

Sintering kinetic of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ based ceramics

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The shrinkage behaviour in based- $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics has been studied by constant heating rate experiments (CHR). Undoped and WO_3 doped BIT ceramics were prepared by two different ways: mixed oxide method and hydroxide-based coprecipitation method. Analyses of the initial and intermediate sintering stages were evaluated using different Coble's based models. Sintering behaviour is modified by both, the dopant and the processing method. Powders obtained by the mixed oxide method sintered through a solid state mechanism, while coprecipitated powders sintered with the presence of a small amount of a transitory liquid phase.

Keywords: bismuth titanate, densification, sintering kinetic.

Cinética de sinterización de cerámicas basadas en $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

Se ha estudiado el comportamiento durante la sinterización de cerámicas basadas en $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT). Muestras sin dopar y dopadas con WO_3 fueron preparadas por dos rutas diferentes: vía convencional por mezcla de óxidos y vía química por el método de coprecipitación de hidróxidos. Las variaciones en la contracción de las muestras se siguieron mediante ensayos de dilatometría. Para determinar los parámetros cinéticos se utilizaron diferentes modelos teóricos basados en los de Coble para los estados inicial e intermedio de la sinterización. Tanto el método de procesamiento como la cantidad de dopante modifican el comportamiento durante la sinterización de estas cerámicas. La sinterización de las muestras obtenidas por vía convencional se produce en estado sólido mientras que en aquellas obtenidas por vía química la sinterización se produce en presencia de una pequeña cantidad de fase líquida.

Palabras clave: titanato de bismuto, densificación, cinética de sinterización.

1. INTRODUCTION

Most of bismuth layer compounds are ferroelectric and present anisotropic electric, ferroelectric and piezoelectric properties due to their crystal structure. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BIT, presents good dielectric and ferroelectric properties and a high Curie temperature ($T_c = 675^\circ\text{C}$) making BIT a good candidate as high temperature piezoelectric material (1).

The crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ can be described as formed by three unit cells of BiTiO_3 with perovskite-like structure interleaved with $(\text{Bi}_2\text{O}_2)^{2+}$ layers. At room temperature $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is monoclinic ($C_{1h} = m$) and ferroelectric, but it can be represented as orthorhombic with the c-axis normal to the $(\text{Bi}_2\text{O}_2)^{2+}$ layers (2). The ferroelectric to paraelectric phase transition in pure BIT is produced at 675°C and the high temperature symmetry is tetragonal ($D_{4h} = 4mmm$) (3). The crystal anisotropy is also reflected in the grain growth habit. Typical microstructure of BIT-based ceramics shows platelet-like grains growing preferentially in the ab plane.

One of the major difficulties for the use of BIT ceramics in piezoelectric applications is its high electrical conductivity, which interferes with the poling process (4). Donor doping, Nb(V), W(VI), significantly decreases the conductivity in BIT-based ceramics (5, 6). This effect has been attributed to a reduction of space charge build up by the compensation of Bi vacancies accompanied by oxygen vacancies. In addition to this, the high anisotropy of electrical conductivity (7,8)

makes the microstructure to play a critical role in the electrical properties, being the electrical conductivity dependent on the aspect ratio (length/thickness) of the platelet-like grains. In this sense, the dependence of the electrical conductivity on microstructure makes ceramic processing a critical step in achieving BIT ceramics for practical use. In addition to this, WO_3 doping controls the grain growth kinetics due to the slowing of grain boundary diffusion processes (9). The doping method which produces microstructures with smaller aspect ratio is the surface doping of the BIT particles. In this manner, WO_3 doping is an appropriate method to decrease the conductivity in BIT ceramics (10).

Several theoretical approaches to analyze the densification process during sintering have been used. These models assume a relatively simple, idealized geometry for the powder system, and for each mechanism, the mass transport equations are solved to provide equations for the sintering kinetics. Due to the microstructure changes during the sintering it is difficult to find a single geometrical model that can represent adequately the entire process. For this reason the sintering process is divided into separate stages: initial, intermediate and final stage and each of them are described with a different model.

In this work these sintering models will be used to identify the main differences in the densification kinetics of bismuth

titanate based ceramics prepared by two different procedures: mixed oxides and coprecipitation method. The effect of the different doping level with WO_3 on the densification of the ceramics will be also evaluated

2. EXPERIMENTAL PROCEDURE

The BIT-based ceramics prepared correspond to the composition $\text{Bi}_4\text{Ti}_3\text{W}_x\text{O}_{12+3x}$ with x between 0 and 0.08. The samples were prepared through two different processing methods:

a) Mixed oxides following a conventional method (11). The estequiometric amount of Bi_2O_3 , TiO_2 and WO_3 powders were mixed in a ball mill, dried, pressed into pellets and calcined at 750°C for 10h. Calcined powders were milled and calcined secondly at 850°C for 10h to both enhance the homogeneity and to complete the formation of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ pure phase.

b) By hydroxide coprecipitation method. Bi_2O_3 and TiO_2 coprecipitated precursors powders (12) were calcined in air at 650°C for 1h to form the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase. Calcined powders were dispersed in ethanol and the corresponding amount of WO_3 precursor, $[\text{W}(\text{C}_2\text{H}_5\text{O})_6]$, was added on the suspension. Through this method surface doping of the BIT particles is attained.

The powders obtained by both methods were isostatically at 200 MPa pressed into cylindrical pellets of 0.5 cm in diameter and 1 cm in length for dilatometric measurements. The compositions are labelled as BIT($x=0$), BITW2 ($x=0.02$), BITW5 ($x=0.05$) y BITW8 ($x=0.08$).

The shrinkage process during sintering was followed using a Netzch 407/E dilatometer. Samples were thermally treated up to 1150°C with a heating rate of $3^\circ\text{C}/\text{min}$. The microstructure was evaluated by scanning electron microscopy (SEM, Carl Zeiss DSM 950) on polished and non-etched surfaces.

3. RESULTS AND DISCUSSION

In the samples prepared by the mixed oxide method the dopant addition delay the beginning of the sintering with regard to undoped samples as it can be seen in the dilatometric experiments (Figure 1). Samples obtained by coprecipitation method show a similar behaviour among them and in these samples obtained by chemical method the shrinkage begins at lower temperatures that the samples obtained by mixed oxide method indicating that the sintering process begins at a temperature lower, around 200° , in the coprecipitated powders.

In figure 2 it can be seen the micrographs obtained by SEM on the polished and non-etched surfaces for some compositions sintered at the temperature of maximum density. Samples obtained by mixed oxide method presented a unique phase. However, in the coprecipitated samples two different phases can be observed, one of them brighter. The EDS analysis showed that the matrix corresponded to the BIT phase and the secondary phase (brighter one) presented a composition qualitatively close to the $\text{Bi}_{12}\text{TiO}_{20}$ phase. As it can be observed in the binary diagram of the system Bi_2O_3 - TiO_2 (13) the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase coexists with the $\text{Bi}_{12}\text{TiO}_{20}$ phase at low temperatures. This secondary phase with sillenite structure is liquid at temperatures lower than the sintering temperatures of the materials studied in this work ($T_f = 795^\circ\text{C}$). According to the morphology of the second phase it seems to come from

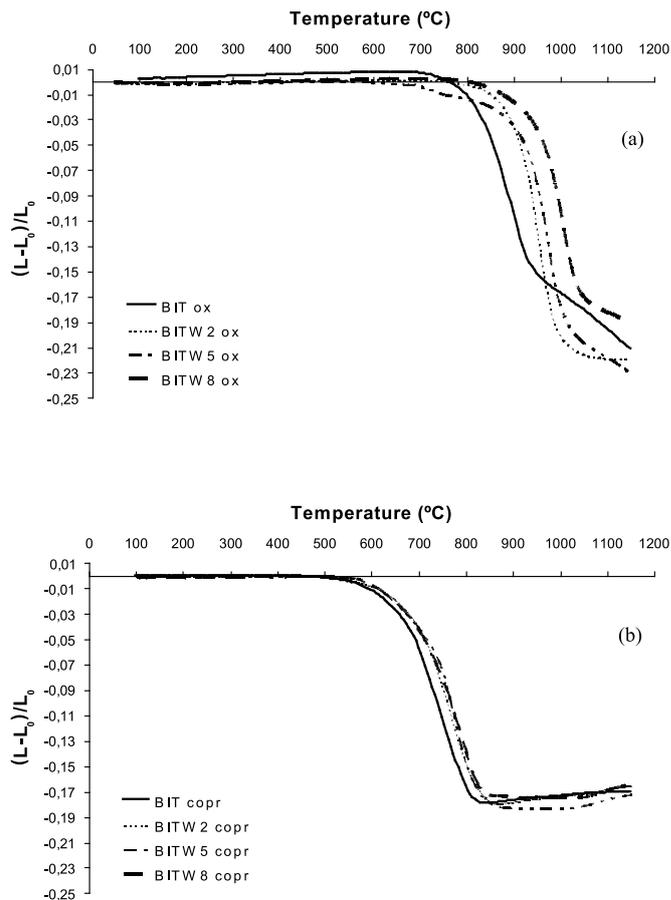


Fig. 1- Linear shrinkage as a function of heating temperature for compositions obtained by: a) mixed oxide method and b) coprecipitation method.

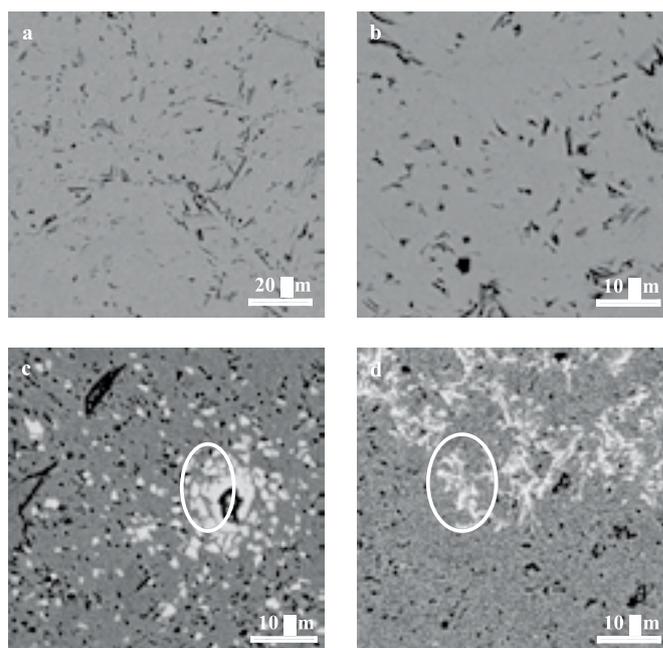


Fig. 2- Micrograph obtained by SEM on polished and non-etched surfaces. a) BITW2 ox sintered at $1000^\circ\text{C}/2\text{h}$, b) BITW5 ox sintered at $1050^\circ\text{C}/2\text{h}$, c) BIT copr sintered at $800^\circ\text{C}/2\text{h}$ and d) BITW5 copr sintered at $850^\circ\text{C}/2\text{h}$.

the crystallization of a liquid. The presence of this transitory liquid phase could play an important role in the sintering of the coprecipitated powders.

Theoretical models for the initial and intermediate stages of sintering were fitted to the experimental data in order to determine the parameters of the sintering kinetic. In this study two models based on Coble's models (14,15,16,17) have been chosen to describe both stages of sintering depending on the conditions of the studied system. Coble obtained the expression [1] to describe the initial stage of the sintering:

$$Y^n \frac{dY}{dt} = K \exp\left(\frac{-Q}{RT}\right) \quad [1]$$

being Y the linear shrinkage, K a constant, Q the activation energy, T the absolute temperature, R the gas constant and n the sintering coefficient. Coble's model is limited to isothermal conditions but it was adapted by Woolfrey and Bannister (18) for non-isothermal conditions, giving the expression [2]:

$$\frac{dY}{Y} = \frac{Q}{(n+1)R} \frac{dT}{T^2} \quad [2]$$

where the activation energy Q is calculated by the Dorn method [3] (18):

$$Q \approx \frac{RT_1T_2}{T_1 - T_2} \ln\left(\frac{Y_1}{Y_2}\right) \quad [3]$$

In this expression it is assumed that, at any combination of shrinkage and temperature, $[d(\Delta l/l_0)/dt]_{\text{non-isotherm}} = [d(\Delta l/l_0)/dt]_{\text{isotherm}}$ if temperature is increased at constant rate. In addition, the method is applicable only when one mechanism is rate-controlling and surface diffusion has a negligible effect.

TABLE I. EDS ANALYSIS OF THE SECONDARY PHASE OBSERVED IN THE BIT BASED SAMPLES OBTAINED BY THE COPRECIPITATION METHOD AT THE TEMPERATURES OF MAXIMUM DENSITY. THE THEORETICAL COMPOSITION OF THE $\text{Bi}_{12}\text{TiO}_{20}$ PHASE CORRESPONDS TO 86% WT OF Bi_2O_3 AND 14% WT OF TiO_2 .

Element	Nets Counts	Weigh Conc %	Atom Conc %	Comp Conc %	Formula
O	0	13.18	62.52	0.00	-
Ti	2096	8.88	9.18	13.11	TiO_2
Bi	797	77.94	28.30	86.89	Bi_2O_3

The theoretical model for the initial stage has been applied to the data corresponding to samples shrunk up to 7% in volume. In order to apply the model $T^2 dY/dT$ vs. Y is represented on this data set. According to the equation a straight line is obtained only when one mechanism is rate-controlling and surface diffusion has a negligible effect. The activation energy, Q , was obtained by Dorn method on the data set which fit to this linear behaviour. Figure 3 is an example showing the curves obtained for undoped compositions prepared by the two processing methods used. Table II shows the activation energies calculated by the same way for all compositions prepared.

All the compositions obtained by mixed oxide method showed similar activation energies for the initial stage of sintering although Q decreases when the dopant level increases.

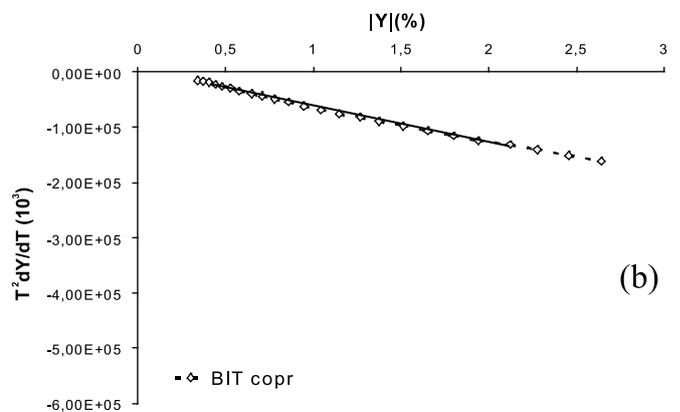
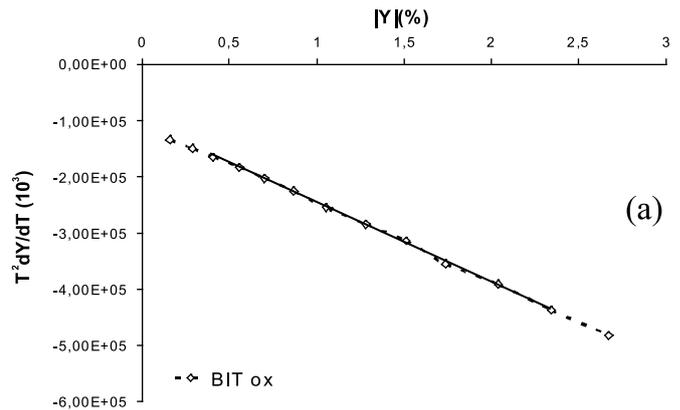


Fig. 3- Diagrams used for the analysis of the initial stage of sintering, using Woolfrey and Bannister model (17), for undoped BIT samples obtained by a) mixed oxide method and b) coprecipitation method. Only the data corresponding to the linear region were used in the analysis.

TABLE II. CALCULATED ACTIVATION ENERGIES BY THE DORN METHOD FOR THE INITIAL STAGE OF THE SINTERING FOR THE COMPOSITIONS OBTAINED BY THE MIXED OXIDE AND THE COPRECIPITATION METHODS.

Initial stage	$Q \pm 30$ (kJ/mol)	Initial stage	$Q \pm 30$ (kJ/mol)
BIT ox	286	BIT copr	113
BITW2 ox	285	BITW2 copr	115
BITW5 ox	211	BITW5 copr	133
BITW8 ox	223	BITW8 copr	140

Likewise, activation energies corresponding to coprecipitated powders are similar among the different compositions within the error interval. However, important differences were observed between activation energies calculated for materials prepared by the mixed oxide method and materials prepared by the coprecipitated method. These differences prove that sintering kinetics are different in the initial stage depending on the processing method used. Compositions prepared by conventional method need higher temperatures to enter into the intermediate stage of sintering than compositions prepared by the coprecipitation method.

Genuist model has been chosen to analyze the intermediate stage of sintering. This model is a generalization of the Coble's

model for systems in non-isothermal conditions [4]. Genuist model leads to the following expressions to describe the intermediate stage:

$$\ln(-T(dy/dt)/(1+y)^4) = -(Q/RT) + C \quad [4]$$

for grain boundary diffusion controlled densification, and [5]:

$$\ln(-Tz(dy/dt)/(1+y)^4) = -(Q/RT) + C \quad [5]$$

for densification controlled by bulk diffusion, being $y = \Delta L / L_0$, $z = (1 - (L_f / L_0)^3 / (1+y)^2)$ and C a constant.

Some assumptions should be taken to make calculations: diffusion coefficients can be calculated using a classical Arrhenius law: $D = D_0 \exp(-Q/RT)$, where Q is the activation energy of the considered mechanism; grain growth occurs only at the end of the sintering; shrinkage corresponding to the intermediate stage occurs over an approximately 100°C range, so surface energy is supposed to be constant; and the last one, thickness of grain boundaries is assumed to be constant.

Therefore, data range corresponding to the intermediate stage of the sintering was selected and Genuist model's was applied. Linear behaviour was obtained and the activation energy over these data was given by the slope of the straight line. Figure 4 shows the curves obtained for undoped

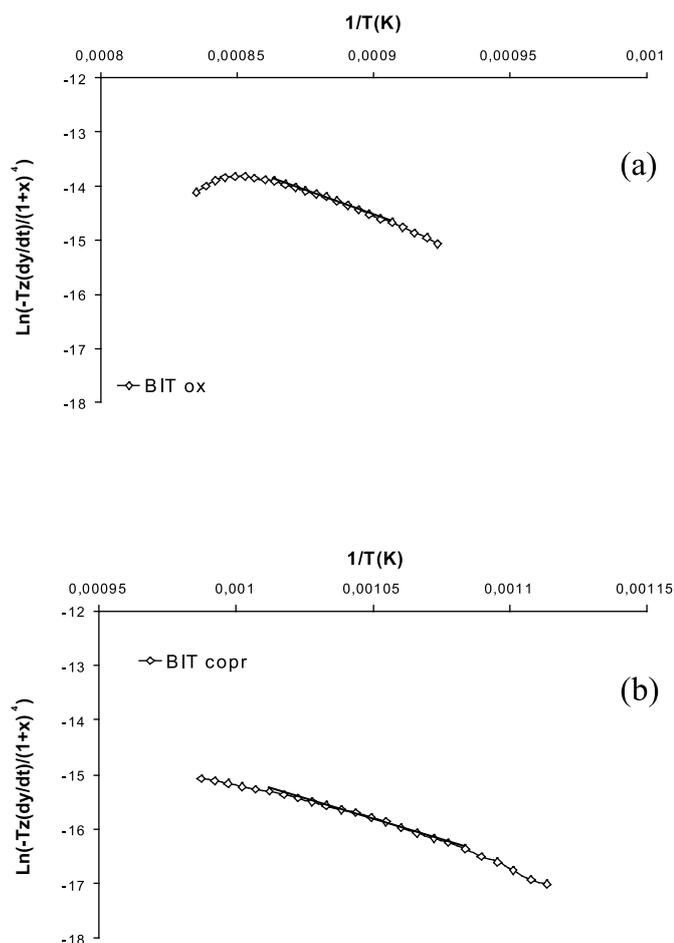


Fig. 4- Diagrams used for the analysis of the intermediate stage of sintering, using Genuist model (19), for undoped BIT samples obtained by a) mixed oxide method and b) coprecipitation method. Only the data corresponding to the linear region were used in the analysis.

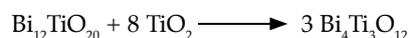
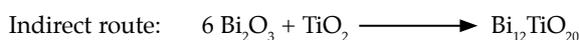
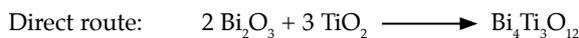
compositions prepared by the two processing methods used. Table III shows the activation energies calculated by the same way for all compositions prepared. Bulk or grain boundary diffusion was considered as predominant mechanism at the intermediate stage of the sintering but no differences were found on the results obtained. Table III shows the values obtained when densification controlled by bulk diffusion is considered.

TABLE III. CALCULATED ACTIVATION ENERGIES BY THE DORN METHOD FOR THE INTERMEDIATE STAGE OF THE SINTERING FOR THE COMPOSITION OBTAINED BY THE MIXED OXIDE AND THE COPRECIPITATION METHODS.

Intermediate stage	Q ± 30 (kJ/mol)	Intermediate stage	Q ± 30 (kJ/mol)
BIT ox	235	BIT copr	116
BITW2 ox	298	BITW2 copr	121
BITW5 ox	306	BITW5 copr	128
BITW8 ox	308	BITW8 copr	95

In the BIT-based materials prepared by the mixed oxide method the activation energies increased greatly with the amount of dopant pointing out that the WO₃ difficults the diffusion processes in these samples. For samples obtained by the coprecipitation method, as occurred in the initial stage of the sintering, the activation energies in the intermediate stage are similar regardless of the level of dopant pointing out that the diffusion processes involved in both stages are similar and no dependent on the dopant level. Moreover, these activation energies are lower than those energies calculated for compositions prepared by the conventional method so the activation energies calculated for the sintering initial and intermediate stages of the sintering in compositions obtained by coprecipitation method indicate that the densification take place through a faster diffusion process. This is in concordance with the early sintering of these samples, around 200°C lower, with respect to the samples obtained by the conventional method. The appearance of a transitory liquid phase during first steps of the sintering in the coprecipitated powders could explain the sintering behaviour in these compositions.

BIT calcined powders obtained by both processing methods used in this study where examined by SEM to explain the presence of a liquid phase in the coprecipitated powders. The particle size is similar in both the coprecipitated and mixed oxide powders, being around 0.5 μm, and in this sense particle size do not explain the different sintering behaviour of both kind of powders. The reaction route of Bi₄Ti₃O₁₂ phase should be considered. The formation of BIT mainly takes place through the direct reaction but an indirect route could occur and the intermediate phase Bi₁₂TiO₂₀ is formed, reacting to form the Bi₄Ti₃O₁₂ phase at higher temperatures (21).



BIT-based compositions prepared by the mixed oxide method were obtained after two calcination steps, at 750°C and 850°C for 10h, which allowed to complete the formation of the Bi₄Ti₃O₁₂ pure phase. On the contrary, samples prepared

by the coprecipitation method were calcined in only one step at 650°C for 1h. This calcination step at low temperature and short time could be the cause of the presence of a small amount of $\text{Bi}_{12}\text{TiO}_{20}$ phase remaining in the compositions prepared by coprecipitation. During the sintering at higher temperatures, as it has been explained before, $\text{Bi}_{12}\text{TiO}_{20}$ remaining phase forms a liquid phase which can be acting as a sintering aid. The micrographs obtained by SEM for the sintering samples of compositions prepared by the coprecipitated method show the presence of this liquid phase. Therefore, the differences observed in the sintering behaviour between compositions prepared by both processing methods described are not caused by the synthesis methods, being the calcinations steps responsible for those differences.

4. CONCLUSIONS

Sintering process took place by solid state mechanism in samples obtained by the mixed oxides method whereas sintering took place through a faster diffusion processes when samples were obtained by the coprecipitation method. The activation energies of the processes are in all cases lower in the samples obtained by the coprecipitation method. Moreover, in these samples the activation energies for the initial and intermediate steps of sintering are similar pointing out that the diffusion mechanism in the two stages is similar. A transitory liquid phase would be present during the initial and intermediate stages of the sintering controlling the diffusion processes in coprecipitated BIT based materials. The origin of this liquid phase seems to be the small amount of the $\text{Bi}_{12}\text{TiO}_{20}$ phase present due to the low calcination temperature. This phase remains as a secondary phase and forms a transitory liquid phase at the sintering temperatures of coprecipitated BIT ceramics. If the sintering takes place by solid state process as in BIT compositions obtained by the mixed oxide method, the addition of WO_3 hinders the diffusion mechanism and the sintering was produced at higher temperatures as the amount of dopant increased.

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REFERENCES

1. S.E. Cummings, L.E. Cross, "Electrical and Optical Properties of Ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Single Crystals", *J. Appl. Phys.*, 39, 2268-74 (1968).
2. J.F. Dorrian, R.E. Newnham, D.K. Smith, "Crystal Structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ", *Ferroelectrics*, 3, 17-21 (1971).
3. B. Aurivillius, "Mixed Bismuth Oxides with Layer Lattices", *Ark. Kemi.*, 1, 463-480 (1949).
4. A. Fouskova, L.E. Cross, "Dielectric Properties of Bismuth Titanate", *J. Appl. Phys.*, 41, 2834-38 (1970).
5. Y.A. Vusevker, V.I. Rivkin, O.P. Kramarov, D.E. Fainrider. *Byull. Izobret.*, 18 (1980).
6. S. Lopatin, T.G. Lupeiko, T.L. Vasil'tsova, N.I. Basenko, I.M. Berlizov, "Properties of Bismuth Titanate Ceramics Modified with Group V and VI Elements", Translate to: *Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy*, 24 [9] 1551-1554 (1989).
7. H. Shulman, M. Testorf, D. Damjanovic, N. Setter, "Microstructure, Electrical Conductivity and Piezoelectric Properties of Bismuth Titanate", *J. Am. Ceram. Soc.*, 79 [12] 3124-3128 (1996).
8. L. Lascano, A.C. Caballero, M. Villegas, C. Moure, J.F. Fernández, "Conductividad Eléctrica en Corriente Alterna de Materiales Cerámicos de Composición $\text{Pb}_x\text{Bi}_4\text{Ti}_{3-x}\text{O}_{12+3x}$ x=0, 1, 2 y 3", *Bol. Soc. Esp. Ceram. V.*, 43 [2] 536-539 (2004).
9. M. Villegas, A.C. Caballero, C. Moure, P. Durán, J.F. Fernández, "Factors Affecting the Electrical Conductivity of Donor-Doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Piezoelectric Ceramics", *J. Am. Ceram. Soc.*, 82 [9] 2411-2416 (1999).
10. M. Villegas, A.C. Caballero, J.F. Fernández, "Modulation of Electrical Conductivity through Microstructural Control in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -based Piezoelectric Ceramics", *Ferroelectrics*, 267, 165-173 (2002).
11. T. Jardiel, A.C. Caballero, M. Villegas, M. Valant, B. Jancar, D. Suvorov, "Equilibrium Phases in the Bi_2O_3 - TiO_2 - WO_3 System". *J. Eur. Ceram. Soc.*, (In press).
12. M. Villegas, T. Jardiel, G. Farías. "Sintering and Electrical Properties of $\text{Bi}_4\text{Ti}_{2.95}\text{W}_x\text{O}_{11.9+3x}$ piezoelectric ceramics", *J. Eur. Ceram. Soc.*, 24 [6] 1025-1029 (2004).
13. S. Miyazawa, T. Tabata, " Bi_2O_3 - TiO_2 Binary Phase Diagram Study for TSSG Pulling of $\text{Bi}_{12}\text{TiO}_{20}$ Single Crystals", *J. Cryst. Growth*, 191 [3] 512-516 (1998).
4. R.L. Coble, "Initial Sintering of Alumina and Hematite", *J. Am. Ceram. Soc.*, 41 [2] 55-62 (1958).
5. R.L. Coble, "Sintering Crystalline Solids. I, Intermediate and Final State Diffusion Models", *J. Appl. Phys.*, 32 [5] 787-792 (1961).
6. R.L. Coble, "Sintering Crystalline Solids. II, Experimental Test of Diffusion Models in Power Compacts", *J. Appl. Phys.*, 32, 793-799 (1961).
7. R.L. Coble, "Intermediate-Stage Sintering - Modification and Correction of a Lattice-Diffusion Model", *J. Appl. Phys.*, 36 [7] 2327 (1965).
8. J.L. Woolfrey, M.J. Bannister, "Nonisothermal Techniques for Studying Initial-Stage Sintering", *J. Am. Ceram. Soc.*, 55 [8] 390-394 (1972).
9. J.J. Bacmann, G.J. Cizeron, "Dorn Method in the Study of Initial Phase of Uranium Dioxide Sintering", *J. Am. Ceram. Soc.*, 51 [4] 209-212 (1968).
20. C. Genuist, F. Haussonne, "Sintering of BaTiO_3 : Dilatometric Analysis of Diffusion Models and Microstructure Control", *Ceram. Int.*, 14 169-179 (1988).
21. H. Shulman, "Piezoelectric Bismuth Titanate Ceramics for High Temperature Applications". Tesis doctoral, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland, 1997.

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