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Processing and dielectric properties of $Bi_4Sr_{n-3}Ti_nO_{3n+3}$ ($n = 3$, 4 and 5) ceramics obtained from mechanochemically activated precursors

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Abstract

The processing of ceramics of ferroelectric, high-Curie temperature $Bi_4Ti_3O_{12}$, $Bi_4SrTi_4O_{15}$ and $Bi_4Sr_2Ti_5O_{18}$ from nanometer particle size powders, obtained by mechanochemical activation, is studied for piezoelectric applications. The effect of the size of the perovskite block (n value) on the density, texture and microstructure of the ceramics processed from the mechanoactivated powders is established. Dielectric properties as a function of temperature and frequency, and piezoelectric coefficients are measured. These powders allow Aurivillius single phase ceramics with good properties to be processed at temperatures significantly lower than conventional solid state reactions.

Keywords: Sintering; Microstructure-final; Dielectric properties; Piezoelectric properties; Bismuth-layer structure

1. Introduction

Bismuth layer-structured ferroelectrics are one of the candidates for lead-free piezoelectric ceramics,[1] and are usually high temperature piezoelectrics thanks to their high ferro-paraelectric transition temperature.[2] The Aurivillius-phases can be described as a regular stacking of $(Bi_2O_2)^{2+}$ slabs and perovskite $(A_{n+1}B_nO_{3n+1})^{2-}$ blocks. The position A is generally occupied by an alkaline, alkaline-earth and rare-earth metal, B by a d^0 transition element and n represents the number of BO_6 octahedra between two Bi_2O_2 layers. The phases studied in this work are $[Bi_2O_2]$ $[Bi_2Sr_{n-3}Ti_nO_{3n+1}]$ with $n = 3$, 4 and 5. Their Curie temperature decrease as n increases,[3] such as it is 675, 520 and 285 °C for $Bi_4Ti_3O_{12}$, $Bi_4SrTi_4O_{15}$ and $Bi_4Sr_2Ti_5O_{18}$, respectively. Properties are also influenced by the microstructure, texture and density, and these factors are related to the synthesis and processing conditions.

The Aurivillius phases that belong to the bismuth–strontium –titanate system ($Bi_4Sr_{n-3}Ti_nO_{3n+3}$) are usually synthesized by solid-state reaction. $Bi_4Ti_3O_{12}$ ceramic powders are prepared at temperatures between 800 and 900 °C, $Bi_4SrTi_4O_{15}$ powders are obtained at 1050 °C, and cumulative treatments up to 1200 °C are necessary for $Bi_4Sr_2Ti_5O_{18}$.[4–7] The high temperature and the long reaction time demanded by the synthesis of these phases, especially that with $n = 5$, entail an important lack of stoichiometry in the final product, along with uncontrolled particle size. This makes necessary to look for alternative routes, such as the mechanochemical activation method. During the mechanical treatment in the mill, the particle size of the initial reactants decreases, while defects and disorder in the sample rise and the homogeneity of the mixture increases. The technique allows amorphous and nanocrystalline precursors to be obtained, for which the synthesis temperatures and reaction times are significantly reduced. It has been demonstrated that the mechanoactivation method facilitates the synthesis of Aurivillius phases.[7,8] Previous work showed that $Bi_4Ti_3O_{12}$ is obtained after the mechanically activated precursor is heated at ~600 °C,[4] that $Bi_4SrTi_4O_{15}$ is obtain when the precursor is thermally treated between 600 and 700 °C,[5,6] and that 900 °C are necessary to obtain $Bi_4Sr_2Ti_5O_{18}$.[6] Like in solid-state reactions, the temperature of crystallization increases with the n value.

In general, the processing of ceramics is facilitated by the high reactivity of the mechanoactivated precursor.[9] In this paper, we report on the processing and properties of $Bi_4Ti_3O_{12}$, $Bi_4SrTi_4O_{15}$ and $Bi_4Sr_2Ti_5O_{18}$ ceramics, from powders prepared by the mechanochemical activation method. Emphasis is

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put on the comparison of the results for the three Aurivillius phases with increasing n.

2. Experimental procedure

$Bi_4Ti_3O_{12}$, $Bi_4SrTi_4O_{15}$, and $Bi_4Sr_2Ti_5O_{18}$ precursor powders were prepared by the mechanochemical activation method. Stoichiometric, 3 g mixtures of analytical grade Bi_2O_3 (Cerac, 99.9%), TiO_2 anatase (Cerac, 99.9%) and $SrCO_3$ (Cerac, 99.9%) were mechanochemically activated in a vibrating mill with stainless steel media: vessel (100 ml) and ball (5 cm diameter).

Identical procedures were used for the processing of ceramics of the three Aurivillius phases. Approximately 1 g of precursor powders were uniaxially pressed into 12 mm diameter discs and further consolidated by isostatic pressing at 200 MPa. Conventional sintering in air was carried out at several temperatures for 5 h with a heating rate of 3 °C min^{-1}. Density was measured by the Archimedes' method using water as immersion liquid. $Bi_4Ti_3O_{12}$ and $Bi_4SrTi_4O_{15}$ crystallographic densities are 8.045 and 7.448 g cm^{-3} from ICDD PDF 35-0795 and 43-0973, respectively. $Bi_4Sr_2Ti_5O_{18}$ density was measured with the AccuPyc 1330 Pycnometer, automatic density analyzer by amount of displaced gas (He), and found to be 7.223 g cm^{-3}. Phases after sintering were studied by Bragg-Brentano $\theta/2\theta$ X-ray diffraction (XRD) with a Siemens D500 diffractometer and a Bruker AXS D8 advance diffractometer, with scan rates of 0.05° (2θ) per second from 5° to 60° (2θ), using Cu Kα radiation ($\lambda = 0.15418$ nm).

A scanning electron microscope (960 Zeiss SEM operated at 10–20 kV with Au and C metallization) was used for characterising the microstructures on polished and thermally etched/quenched surfaces.

Ag or Pt electrodes were painted on the disc faces and sintered at 650 and 900 °C, respectively for electrical characterization. The dependence of the dielectric permittivity and losses on temperature at 10 frequencies between 1 and 500 kHz was dynamically measured, during cooling at −1 °C min^{-1} from above the Curie temperature down to room temperature, with a HP4194A impedance/gain phase analyzer. Poling was attempted at fields and temperatures up to 5 kV mm^{-1} and 200 °C, respectively, and the d_{33} piezoelectric coefficient was measured with a Berlincourt-type meter.

3. Results and discussion

The evolution of the precursor during the mechanical treatment was followed by XRD. The diffraction peaks of the initial products broadened and progressively became less intense with activation time. The mechanical treatment was considered completed when XRD patterns corresponding to an amorphous were obtained, which occurred after 168 h for $Bi_4Ti_3O_{12}$ and $Bi_4SrTi_4O_{15}$. However, in the case of $Bi_4Sr_2Ti_5O_{18}$, there was still a peak indicating the presence of $SrCO_3$ after 168 h of mechanical treatment. Activation was thus prolonged up to 672 h, when the ceramic powders obtained were amorphous. Fe contamination was not found by EDXS analysis.

For all cases, the DTA curve (not shown in the article) presents two exothermic peaks on heating. The first peak appears at 308 and 376 °C for the $Bi_4Ti_3O_{12}$ and $Bi_4SrTi_4O_{15}$ precursors, respectively, and corresponds to the formation of a fluorite-type (Sr)–Bi–Ti–O phase.[4–6] In the case of the $Bi_4Sr_2Ti_5O_{18}$ precursor, the peak occurs at 462 °C, and cannot be associated with a fluorite-type phase because this was not observed by XRD. This peak for $n = 5$, and the second exothermic peak for $n = 3$, 4 and 5 at 441, 455 and 491 °C, respectively, are attributed to the formation of the Aurivillius phases. It is observed that the temperature of formation of the Aurivillius phases increases with the n value. Intermediate fluorite phases were observed during the heating of $n = 5$ activated for shorter times, which shows the influence of the milling time in the path-way reaction. Thermogravimetry shows a first weight loss evolution attributed to moisture (starting at 100 °C). For the case of $Bi_4SrTi_4O_{15}$ and $Bi_4Sr_2Ti_5O_{18}$ powders, there are additional losses due to the CO_2 evolved from $SrCO_3$, which occurs in two steps (at 405 and 560 °C) and one step (at 561 °C), respectively.

Fig. 1 shows the XRD patterns for ceramics of the three Aurivillius phases, obtained from the mechanoactivated amorphous precursors. Sintering was accomplished at 1050 °C for 5 h. These conditions were chosen after a sintering study at temperatures ranging from 1000 to 1200 °C. Dense ceramics cannot be obtained for $Bi_4SrTi_4O_{15}$ and $Bi_4Sr_2Ti_5O_{18}$ at 1000 °C. Decomposition of the Aurivillius phases and Bi losses were observed above 1100 °C for $Bi_4SrTi_4O_{15}$ and $Bi_4Sr_2Ti_5O_{18}$.

Densification values are given in Table 1. This magnitude decreases as n increases for ceramics sintered at the same temperature, which is most probably a consequence of the presence of increasing amounts of $SrCO_3$.

Ceramics processed from mechanochemically activated powders do not show any texture, as a consequence of the equiaxial morphology of the particles in the precursor. SEM confirmed the random orientation of the Aurivillius anisometric particles (Fig. 2). $Bi_4Ti_3O_{12}$ presents platelet-like grains with 3 μm thickness and length up to 20 μm. Both the thickness and length decrease when n increases. Besides platelets, there are pockets of equiaxed, small (0.25 μm) grains for the $Bi_4SrTi_4O_{15}$ ceramic. The fraction of equiaxed grains increases for the $Bi_4Sr_2Ti_5O_{18}$ ceramics. These results indicate that grain growth and densification are delayed as n increases. Nevertheless, single phase ceramics with a density high enough for electrical characterization have been successfully processed from the mechanoactivated precursors.

Dielectric permittivity as a function of temperature and frequency is shown in Fig. 3. The dielectric permittivity curve

Table 1
Densification (ρ), dielectric permittivity ($\varepsilon_{33}^{\sigma}$), Curie temperature ($T_C$) and piezoelectric coefficient (d_{33}) for $Bi_4Ti_3O_{12}$, $Bi_4SrTi_4O_{15}$ and $Bi_4Sr_2Ti_5O_{18}$ ceramics sintered at 1050 °C

	ρ (%)	$\varepsilon_{33}^{\sigma}$ ($\times\varepsilon_0$)	T_C (°C)	d_{33} ($\times 10^{-12}$ C N^{-1})
$n = 3$	96	120	644	–
$n = 4$	90	170	503	25
$n = 5$	87	255–280	267	26

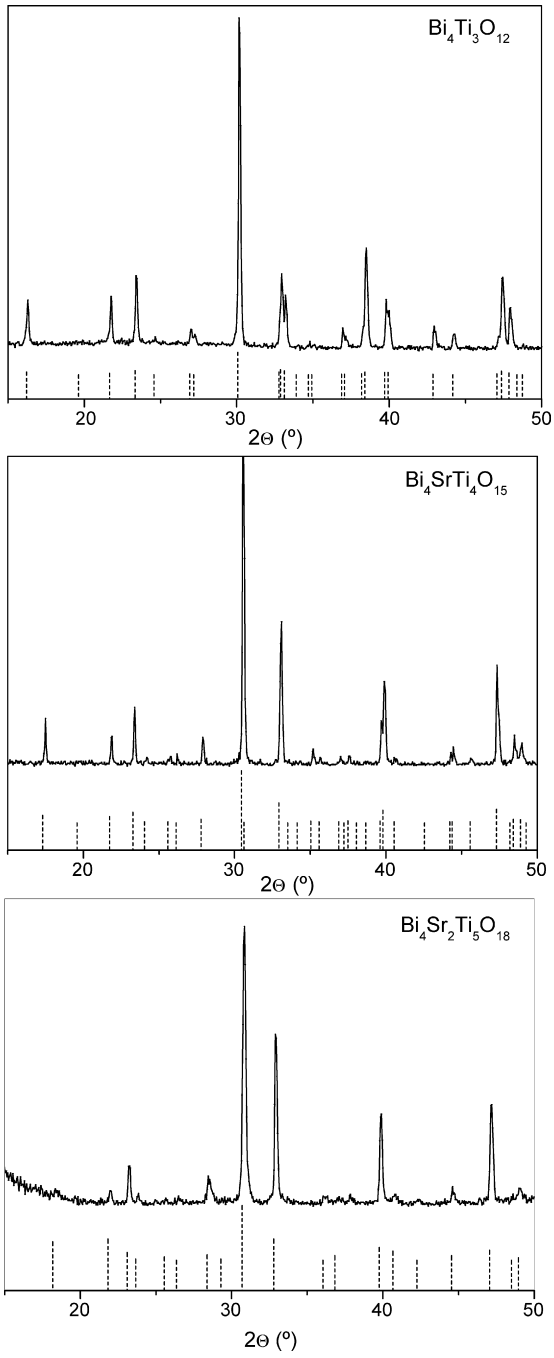

Fig. 1. XRD patterns of $Bi_4Ti_3O_{12}$, $Bi_4SrTi_4O_{15}$ and $Bi_4SrTi_5O_{18}$ ceramics processed at 1050 °C (vertical bars at the bottom indicate the Bragg positions from the ICDD PDF files).

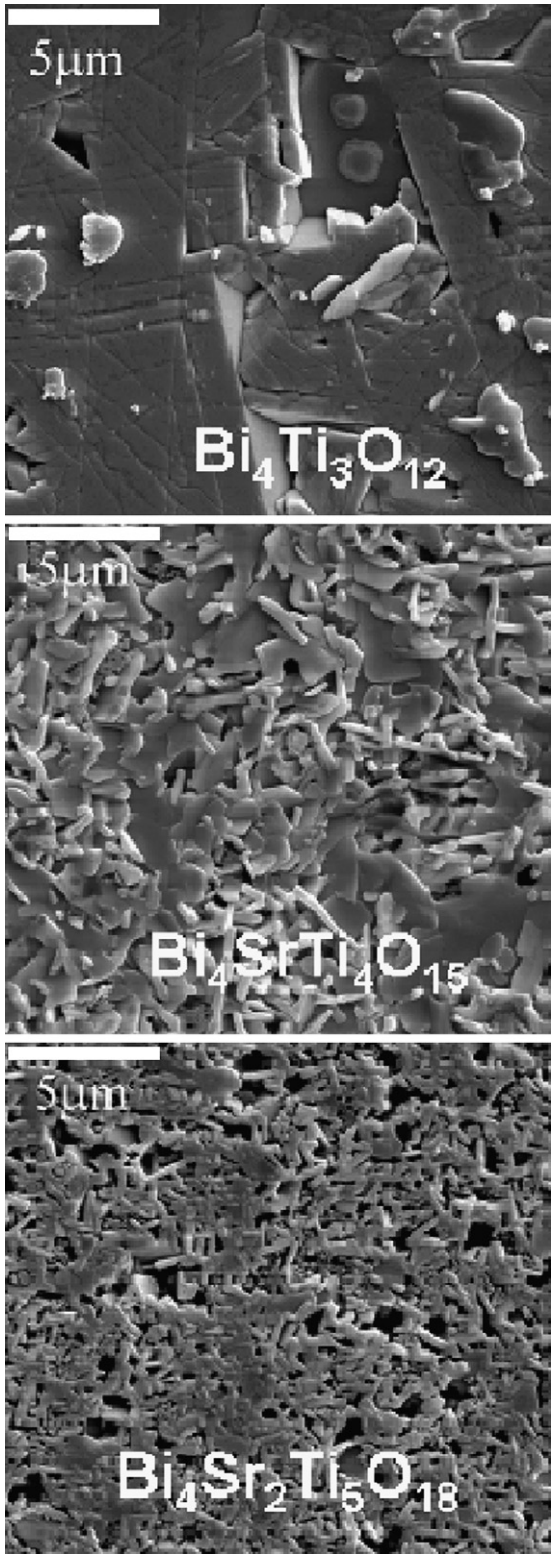

Fig. 2. Microstructures of $Bi_4Ti_3O_{12}$, $Bi_4SrTi_4O_{15}$ and $Bi_4SrTi_5O_{18}$ ceramics processed at 1050 °C.

of $Bi_4Ti_3O_{12}$ ceramic presents the two dielectric relaxation peaks associated with the dynamics of vacancies.[10,11] A previous investigation[12] showed two similar anomalies below T_C in the curve of $Bi_4Sr_2Ti_5O_{18}$ ceramics obtained by the solid-state method. Authors[12] suggested that the peaks were originated by oxygen vacancies related to Bi vaporization. In our case, no peaks below T_C were observed in the curves of $Bi_4SrTi_4O_{15}$ and $Bi_4Sr_2Ti_5O_{18}$ ceramics. This could be a consequence of the smaller sintering temperature (1050 °C as compared with 1195 °C[12]), and thus, of the absence of bismuth vacancies. Also, $n = 4$ and 5 present strontium in the pseudo-perovskite block. The Sr–Ti–O block is more stable than Bi–Ti–O, which could cause the concentration of oxygen vacancies in $Bi_4SrTi_4O_{15}$ and $Bi_4Sr_2Ti_5O_{18}$ to be smaller than in $Bi_4Ti_3O_{12}$ ceramics.[13]

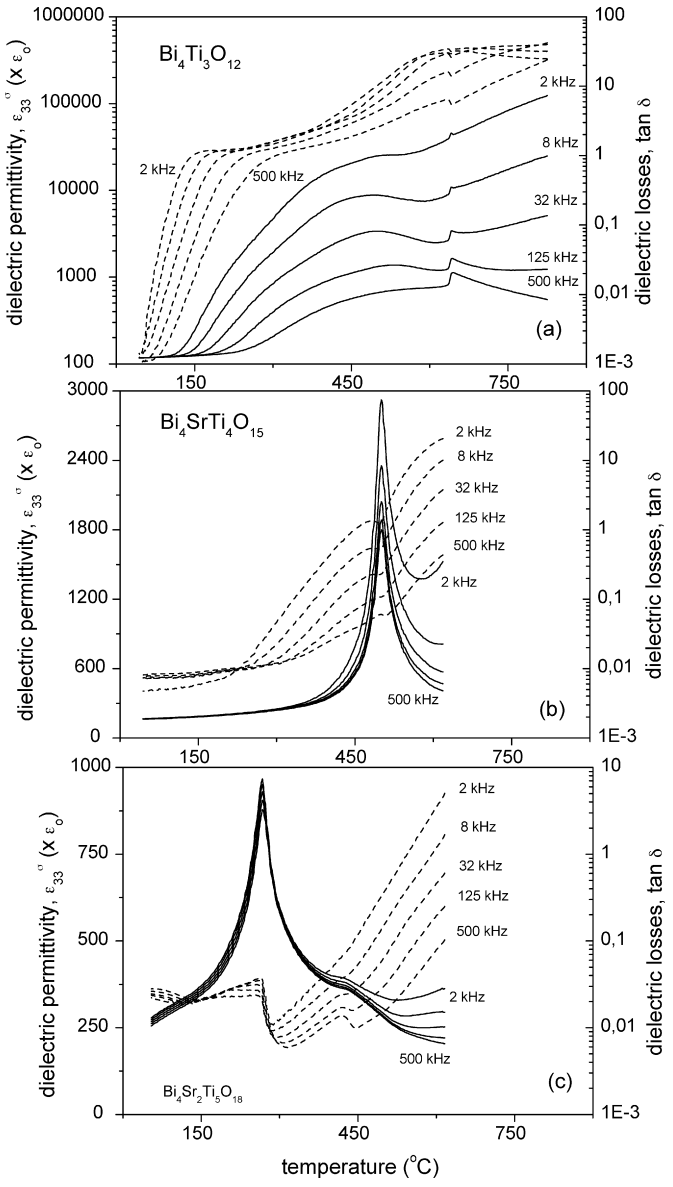

Fig. 3. Dielectric permittivity and losses as a function of temperature at several frequencies for (a) $Bi_4Ti_3O_{12}$, (b) $Bi_4SrTi_4O_{15}$ and (c) $Bi_4Sr_2Ti_5O_{18}$ ceramics sintered at 1050 °C.

An anomaly appears in the dielectric permittivity curve of the $Bi_4Sr_2Ti_5O_{18}$ ceramics around 420 °C, above T_C. We have not found mention of this anomaly in the literature. A similar anomaly has been described for $Bi_4Ti_3O_{12}$, and interpreted to be of extrinsic and not of structural origin.[14] However, the anomaly for $n = 5$ is observed on heating and cooling and shows no dispersion, which suggest it being related to a second transition. Dielectric curves for the three compositions reflect the known decrease of T_C with n (see the table). $Bi_4Ti_3O_{12}$ presents high conductivity that prevents poling. This is not the case for $Bi_4SrTi_4O_{15}$ and $Bi_4Sr_2Ti_5O_{18}$ materials, and poling was possible. Values of the longitudinal d_{33} piezoelectric coefficients of $Bi_4SrTi_4O_{15}$ and $Bi_4Sr_2Ti_5O_{18}$ ceramics are given in the table, and are comparable to those reported by other authors.[14,15]

4. Conclusions

The temperature of formation of the $Bi_4Sr_{n-3}Ti_nO_{3n+3}$ with $n = 3$, 4 and 5 Aurivillius phases from mechanochemically activated precursors increases with n. Grain growth and densification during sintering are delayed as the size of the perovskite block increases. Nevertheless, single phase ceramics can be processed at 1050 °C from these precursors for the three cases. Dielectric permittivity curves for $Bi_4SrTi_4O_{15}$ and $Bi_4Sr_2Ti_5O_{18}$ ceramics do not show relaxation peaks at temperatures below T_C, due to the stability of the Sr–Ti–O block and to the decrease of the bismuth vaporized as a result of the low sintering temperature. Conductivity is reduced for $n = 4$ and 5, which allows poling. Piezoelectrics coefficients of $\sim$25 pC N^{-1} are obtained.

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