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Low-temperature Sintering and Electrical Properties of Chemically W-doped $Bi_4Ti_3O_{12}$ Ceramics

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Abstract

High temperature piezoelectric ceramics based on W^{6+}*-doped* $Bi_4Ti_3O_{12}$*(W-BIT) have been prepared by a chemical route based on hydroxides coprecipitation. The low calcination temperature (650°C for 1 h) gave rise to a BIT powder consisting of small reactive particles. The characteristics of the calcined powder along with the narrow pore size distribution in the green compacts allowed a rapid densification,* $>99\%$ ρ_{th} *at a very low temperature (900°C for 2 h). The microstructure study revealed a plate-like morphology with small platelets that did not grow significantly until high temperature (1100°C). The chemically prepared* W^{6+}*-doped BIT materials showed an electrical conductivity value 2–3 orders of magnitude lower than undoped samples. The decrease in the electrical conductivity allowed the W-doped samples to be poled and preliminary piezoelectric results were obtained. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: powders-chemical preparation, sintering, microstructure-final, electrical conductivity, piezoelectric properties.

1 Introduction

Bismuth titanate $Bi_4Ti_3O_{12}$ (BIT), which belongs to the Aurivillius family,[1] is perhaps one of the most studied compounds among the bismuth-based layered ceramics.

As many other compounds of this bismuth-based layered family, BIT is ferroelectric. The T_c of pure BIT is about 675°C. Due to this high transition temperature, BIT ceramics are good candidates for high temperature piezoelectric applications. The main problem concerning their practical application as piezoelectrics is that bismuth titanate has a relatively low electrical resistivity. The electrical conductivity in BIT is highly anisotropic, with the maximum value in the same plane as the polarization.[2,3] As a consequence BIT ceramics are very difficult to pole. The reduction of electrical conductivity is, then, one of the main goals of BIT worldwide investigations. As it is expected in a p-type material, as BIT, acceptor dopants such Fe^{3+} in Ti^{4+} positions or Sr^{2+} in Bi^{3+} positions increase the BIT electrical conductivity,[4] whereas it has been shown that doping with donor cations such as Nb^{5+}, Sb^{5+} or Ta^{5+} in the Ti^{4+} positions decreases BIT conductivity.[4,5]

The aim of the present work is to study the influence of chemical processing on the sinterability and the microstructure development of BIT ceramics and the effects of WO_3 doping on electrical conductivity and piezoelectric properties of $B_4Ti_3O_{12}$ ceramics.

2 Experimental Procedure

Donor-doped (5 at% W^{6+}) $Bi_4Ti_3O_{12}$ materials ($Bi_4Ti_{2{\cdot}95}W_{0{\cdot}05}O_{12{\cdot}05}$) were prepared using a hydroxide-based coprecipitation method. Titanium tetrabutoxide $Ti(C_4H_9O)_4{\cdot}C_4H_9OH$ (Alfa Products), $Bi(NO_3)_3{\cdot}5H_2O$ (Riedel) and WO_3 were used. Stoichiometric amounts of Ti^{4+} and Bi^{3+} precursors were dissolved in a slightly acid isopropyl alcohol solution. This solution was carefully added to an aqueous suspension of WO_3 by dropping while stirring. Then, with a carefully pH control, an aqueous solution of NH_4OH (50/50) was

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*To whom correspondence should be addressed. Fax: +91-870-0550; e-mail: mvillegas@icv.csic.es slowly added to achieve the complete precipitation of the hydroxides. The coprecipitated powders were washed and redispersed several times with isopropyl alcohol until a neutral pH was achieved. After drying an amorphous powder was obtained. These coprecipitated powders were air-calcined at 650°C/1 h and attrition milled for 2 h in isopropanol. Then, the calcined powders were granulated, uniaxially pressed and sintered between 800–1150°C for 2 h. The densification process was also studied by dilatometry between 25 and 1100°C with a heating rate of 10°C min^{-1} using a dilatometer Adamel L'homargy DI-24.

WBIT calcined powders were characterized by X-ray diffraction (D-5000 Siemens) and scanning electron microscopy (DSM950 Carl Zeiss). Green compacts were characterized by Hg porosimetry (Micromeritics Autopore II 9215).

The density of the sintered compacts was measured by the Archimedes' method in water and the microstructure of sintered compacts was studied on polished and thermally etched surfaces by SEM.

Electrical measurements were carried out on disks ground with 6 μm diamond paste, electroded with Ag-paste. Electrical conductivity measurements were done by complex impedance spectroscopy using a HP4192A impedance analyzer. Sliced disks were poled at 60 kV cm^{-1} at a temperature of 160°C during 1 h and piezoelectric properties were measured by the resonance–antiresonance method[6] on poled samples.

3 Results and Discussion

SEM micrograph of WBIT calcined powders is shown in Fig. 1. WBIT powders consisted of small soft-like agglomerates of 1 μm formed by very small equiaxed particles of ~100 nm. Apparently neither platelets nor needle-like particles were developed during calcination. XRD analysis of the calcined powders revealed the presence of an unique $Bi_4Ti_3O_{12}$-type phase.

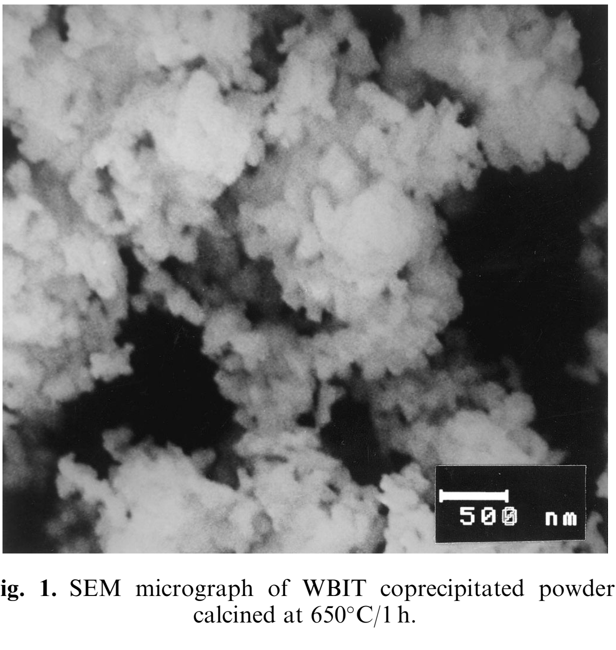

Fig. 1. SEM micrograph of WBIT coprecipitated powders calcined at 650°C/1 h.

After uniaxial compaction, the density of the green compacts was 66% ρ_{th}. The pore size distribution curve (Fig. 2) showed a narrow pore size distribution with an unique maximum centered at 0·11 μm.

The green compacts of WBIT powder were sintered between 800 and 1150°C for 2 h (Fig. 3). Coprecipitated WBIT powders densified at a temperature lower than that reported for the conventional BIT powders.[7] Thus a maximum density >99 ρ_{th} was achieved at 900°C (Fig. 3) whereas ~90% ρ_{th} was reported at a temperature as high as 1150°C for platelike BIT powders.[7] A rapid densification occurred above 800°C in a temperature interval as narrow as 50°C in coprecipitated WBIT powders, contrary to a rather slow densification process found in conventional BIT powders.[7,8] This rapid densification can be attributed to the very uniform pore-size distribution in the green compacts (see Fig. 2).

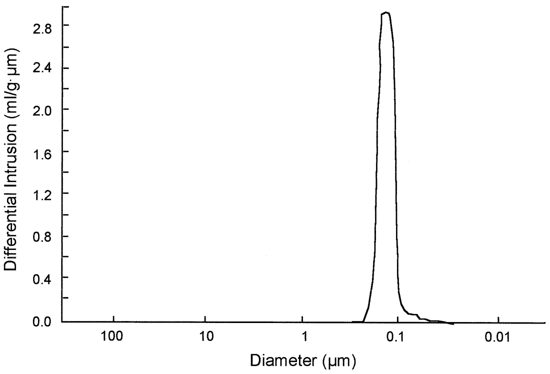

Fig. 2. Pore-size distribution of WBIT green compacts.

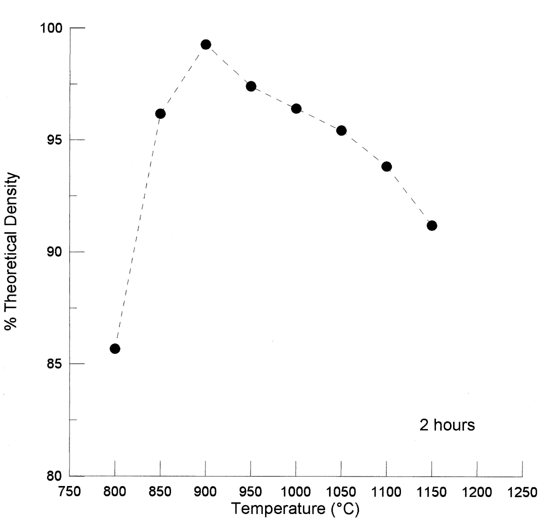

Fig. 3. Densification behavior as a function of temperature for WBIT ceramics.

The densification process was also studied by constant heating rate (CHR) experiments. As it is shown in Fig. 4, WBIT compacts started to shrink at about 650°C and an end point was reached at a temperature of 950°C with a shrinkage of ~27%. The shrinkage-rate curve showed an unique maximum centered at 820°C. Above this temperature the shrinkage rate decreased. The shrinkage curve also supports the influence of the narrow pore-size distribution on the rapid densification of coprecipitated WBIT powders. Only one maximum in the shrinkage-rate curve was registered (820°C) and it can be attributed to a rapid elimination of the inter-particle pores and agreed well with the maximum of density found in the isothermal sintering experiments (see Fig. 3). No other peaks were registered in the shrinkage-rate curve, demonstrating the presence of very soft-flowable agglomerates in the calcined powders which were completely broken during the pressing step.

Figure 5 shows the microstructure evolution of the WBIT ceramics.The plate-like morphology was observed in all the samples. The WBIT-H average length of plate-like grains ranged from $1{\cdot}20 \pm 0{\cdot}13\,\mu$m at 900°C to $7{\cdot}20 \pm 0{\cdot}30\,\mu$m at 1100°C, showing a small increase of platelets length with sintering temperature up to 1100°C.

Microstructure development is the expected in a bismuth layered ceramic, with the appearance of plate-like grains. No exaggerated grain growth was observed up to 1100°C. At lower temperatures platelets are smaller than observed in undoped coprecipitated BIT[9] indicating a grain growth control exerted by the WO_3 doping. At 1100°C this control disappeared indicating the possible formation of a complete solid solution between the dopant and the $Bi_4Ti_3O_{12}$.

The temperature dependence of the electrical conductivity in W^{6+}-doped BIT ceramics sintered at 1050°C for 2 h is plotted in Fig. 6, along with the data of the chemically prepared undoped BIT.[9] The inverse temperature dependence of the conductivity in a logarithmic scale was a straight line with an activation energy of $1{\cdot}1 \pm 0{\cdot}1$ eV in the

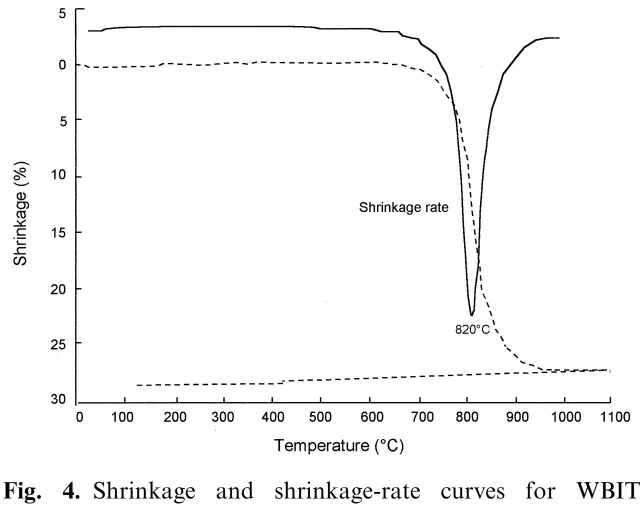

Fig. 4. Shrinkage and shrinkage-rate curves for WBIT compacts.

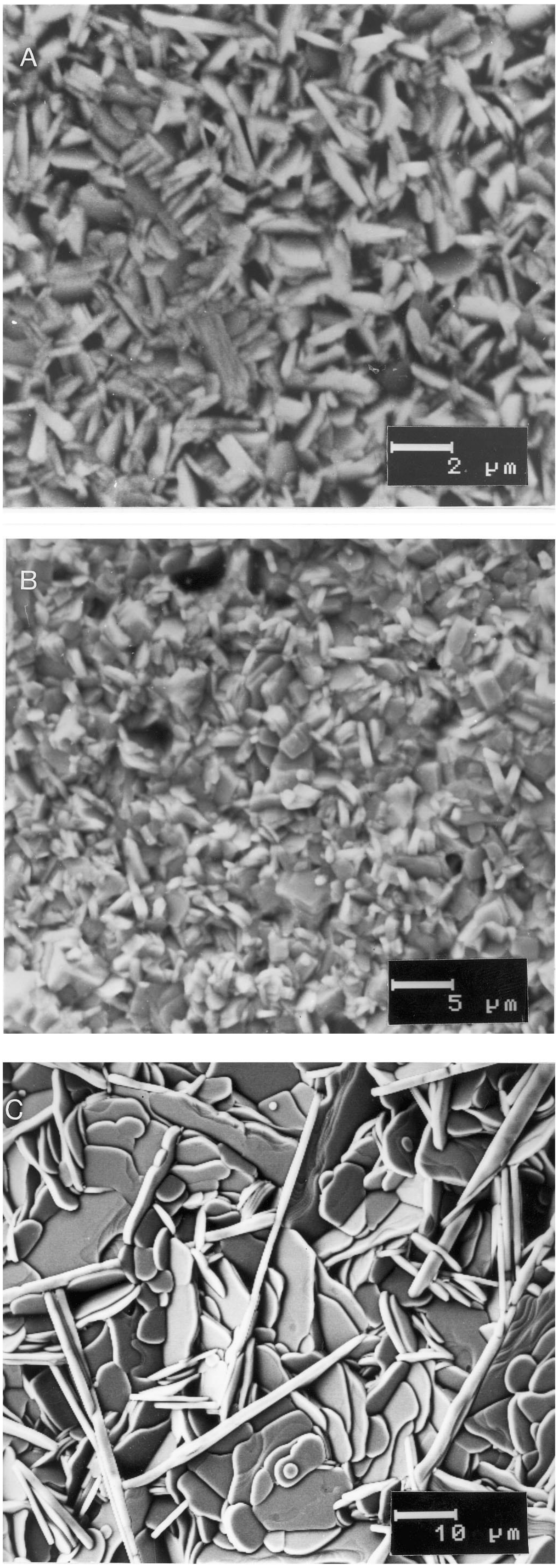

Fig. 5. SEM micrographs of polished and thermally etched surfaces of WBIT ceramics sintered at (a) 900°C, (b) 1000°C, and (c) 1100°C (soaking time 2 h).

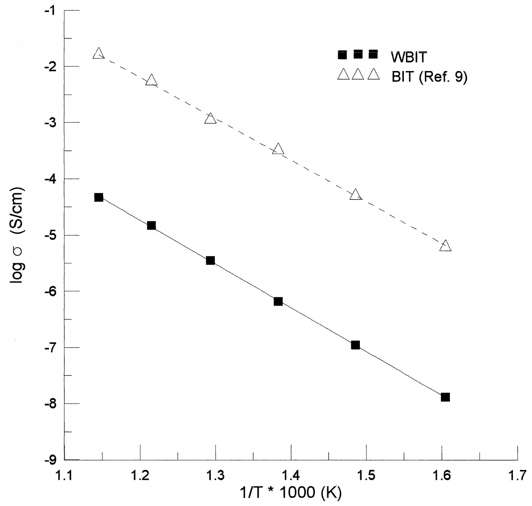

Fig. 6. Arrhenius plots of the log of the conductivity as a function of the inverse of the temperature for the W-doped and undoped BIT ceramics sintered at 1050°C/2 h.

range 350°–650°C, in agreement with the E_a data given by Shulman *et al.*[4] for Nb^{5+} doped and undoped BIT. As it can be seen in Fig. 6, W^{6+} doping decreased the electrical conductivity in BIT-based materials by 2–3 orders of magnitude when compared to the undoped BIT. Piezoelectric response in W^{6+}-doped $Bi_4Ti_3O_{12}$ materials has been obtained. The decrease in electrical conductivity in about two orders of magnitude when compared with pure BIT[9] allowed us to pole the samples at high electric fields. A piezoelectric thickness factor of $k_t = 0{\cdot}09 \pm 0{\cdot}01$ was measured. A deeper study related to the piezoelectric behaviour of these materials at room and high temperature is now in progress.

4 Conclusions

The preparation of $Bi_4Ti_3O_{12}$ (BIT) ceramics doped with WO_3 by a chemically (hydroxide coprecipitation) method produced high density ceramics at low temperature with a maximum density $> 99\%\ \rho_{th}$ at a temperature as low as 900°C. The soft agglomerates present in the calcined powders along with the narrow pore size distribution in the green compacts allowed a rapid densification of the chemically prepared WBIT ceramics. The platelets growth seems to be controlled up to 1100°C by the WO_3 addition.

As it was expected, the doping with WO_3 reduced the electrical conductivity by about two orders of magnitude when compared with the undoped BIT. Piezoelectric response in W^{6+}-doped materials was obtained. k_t values of $0{\cdot}09 \pm 0{\cdot}01$ were measured.

Acknowledgements

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