

Study and control of the conductivity of Nb-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ for high temperature piezoelectric applications

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Bismuth-based layered compounds have been considered during the last years as interesting materials for high temperature piezoelectric applications, due to their stability and wide thermal range of the ferroelectric activity. The high electrical conductivity present at high temperatures has been a disadvantage for the potential applications of these compounds. On $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT), different doping, such as Nb^{5+} and W^{6+} were used to increase resistivity. It has been shown that Nb^{5+} doping modifies piezoelectric response, passing from relatively high hysteretic to linear and almost completely non-hysteretic. In the present work, the effect of Nb^{5+} doping related to the conduction response is investigated. Studies of the I-V curves as a function of the temperature allows us, for the first time, to measure the conductivity of these compounds at room temperature (RT) and to discuss which are the microstructural elements that control the conductivity of the material using a serial electrical model. It is shown that at temperatures between RT and 125°C the grain boundary conductivity limits the total conductivity. At higher temperatures, the material conducts mainly through the bulk of grains. Conduction type, conductivity thermal regimes and chemical composition may explain the change in the piezoelectric behaviour.

Keywords: BIT, Conductivity, Piezoelectricity.

Estudio y control de la conductividad en compuestos de $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ dopados con Niobio, para aplicaciones de alta temperatura

Compuestos laminares de bismuto han sido considerados en los últimos años materiales interesantes como piezoeléctricos en aplicaciones de alta temperatura, debido a su estabilidad y amplio rango térmico de existencia de actividad ferroeléctrica. Sin embargo, la elevada conductividad presente a altas temperaturas ha sido una desventaja para las potenciales aplicaciones de estos compuestos. En el caso de $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT), diferentes dopantes como Nb^{5+} o W^{6+} han sido empleados para aumentar la resistencia eléctrica del material. Es conocido que el dopado con Nb^{5+} modifica la respuesta piezoeléctrica del material pasando de presentar una elevada histéresis a prácticamente lineal y no histerética. En este trabajo se estudia el efecto de este tipo de dopado sobre la respuesta de la conductividad. Estudios eléctricos mediante la medida de curvas I-V en función de la temperatura nos permiten, por primera vez en la literatura, medir la conductividad de estos compuestos a temperaturas entorno a la ambiente (TA) y discutir qué elemento mesoestructural controla la conductividad total del material, usando un model eléctrico en serie. Como resultado, se ha visto que a temperaturas entre TA y 125°C es la conductividad del borde de grano la que limita la conductividad de todo el compuesto. A temperaturas superiores, el material conduce principalmente a través del interior de grano. Combinaremos los resultados de los estudios sobre tipo de conducción, regímenes térmicos y la composición química para interpretar los cambios en la respuesta general introducidos por el dopado.

Palabras Clave: BIT, Conductividad, Piezoelectricidad.

1. INTRODUCTION

The bismuth titanate family of layer-structure ferroelectrics has recently attracted considerable interest for high temperature piezoelectric applications (1) and non-volatile ferroelectric memories (2). In both cases materials are expected to exhibit low conductivity. For piezoelectric sensor applications a low conductivity is essential to prevent decay and charge drift of slowly varying piezoelectric signal. For memory applications, high electric fields used for polarization switching also require low leakage current of the ferroelectric. Another aspect common for these two very different applications is the role of ferroelectric domain-walls. In piezoelectric effect, domain-walls displacement is known to be a major extrinsic contribution responsible for the hysteresis and field dependence of piezoelectric response (3). In memories, polarization fatigue is

closely related to movement, nucleation and growth of domain walls. Thus, electrical conductivity and mechanisms related to domain-wall processes in these materials must be well understood. In this paper, we study conductivity of pure and donor-doped bismuth titanate for the first time at temperatures as low as 25°C. Such study is of interest as most piezoelectric data are also available at the room temperature. The conductivity is reduced by doping BIT with Nb^{5+} (4), which was also found to suppress the piezoelectric nonlinearity and hysteresis (5). Thus, this study could be a starting point for finding possible links between mechanisms responsible for the conductivity decrease and reduction of domain-wall contributions to the piezoelectric properties in bismuth titanate based materials.

2. EXPERIMENTAL, PROCEDURE

2.1.- Samples Preparation

The doping of BIT with Nb^{5+} gave the solid solution $\text{Bi}_4\text{Ti}_3\text{O}_{12-x/4}\text{Nb}_{x/5}\text{O}_{12}$ under study. The solubility limit of Nb^{5+} in the lattice at the Ti^{4+} -site has been found to be $x \leq 0.7$ (6). This solid solution is non-stoichiometric, that is the number of cations is not kept constant, but we do assure the electroneutrality of the solution. That means that the different compounds have concentration of Ti^{4+} vacancies, equal to $x/20$ per mol. The sample preparation was carried out by solid state reaction of the mixture of the precursor powders, Bi_2O_3 (FERRO 320-A, 99.9%), TiO_2 (ALFA 88221, >99%) and Nb_2O_5 (ALFA, >99.9%). The calcination was performed at 850°C during 4h in air. Sintering process of the 1-2mm thick green pellets was made at 1125°C during 4h for all compositions. Those procedures are described in detail elsewhere (7). The obtained densities were always higher than 97% of the theoretical density. Samples were polished down to the right thickness (0.5-1mm), gold sputtered electroded and then characterized as will be described below.

2.2.- Experimental Settings

To pole samples, they are introduced into a silicone oil bath and heated up to a temperature between 125 and 200°C , depending on the composition. A dc electric field from 20 to 80kV/cm is applied to the sample at this temperature and kept applied while the sample was cooled down to room temperature. The poling conditions are optimized for each composition as described in (6). Piezoelectric properties of the samples were measured 1 day after poling, according to the IRE standards (8). The polarization degree was controlled by measuring the d_{33} - piezoelectric coefficient with a Berlincourt-meter, at room temperature.

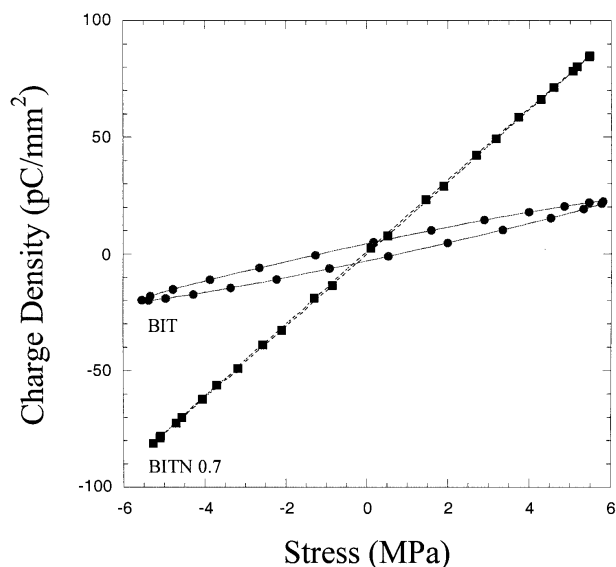


Figure 1.- Comparative direct piezoelectric response for undoped BIT (●) and BITN($x=0.7$) (■) samples, measured at 1Hz.

Two different systems have been used to make the macroscopic characterization of the solid solution. The piezoelectric characterization was performed via direct piezoelectric effect as a function of the amplitude and frequency of the applied sinusoidal stress. For the conductivity measurements in dry air atmosphere at different temperatures, the time-domain voltage-step technique was used, because frequency-domain techniques, like ac impedance spectroscopy, show experimental limitations for very high impedance measurements (9). This is the case of our materials at low frequencies and low temperatures. Such technique is based on applying a dc voltage step (1 hour long) to the sample and analyzing the charge-discharge current response. The set up consists of a precision electrometer Keithley 6145 and a Delta Chamber 9023 which was used to control the temperature of the sample.

3. RESULTS

3.1.- Piezoelectric Measurements

Figure 1 shows the comparative piezoelectric response measured at 0.1Hz for the two extreme compositions of the solid solution, $x=0$ and 0.7 . We can observe the change of behaviour from largely hysteretic for undoped BIT($x=0$) to almost non-hysteretic on Nb-doped sample ($x=0.7$). Furthermore, the d_{33} value increases with Nb^{5+} amount ($x/5$). This result is itself very important, because phases with lower hysteresis and d_{33} higher than in pure BIT increase the potential applications. In Figure 2 and 3, the evolution of the piezoelectric coefficient d_{33} as a function of the amplitude of the applied stress, X_σ , at several frequencies (0.01Hz to 100Hz) is shown for these two compounds. In the case of undoped BIT ($x=0$), the dependence is clearly non-linear. When introducing Nb^{5+} in the composition this response become perfectly linear with the field and the frequency dispersion disappears. The field dependence of the piezoelectric coefficients has been interpreted in terms of domain wall pinning mechanisms (5,10,11). The absence of

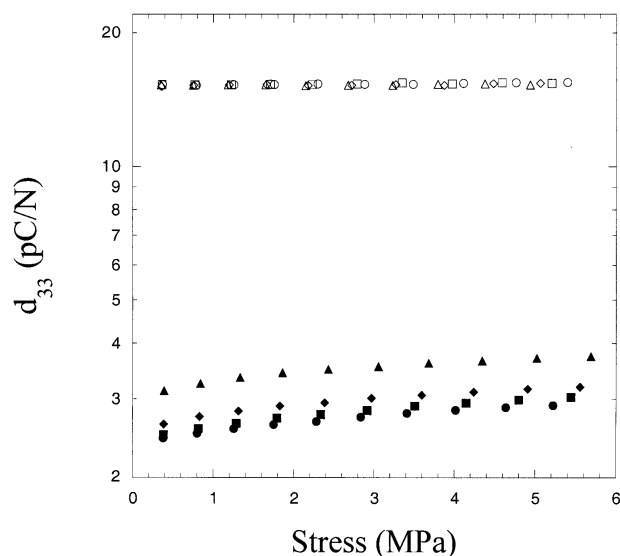


Figure 2.- Dependence of the piezoelectric coefficient d_{33} of undoped BIT (closed symbols) and Nb-doped BITN($x=0.7$) (open symbols), as a function of the amplitude of the applied ac pressure, X_σ , measured at different frequencies from 0.01Hz to 100Hz.

hysteresis in Nb-doped materials ($x \geq 0.5$) indicate complete pinning of walls that reduces extrinsic contributions to the piezoelectric effect. In case of $x=0.7$ sample, this extrinsic part is very weak as indicated by the slope of the linear dependence (Figure 3), and confirmed by the absence of hysteresis in piezoelectric effect (Figure 1). The exact origin of large extrinsic contribution to piezoelectric effect in pure BIT is presently not understood, but is probably related to domain wall processes.

3.2.- Conductivity Measurements

Figure 4 presents the dc conductivity as a function of $1/T$ for all compositions under study. All of them show similar activation energies around 1 eV. However a drastic change in the conductivity values is shown with Nb^{5+} doping. In Figure 5, we represent the conductivity variation as a function of the Nb^{5+} content for three different temperatures. For all temperatures the behaviour shows the same trend: after slight increase ($x=0.05$), the conductivity decreases continuously with increasing Nb amount. At temperatures higher than 50°C , in fact the conductivity decreases until reaching a minimum at $x=0.5$, and increases slightly again for $x=0.7$. Therefore, the desired reduction of the conductivity is achieved, making these compositions more useful for piezoelectric applications. This is the behaviour already reported by H.S. Shulman et al (4) at temperatures higher than 125°C in previous studies. In fact, the temperature region around room temperature is the more interesting one because it is there where the piezoelectric characterization is performed. However, the frequency region at which the dc conductivity measurements are made (relaxation times of 1h) does not correspond to the frequency region of piezoelectric measurements ($\sim 1\text{Hz}$), so a more powerful analysis of the charge-discharge data is needed.

Some authors (12-14) have shown the possibility to extract more information from the charge-discharge (15) curves than simple dc conductivity data. The polarization mechanism in a dielectric ceramic can be understood as a relaxation process of

the different electrical elements conforming the ceramic, clearly identifiable when representing I-t curves in bi-logarithmic scale (12). In the different steady states, after capacitive relaxation, we can calculate the pure resistive impedance of the system, according to the Kirchhoff's laws. These values will correspond to a combination of the different microstructural elements, grain, grain boundaries and electrodes, depending on the model used to simulate the electrical response of the material. Regarding the experimental I-t curves of our materials we observe two steps, one the long term current corresponding to the dc response, and another at short term measuring time (100Hz to 1Hz).

Electrical response in dielectric ceramics is very commonly represented using a geometrical serial model, consisting of parallel RC circuits for each electric element, interconnected in a series (16-18). As first approach, we will use this model to explain the response of our materials. Applying the model we get the conductivity values corresponding to the grains, σ_g , to the grain boundaries, σ_{gb} and the total conductivity, σ_{total} , at each temperature. To increase the accuracy of the results we first fit the I-V curves in the Ohmic regime at each temperature.

In Figure 6 we show the conductivity as a function of the temperature, between 25° and 225°C , for $x=0.5$ sample as an example. As can be shown, the total or dc conductivity is fully controlled by the conductivity of the grain boundary at temperatures below 125°C . Above 200°C the grain conductivity, being lower than grain boundary one, controls the material conductivity. In the intermediate range, 125° to 200°C , both grain and grain boundary share the control of the conductivity due to their similar values. The same behaviour has been found in all samples of the solid solution, Figures 7 a, b and c.

4. DISCUSSION

From earlier works (4,6) it has been shown that the grain size of samples sintered at the same temperature decreases when doping with Nb. Thus the volume fraction of the grain bound-

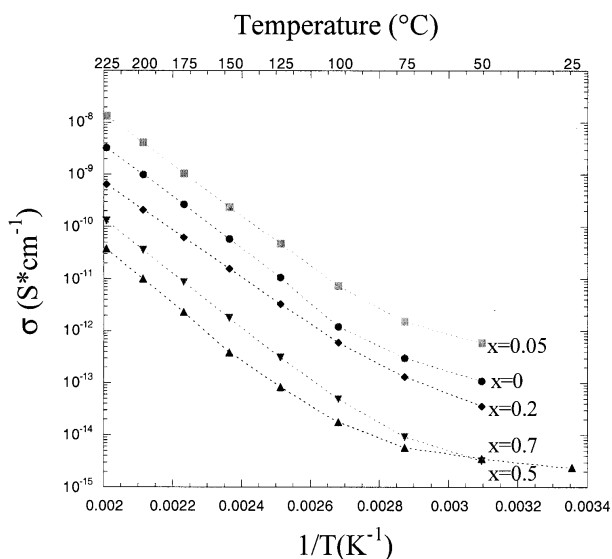


Figure 3.- Arrhenius plot of the dc conductivity as a function of $1/T$ for all samples of the BITN solid solution: $x=0$ (●), 0.05 (■), 0.2 (◆), 0.5 (▲) and 0.7 (▼).

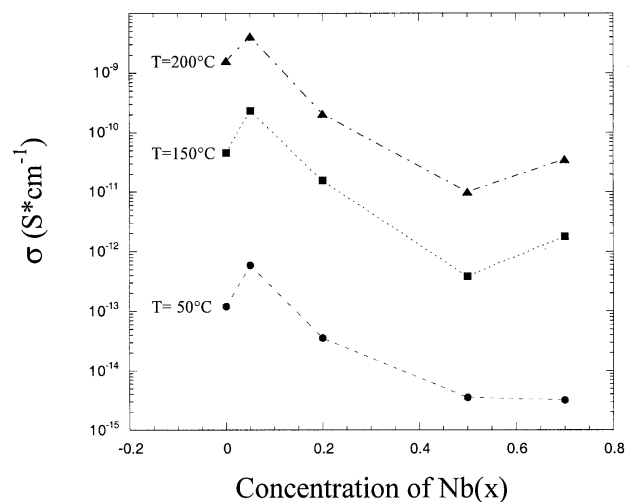


Figure 4.- Variation of the dc conductivity as a function of the Nb doping amount present in the phase, at three different temperature regimes (● - 50°C , ■ - 150°C and ▲ - 200°C).

dary is expected to increase with doping and therefore its electrical influence in the system should increase. On the other hand, TEM experiments show no evidence of change in the chemical composition of the grain boundaries. The grain boundaries seem to be just a twinning of the crystallographic structure.

From the conductivity measurements, using the serial model (let us keep in mind that in a serial model the higher resistance element of the circuit controls and limits the total dc conductivity of the system) it is shown that at temperatures between RT and 125°C the grain boundary conductivity limits the total conductivity.

We must compare conductivity and piezoelectric responses measured in the same frequency and temperature ranges to assure that we are looking at the response of the material under similar conditions. Thus, it is the conductivity at high frequency ($\geq 1\text{Hz}$) and low temperature (around RT) which must be studied to explain the change in piezoelectric behaviour. According to the model, the conductivity at high frequency, σ_g , is limited by the conductivity of the grain boundary, σ_{gb} , at RT. The Nb doping increases both the volume fraction of the grain boundary and its intrinsic conductivity (figure 7). On the other hand, Fousek (19) has shown that a reduction in the conductivity implies a reduction of the effectiveness on the domain wall motion. All these facts lead us to suggest that it is the reduction of grain boundary conductivity induced by Nb doping, which is responsible for the reduction of extrinsic contribution to the piezoelectric effect, by, for example, a more effective pinning of domain walls at the grain boundaries.

5. CONCLUSIONS.

For the first time, low temperature and high frequency (short times) conductivities have been measured in bismuth layered compounds. This study of conductivity as a function of the Nb^{5+} doping concentration gives us several interesting results:

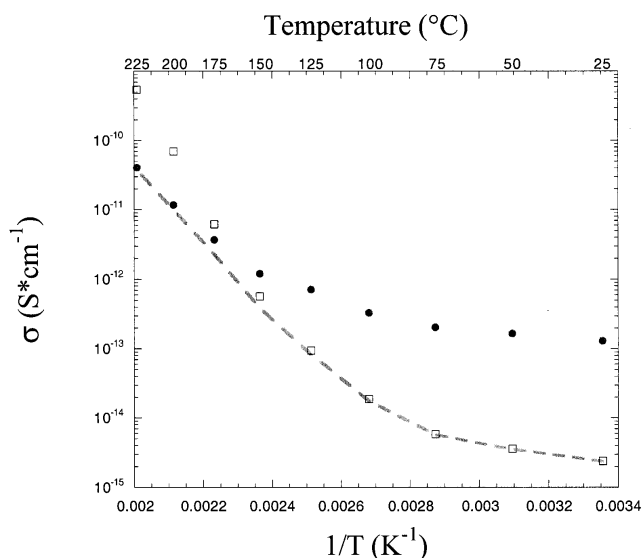


Figure 5.- Conductivity contributions of different microstructural elements (grains (●), grain boundaries (□), and the total dc (—)) as a function of 1/T calculated using an electrical serial model, for a sample BITN(x=0.5).

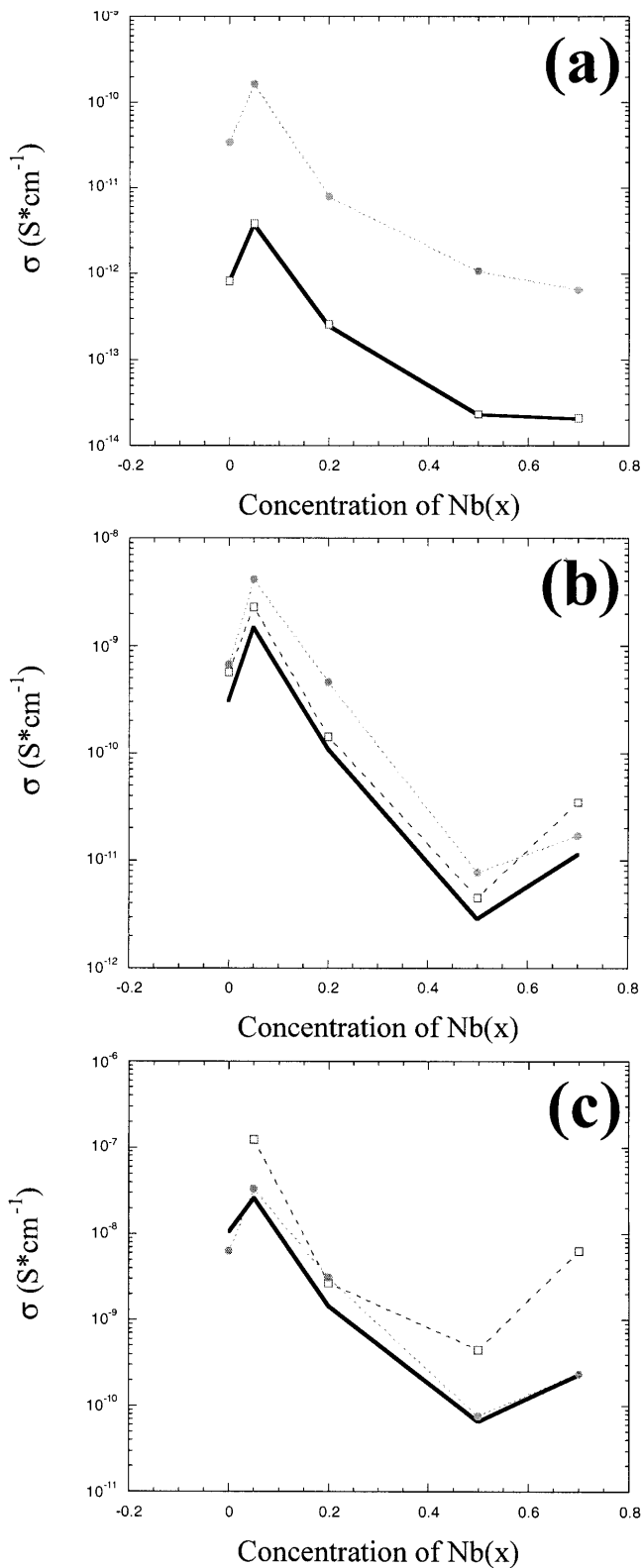


Figure 6.- Conductivity regimes as a function of the Nb concentration in BITN solid solution. The contribution of the grain (●) and grain boundary (□) conductivities to the total dc conductivity (æ) change with the temperature: conductivity measured at 50°C(a), at 150°C(b), and at 200°C(c).

Using a classical serial model to analyze the conductivity it is obtained that the grain boundary is the structural element that governs the material response in the low temperature and high frequency domain.

It is suggested that the grain boundary reduces the total conductivity of the material, being the electrical element with the lower conductivity. This reduction of conductivity could decrease hysteresis and non-linearity by promoting strong pinning of the domain walls.

The validity of the serial model and domain wall pinning mechanisms must be confirmed with complementary measurements. Other models must be tested as well.

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