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Thermal Behavior of the Elastic (Young's) Modulus in SBN-derived Compounds ($Bi_2SrNb_2O_9$)

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Abstract

Measurements of the elastic (Young's) modulus, mechanical losses and d.c. electrical conductivity as a function of the temperature in Aurivillius type structure ferroelectric ceramics have been performed. The results suggest that the anomalies appearing in macroscopic complex elastic modulus and electrical conductivity near the temperature of 300°C, do not correspond to a ferro- paraelectric or ferro-ferroelectric phase transition. These anomalies could be caused by a change in the defect structure coming from unstable Bi^{3+} cation. © 1999 Elsevier Science Limited. All rights reserved

Keywords: phase transitions, defects, electrical conductivity, mechanical properties.

1 Introduction

The interest of the ferroelectric thin films for application in non volatile memories and infrared sensors is continuously growing. New compositions are being investigated to overcome some problems, such as aging and retention of polarization, which are limiting the use of the classical compositions based on lead titanate circonate. Recently, thin films of lead free ferroelectric compositions have been prepared that could solve these problems.[1] These compositions are the layered perovskites with Aurivillius type structure that contain Bi in, at least, one of the layers.

According to the most recent works,[2,3] the limitation of these new compositions to get thin films with nice characteristics would come from the instability of the Bi^{3+} cation that diffuses to the surface of the films when the temperature increases.

The ferroelectric Aurivillius also become very interesting materials for devices that have to work in limited conditions of temperature, like high temperature ultrasonic sensors, accelerometers, etc.

It is well known[4,5] that the existence of point defects in ferroelectric materials produces interactions between defects and domain walls of relaxational character in the low frequency region. Measurements as a function of the temperature on metals and alloys with high concentration of oxygen vacancies exhibit big anomalies in the behavior of the elastic modulus and internal friction coefficient at certain temperatures,[6–8] which are some hundred of degrees apart in the heating and cooling runs.

We see that measurements of the internal friction coefficient and Young's modulus may deliver important information on the point defects stabilization and interaction processes in many materials.

In this work we have studied the behavior of the Young's modulus as a function of the temperature in ceramics which compositions have Aurivillius type structures with two perovskite layers sandwiched between bismuth oxide layers and different substitute cations. The aim of the work is to deliver information on the mechanisms that could give rise to the above mentioned anomalies and their relationship with possible structural phase transitions that could occur at temperatures far from those of the well-stablished ferroparaelectric transitions.

2 Experimental

Ceramics with Aurivillius structure, two perovskite layers ($n=2$) between Bi_2O_2 layers, and nominal compositions shown in the Table 1 were obtained

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from oxides and carbonate mixtures and a synthesis procedure that allows the making of Te-substitutions for Bi in the Bi_2O_2 layer.[9] Sintering was performed at the temperature of 850–950°C under an applied axial pressure of 275 kgcm^{-2}. The sintering process delivers very textured ceramics with some grade of grain preferential orientation and densifications of 97–98%.

To measure the low frequency complex Young's modulus as a function of the temperature the three point bending (TPB) technique with dynamic mechanical analysis was used. The measurements were performed on 12×2×0·5 mm samples at a thermal rate of 1°Cmin^{-1} d.c. Electrical conductivity was obtained from a.c. (1–100 kHz) impedance arcs. EPR spectra were obtained at the N_2-liquid temperature

Table 1.

Composition		Tc*(°C)*
$Bi_2SrNb_2O_9$	(SBN)	420
$Bi_{1{\cdot}75}Te_{0{\cdot}25}Sr_{0{\cdot}75}Na_{0{\cdot}25}Nb_2O_9$	(SNBTeN25)	350
$Bi_{1{\cdot}50}Te_{0{\cdot}50}SrTiNbO_9$	(SNBTeN50)	400
$(Bi_2SrNb_2O_9)_{0{\cdot}25}(Bi_3TiNbO_9)_{0{\cdot}75}$	(SBN25/BTN75)	740

3 Results and Discussion

The behavior of the relative elastic modulus and mechanical loss tangent of the base sample is presented in the Fig. 1. Curves A,A′ correspond to the first heating-cooling cycle for modulus and Tanδ respectively, curve B was obtained immediately after the cooling of curve A. The curve C, 7 days

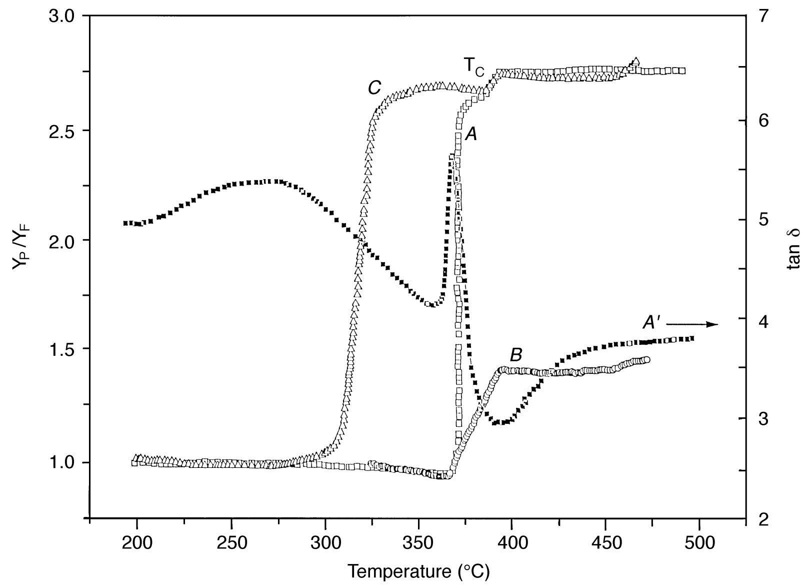

Fig. 1. Relative Young's moduli for SBN sample: A, first heating; B, second heating; C, third heating; A′, Tanδ in the first heating.

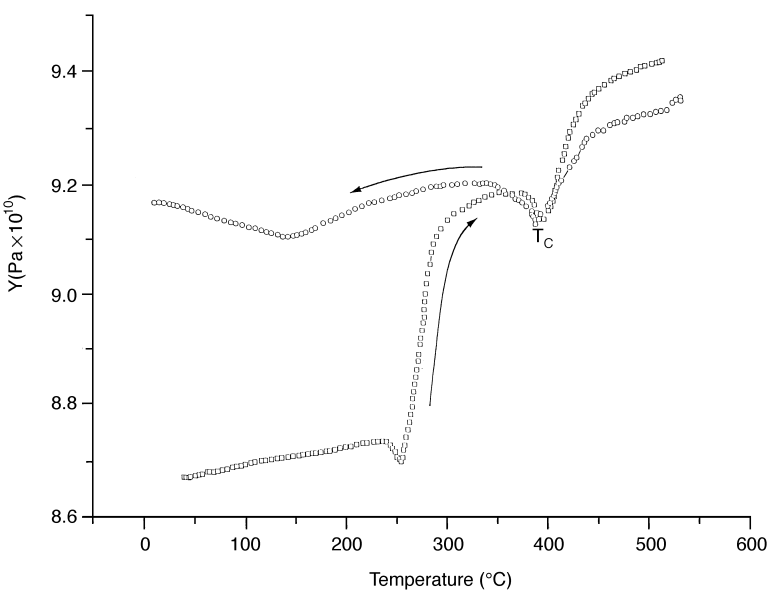

Fig. 2. Relative Young's moduli as a function of the temperature for samples SBN (□), SNBTeN25 (○) and SNBTeN50 (△).

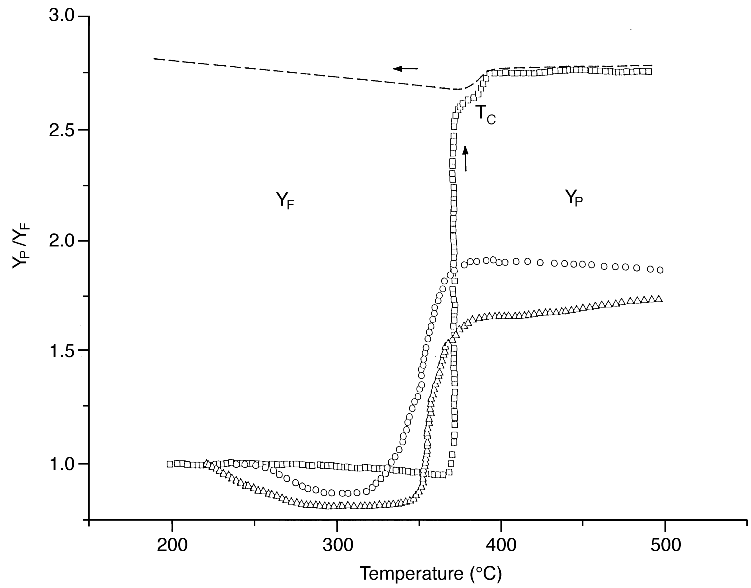

Fig. 3. Young's modulus as a function of the temperature for the sample SBN three months after the first heating.

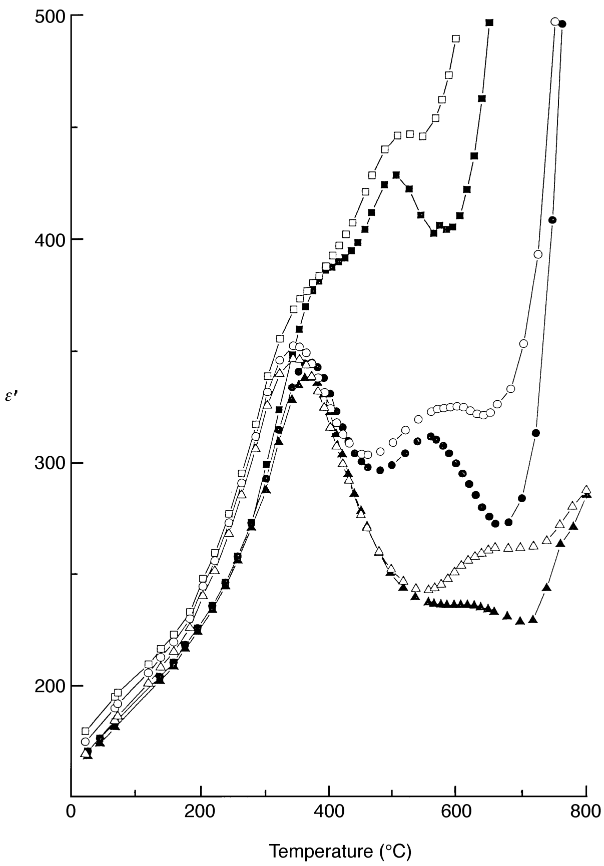

Fig. 4. Dielectric constant as a function of the temperature for the sample SNBTeN25 at frequencies of: (□) 1 kHz, (○) 10 kHz and (△) 100 kHz. Black points: increasing temperature.

after the curves A,A′. The anomalies in curves A,A′ are much more remarkable than those of curve B, and the temperature where the anomalies appear in curve C is lower than that of the first thermal cycle. In the Fig. 2 the elastic modulus as a function of the temperature for SBN sample three months after the first thermal treatment is plotted. We can observe a big decrease in the height of the jump of the modulus and the anomaly at the phase transition temperature.

Figure 3 shows the relative elastic moduli as a function of the temperature for samples with Te-substitution in the Bi- site cations and the base sample. Y_F and Y_P represent the Young's modulus in the ferroelectric and paraelectric phase respectively. The results show that the value of the jump of the anomaly close to 300°C decreases when the Te-substitution increases. In all the cases the behavior of the elastic moduli is not reversible in the heating–cooling run.

Dielectric constant as a function of the temperature for sample SNBTeN25 is plotted in Fig. 4. Maxima appear at 350°C and 500–600°C that are reversible in the thermal cycle. The temperature position of the higher temperature maximum changes with the measuring frequency.

In the Fig. 5 the Arrhenius of the d.c. conductivity for the SBN25/BTN75 sample has been represented. Changes in the slope of the conductivity curve versus K^{-1} appear at the temperatures of 250°C and 350°C that not correspond to structural phase transitions. The 0·74 eV slope must be due to the ionization of defects[10] and that of 4·1 eV to the liberated charge carriers movement. The behavior of the conductivity thermal process is irreversible. The defect ionization has been corroborated by mean of EPR measurements before and after heating the sample at 500°C for samples SBN and BTN (Bi_3TiNbO_9). The presence of free carriers give rise to the EPR-line with $g = 2{\cdot}0024$ in the after heating spectrum, Fig. 6. It has been proposed[11] that holes trapped in Bi^{3+} or

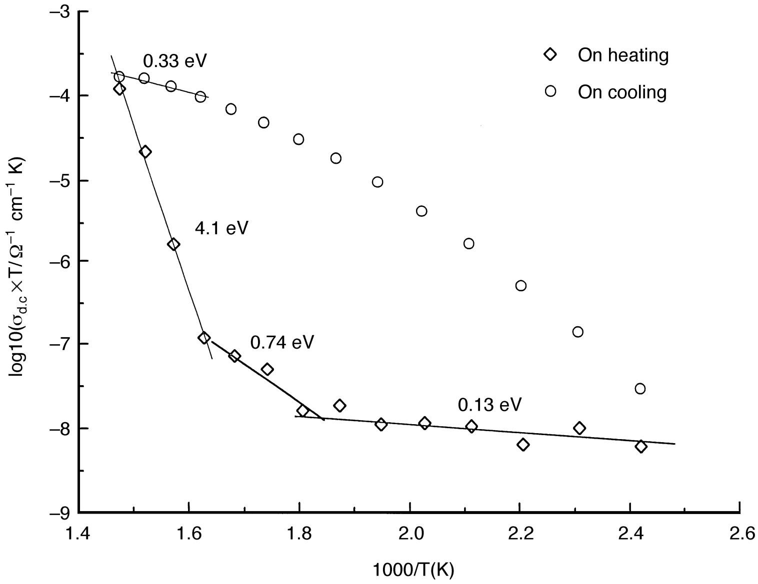

Fig. 5. Arrhenius of the d.c. electrical conductivity for the sample SBN25BTN75 showing three slopes in the heating run.

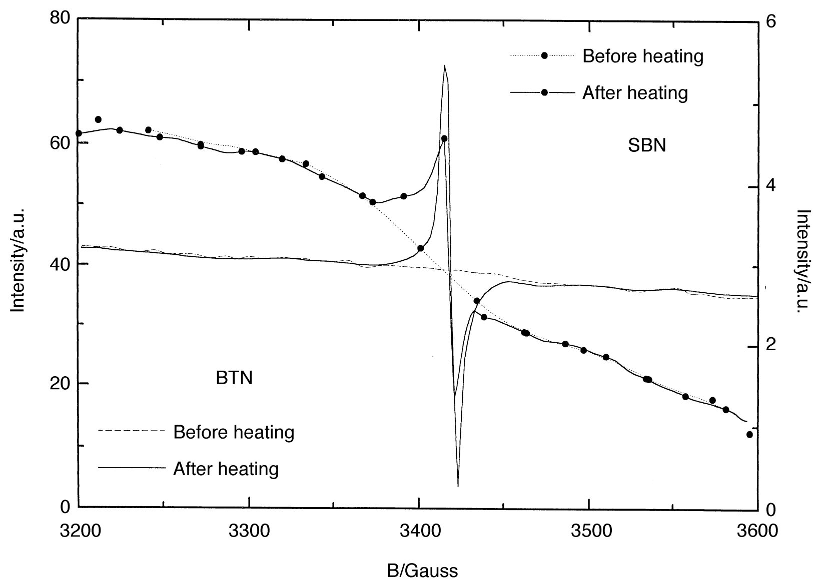

Fig. 6. EPR spectra for BTN and SBN compositions before (– – –) heating and after (_) heating at 500°C, 5 min.

electrons trapped in Ta^{5+} cations form Bi^{4+} and Ta^{4+} shallow centers with low activation energy.

Considering these results it is possible to give an explanation for the thermal Young's modulus behavior: At low temperatures the existence of defects leads to low values of Y.[6] When the charge carriers leave the defects and pin the domain walls which results in the increase of the Young's modulus in the low frequency region.[4,5] As the height of the jump of the modulus decreases with the amount of Bi-substitution, it seems clear that this cation is the main defect influencing the electrical and elastic properties of the Aurivillius type compounds.

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