

Processing and dielectric properties of the mixed-layer bismuth titanate niobate $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ by the metal-organic precursor synthesis method

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Abstract

The preparation of homogeneous $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ single phase nanosized ceramic powders at temperatures as low as 400–500°C using a metal-citrate complexes method, based on the Pechini-type reaction route, is described. The thermal decomposition/oxidation of the polymerized resin, as investigated by TG/DTA, XRD, Raman spectroscopy and SEM, led to the formation of a well defined orthorhombic $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ compound with lattice parameters $a=0.544$, $b=0.540$ and $c=2.905 \pm 0.0005$ nm. Reaction formation takes place through an intermediate binary phase with a stoichiometry close to $\text{Bi}_{20}\text{TiO}_{32}$ which forms between 300 and 375°C. The metal-organic precursor synthesis method, allows the control of the Bi/Ti/Nb stoichiometric ratio leading to the rapid formation of the nanosized bismuth titanate niobate, $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$, ceramic powders, at temperatures much lower than usually needed in the conventional route. Sintering of the as-prepared ceramic powders led to near full density samples in the temperature range 1100–1130°C. The mixed-layer structure $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ ceramics showed two phase transitions at about 650 and $850 \pm 5^\circ\text{C}$, and a piezoelectric modulus, d_{33} , as high as 20×10^{-12} C/N. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$; Dielectric properties; Powders-chemical preparation; Reaction sequence; Sintering

1. Introduction

Within the family of layered bismuth-bearing perovskite compounds, so called Aurivilius phases,¹ with the general formula $\text{Bi}_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+3}$, the $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ (BTN) is one of the most complex layered bismuth compounds, where the structure type is represented by $\text{Bi}_4\text{A}_{2m-1}\text{B}_{2m+1}\text{O}_{6m+9}$, with $m=1, 2, 3$.² The structure of BTN appears to consist of a regular intergrowth of $\text{Bi}_3\text{TiNbO}_9$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ layers along the c axis.³ The BTN compound has been indexed² on the basis of an orthorhombic unit cell having parameters $a=0.544$, $b=0.540$ and $c=2.905$ nm. The crystal structure of the BTN compound was also studied by Horiuchi et al.⁴ by means of super-high resolution electron microscopy, confirming the regular sequence of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and

$\text{Bi}_3\text{TiNbO}_9$ — like layers in the structure of the $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ compound.

The dielectric properties of BTN ceramics have also been studied and there is a current consensus on the two dielectric anomalies observed in this compound at about 670 and 850°C, albeit both of them being attributed to a different phenomenon depending on the author. Thus, for example, Korzunova et al.³ suggested that the low-temperature anomaly was due to the ferroelectric transition of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, and the high temperature one could be due to the ferroelectric transition of the BTN itself. However, Chu et al.⁵ attributed the dielectric anomalies observed in BTN to an irregular stacking of $\text{Bi}_3\text{TiNbO}_9$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ layers suggesting, thus, that the low temperature dielectric anomaly could be due to a phase transition of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ present as clusters in the structure of BTN compound. Such a suggestion which is in contradiction with the reported structure for BTN by Horiuchi et al.,⁴ allows us to assume that the processing conditions to prepare the BTN compound could affect the homogeneity in the arrangement of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_3\text{TiNbO}_9$

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layers and, therefore, the dielectric response of the BTN ceramics.

$\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ has been synthesized by solid-state reactions from Bi_2O_3 , TiO_2 and Nb_2O_5 powder mixtures,^{2,3,5} but in most of the cases the $\text{Bi}_3\text{TiNbO}_9$ phase is generally present as a parasite minor impurity even after extended heating to 1100°C. Furthermore, the solid-state reaction between the above oxides does not proceed homogeneously but sequentially.³ Therefore, nonhomogeneous samples are obtained by this solid-state process. Such a problem can be solved by using a nonconventional method of synthesis, and the polymeric precursors method, based on that of Pechini,⁶ could be the most suitable in this specific case, in which both the Bi and Nb ions are strongly hydrolyzable in aqueous media. In addition, Bi_2O_3 is highly volatile under the temperature conditions of either powder synthesis or subsequent sintering and, therefore, control of cation stoichiometry becomes very difficult. To our knowledge no reports have been published on the synthesis by chemical routes of these bismuth-layer compounds, and only various complex oxides such as $\text{Pb}_3\text{MgNb}_2\text{O}_9$,^{7,8} $\text{Y}_2\text{Ti}_2\text{O}_7$,⁹ and some superconductors with multiple cationic compositions¹⁰ have already been successfully prepared.

Within this framework, we report in the present paper the successful preparation, for the first time, of homogeneous $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ samples at temperatures as low as 400°C by the metal-citrate complexes method, the sintering behavior of the $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ ceramics obtained by that chemical synthesis route, and the piezoelectric properties.

2. Experimental procedure

Powders of $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ were prepared by the metal citrate polymeric-organic precursor method as detailed elsewhere.¹¹ Briefly, the required amount of titanium (IV) tetrabutoxide ($\text{Ti}[\text{C}_4\text{H}_9\text{O}]_4 \cdot \text{C}_4\text{H}_9\text{OH}$ Alfa Product, Karlsruhe, Germany) was dissolved in 4 mol ethylene-glycol ($\text{C}_2\text{H}_6\text{O}_2$; EG, E. Merck, Darmstadt, Germany); then 1 mol anhydrous citric acid ($\text{C}_6\text{H}_8\text{O}_7$; CA, E. Merck, Darmstadt, Germany) was added to this solution by stirring at 60°C up to achieve complete dissolution. On the other hand, the required amounts of bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and niobium pentachloride, NbCl_5 , (Riedel de Hach, Seelze, Germany) were separately dissolved into aqueous nitric acid and hydrochloric acid, respectively, and then mixed together to obtain a clear solution containing Bi and Nb cations. The solution containing bismuth and niobium ions was directly mixed with the CA-EG solution containing titanium ions, and this was slowly heated up to 80°C during 3–5 h. The resultant transparent solution was then heated at 130°C for several hours on a hot plate with magnetic stirring to promote esterification between CA and EG. During the heat treatment, a change in color from colorless

to yellow or brown was observed, indicating the formation of a polymeric gel. In order to remove undesirable solvent and organics, the viscous polymeric product was heat-treated at $\sim 280^\circ\text{C}$ in the beaker. The solid black resin thus obtained was precalcined at 350°C for 2 h resulting in the formation of a green yellowish powder. After milling, the precalcined powder was heat-treated at different temperatures between 400 and 800°C for 2 h.

Thermal reactions taking place during the calcination of the solid black resin were analyzed in air by thermogravimetric and differential thermal analysis (STA 409, Netzsch-Geratebau, Selb-Bayern, Germany), using a sample weight of about 80 mg, and a heating and cooling rate of 3°C/min. The existing phases in the calcined samples were studied by X-Ray diffraction (XRD), $\text{CuK}\alpha$, 40 kV–40 MA, (Siemens D-5000, Erlangen, Germany). The scan rate was 2°/min for the phase identification in the 2θ range 2–80, and step scanning (step size 0.02°, counting time 10°/step) for the determination of lattice parameter, where standard silicon powder was used for the angle calibration. Crystallite size of calcined powders were determined by X-ray line broadening using the Scherrer equation.¹² Raman spectra at room temperature of the calcined samples were registered with a single monochromator Renishaw system 1000 equipped with a cooled CCD detector (200 K) and a holographic Notch filter. The elastic scattering is filtered by the holographic Notch filter, and the Raman signal remain higher than with triple monochromator spectrometers. The samples were excited with the 514 nm Ar line in an in situ treatment under flowing air. The spectral resolution is better than 2 cm^{-1} , and the spectra acquisition consisted of five accumulations of 60 s.

The specific surface area of the powder samples was determined with nitrogen by single-point BET (Quantachrome MS-16 model, Syosset, NY, USA). The evolution of the powder morphology with the calcination temperature, as well as the microstructure on polished and thermally etched sintered samples, were studied by scanning electron microscopy (SEM) (Zeiss DSM 950, Oberkochen, Germany) equipped with energy dispersion spectroscopy (EDS) with a beryllium window. The sintering of the BTN calcined powders was performed on 200 MPa isopressed samples in the temperature range of 1050–1120°C.

Polished disks (10 mm diameter and 1 mm thick) were prepared for dielectric measurements by painting on Pt electrodes. Samples were annealed at 800°C for 30–60 min to improve the mechanical and electrical characteristics of the electrodes. The temperature dependence of the dielectric permittivity in sintered BTN samples was measured with an HP 4290 A LCR meter. The precision of the temperature measurement was within $\pm 5^\circ\text{C}$.

Poling of BTN sintered samples was performed in a silicon oil bath at 220°C in a field of 60 kV/cm for 10 min. Piezoelectric response, d_{33} , was determined with a

Berlincourt meter, and the electromechanical coupling factor was derived from resonance-antiresonance measurements.

3. Results and discussion

3.1. Thermal decomposition and powder characterization

The chemical sequence for the preparation of BTN powders, i.e. (a) Chelate formation, (b) Esterification process and (c) Polymerization, are found to have taken place correctly. The fact that no visible precipitation could be observed throughout the entire process support is such a contention. On the other hand, the relative weight loss (–85%) and differential thermal analysis of the polymeric precursor, as shown in Fig. 1, indicate that heat begins to evolve at about 300°C and all the weight loss occurs below 520°C. The DTA curve shows an exothermic shoulder at about 340°C which, probably, corresponds to the initial decomposition/oxidation of the polymeric precursor. With an increase in temperature a second exothermic effect, which maximum appears to be located at ~ 394°C was also present. Between 400 and 500°C a relatively well defined plateau also appeared in the DTA curve. Although no previous thermodynamic data have been found in the literature, the second exothermic effect could be attributed to the first nucleation events, and the crystallization process of BTN is completed through the plateau before 520°C. At that temperature the weight loss is finished. This crystallization process takes place simultaneously with the combustion of residual organic products and/or carbon.

The X-ray diffraction study on the samples calcined at different temperatures, as shown in Fig. 2, revealed that, in close agreement with the DTA results, in the short temperature interval of 394–494°C the amorphous black resin converts completely into the $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ compound.

Such a reaction formation takes place through the previous formation of an intermediate phase, which has been identified as a complex bismuth-titanium oxides binary compound of the type $\text{Bi}_{20}\text{TiO}_{32}$ with tetragonal

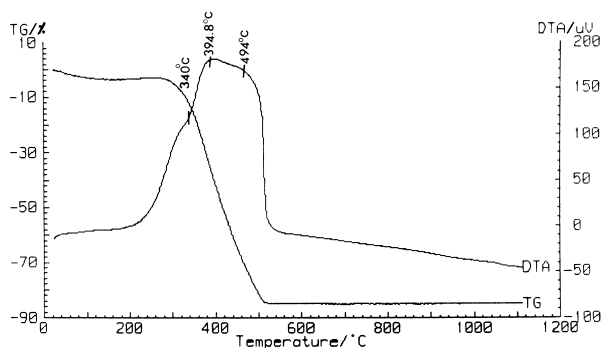


Fig. 1. TG/DTA curves for BTN precursors.

structure.¹³ Such a compound along with a small amount of metallic bismuth were present in the black resin calcined at 375°C for 2 h. The presence of metallic bismuth is only justifiable by the reducing conditions that, induced by the combustion of organic products at that temperature, may give rise to metal ions with lower valence state. Neither titania nor niobia were detected at this thermal level, but a large amount of the amorphous polymeric precursors was still present. Between 375 and 494°C all the amorphous phase (presumably containing the Nb^{5+} and part of Ti^{4+} cations) and the metallic bismuth are transformed by thermal decomposition/oxidation and react rapidly with the $\text{Bi}_{20}\text{TiO}_{32}$ intermediate phase leading to the formation of the $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ compound. The appearance of the $\text{Bi}_{20}\text{TiO}_{32}$ intermediate phase is in agreement with the presence of a plateau in the DTA curve in which the two compounds $\text{Bi}_{20}\text{TiO}_{32}$ and $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ coexist; no other intermediate phases were detected during the calcination process.

It must be mentioned that a sample heat-treated at 400°C for 20 h led to the synthesis of >85% of BTN. These results are in contradiction with those of Korzunova et al.,³ who proposed the formation of the binary and ternary $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_3\text{TiNbO}_9$ intermediate phases prior to the final formation of the $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ compound. It is suggested in our case that the small particle size of the calcined powders (~ 55 nm), accelerated the reaction kinetics leading to the formation of an intermediate phase different to those found by Korzunova et al.³ On the other hand, the enthalpy for the

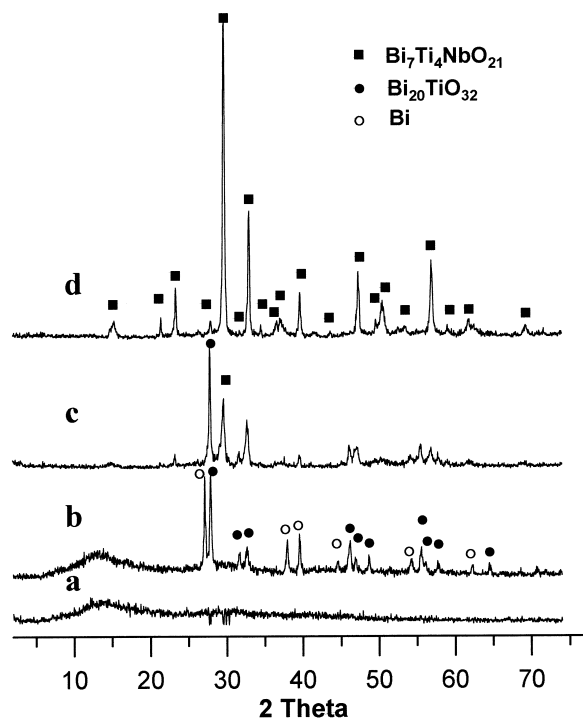


Fig. 2. X-ray diffraction patterns of BTN precursor calcined at 180 (a), 375 (b), 400 (c), and 500°C for 2 h (d).

formation of a binary compound such as $\text{Bi}_{20}\text{TiO}_{32}$ will be much lower than that required for the formation of a ternary one. At 800°C for 2 h the samples were a well crystallized $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ orthorhombic phase, and the measured lattice parameters $a=0.544$, $b=0.540$ and $c=2.905$ nm match well with the orthorhombic BTN structure previously reported.²

To further support the belief that the formation of BTN in the polymeric complex method is completed at a much lower temperature than that in the conventional mixed oxides one, the powder precursors calcined at several temperatures were characterized using a Raman spectroscopy. Fig. 3 shows the Raman spectra of powders calcined at the higher temperature (1120°C), and this is compared with that obtained on a $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ sample sintered at 1130°C . Twelve phonon modes of BTN, at about 44, 60, 79, 89, 117, 227, 268, 320, 351, 542, 609 and 848 cm^{-1} are observed. All of these modes are the same as those found for the bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, single crystal,¹⁴ with the only difference of a splitting of the phonon mode 84 into two peaks at 79 and 89 cm^{-1} , and the mode at 326 cm^{-1} into two peaks at 320 and 351 cm^{-1} . In Raman spectra of powders calcined at $375\text{--}540^\circ\text{C}$ for 2 h, Fig. 4, a few extra peaks or shoulders not identified with BTN were detected at 178, 203, 310 and 428 cm^{-1} at 375°C , and 160, 252, 310 and 627 cm^{-1} at 400°C . In the samples calcined at 540°C three broad peaks at 251, 548 and 845 cm^{-1} were observed.

From the above results the following can be pointed out. (a) The sharp increase in the intensity of the 313 cm^{-1} band and the appearance of a band at 428 cm^{-1} along with three other peaks at 178, 203 and 614 cm^{-1} in the sample calcined at 375°C , indicated the rearrangement of a binary $\text{Bi}_2\text{O}_3\text{--TiO}_2$ intermediate structure^{15,16} before the formation of BTN phase. Such a binary intermediate phase, according to the X-ray diffraction results, seems to correspond to the $\text{Bi}_{20}\text{TiO}_{32}$ compound, albeit this is not clearly established. (b) Although the spectrum for the sample heated at 400°C was similar to that after 540°C except for the almost disappearance of the bands at 310 and 428 cm^{-1} , but the appearance of a shoulder at 147 and a band at 252 cm^{-1} indicated the coexistence of the two $\text{Bi}_{20}\text{TiO}_{32}$ and BTN phases, which is in agreement with the DTA and X-ray diffraction results. (c) The complete disappearance of all the Raman bands corresponding to the intermediate phase and, on the other hand, the increase in the intensity of the peaks at 250, 548 and 845 cm^{-1} , which are representative of a typical mixed-layered perovskite structure,¹⁶ indicated the formation of a not well crystallized BTN ternary phase close to the $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ composition. It must be noted that the extremely broad bands present in such a spectrum can be indicating a disordered structure similar to that seen for glasses.

On the other hand, from the above Fig. 3 some differences can be noted in the room temperature Raman spectra registered on the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ high temperature sintered samples. As the Bi_2O_3 concentration increased, the Raman modes were displaced towards higher frequencies, and the intensity of the Raman bands decreased. If it is assumed that the higher

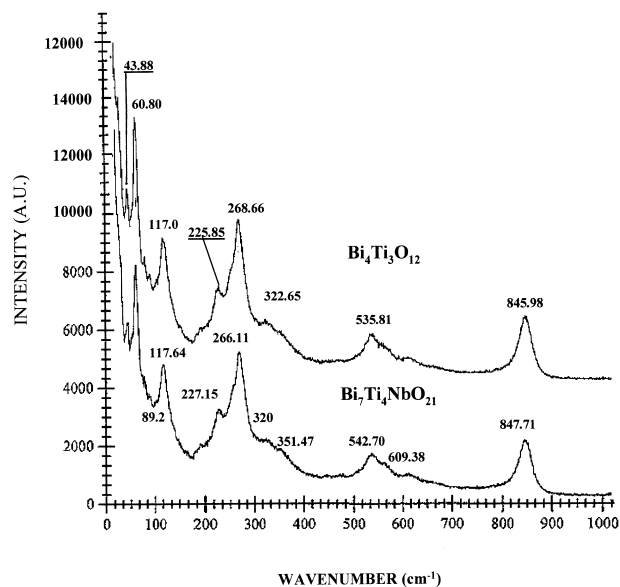


Fig. 3. Room temperature Raman spectra of $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ sintered samples.

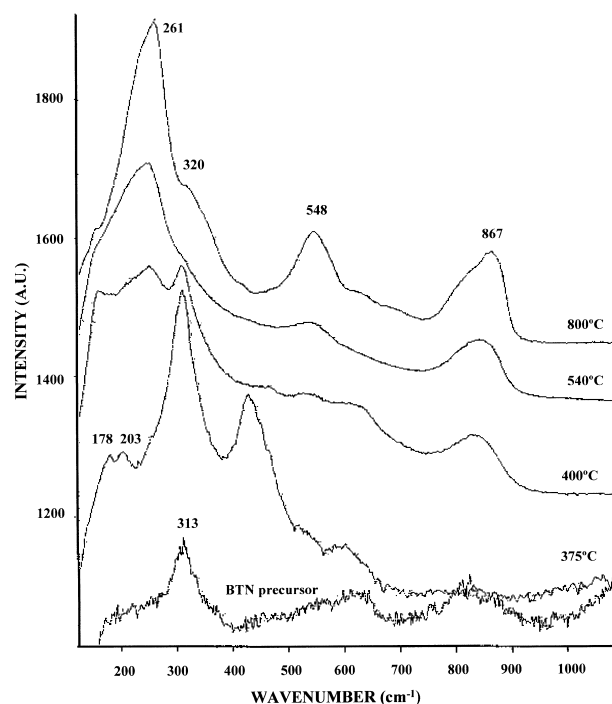


Fig. 4. The evolution of the BTN Raman bands with temperature.

wavenumber phonon modes can be attributed to vibrations of Ti–O or Nb–O atoms inside the perovskite layer O_6 octahedra, and the lower wavenumber phonon modes to vibrations of Bi–O atoms within the Bi_2O_2 layer, then the lowest phonon mode below 50 cm^{-1} , is considered to be associated with vibrations of Bi–Bi atoms with weak metal bonds on a–c surfaces.¹⁷

After calcining at 500°C , the polymeric organic precursor retained, as observed by SEM and shown in Fig. 5, an expanded and friable structure. A high magnification of the same figure, not shown here, revealed the formation of small agglomerates, about $0.2\ \mu\text{m}$ in size, of pure $Bi_7Ti_4NbO_{21}$ ceramic powders. Considering the line broadening in XRD measurements, where the size particle was revealed to be $\sim 55\text{ nm}$, there is a strong tendency of these particles to agglomerate. After calcining at 600°C a coarsening of the bismuth titanate niobate crystallites takes place. The size of these crystallites, $\sim 100\text{ nm}$, indicates rapid surface diffusion. At this point, the specific surface area of the ceramic powder decreased from 13.5 to $7.6\text{ m}^2\text{ g}^{-1}$, as determined by the BET single point method. From the above results, and also taking into account the SEM observations, we can suggest that, in a first step, the formation of $Bi_{20}TiO_{32}$ particles might be consistent with an Avrami-type nucleation and growth mechanism,¹⁸ in which the particles continuously nucleated three-dimensionally within the amorphous polymeric precursor matrix below 400°C . After the nucleus of crystal appears, the primary particle size gradually increases from the randomly distributed nuclei with the increasing temperature. The amount of the intermediate $Bi_{20}TiO_{32}$ phase rapidly decreased with the $Bi_7Ti_4NbO_{21}$ formation and, finally, crystal growth of $Bi_7Ti_4NbO_{21}$ by a solid-state reaction as the heat-treatment temperature increased takes place.

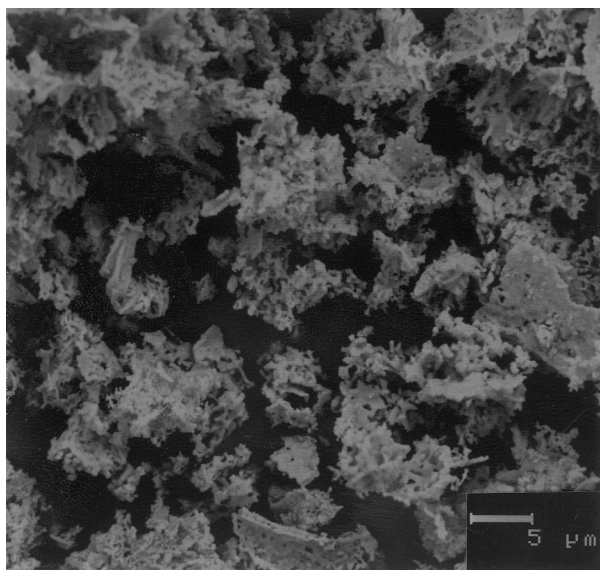


Fig. 5. SEM image of BTN powder precursor after calcining at 600°C .

3.2. Densification and microstructure

BTN sample densities after sintering are plotted as a function of the sintering temperature in Fig. 6. Moderately high density samples [more than 96% ($7.7\text{ g}\cdot\text{cm}^{-3}$) of the theoretical density] were obtained when sintered in the narrow temperature range 1050 – 1120°C . On the basis of no refinement in particle characteristics after powder milling, it can be considered as a highly densified BTN ceramic at this relatively low sintering temperature, and comparable to the density achieved by hot-forging sintering.¹⁹ Samples obtained by the conventional route of mixing oxides when sintered in the same conditions showed much lower density [$\sim 91\%$ ($7.25\text{ g}\cdot\text{cm}^{-3}$) of the theoretical density].³

Typical SEM micrographs of polished and thermally etched surfaces of annealed samples are shown in Fig. 7(a)–(c). As expected from these layered bismuth compounds, the microstructure consisted of elongated grains randomly oriented and their sizes depended on the sintering temperature. As it is shown, the average grain size increased with sintering temperature ranging from about $0.3\ \mu\text{m}$ to $1.5\ \mu\text{m}$ in thickness, and from 0.7 to $6.0\ \mu\text{m}$ in length at 1050 and 1130°C , respectively. Taking into account the strong crystal structure anisotropy of this BTN compound, the small grain size measured indicated the high-purity of the raw materials obtained by the complex polymeric method, and no liquid-phase was formed during sintering.

3.3. Dielectric and piezoelectric properties

The temperature dependence of the dielectric constant, as shown in Fig. 8, presents two peaks at ~ 655

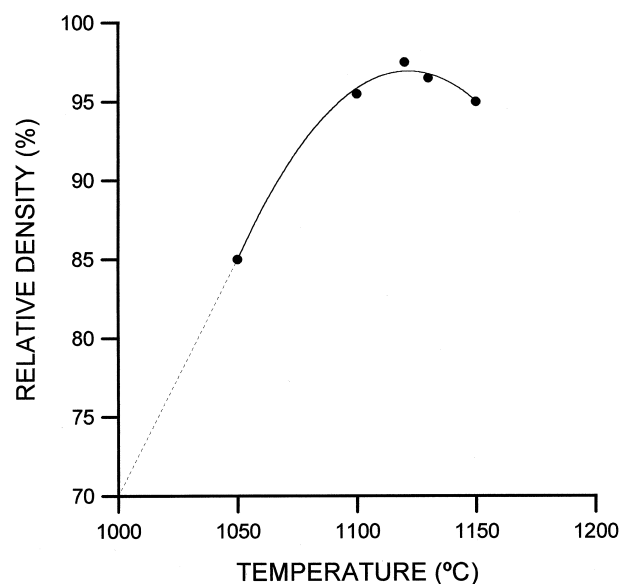


Fig. 6. Sintering behavior of BTN samples as a function of temperature.

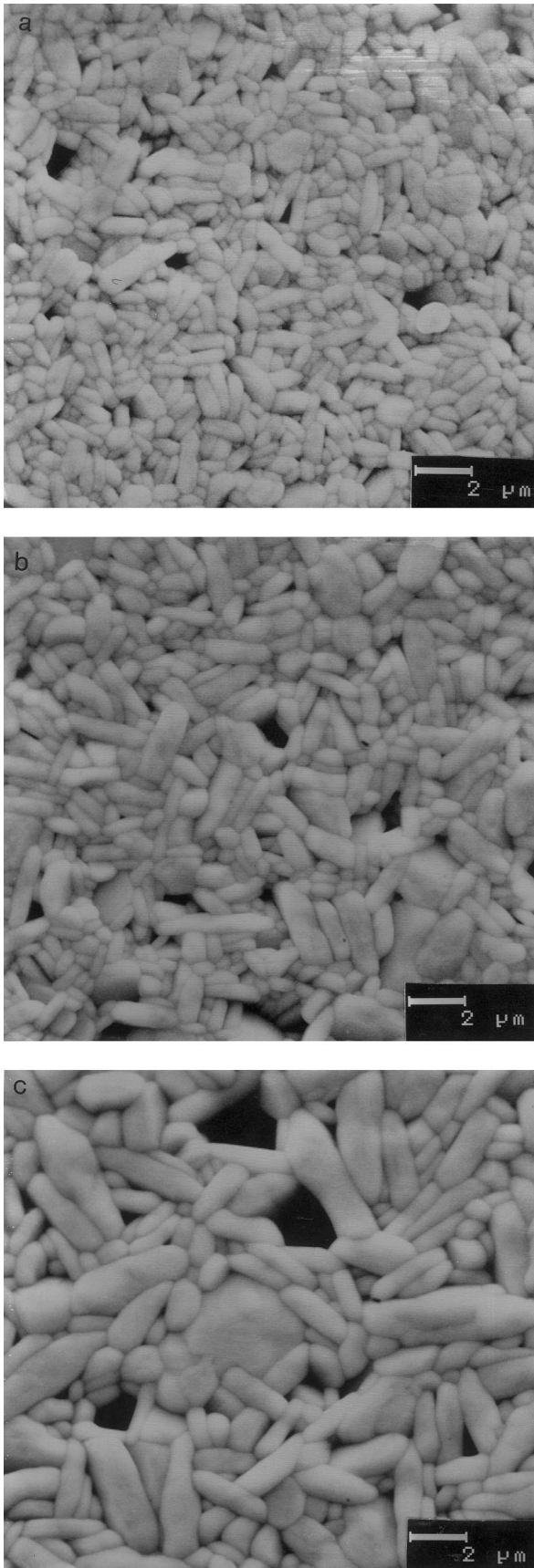


Fig. 7. Microstructural evolution of BTN sintered samples with temperature.

and $855 \pm 5^\circ\text{C}$. These temperatures at which the dielectric anomalies were found are somewhat lower than those observed by Kikuchi et al.,² 670 and 870°C , and by Chu et al.,⁵ 676 and 856°C , respectively. However, our data coincides well with those of Kornuzova et al.³ whose observed these two same anomalies at 630 and above 830°C , respectively. Maalal et al.²⁰ also reported a low-temperature anomaly at 675°C , and a high-temperature one at 850°C . Assuming that the phase transition at $\sim 850^\circ\text{C} \pm 5^\circ\text{C}$ is a true ferroelectric-paraelectric phase transition of the BTN phase,⁵ the discrepancies for the temperature at which the dielectric anomalies appeared can be related to the microstructure and grain size of the sintered BTN ceramics.²¹ In our case, the lower temperature observed may be due to the high density and small grain size of the BTN sintered samples. In the same way, the room temperature permittivity (~ 130) and the dissipation factor (1.2%) are in agreement with the microstructure features. It must be mentioned that these two parameters were kept almost constant up to about 450°C .

The electromechanical properties of these bismuth layered compounds depend strongly on the poling conditions and, thus, the observed polarization-electric field loops, not shown here, were not fully saturated. From these experiments a value of 27 kV/cm for the coercive field and $-1 \mu\text{C}/\text{cm}^2$, see Table 1, were determined. Although low values must be generally expected for the electromechanical properties of these ceramics, Table 1 shows the coupling factor, k_{33} , of the longitudinal mode, the piezoelectric constant, d_{33} , and the frequency constant, N_{33} , for the BTN ceramics sintered at 1120°C for 2 h, and poled at 220°C for 15 min in silicon oil under a field of 60 kV/cm. A piezoelectric modulus d_{33} as high as $20 \times 10^{-12} \text{ C}/\text{N}$ was measured which indicated

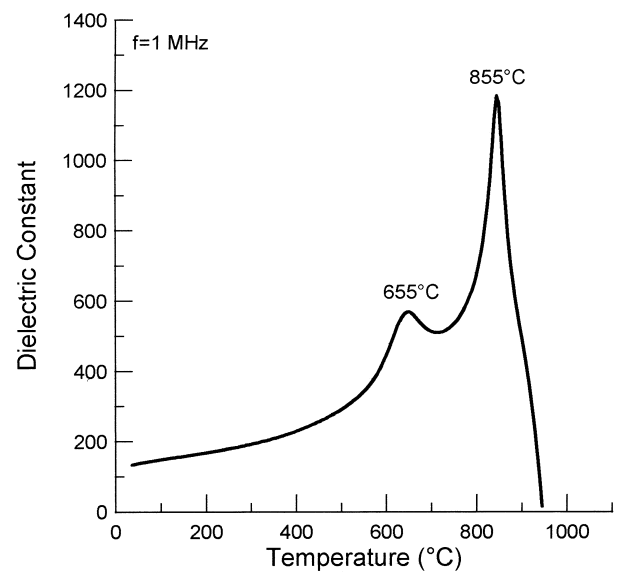


Fig. 8. Temperature dependence of the dielectric constant of BTN ceramics.

Table 1
Dielectric and piezoelectric properties of Bi₇Ti₄NbO₂₁ ceramics

Property	Bi ₇ Ti ₄ NbO ₂₁
Density (g cm ⁻³)	7.7
Dielectric constant	130
Curie temperature, T _c (°C)	855
Dissipation factor (%)	1.2
Coercive field (kV·cm ⁻¹)	27
Remanent polarization (μC/cm ²)	-1
Coupling factor, k ₃₃ (%)	10
Piezoelectric constant, d ₃₃ , (10 ⁻¹² C/N)	20
Frequency constant, N ₃₃ , (Hz·m)	1500

that the Bi₇Ti₄NbO₂₁ mixed layered compound is a ferroelectric ceramic piezoelectrically very active. Such a piezoelectric modulus value is four times larger than that found for Bi₃TiNbO₉ ceramics³ confirming, thus, the possible applications of these ceramics as a high temperature piezoelectric material.

4. Conclusions

Homogeneous and fine Bi₇Ti₄NbO₂₁ ceramic powders have been prepared by the metal citrate-based polymeric-organic Bi, Ti, Nb precursor method. The synthesis temperatures employed are substantially lower than those currently used in the conventional route. The thermal decomposition/oxidation of the organic products and the subsequent heat evolution favored the crystallization of the Bi₇Ti₄NbO₂₁ compound at very low temperatures (~ 400°C). Based on TGA/DTA, XRD and Raman results, we conclude that the synthesis of the Bi₇Ti₄NbO₂₁ compound takes place through the formation of an intermediate binary phase of composition close to Bi₂₀TiO₃₂, which is formed during the heating between 300 and 375°C. At 400°C for 2 h a mixture of Bi₇Ti₄NbO₂₁ and the intermediate phase was present. Prolonged heat treatment between 400 and 500°C promoted a rapid consumption by solid-state reaction of the intermediate phase with the formation of Bi₇Ti₄NbO₂₁, without any indication on the formation of other different phases or segregation of the individual metal oxides. The high sinterability of the as prepared BTN ceramic powders, consisting of relatively soft agglomerates of 100 nm in size, led to highly dense BTN bodies with small grain size and quite uniform microstructure. Dielectric property measurements on these ceramics have shown a double dielectric anomaly as a function of temperature, with a piezoelectric constants d₃₃ as high as 20 pC/N and a longitudinal electro-mechanical coupling coefficient (10%), indicating the high piezoactivity of these materials. These results support the contention for the metal-organic precursor synthesis method as useful to prepare dense ceramics with complex composition such as those of bismuth titanate niobates.

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