Journal of the European Ceramic Society **19** (1999) 2015–2020
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PII: S0955-2219(99)0010-2
0955-2219/99/$ - see front matter

Dependence of the Structural and Dielectric Properties of $Ba_{1-x}Sr_xTiO_3$ Ceramic Solid Solutions on Raw Material Processing

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(Received 10 November 1998; accepted 30 December 1998)

Abstract

The structures and dielectric properties of $Ba_{1-x}Sr_xTiO_3$ *ceramic solid solutions in the whole* x *range and their dependence on the material processing are investigated. A short time pre-calcination milling–mixing of the precursor powders causes compositional inhomogeneity and thus a diffuse phase transition. For long milling–mixing time, the diffuse phase transition is observed only in the* $SrTiO_3$ *rich compositions (*$x > 0{\cdot}8$*). © 1999 Elsevier Science Limited. All rights reserved*

Keywords: milling, mixing, microstructure: final, dielectric properties, $BaTiO_3$ and titanates.

1 Introduction

Barium titanate ($BaTiO_3$) is known as a typical ferroelectric material which exhibits three sharp transitions: a first-order ferroelectric-paraelectric phase transition (cubic-tetragonal) around 130°C (also called Curie temperature T_c), a tetragonal-orthorhombic phase transition around 5°C and an orthorhombic-rhombohedral phase transition around −80°C. $BaTiO_3$ based solid solutions have been a subject of extensive study since the early 1950s. With partial substitution of the titanium by other tetravalent ions like in $Ba(Ti,Sn)O_3$,[1] $Ba(Ti,Zr)O_3$[2] and $Ba(Ti,Ce)O_3$[3] etc., the variation of the permittivity around the Curie temperature T_c was found to get smeared out in both ceramics and single crystal specimens, i.e. to exhibit diffuse phase transition (DPT), a similar behaviour to well known complex lead perovskite ferroelectric relaxors.[4] However, this kind of DPT behaviour was rarely observed in solid solutions with substitution of barium ions. The permittivity curves were sharp and the permittivity maximum temperatures were frequency independent for $(Ba,Ca)TiO_3$[5] and $(Ba,Yb)TiO_3$[6] solid solutions, although a broad permittivity maximum was also observed when the substitution ions exceeded the solubility limit, this being interpreted as due to the very small grain size caused by the inhibition of grain growth by the second phase present at the grain boundaries.[6] However, for the substitution of barium by strontium, i.e. for the $Ba_{1-x}Sr_xTiO_3$ solid solutions, conflicting results for the diffuseness data have appeared in the literature. Smolenskii *et al.*[7] obtained enlarged permittivity maxima around T_c for ceramic samples, while Benguigui *et al.*[8] reported diffuse phase transition for $x > 0{\cdot}6$ in single crystals and Barb *et al.*[9] reported similar results for ceramic samples. Lemanov *et al.*[10] reported a diffuse phase transition and glasslike behavior only in the $SrTiO_3$ rich region ($x > 0{\cdot}85$). Tiwar *et al.*[11] observed a DPT behavior in ceramic samples prepared by the 'semi-wet' process even when x was very small, e.g. $x = 0{\cdot}08$, 0·12, 0·16 and 0·2.

The disagreement on the diffuseness data of the $Ba_{1-x}Sr_xTiO_3$ solid solutions especially for low Sr concentrations questions whether the diffuse phase transition is an intrinsic property of this solid solution. An impurity could cause a diffused dielectric permittivity. A non-homogeneous distribution of Ba^{2+} and Sr^{2+} would also lead to a DPT response, if the origin of the DPT was due to compositional fluctuations, as proposed by Smolenskii.[12]

The present work reports the dielectric properties of $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions in the whole range of x from $x = 0{\cdot}0$–$1{\cdot}0$. Different pre-calcination milling–mixing times were used in order to investigate its influence on the dielectric properties of the solid solutions in an attempt to examine possible effects of inhomogeneities on the DPT behavior.

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2 Experimental

Ceramic samples were prepared by the conventional mixed oxide method. Reagent grade $BaCO_3$, $SrCO_3$ and TiO_2 were weighed according to the composition $Ba_{1\text{-}x}Sr_xTiO_3$ where $x = 0$, 0·2, 0·4, 0·6, 0·8, 0·9, 0·95 and 1, respectively. After mixing by milling in alcohol for 6 h using agate pots and agate balls in a planetary mill, the powders were dried, and then calcined at 1150°C for 6 h. For the $x = 0{\cdot}6$ and 0·8 compositions, different mixing time, 0, 3, 6 and 9 h (0 h means that the weighed oxides were only mixed by hand for 5–10 min in an agate bowl) were used, in order to investigate the effects of the milling–mixing time on the properties of the ceramics.

The calcined powders were milled again for 8–10 h, to obtain powders of less than 5 μm of particle size. Pellets of 10 mm in diameter and 2–3 mm in thickness were uniaxially pressed at 100 MPa and then isostatically pressed at 250 MPa. The samples were sintered between 1300 and 1400°C for 4 h; the higher the x value, the higher the sintering temperature.

The density of the sintered samples was measured by the Archimedes method. The specimens were 91–96% of theoretical density for all the compositions.

Some of the sintered samples were ground into powder and the phases were identified by X-ray diffraction analysis. The SEM (Scaning Electron Microscopy) microstructures of the samples were observed in polished sections followed by a thermal etching using a Hitachi S4100 microscope.

For the dielectric measurements, sintered samples were polished and gold electrodes were sputtered on both sides. Dielectric permittivity and loss factor were measured, at different frequencies between 10 Hz and 1 MHz, as a function of temperature, using a Solartron 1260 Impedance/Gain-Phase Analyzer and a Displex APD-Cryogenics cryostat during heating up at a rate of 1 Kmin^{-1} in the temperature range of 12–320 K. Measurements in the range of 320–500 K were done in a furnace during heating up at a rate of 1 Kmin^{-1}.

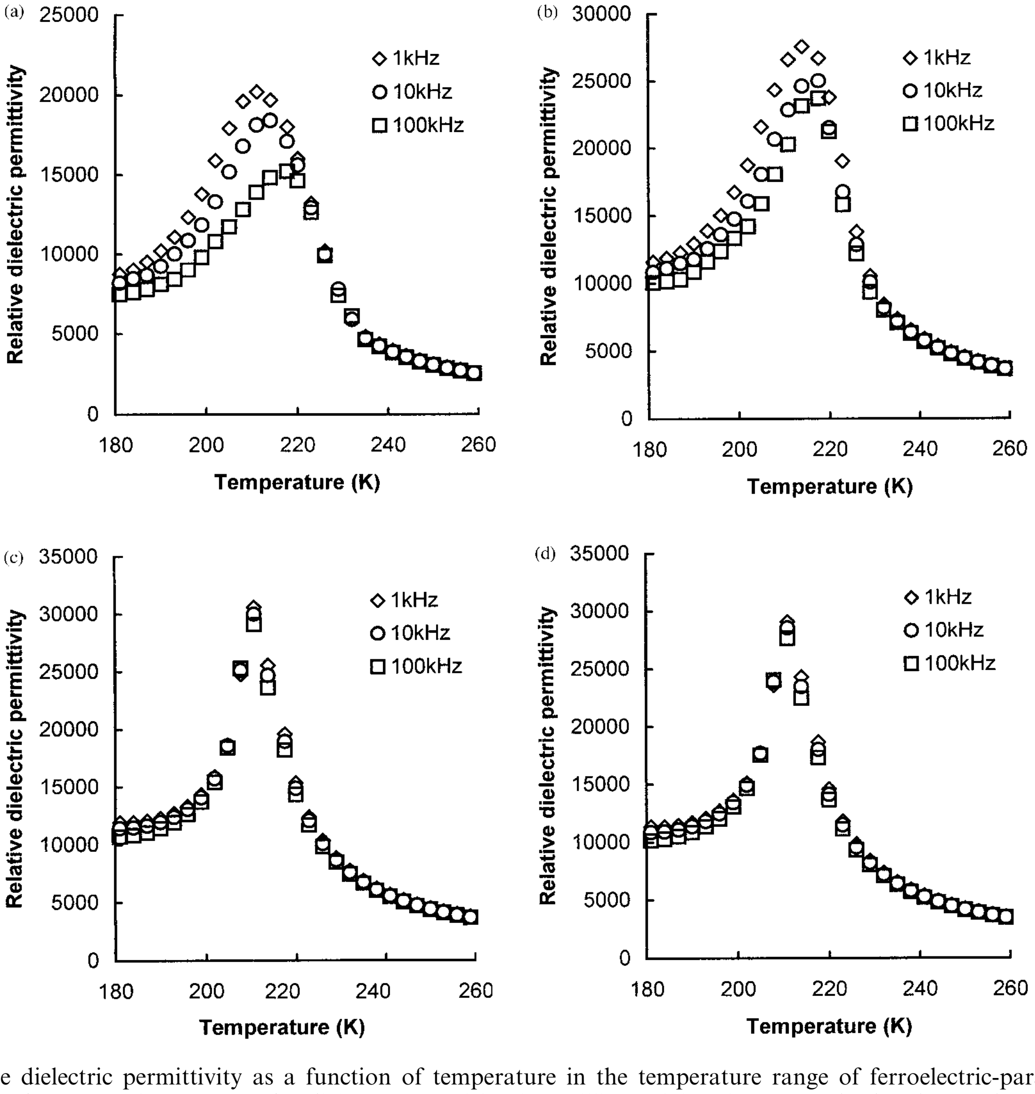

Fig. 1. Relative dielectric permittivity as a function of temperature in the temperature range of ferroelectric-paraelectric phase transition of $Ba_{1\text{-}x}Sr_xTiO_3$ ($x = 0{\cdot}6$) for different pre-calcination milling–mixing times: (a) 0 h, (b) 3 h, (c) 6 h and (d) 9 h.

3 Results

Figure 1 shows the temperature dependence of the dielectric permittivity in the temperature range of the ferroelectric-paraelectric transition for the $x = 0{\cdot}6$ composition for different milling–mixing time. A broad permittivity maximum and frequency dependence of maximum temperatures can be seen in the 0 and 3 h mixed samples. Sufficient mixing time (6 and 9 h) eliminates the diffuseness and no evident change in permittivity curves can be seen between the results for samples mixed for 6 and 9 h.

Figure 2 shows the SEM microstructures of the samples mixed for 0 and 6 h. No significant difference can be seen. All the samples, irrespective of mixing time, exhibit similar microstructures. The average grain size is around 3 μm.

Although all the X-ray diffraction patterns of the samples mixed for different times correspond to single phase cubic perovskite specimens, a peak broadening is seen as the milling–mixing time decreases, as shown in Fig. 3. This could be due to the compositional inhomogeneities, most probably, inhomogeneities in the Ba^{2+} and Sr^{2+} distribution. The fact that almost no difference can be seen in the broadness of the X-ray diffraction peaks between the samples milled for 6 and 9 h indicates that more than 6 h of pre-calcination milling–mixing can not further improve the compositional homogeneity.

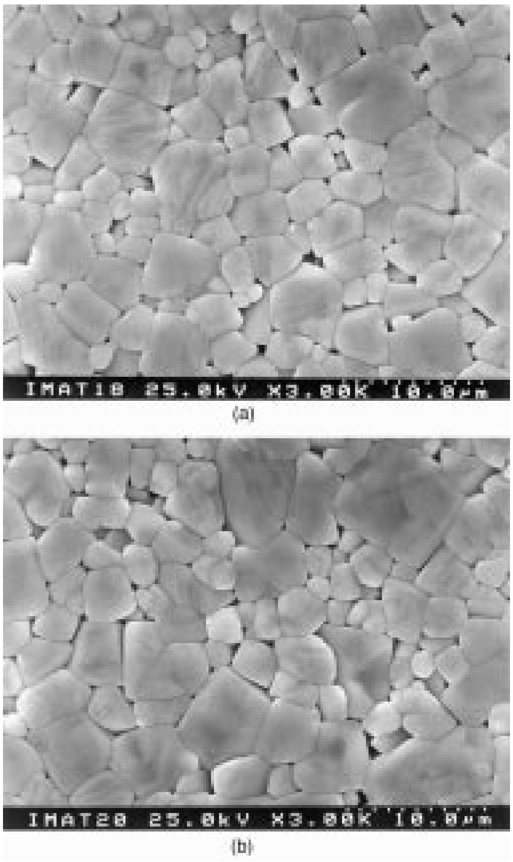

Fig. 2. SEM microstructures of $Ba_{1-x}Sr_xTiO_3$ ($x = 0{\cdot}6$) mixed for (a) 6 h and (b) 0 h.

The same milling–mixing time investigation was carried out for the $x = 0{\cdot}8$ composition. A similar behaviour was observed.

In the study of the structural and dielectric properties of $Ba_{1-x}Sr_xTiO_3$ solid solutions in the whole x range, data for a pre-calcination milling–mixing time of 6 h is presented.

The X-ray diffraction patterns of $Ba_{1-x}Sr_xTiO_3$ at room temperature are shown in Fig. 4. A single phase was observed for all the samples, suggesting that $BaTiO_3$ and $SrTiO_3$ form a complete solid solution for the whole x range. For $x = 0$ and 0·2, the structure is tetragonal while it is cubic for $x = 0{\cdot}4$, 0·6, 0·8, 0·9, 0·95 and 1. Moreover, a clear shift of the diffraction peaks to higher 2θ values with increasing x can be seen in Fig. 4; an indication of a decrease of the unit cell volume with x. As can be seen in Fig. 5, the lattice constant decreases linearly with increasing x value (for $x = 0$ and 0·2, the average lattice constant $\bar{a} = (a^2c)^{1/3}$ is taken, where a and c are the lattice parameters of the tetragonal cell), this being due to the smaller ionic radius of Sr^{2+} (1·40Å[13,14]) when compared to that of Ba^{2+} (1·60Å[13,14]) and also indicates that the Sr ions are substituting Ba into the lattice.

Figure 6 shows the curves of dielectric permittivity versus temperature for various compositions. The dielectric permittivity curves are sharp and the permittivity maxima temperatures are frequency independent when $x \leq 0{\cdot}8$, while a diffused phase transition is observed for $x = 0{\cdot}9$ and 0·95 and no peaks can be seen for $x = 1$.

From Fig. 6, it can also be seen that as x increases, the three phase transitions shift to lower temperatures, at a shifting rate of 3·3, 2·3 and 1·0 K mol%$^{-1}$ of Sr^{2+}, respectively, in agreement with the previously presented results .[7,15] For $x = 0$, 0·2, 0·4 and 0·6, three sharp peaks, originated from cubic-tetragonal, tetragonal-orthorhombic and orthorhombic-rhombohedral phase transition, respectively, are evident. For $x = 0{\cdot}8$, the three peaks seem to coalesce. The dielectric permittivity maximum at T_c increases with an increase in the x value, reaching the highest value at around $x = 0{\cdot}6$ and then decreases. A maximum T_c permittivity value at $x = 0{\cdot}6$ was previously reported by Smolenskii.[7]

4 Discussion

From X-ray diffraction patterns, it seems that a short time pre-calcination milling-mixing could cause an inhomogeneous distribution of Ba^{2+} and Sr^{2+} ions in the calcined/sintered samples. According to Smolenskii,[12] such an inhomogeneity would cause

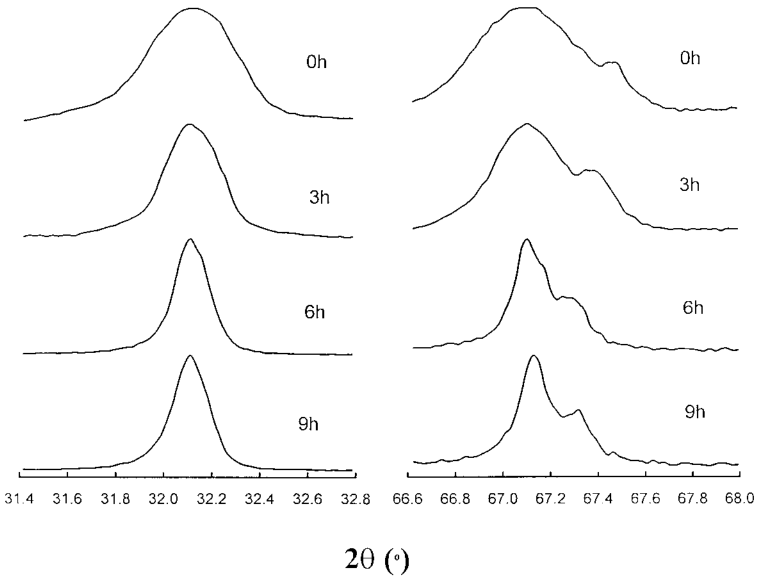

Fig. 3. X-ray diffraction patterns of $Ba_{1-x}Sr_xTiO_3$ ($x = 0{\cdot}6$) for different pre-calcination milling–mixing times.

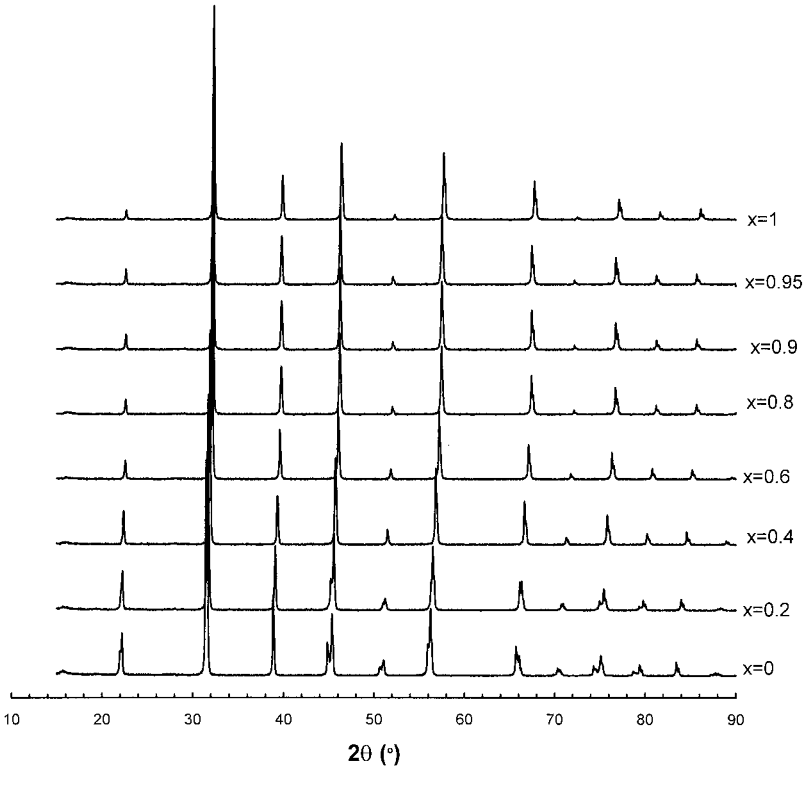

Fig. 4. X-ray diffraction patterns for $Ba_{1-x}Sr_xTiO_3$ compositions.

a distribution of Curie points in different regions and thus a diffuse phase transition. A DPT behaviour was observed for samples mixed for the short times, but not in samples mixed for long periods. These results seem to support the idea proposed by Smolenskii[12] that compositional fluctuations are the origin of DPT behavior and also suggest that the diffuseness observed in the $BaTiO_3$ rich region of the $Ba_{1-x}Sr_xTiO_3$ solid solutions is not an intrinsic property of the solid solution.

Strontium titanate ($SrTiO_3$) is a quantum paraelectric which shows very high dielectric permittivity at low temperature and no ferroelectric phase transition occurs at temperature down to almost 0 K.[16] However, a low temperature relaxation behaviour, similar to that observed in ferroelectric relaxors, has been observed in doped $SrTiO_3$ such as $Sr_{1-x}Ca_xTiO_3$[17] and $Sr_{1-1.5x}Bi_xTiO_3$.[18] A widely accepted viewpoint is that the relaxation of these systems is due to a random field induced domain

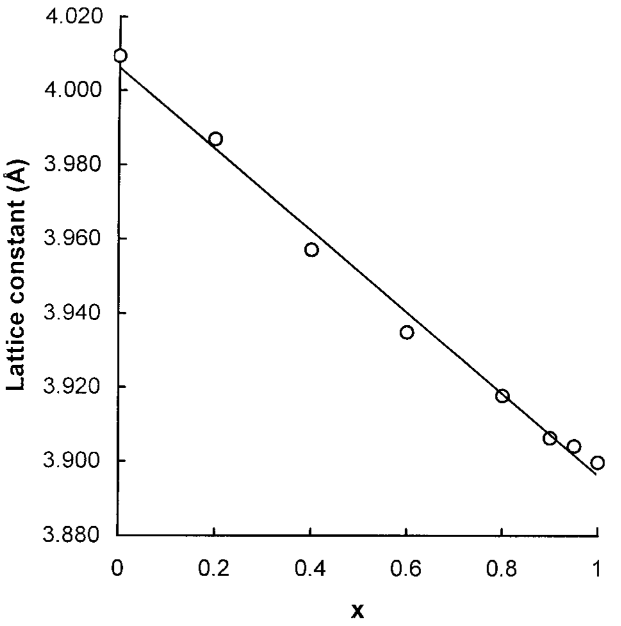

Fig. 5. Concentration dependence of lattice constant for $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions (for $x=0$ and 0·2, the average lattice constant $\bar{a}=(a^2c)^{1/3}$ is taken).

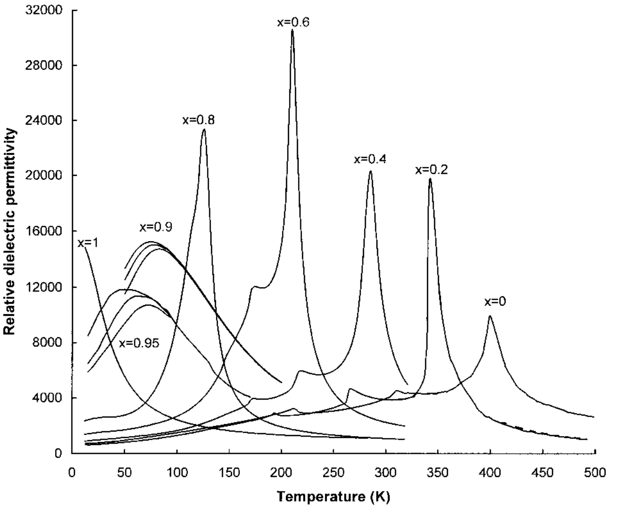

Fig. 6. Relative dielectric permittivity as a function of temperature for $Ba_{1-x}Sr_xTiO_3$ ceramics. For $x=0{\cdot}9$ and 0·95 compositions, the top curve corresponds to 1 kHz, the middle one to 10 kHz and the bottom one to 100 kHz. For the other compositions, the frequency is 1 kHz.

state.[17,18] A similar mechanism was suggested to be the origin of the relaxation behaviour of $KTaO_3$ with impurities such as $K_{1-x}Li_xTaO_3$.[19]

High x value $Ba_{1-x}Sr_xTiO_3$ solid solutions can also be regarded as a barium substitution for strontium in $SrTiO_3$. As shown in Fig. 6, a DPT behavior was observed in the samples with small amount of Ba^{2+} substituting for Sr^{2+}. The relaxation of $Sr_{1-x}Ca_xTiO_3$ and $Sr_{1-1.5x}Bi_xTiO_3$ was interpreted to be due to the off-center location of Ca^{2+} or Bi^{3+} in the Sr^{2+} sites.[17,18] This followed suggestions that the substituting ions, which have smaller ionic radius and greater polarisation forces as compared to the lattice ions, will generally be off-center located. Ca^{2+} and Bi^{3+} ions are in such cases. However, Ba^{2+} has a bigger ionic radius (1·60Å[13,14]) compared to Sr^{2+} (1·40Å[13,14]) and thus should not be an off-center ion. Thus, the observation of a relaxor behavior in $Ba_{1-x}Sr_xTiO_3$ solid solutions in the $SrTiO_3$ rich region can not be attributed to this mechanism. The relaxation mechanism of $Ba_{1-x}Sr_xTiO_3$ is being further studied.

5 Conclusions

The pre-calcination milling–mixing time of raw powders significantly influences the dielectric properties of $Ba_{1-x}Sr_xTiO_3$ solid solutions. A short time milling–mixing could cause compositional inhomogeneity and thus a diffuse phase transition behaviour. More than 6 h of mixing does not appear to improve the compositional inhomogeneity.

Increasing the Sr^{2+} concentration in the $BaTiO_3$-$SrTiO_3$ solid solutions systematically lowers the three phase transition temperatures, at a rate of 3·3, 2·3 and 1·0 K mol%$^{-1}$ of Sr^{2+}, respectively. The dielectric permittivity at T_c increases with increasing Sr^{2+} content, reaching the highest value at 0·6 of Sr^{2+} and then decreases. When $x>0{\cdot}8$, a diffuse phase transition is observed.

Acknowledgements

The authors acknowledge the FCT (Portuguese Foundation for Science and Technology) for financial support and one of us Liqin Zhou thanks Praxis XXI for a maintenance grant.

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