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# Relaxor properties of $\text{Ba}_{0.9}\text{Bi}_{0.067}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics

Simon Annie, Ravez Jean, Maglione Mario

## Abstract :

Starting from the well-known ferroelectric material  $\text{BaTiO}_3$ , we show that coupled substitutions at the Ba and Ti cationic sites are able to improve the material properties. The compositions  $\text{Ba}_{0.9}\text{Bi}_{0.067}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$  display a relaxor behaviour close to room temperature which open the way for possible use of it for capacitor applications. The origin of such optimization is related to the Bi cations which share similar electronic structure with Pb without raising environmental concerns related to the volatility of  $\text{PbO}$ . In addition, we have found a very peculiar transition sequence in this compound from paraelectric to ferroelectric and then to relaxor on cooling.

**Keywords :** Ferroelectric; Relaxor; Perovskite

## 1. Introduction

According to their behaviour, ferroelectric materials may be divided into two different classes depending on whether they are classical or relaxor ferroelectric [1]. The typical characteristic of the latter is that a least two different cations have to be localised in the same crystallographic site. Indeed, the  $\text{ABO}_3$  oxidic perovskites display fully ordered transitions ( $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ ), mesoscopic disorder leading to the relaxor behaviour ( $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ , ...) and dipolar glass states ( $\text{KTaO}_3\text{:Li}$ ,  $\text{KTaO}_3\text{:Na}$ ) [2], [3], [4], [5] and [6]. In addition to the usual applications of ferroelectric materials, relaxors are of great interest for dielectrics in capacitors and actuators [7]. The relaxor materials usually used are lead-based ceramics, for example  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN) and derived compounds. However these materials have a drawback due to the volatility and the toxicity of  $\text{PbO}$ . At the present time current research is oriented to environment-friendly applications using lead-free materials. In addition, the aim for application was to prepare lead-free relaxor ceramics with such properties close to room temperature (RT) ( $T \approx 295 \text{ K}$ ). In fact, up to now, lead-free relaxor presented value of  $T_m$  often widely less than RT [8].

The present report is aimed as designing and characterizing new lead-free ferroelectric relaxors. The selected compositions belong to the perovskite family  $\text{AMO}_3$  and are derived from  $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ . This solid solution is characterized by both ferroelectric and relaxor properties depending on the composition: the original ferroelectric transitions of  $\text{BaTiO}_3$  continuously transform into the relaxor state whose temperature of occurrence decreases to very low temperatures as the Zr content increases up to about 42% [9]. To trigger the coexistence between order (ferroelectric) and disorder (relaxor), we decided to add another degree of freedom on introducing a disorder on the Ba site. This can be achieved with the heterovalent substitution of  $\text{Ba}^{2+}$  cations with the  $\text{Bi}^{3+}$  ones. To account for this charge unbalance, vacancies on this site are introduced a level of 1 vacancy for 2  $\text{Bi}^{3+}$  substitutions, leading to the chemical formula  $\text{Ba}_{1-y}\text{Bi}_{2y/3}\square_{y/3}\text{TiO}_3$ . Fixing a given Bi content, we then proceed to the Zr/Ti substitution to achieve the already recalled BTZ trends. Doing so, we thus have the co-existence between a fixed disorder on the Ba site and a tunable disorder on the Ti site. In the present paper, the Bi content will be fixed at 2/30 leading to the formula  $\text{Ba}_{0.9}\text{Bi}_{0.067}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ . The cation  $\text{Bi}^{3+}$  (substituted to  $\text{Ba}^{2+}$ ) was chosen due to its  $6(\text{sp})^2$  lone pair; such electronic environment (favourable for the relaxor effect) was previously involved also in lead-compositions, but without here the disadvantage of lead pollution [1].

## 2. Lead-free relaxor ferroelectrics ceramics derived from $\text{BaTiO}_3$

Depending on both the substitution and the composition, different types of behaviour have been evidenced in binary systems derived from  $\text{BaTiO}_3$ :

– for homovalent substitutions in the  $M$  site (e.g.,  $\text{Ba}(\text{Ti}_{1-x}\text{M}_x)\text{O}_3$ ,  $M=\text{Zr}$ ,  $\text{Sn}$ ,  $\text{Ce}$ ), the transition sequence was the same as that of  $\text{BaTiO}_3$  for low values of  $x$  (e.g.,  $x \leq 0.10$ ,  $M=\text{Zr}$ ). For greater values of  $x$  (e.g.,  $0.10 < x \leq 0.27$ ,  $M=\text{Zr}$ ) there was only one rhombohedral, ferroelectric –  $T_C$  → cubic, paraelectric transition after the disappearance of the orthorhombic and tetragonal phases. For the highest values of  $x$  (e.g.,  $0.27 < x \leq 0.40$ ,  $M=\text{Zr}$ ) the behaviour was of relaxor type [8], [9] and [10].

– for heterovalent substitutions in the A site, the transition sequence was the same as that of BaTiO<sub>3</sub> up to relatively high values of  $\gamma$  ( $\gamma < 0.02$  for Ba<sub>1- $\gamma$</sub> Bi<sub>2 $\gamma$ /3</sub>TiO<sub>3</sub>). For higher values of  $\gamma$  ( $0.09 \leq \gamma \leq 0.15$ ), a relaxor behaviour was observed [11].

The main relaxor characteristics  $\Delta T_m = T_m(10^5 \text{ Hz}) - T_m(10^2 \text{ Hz})$  and  $\Delta \epsilon'_r / \epsilon'_r = [\epsilon'_{r, \text{max}}(10^2 \text{ Hz}) - \epsilon'_{r, \text{max}} \times (10^5 \text{ Hz})] / \epsilon'_{r, \text{max}}(10^2 \text{ Hz})$  become higher as the composition deviates from BaTiO<sub>3</sub>. Moreover, the composition range of solid solutions showing a relaxor behaviour depends on the type of substitution. When we compare the concentration range leading to the same shift of  $T_m$  ( $\Delta T_m = 10 \text{ K}$ ) [10]:

– for homovalent substitutions in the M site, the cations charge balance (e.g., Ti<sup>4+</sup> and Zr<sup>4+</sup>) requires a high substitution rate for the relaxor effect to set in ( $x=0.35$ ).

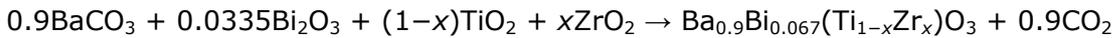
– for heterovalent substitutions in the A site, relatively high substitution rate is required because this site is not the ferroelectric active one in Lead-free compounds.

– for heterovalent substitutions in the M site, which are coupled of course with heterovalent ones in another site, the values of  $x$  are the lowest. This implies that the relaxor effect is mainly dependent on heterovalent substitutions in the M site.

In addition, the value of  $T_m$ , which is a typical feature of the relaxor effect was the highest for the limit composition of the solid solution Ba<sub>1- $\gamma$</sub> Bi<sub>2 $\gamma$ /3</sub>TiO<sub>3</sub> chosen in the present work.

### 3. Preparation

The various compositions of the Ba<sub>0.9</sub>Bi<sub>0.067</sub>(Ti<sub>1- $x$</sub> Zr <sub>$x$</sub> )O<sub>3</sub> system were obtained from BaCO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> (Aldrich 99%) using the following reaction:



Before the two heat treatments, 1 h grinding was done and powders were pressed under 100 Mpa into 8 mm diameter disks about 1 mm thick. Calcination at 1200 °C for 15 h was followed by 4 h sintering at 1400 °C under oxygen atmosphere.

Room temperature powder X-ray diffraction patterns were recorded on a Philips diffractometer using CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the angular range  $5 \leq 2\theta \leq 80^\circ$ . This made it possible to verify that the samples were single phases and of perovskite type. This allows us to determine the limits of the solid solutions. The single phase corresponds here to  $0 \leq x \leq 1$ .

The diameter shrinkage  $(\phi_{\text{init}} - \phi_{\text{final}}) / \phi_{\text{init}}$  and the compactness (experimental density / theoretical density) were systematically determined. Their values were in the range 0.15 to 0.17 and 0.92 to 0.96, respectively.

### 4. Dielectric results

Dielectric measurements were performed on ceramic disks after deposition of gold electrodes on the circular faces by cathodic sputtering. The real and imaginary relative permittivities  $\epsilon'_r$  and  $\epsilon''_r$  were determined under helium as a function of both temperature (77–600 K) and frequency ( $10^2$ – $2 \cdot 10^5$  Hz) using a Wayne–Kerr 6425 component analyzer.

Two different behaviours appeared in the thermal evolution of  $\epsilon'_r$  versus frequency:

– for  $0 \leq x < 0.075$ , we observed one relatively sharp peak of  $\epsilon'_r$ , no dependent on frequency, at  $T_c$  and a shoulder in the slope with a dispersion of  $\epsilon'_r$  and an increase of  $T_m$  with frequency. As an example we reported on Fig. 1 the result for a ceramic corresponding to  $x=0.040$ . The behavior is of classical ferroelectric type;

– for  $0.075 \leq x \leq 1$ , only one peak was observed.

Fig. 2 and Fig. 3 give the temperature dependence of  $\epsilon_r'$  and  $\epsilon_r''$  at various frequencies for a ceramic with composition  $x=0.15$ . The temperature  $T_m$  of  $\epsilon_r'$  maximum was shifted to higher values at greater frequencies. A frequency dispersion took place for  $T \leq T_m$ , the value of  $\epsilon_r'$  decreasing when the frequency increased. The temperature and frequency variations of the imaginary part  $\epsilon_r''$  of the permittivity were also specific: the temperature  $T_m$  of  $\epsilon_r''$  maximum was shifted to higher values on increasing frequency, but contrary to the evolution of  $\epsilon_r'$ , the evolution of the frequency dispersion was here characterized by an increase in  $\epsilon_r''$  when frequency increased. In addition, there was a deviation from the Curie–Weiss law (Fig. 4). The value of the Curie–Weiss temperature  $T_0$  was greater than that of  $T_m$ , and that of  $T_{dev.} - T_m$  was about 153 K. A strong dielectric dispersion is evidenced leading to a Vogel Fulcher (VF) behaviour. The latter was computed using the equation  $\log f = \log f_0 - E_a/k_B(T_m - T_{VF})$  where  $f_0$  is the high temperature extrapolation of the attempt frequency,  $E_a$  the activation energy,  $k_B$  the Boltzmann constant and  $T_{VF}$  the static freezing temperature [12] and [13]. All these dielectric characteristics are typical of relaxor behavior [1]. Fig. 5 shows the variations in  $T_C$  and  $T_m$  with the composition at 1 kHz.  $T_m''$  decreased from  $x=0.075$  to  $x=0.8$ . For  $0.8 < x \leq 1$ , values of  $T_m''$  are not plotted on Fig. 5, due to low temperature experimental limitations.

## 5. Discussion

Most part of substitutions carried out from  $\text{BaTiO}_3$  and showing a relaxor effect unfortunately lead to values of  $T_m$  widely below room temperature (295 K). Moreover it was known that the replacement of the  $\text{Ba}^{2+}$  cation by a cation owning a  $6(\text{sp})^2$  lone pair allowed an increase of the Curie temperature: for example, the solid solution  $\text{Ba}_{1-x}\text{Pb}_x\text{TiO}_3$  where the value of  $T_C$  varies from 400 K ( $\text{BaTiO}_3$ ) to 760 K ( $\text{PbTiO}_3$ ). In the present work, for reasons mentioned in the introduction of this article (toxicity of  $\text{PbO}$ ), we consider the cation  $\text{Bi}^{3+}$ .

Previous study of ceramics with composition  $\text{Ba}_{1-y}\text{Bi}_{2y/3}\text{TiO}_3$  shown that the value of  $T_C$  was practically stable up to the value  $y=0.10$  (Fig. 6). However, the two transitions temperatures  $T_1$  and  $T_2$  present in the ferroelectric region of  $\text{BaTiO}_3$  merged into a ferroelectric transition for  $y \approx 0.02$ . It is the composition  $y=0.10$  belonging to this solid solution which is the starting composition of this present work. For this composition, the merged  $T_1$  and  $T_2$  resulted in a relaxor behavior at a temperature  $T_m'$  which was further perturbed by Zr substitution in the Ti site.

The examination of the Fig. 5 shows that for a relatively low substitution rate  $\text{Zr} \_\_ \text{Ti}$ , the value of  $T_C$  is decreasing while that of  $T_m'$  is increasing up to a composition  $x \approx 0.070$ , beyond what remains a single effect at  $T_m''$  between a relaxor state and a paraelectric one. This value of  $T_m''$  is slowly decreasing down to values close to 100 K when  $x$  is still increasing (the last values of  $T_m''$  for  $x$  between 0.8 and 1 are not reported on Fig. 5, due to experimental limitation). We point out the very peculiar features of the phase diagram displayed on Fig. 5. For compositions close to  $\text{Ba}_{0.9}\text{Bi}_{0.067}\text{TiO}_3$ , i.e.,  $x \leq 0.07$ , the ceramics undergo two phase transitions on cooling. The first, at  $T_C$  is from a paraelectric to the ferroelectric state similar to  $\text{BaTiO}_3$ . The second one, which occurs within the ferroelectric state, is of relaxor type. This is very unusual in the field of relaxors where the succession of transitions is always in the thermodynamically favourable sequence on cooling: paraelectric  $\rightarrow$  relaxor  $\rightarrow$  ferroelectric. The latter ordering transition can be either electric field induced like in PMN [14] and [15] or chemically driven like in PSN and PST [16]. The very peculiar behaviour  $\text{Ba}_{0.9}\text{Bi}_{0.067}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$  is ascribed to the dual substitution on the A and B sites. The Bi substitution on the A site lead to the low temperature relaxor state while the Zr substitution on the B site keeps the ferroelectric high temperature at low rates. This special chemistry explains the apparent contradiction of our results with thermodynamics which always call for ordering on cooling. Detailed investigations of the possible segregation of both substituted cations at nanoscale are needed to clear out the microscopic origin of the transition sequence that we have observed.

In relation with a future use in electronic components, we focus our attention on the ceramic corresponding to the composition  $x=0.08$ . Its relaxor characteristics are reported on Table 1, showing that high permittivities are achieved close to room temperature for this composition.

In addition, there is also a strong deviation from the Curie–Weiss law ( $T_m'' < T_0$ ). A deviation for  $T < T_{dev.}$  (e.g.,  $T_{dev.} = 418 \text{ K}$  at  $10^5 \text{ Hz}$ ) is characteristic of dipole interactions responsible of some type of short range order. The large curvature of  $1/\epsilon_r'$  around  $T_m$  is in good agreement with a strongly

diffuse phase transition. The value of the frequency dispersion  $\Delta\epsilon'_r/\epsilon'_r$  at a normalized temperature  $T = T_m'' - 60 \text{ K}$  is about 0.091. The good fit of the data  $\log f$  vs  $T_m''$  with a Vogel Fulcher law leads to the value  $T_{VF} = 238 \pm 10 \text{ K}$ .

It appears that such a composition satisfies the aim of the fixed purpose:

– the value of  $T_m''$  is next to room temperature, allowing to use relaxor properties in normal conditions.

– the values of  $\Delta T_m''$  and that of  $\Delta\epsilon'_r/\epsilon'_r$  are high ( $\Delta T_m = 32 \text{ K}$ ,  $\Delta\epsilon'_r/\epsilon'_r = 0.91$ ); they are higher than those of the PMN ceramic ( $\Delta T_m = 15 \text{ K}$ ,  $\Delta\epsilon'_r/\epsilon'_r = 0.19$ ), usually used for applications.

– the value of  $\epsilon'_r$  lies between 3400 and 4000; these values are promising. Actual studies lead at increasing these values, thanks to an optimization of elaboration parameters.

The different characteristics of this ceramic present a real interest for applications, pointing out that the lack of lead prevents all the toxic pollutions during the preparation state.

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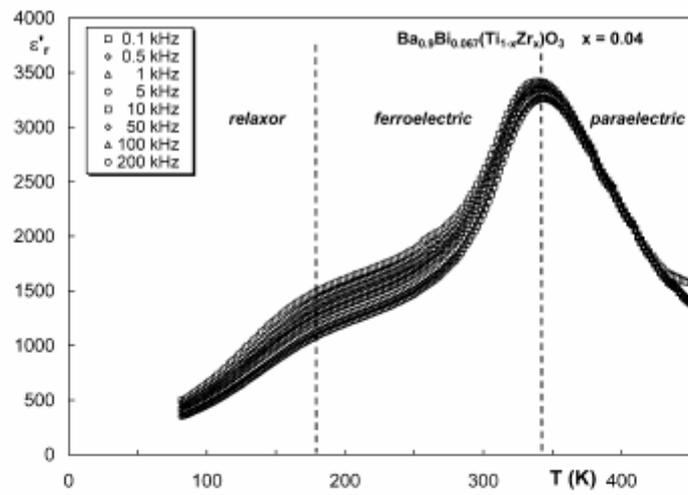


Fig. 1. Temperature dependence of  $\epsilon'_r$ , the real part of the permittivity, for a ceramic with composition  $\text{Ba}_{0.9}\text{Bi}_{0.067}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$  corresponding to  $x = 0.04$ .

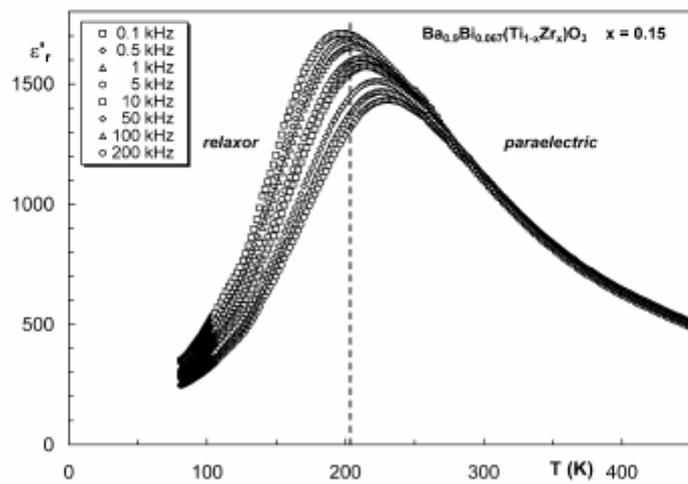


Fig. 2. Temperature dependence of  $\epsilon'_r$ , the real part of the permittivity, for a ceramic with composition  $\text{Ba}_{0.9}\text{Bi}_{0.067}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$  corresponding to  $x = 0.15$ .

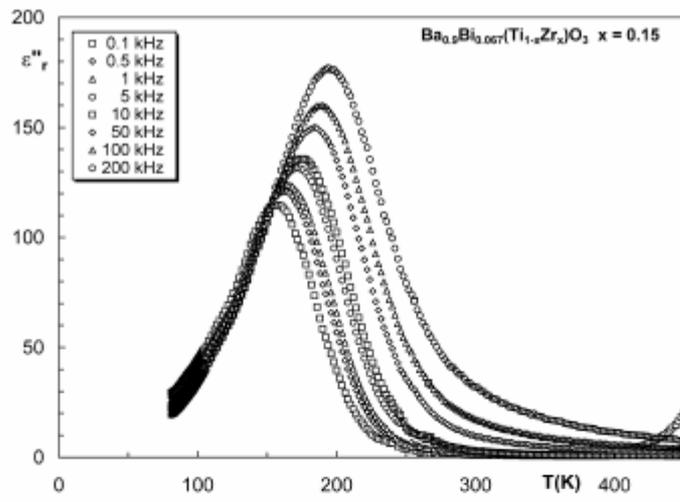


Fig. 3. Temperature dependence of  $\epsilon''_r$ , the imaginary part of the permittivity, for a ceramic with composition  $\text{Ba}_{0.9}\text{Bi}_{0.067}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$  corresponding to  $x = 0.15$ .

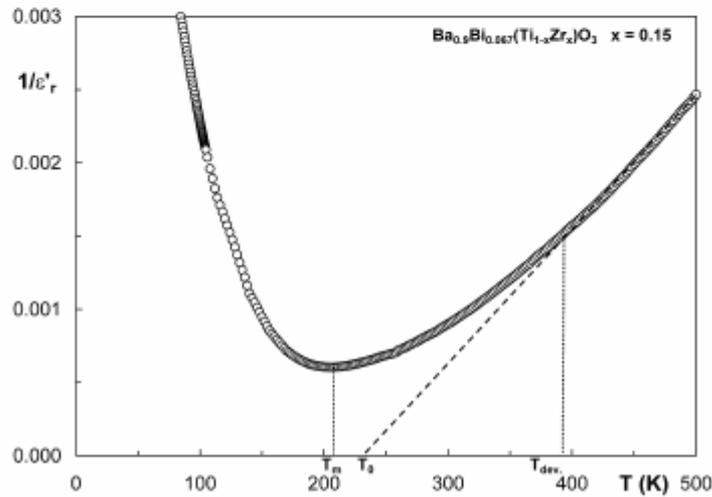


Fig. 4. Temperature dependence of  $1/\epsilon'_r$ , at 1 kHz, for a ceramic with composition  $\text{Ba}_{0.9}\text{Bi}_{0.067}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$  corresponding to  $x = 0.15$ .

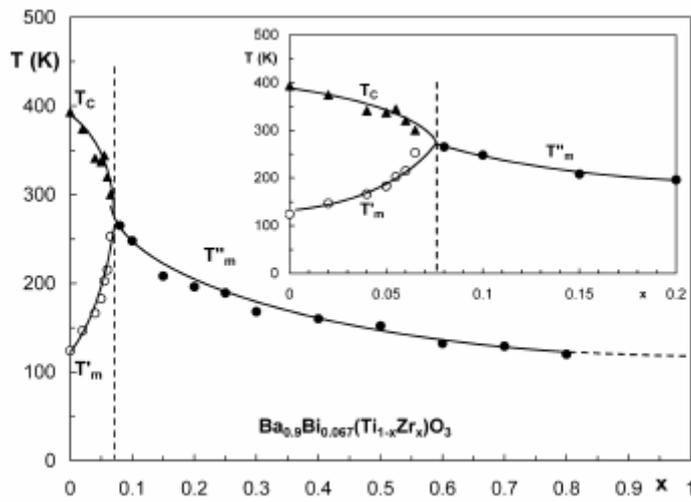


Fig. 5. Thermal variation of the dielectric anomalies, at 1 kHz, for ceramics with composition  $\text{Ba}_{0.9}\text{Bi}_{0.067}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ .

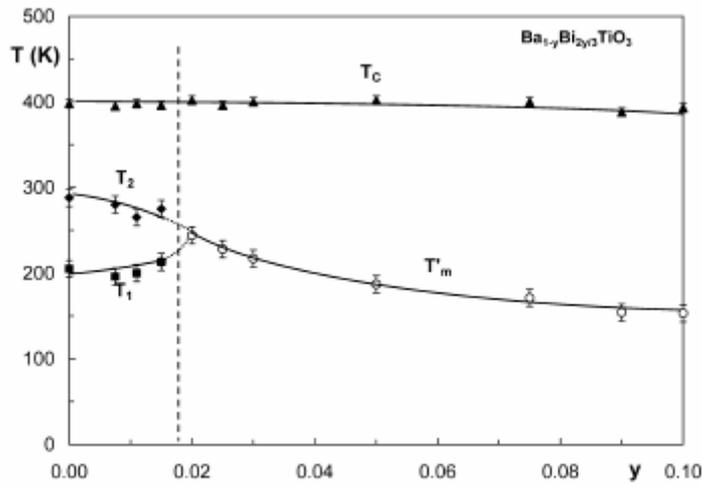


Fig. 6. Variation of  $T_c$  or  $T_m$  with  $x$  for ceramics with composition  $\text{Ba}_{1-y}\text{Bi}_{2y/3}\text{TiO}_3$ .

Table 1			
Some relaxor characteristics of ceramic with composition $x = 0.08$			
$f$ (kHz)	$T_m''$ (K)	$\epsilon'_{r, \max}$ at $T_m''$	FWHM <sup>a</sup> (K)
0.1	255	3930	227
1	264	3810	224
10	275	3650	221
100	287	3470	219

<sup>a</sup> FWHM: full width at half maximum.