIGURE CAPTIONS

Figure 1. X-Ray patterns of compounds $CaBi_4Ti_4O_{15}$ (A), and $Ca_2Bi_4Ti_5O_{18}$, (B)

Figure 2. SEM Micrographs corresponding to polished and thermally etched surfaces of ceramic samples of compounds $CaBi_4Ti_4O_{15}$ (A), and $Ca_2Bi_4Ti_5O_{18}$, (B)

Figure 3. Permittivity-Temperature curves, (heating cycle) of the compounds $CaBi_4Ti_4O_{15}$ (A), and $Ca_2Bi_4Ti_5O_{18}$, (B)

TABLE 1
LATTICE PARAMETERS OF $CaBi_4Ti_4O_{15}$

$CaBi_4Ti_4O_{15}$ Lattice parameters: $a_0=0.5410_5$ nm, $b_0=0.5419_5$ nm, $c_0=4.079_8$ nm, $V=1.196_3$ nm^3		
d	h k l	I, (%)
20.3430	0 0 2	3.9
10.1768	0 0 4	3.4
6.781	0 0 6	6.3
5.0882	0 0 8	8.8
4.0716	0 0 10	9.7
3.8158	1 1 1	19.6
3.6885	1 1 3	4.1
3.4694	1 1 5	3.7
3.3903	0 0 12	3.4
3.2002	1 1 7	11.5
2.9247	1 1 9	100
2.7106	1 0 13, 0 2 3	24.2
2.5436	0 0 16	5.4
2.5180	2 0 6	2.1
2.4247	1 1 13	2.8
2.3967	2 0 8	2.9
2.2586	0 2 10	21.5
2.2153	1 1 15	2.9
2.1209	2 0 12	2.0
2.0345	0 0 20	4.7
1.9835	2 0 14	2.0
1.8832	2 2 4	2.9
1.8704	1 1 19	8.9
1.8555	0 0 22	5.4
1.7940	2 2 8	2.4
1.7362	1 1 21	14.0
1.7157	1 3 1	4.1
1.7106	3 1 1	3.7
1.6449	1 3 7	2.0
1.6369	3 1 7	7.3
1.6276	2 0 20	2.6
1.6154	1 1 23	3.2
1.6022	3 1 9	14.6
1.5307	2 0 22	3.2
1.4990	3 2 1	4.7
1.4625	2 2 18	6.5
1.4539	1 0 27	2.5
1.4486	3 1 15	1.7
1.4033	1 1 27	4.1
1.3960	3 1 17	2.6
1.3580	3 2 13	4.3
1.3530	0 4 0	3.8
1.3392	4 0 4	2.6
1.2818	2 0 28	2.7
1.2459	3 3 7	4.6

TABLE 2
LATTICE PARAMETERS OF $Ca_2Bi_4Ti_5O_{18}$

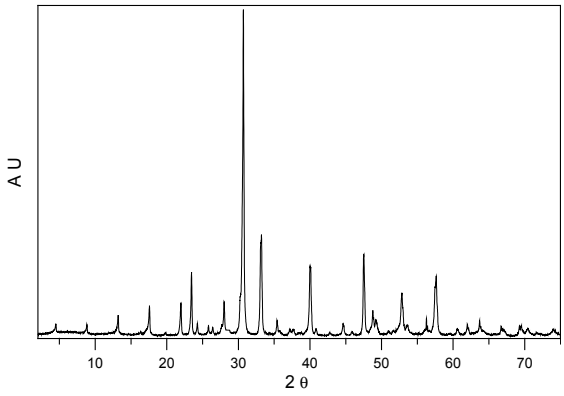
$Ca_2Bi_4Ti_5O_{18}$ Lattice parameters: $a_0=0.5381_1$ nm, $b_0=0.5390_9$ nm, $c_0=4.828_8$ nm, V=1.400_8 nm^3		
d	h k l	I, (%)
24.2951	0 0 2	11.2
12.1371	0 0 4	5.8
8.1025	0 0 6	7.9
6.0742	0 0 8	15.9
4.8558	0 0 10	9.4
4.0298	0 0 12	16.8
3.8117	1 1 1	11.4
3.7209	1 1 3	6.7
3.4602	0 0 14	8.8
3.3442	1 1 7	3.8
3.1101	1 1 9	19.4
3.0179	0 0 16	5.6
2.8848	1 1 11	100
2.6997	2 0 0	37.5
2.4674	2 0 8	3.3
2.4205	0 0 20	9.7
2.2411	2 0 12	21.5
2.1967	0 0 22	9.4
2.1158	1 1 19	3.4
2.0129	2 0 16	4.7
1.9053	2 2 0, 2 0 18	2.0
1.8560	2 2 6	3.7
1.8393	1 1 23	9.0
1.7977	2 0 20	7.3
1.7222	2 2 12, 1 1 25, 0 0 28	5.7
1.7021	1 3 0, 3 1 0	11.6
1.6212	1 1 27	5.8
1.6099	2 0 24	6.7
1.5857	3 1 11	14.9
1.5248	2 0 26	3.7
1.4948	2 2 20	3.6
1.4403	1 1 31	5.6
1.4188	1 3 19	3.2
1.3819	2 2 24	2.8
1.3448	0 4 2	4.5
1.2953	4 0 10	3.1

Table 3
Some electrical parameters of $CaBi_4Ti_4O_{15}$ and $Ca_2Bi_4Ti_5O_{18}$ sintered ceramic samples

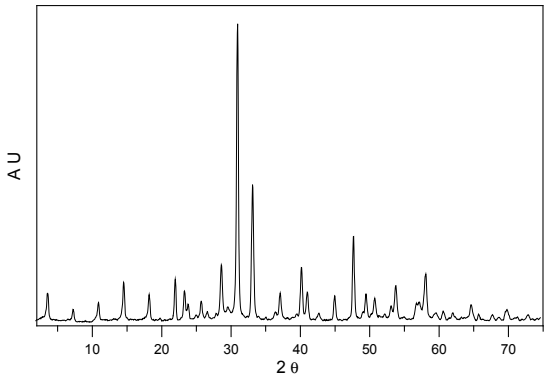
SAMPLE	K_{33}	d_{33}, (CN^{-1})	k_t	k_p	tan δ, 10kHz	Q_m	ρ, (Ωcm^{-1})
$CaBi_4Ti_4O_{15}$	180	$40.00x10^{-12}$	0.46	0.11	$1.1x10^{-3}$	114	$>10^{11}$
$Ca_2Bi_4Ti_5O_{18}$	93	$8.83x10^{-12}$	0.16	0.10	$1.0x10^{-3}$	106	$>10^{10}$

Table 4
Symmetry type of different $Bi_4Ti_3O_{12}$-ABO_3 derived compounds as a function of the perovskite type

ABO_3 COMPOUND	Symmetry of the corresponding Aurivillius phase $A_{m-1}Bi_2B_mO_{3m+3}$
$SrTiO_3$	Cubic
$BaTiO_3$	Tetragonal c/a≈1
$PbTiO_3$	Tetragonal c/a=1.047
$BiFeO_3$	Rhombohedral
$CaTiO_3$	Monoclinic

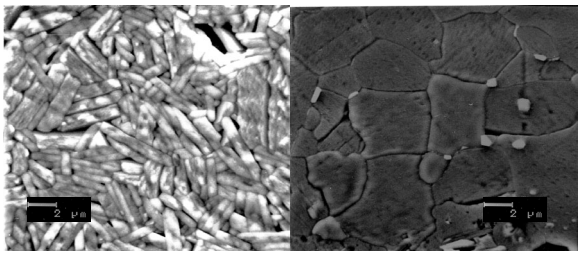


A



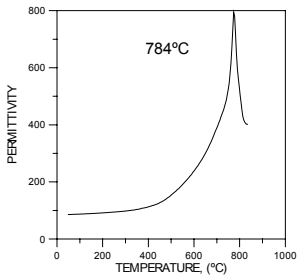
B

Figure 1



A B

Figure 2.


784°C
PERMITTIVITY
TEMPERATURE, (°C)
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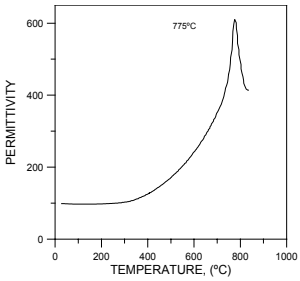
200
400
600
800
1000

A


775°C
PERMITTIVITY
TEMPERATURE, (°C)
0
200
400
600
800
1000

B

Figure 3.