

Structural evolution and polar order in $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$

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We perform a combination of diffraction and diffusion of neutron and high-resolution x-ray experiments on the $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ system as well as dielectric susceptibility and polarization measurements. We show the SrTiO_3 -type antiferrodistortive phase up to a concentration of barium $x_c \approx 0.094$: the progressive substitution of Sr by Ba leads to a monotonic decrease and to a vanishing of the oxygen octahedra tilting. The critical concentration x_c separates the phase diagram in two regions, one with a sole antiferrodistortive phase transition ($x < x_c$) and one with a succession of three BaTiO_3 -type ferroelectric phase transitions ($x > x_c$). Inside the nonferroelectric antiferrodistortive phase a local polarization is observed, with a magnitude which is comparable to the values of the spontaneous polarization observed in the ferroelectric phases of the rich in barium-compounds. In these compounds a relative shift of Ti and Ba from the oxygen skeleton is measured and the spontaneous (long-range) polarization calculated from structural refinements. Its concentration and temperature evolution is in qualitative agreement with the values deduced from our dielectric susceptibility study.

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I. INTRODUCTION

The influence of impurities in incipient ferroelectrics, in which ferroelectricity is suppressed by quantum fluctuations, has been extensively studied. In particular niobium, lithium or sodium (etc.)-doped potassium tantalate KTaO_3 , or calcium-doped strontium titanate SrTiO_3 ,¹ display a dipole glass state for small doping rate and a ferroelectric state above a critical concentration. In these compounds the dipole moment of the off-center ions and the corresponding reorientation dynamic are considered to have a drastic influence upon the properties of these systems. On the other hand, such properties have also been observed when barium is inserted in the structure of SrTiO_3 ,² although the difference in ionic size between Ba and Sr cannot lead to such off-center dipole moments. Therefore, the $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ system appears to be important for the understanding of dipole glasses.

The study of the $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ phase diagram started a long time ago: in 1945 Jackson and Reddish³ reported the unusual dielectric properties of this system. A huge number of papers were reported afterward: for instance, a room-temperature lattice parameter versus concentration study was reported from x-ray experiments by several authors^{4,5} as well as the temperature/concentration dependence of the dielectric properties.^{6,7} Many data were gathered by Barb the authors of Ref. 8, who proposed a tentative phase diagram in 1982.

More recently the $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ system has received lot of attention due to its very promising dielectric properties when used as thin film.⁹ This interest was also motivated by the general wish of replacing lead based perovskites by “cleaner” materials. In this framework the weakening of the dielectric properties when downsizing from ceramics to thin films is less important in $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ than in other lead-free material. In particular, many of studies have been devoted to compounds with concentration in barium close to

0.8, because of a strong value of the dielectric susceptibility at room temperature inside a paraelectric phase, which avoids aging due to ferroelectric domain pinning. This strong value at room temperature is due to the decrease of the tetragonal-cubic Curie temperature when BaTiO_3 is doped with Sr one deals with a technological property directly connected to the knowledge of the structural evolution.

This induced a renewal of interest for these materials and in this context Lemanov *et al.* proposed a phase diagram deduced from ultrasonic and dielectric measurements² and light refraction.¹⁰ Recently an extensive study of the rich in barium region of the phase diagram ($0.7 \leq x \leq 1$), using a combination of x-ray high-resolution diffraction with dielectric measurements has been published (see Ref. 11). In particular the authors of Ref. 11 showed that the diffusivity of the phase transitions was intrinsic and does not arise from compositional inhomogeneities, though they could enhance the smearing.

The purpose of our paper is to report a structural evolution study which combines both neutron (powder diffraction and single crystal inelastic scattering) and high-resolution powder x-ray experiments of the whole phase diagram and to compare it with the papers mentioned above, in order to give further insights on this system. In particular, a comparison of the diffraction results with polarization measurements allows us to discuss local versus long range polar ordering.

II. EXPERIMENT

The conventional dry route of mixing BaCO_3 , SrCO_3 , and TiO_2 in adequate proportions was used for preparation of powders and ceramics. Single crystal grown by a flux method was kindly supplied by Dr. M. Maglione (Lcmcb, Bordeaux, France). The neutron experiments were performed at Laboratoire Léon Brillouin using the Orphée reactor facili-

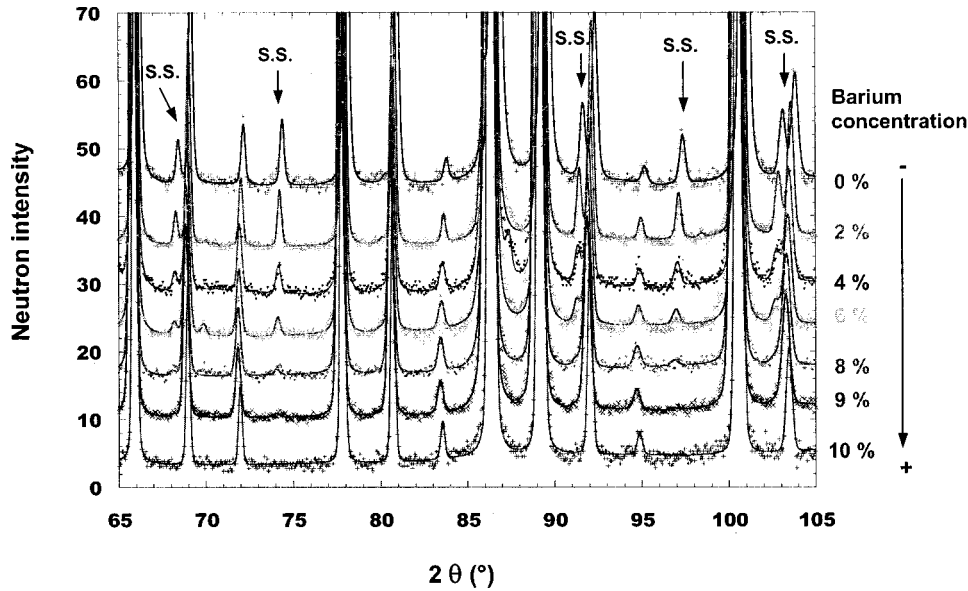


FIG. 1. Neutron powder diffraction patterns for the $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ compounds ($x \leq 0.1$) at 2 K ($\lambda = 1.226 \text{ \AA}$). S.S. refers to superstructure peaks due to the tilting of the oxygen octahedra. The lines are the calculated profiles from the Rietveld analysis.

ties (Saclay, France). Powder diffraction patterns were collected on a high-resolution two-axis diffractometer 3T2 ($\lambda = 1.226 \text{ \AA}$), using steps of 0.05° between 6° and $120^\circ 2\theta$. Inelastic measurements were carried out on the 4F1 triple-axis spectrometer [$k_i = 1.55 \text{ \AA}^{-1}$, with a bent pyrolytic graphite (PG) monochromator, a bent PG analyzer, and a polycrystalline beryllium nitrogen-cooled filter]. X-ray-diffraction studies were performed using a two-axis diffractometer with Bragg-Brentano geometry with $\text{CuK}\beta$ monochromatic radiation from an 18 kW Rigaku rotating anode; patterns were scanned through steps of $0.006^\circ (2\theta)$ with a typical counting time of 15 s up to 120 s. In each case for the low-temperature experiments a He cryostat or closed-cycle cryogenerator with thermal stability of 0.1 K and precision within 1 K was used. Structural Rietveld refinements were carried out with the XND (Ref. 12) program.

The dielectric susceptibility and polarization measurements have been performed using a Hewlett Packard 4192A LF impedance analyzer (5 Hz–13 MHz), a Keithley 617 electrometer, and a He cryostat.

III. EXPERIMENTAL RESULTS

A. Influence of weak substitution of Ba on the structural evolution of SrTiO_3

We have recorded full neutron Rietveld patterns at 300 and 2 K for samples with concentrations of Ba between 0% and 10%. At room temperature all the structures were observed to be cubic, with classical B thermal parameters. At 2 K, as we previously reported¹³ in pure SrTiO_3 we have observed the superstructure peaks associated to the rotation of oxygen octahedra, the intensity of which is decreasing as concentration of Ba increases (Fig. 1). For samples with $0 \leq x \leq 0.09$, these patterns could be refined using as a starting model the tetragonal ferroelastic structure ($14/mcm$ space group) of pure SrTiO_3 . The refinements converged rapidly to good values of R_{wp} and R_B (typically 5.5% and 1.3%) with a typical R_{exp} of 2.3%. No anomalously high values of the B

thermal parameters which could be an indication of some possible disorder (as observed for instance in lead based relaxor compounds¹⁴) were evidenced. The high-resolution x-ray experiments revealed no additional splittings or widenings which could have indicated supplementary distortions (e.g., BaTiO_3 -like).

Clearly, the low-temperature structure of these compounds is tetragonal with a ferroelastic nonferroelectric $14/mcm$ space group. From the structural refinement we have extracted the angle φ of tilting of the oxygen octahedra (Fig. 2). A monotonic diminution is observed when doping with Ba up to a critical concentration extrapolated according to a power law at $x_c \approx 0.094$.

In order to obtain further insights into the structural evolution of the low concentration ($x < x_c$) compounds, in the $\text{Sr}_{0.98}\text{Ba}_{0.02}\text{TiO}_3$ compound we have measured the temperature dependence of the φ angle (from neutron powder diffraction) and of the intensity of the $(\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$ superstructure peak (from a single crystal with a neutron triple-axis spectrometer) (Fig. 3). The critical tetragonal-cubic transition temperature was observed to be $T_{c2\%} = 105(2)$ K. The critical exponents β could be extracted from these evolutions, and were found to be equal to 0.33(1), the same value which is observed in pure SrTiO_3 .¹⁵ Following the work of Refs. 16, 17, etc., an inelastic study of the $\text{Sr}_{0.98}\text{Ba}_{0.02}\text{TiO}_3$ single crystal has been performed. The crystal sample was a colorless cube of 0.5 cm^3 with an effective mosaic spread of 0.4° and was glued in a $(1\bar{1}0)$ plane. Energy scans at $Q = (\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$ have shown a central peak and a soft mode (Fig. 4) with temperature evolutions very similar to the one observed in pure strontium titanate (Refs. 16 and 17), and therefore are not detailed here.

This set of experiments has revealed no change in the mechanism of the cubic-tetragonal phase transition when adding a few percent of barium. Experiments at higher concentrations, i.e., close to x_c should be highly interesting but probably very difficult due to the weakening of the superstructure peaks intensities (Fig. 2).

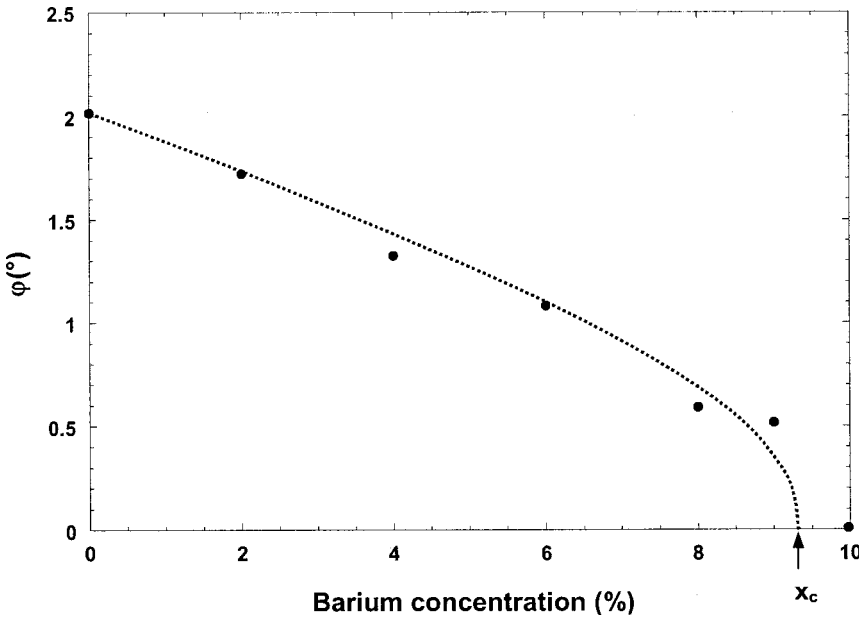


FIG. 2. Tilt angle ϕ of the oxygen octahedra at 2 K deduced from neutron Rietveld refinements. The dotted line [fitted according to a power law $(x - x_c)^{0.5}$] is a guide for eyes.

B. Structural evolution of $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ for a high concentration of Ba ($x > x_c$)

The experiments described above have shown a ferroelastic nonferroelectric phase up to $x_c \approx 0.094$. Using the same combination of neutron and x-ray diffraction on powders we have studied samples with concentrations $x > x_c$ up to $x = 0.5$. In Fig. 5 we plot the temperature evolution of the full width at half maximum (FWHM) for $(h00)$ Bragg peaks for three concentrations. For all samples ($x \geq 0.10$) changes of the FWHM associated with the cubic-tetragonal-orthorhombic-rhombohedral phase transitions could be detected. Indeed the $(h00)$ peaks widen due to the resulting orthorhombic and tetragonal distortions, whereas the (hhh) peaks widen only inside the rhombohedral phase. When Sr is substituted into the structure of BaTiO_3 , these results indi-

cate a progressive decrease of all critical temperatures as well as a decrease of the different distortions associated to the different ferroelectric phases.

Inside each ferroelectric phase we have performed a neutron powder data collection for several concentrations. We have refined the data using as starting models those of the three ferroelectric phases of pure BaTiO_3 from Ref. 18, with $R3m$ (rhombohedral), $Amm2$ (orthorhombic), and $P4mm$ (tetragonal) space groups. The Rietveld refinements also converged rapidly to good values of R_{wp} and R_B . From the structural refinements we could calculate the magnitude of the polarization using the apparent charges from Hewat.¹⁹ The results (Fig. 6) indicate a monotonic decrease and convergence of the different polarizations with decreasing content of barium, down to the critical concentration x_c , where all the values collapse to zero.

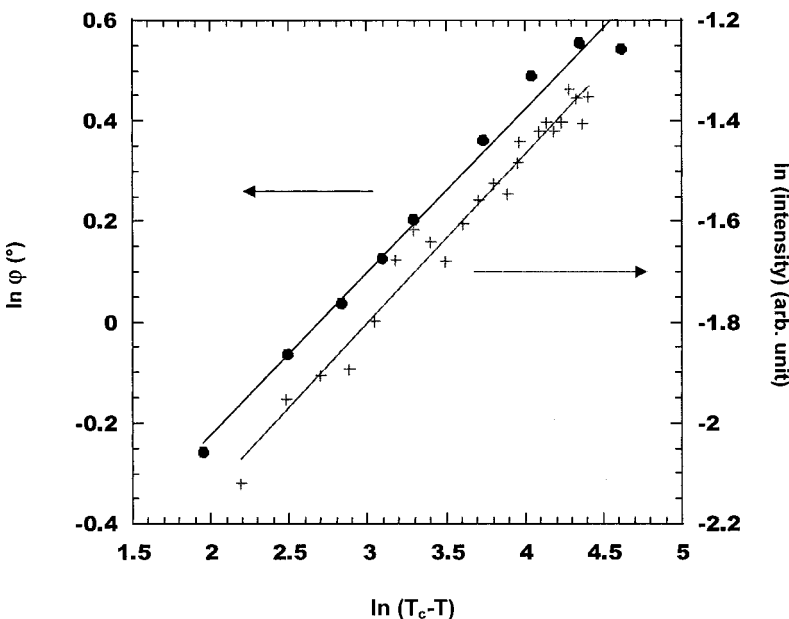


FIG. 3. Intensity of the $(\frac{1}{2} \frac{1}{2} \frac{3}{2})$ superstructure peak and tilt angle ϕ of the oxygen octahedra for the $\text{Sr}_{0.98}\text{Ba}_{0.02}\text{TiO}_3$ single crystal and powder sample respectively, as a function of temperature.

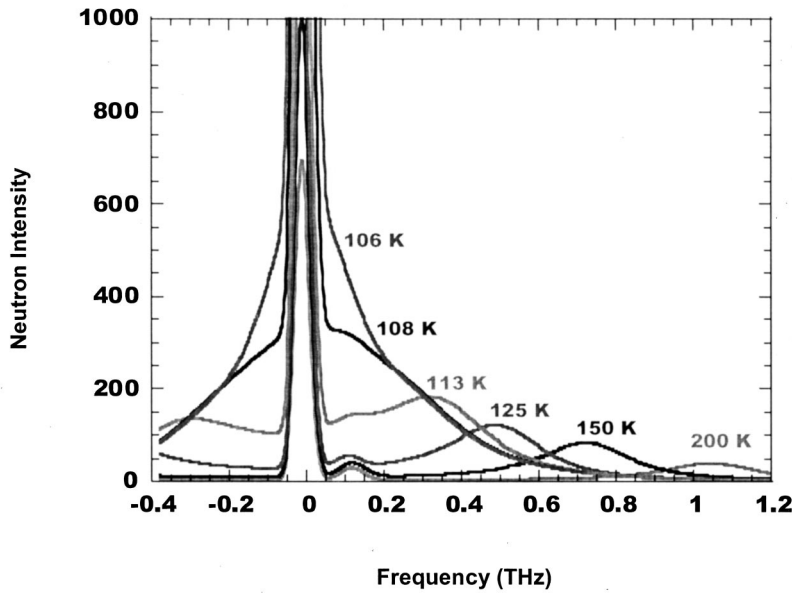


FIG. 4. Neutron inelastic scans showing the soft mode and the central peak of the $\text{Sr}_{0.98}\text{Ba}_{0.02}\text{TiO}_3$ crystal (the weak mode near 0.1 THz is a spurious temperature-independent effect).

C. Dielectric susceptibility, polarization in the nonferroelectric and ferroelectric phases

Dielectric properties and polarization measurements of $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ have been reported and discussed many times. In particular the diffuse character of the temperature dependence of the ϵ dielectric susceptibility has been pointed out.^{6,7,11} In the present study we want to compare these properties when the concentration of Ba is increased from the nonferroelectric compounds ($x < x_c$) to the ferroelectric compounds ($x > x_c$).

Regarding quantum, glassy, and conventional paraelectrics and ferroelectrics, an accurate description of the susceptibility data has been achieved by Dec and Kleeman.²⁰ Indeed these authors have shown that one should use a generalization of the classical Barrett formula by changing the temperature scale and use

$$\epsilon = \frac{C}{(T^Q - T_0^Q)^\gamma} + B,$$

where the quantum temperature scale $T^Q = T_S \coth(T_S/T)$ replaces the real temperature, C is the Curie constant, B is independent of the temperature, T_S is the saturation temperature related to the ground state energy of the quantum oscillator, T_0^Q is the quantum critical temperature, and γ is the exponent of the susceptibility. This formula (which has been justified in Ref. 21) reduces for high temperatures (i.e., $T_0^Q \gg T_S$) to the classical law for “dirty” ferroelectrics,

$$\frac{1}{\epsilon} = \frac{(T - T_m)^\gamma}{C} + \frac{1}{\epsilon_m}, \tag{1}$$

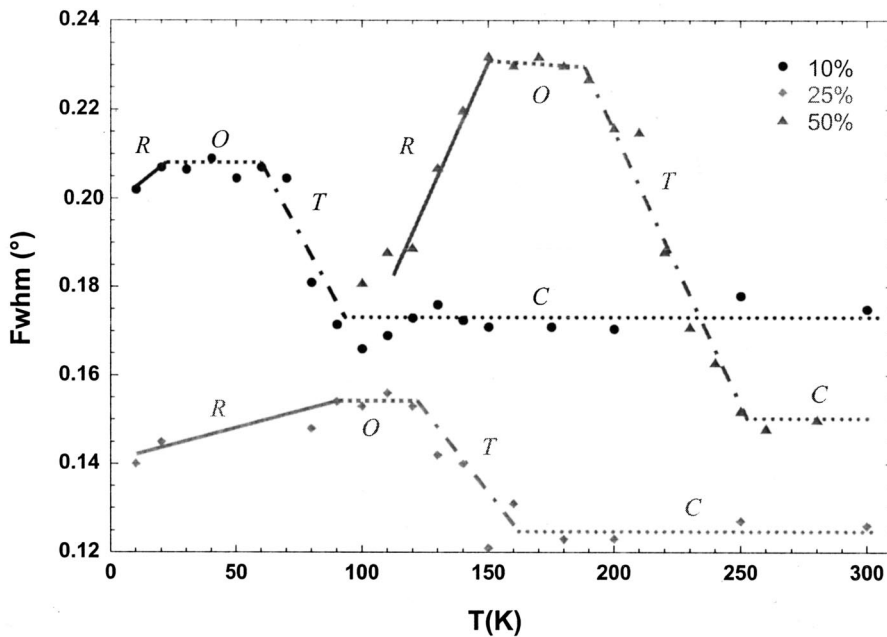


FIG. 5. Full width at half maximum vs temperature for the (200) peaks ($x=0.5$ and 0.25) and the (400) peak ($x=0.1$). Slope changes indicate the ferroelectric transition temperatures, and are in agreement with the evolution of the (hhh) peaks (not shown). The initials C, T, O, and R indicate the cubic, tetragonal, orthorhombic, and rhombohedral phases, respectively.

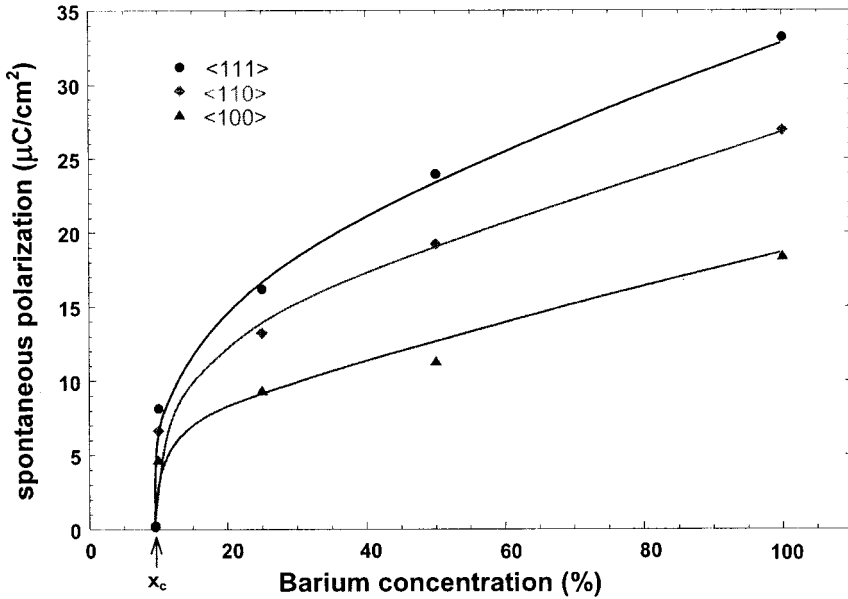


FIG. 6. Spontaneous polarizations for the $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ compounds ($x=1, 0.5, 0.25,$ and 0.1) calculated from the neutron Rietveld refinements.

with T_m the temperature of the maximum of the dielectric susceptibility ϵ_m , $\gamma=1$ for classical ferroelectrics and $1 \leq \gamma \leq 2$ for dirty or diffuse ferroelectrics. In the case of pure SrTiO_3 , it is well known that $\gamma \cong 2$; on the other hand, the authors of Ref. 11 showed that $\gamma=1.10$ in pure BaTiO_3 ($x=1$), and increases linearly up to 1.8 for $x=0.80$, but this result is in contradiction with the result by Lemanov *et al.*,² who reported γ values equal to 1 for the whole range $x \geq 0.12$. Therefore, we have performed a fitting of our ceramics high temperature susceptibility data with formula (1): the usual procedure consists in extracting γ from the linear part of the plot $\ln(1/\epsilon - 1/\epsilon_m) = f[\ln(T - T_m)]$. The results (Fig. 7) have confirmed a $\gamma=2$ value (within the precision of measurement) in the whole range of concentration studied ($0 \leq x \leq 0.5$) in agreement with Ref. 11.

In the second part of this study we are interested in comparing the magnitude of the local (short-ranged) polarization detected in the (nonferroelectric) ferroelastic phase with the spontaneous (long-ranged) polarization of the true ferroelectric phases. For the polarization measurements we have first used the conventional method based on the integration of the pyroelectric current (Fig. 8). However, this method is supposed to apply in ceramics to relatively high electric fields (up to 5 kV/cm). In the case of SrTiO_3 there are contradictory reports regarding the effect of an electric field: on the one hand, Hemberger *et al.*²² reported an electric-field-induced phase on the basis of dielectric measurement; on the other hand, Worlock and Fleury²³ reported, in Raman experiments, the hardening under electric field of the TO-phonon mode which should soften at zero field in absence of quan-

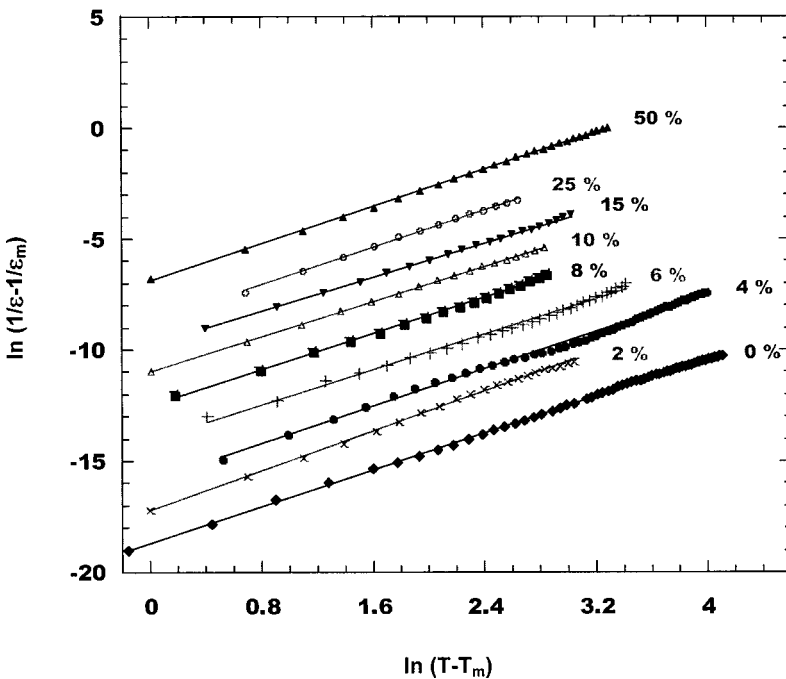


FIG. 7. Linear part of the variation of $\ln(1/\epsilon - 1/\epsilon_m)$ with $\ln(T - T_m)$, measured at $f = 10$ kHz. The curves are shifted on the ordinate axis for the clarity and give a critical exponent γ close to 2 ± 0.2 for all the samples. ϵ_m is the maximum value of the dielectric susceptibility obtained at $T = T_m$.

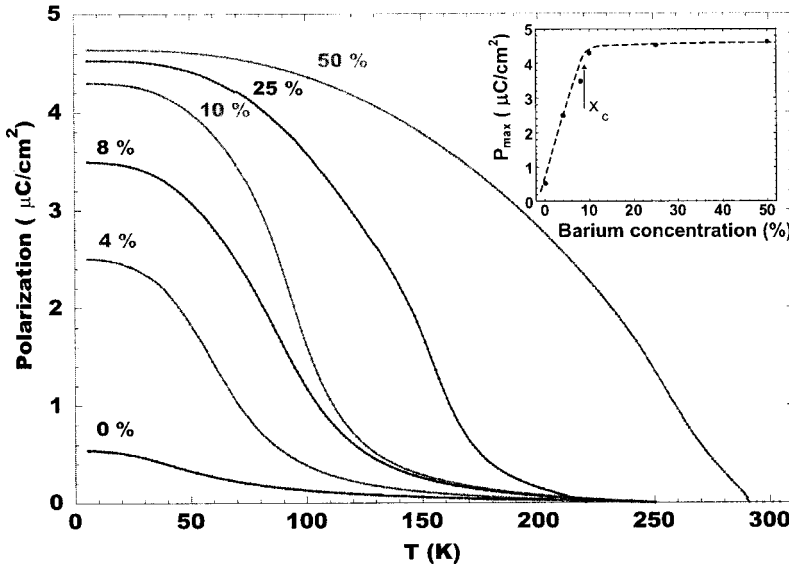


FIG. 8. Values of polarizations stemming from pyroelectric measurements at $f=10$ kHz. The inset shows the maximum of polarization P_{\max} as a function of the barium concentration.

tum fluctuations. We have recently clarified this problem by combining x-ray experiments and second-harmonic generation microscopy under electric field which showed the absence of long-range polar order²⁴ in SrTiO₃ under an electric field. However, as the effects of electric fields have not been studied in Ba-doped SrTiO₃, we have also extracted the polarization from our set of ceramics dielectric susceptibility measurements, because this kind of experiments is performed at very low field; in this way we ensure any high electric field effect on the Sr_{1-x}Ba_xTiO₃ system.

Following the common procedure initiated in PbMg_{1/3}Nb_{2/3}O₃ by Burns and Dacol²⁵ in the measurement of refractive index, by Darlington²⁶ in the lattice parameter expansion of Pb_{1-x}La_x(Zr_{1-y}Ti_y)_{1-x/4}O₃ (PLZT), and by Kirsch, Schmitt and Müser²⁷ in the measurement of the dielectric susceptibility ϵ of PLZT the deviation from simple Curie laws below a T_d temperature is supposed to arise here from the existence of local dipoles (the limits of this modeling was discussed by Viehland *et al.*²⁸). Therefore, from the measurement of the dielectric susceptibility ϵ , we have extracted the temperature dependence of the polarization from the laws

$$\frac{1}{\epsilon} = \frac{T-T_0}{C} + g^* \langle P_{\text{loc}}^2 \rangle \quad \text{for } T > T_c$$

$$\frac{1}{\epsilon} = \frac{2(T-T_0)}{C} + g^* \langle P_s^2 \rangle \quad \text{for } T < T_c,$$

in which C is the Curie constant, T_0 the Curie temperature, T_c is the critical temperature of the ferroelectric phase transitions ($T_c=0$ for $x < x_c$), g^* is the coupling constant (related to the quadratic electro-optic tensor; see Ref. 27) which is unknown in the case of Sr_{1-x}Ba_xTiO₃, and P_{loc} and P_s are the local (nonzero below T_d) and spontaneous polarizations.

The Curie constants and temperatures are classically determined by a linear fitting and extrapolation of the high-temperature data for which P_{loc} is zero. The quantity $\sqrt{g^* \langle P^2 \rangle}$ is plotted vs temperature and concentration in Fig. 9.

The measurements of polarization via the pyroelectric current (Fig. 8) and via the dielectric constant (Fig. 9) give qualitatively the same results. In pure SrTiO₃ a weak but

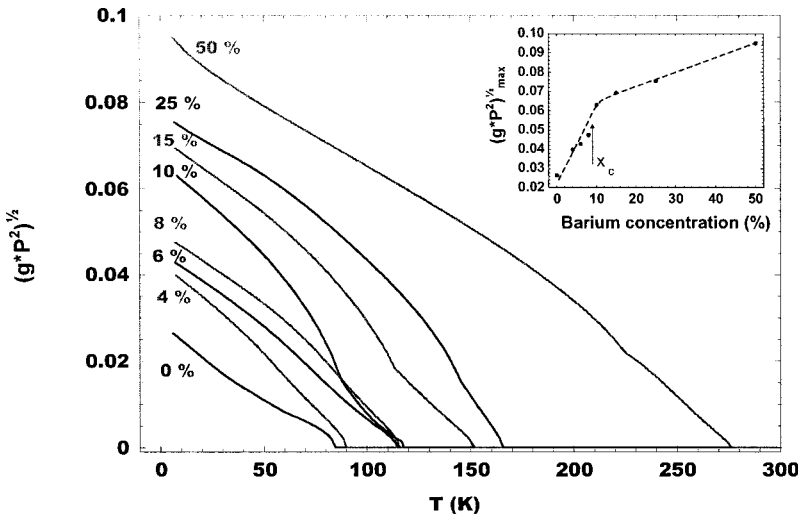


FIG. 9. $\sqrt{g^* \langle P^2 \rangle}$ vs temperature and concentration (where g^* is the coupling constant related to the quadratic electro-optic tensor). The inset is the maximum of $\sqrt{g^* \langle P^2 \rangle}$ vs barium concentration.

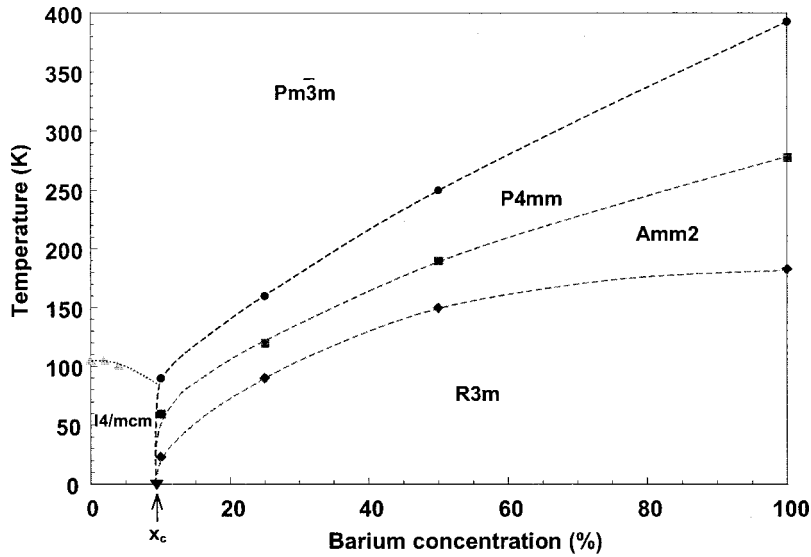


FIG. 10. Critical temperature vs concentration phase diagram of $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$, deduced from our x-ray and neutron-diffraction studies. The critical temperatures for BaTiO_3 are derived from the literature (Ref. 35).

nonzero P polarization, already reported by several authors,²² is evidenced at low temperature and continuously increases with decreasing temperature up to a P_{\max} value (Fig. 8). When substituting Ba for Sr the polarization P_{\max} increases: at a concentration close to x_c , P_{\max} is about 7.5 times the value observed in pure SrTiO_3 . For compounds with higher concentrations of Ba, i.e. $x > x_c$, a local polarization is still observed, which transforms at lower temperature ($T < T_c$) into the spontaneous polarization P_s associated with the onset of the ferroelectricity. The spontaneous polarization P_{\max} is still increasing with the concentration of Ba, but its magnitude remains comparable to that of the local polarization observed in the concentration range $x < x_c$. Indeed, the polarization P_{\max} show no discontinuity at x_c , but saturate for $x > x_c$ (inset of Fig. 8). All these results are also observed in the measurements of polarization via a dielectric constant, i.e., a local polarization in the concentration range $x < x_c$ (Fig. 9) with no discontinuity in the concentration evolution when the polarization becomes spontaneous ($x > x_c$) (inset of Fig. 9). These data are in qualitative agreement with those from Refs. 10 and 29, whose authors extracted the polarization from temperature dependence of the index of refraction; however, our conclusions are slightly different (see below, in Sec IV). In addition, the spontaneous polarizations calculated from the Rietveld analysis (Fig. 6) are in qualitative agreement with the evolution observed for $x > x_c$ via dielectric and pyroelectric measurements. However, the latter values are weaker as they are obtained on ceramic samples whereas the values deduced from Rietveld should be equivalent to those measured in a perfectly monodomain single crystal.

IV. SUMMARY AND DISCUSSION

Thanks to the neutron diffraction, we have evidenced the SrTiO_3 -type antiferrodistortive phase up to a concentration of barium $x_c \approx 0.094$: the progressive substitution of Sr by Ba leads to a decrease and vanishing of the oxygen octahedra tiltings. The critical concentration x_c which separates the phase diagram in two regions (Fig. 10), one with a sole an-

tiferrodistortive phase transition and the other with a succession of three ferroelectric phase transitions, is in good agreement with the value proposed in Ref. 8 and also in Ref. 7 ($x_c \approx 0.1$), but is much stronger than that ($x_c \approx 0.035$) proposed by Lemanov *et al.*² We believe that in the latter study this value has been underestimated as it results from combination of indirect methods, i.e., dielectric and ultrasonic measurements. In pure SrTiO_3 it was obvious for a long time that dielectric anomalies are not obligatorily associated to onset of ferroelectric phase transitions: the authors of Ref. 11, and this present work have demonstrated this fact for the $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ system. Moreover elastic constants measurements on pure SrTiO_3 , by Scott and Ledbetter³⁰ have shown some anomalies at temperatures below 105 K, which are not indicative of a true structural ferroelectric phase transition but rather interpreted in terms of dynamics. In our opinion, diffraction is more relevant than macroscopic measurements to detect structural changes.

Inside the nonferroelectric antiferrodistortive phase and below a T_d temperature a local polarization is observed with a magnitude comparable to the values of spontaneous polarization observed in the ferroelectric phases of the rich in barium compounds, i.e. with $x > x_c$. In these compounds we have observed BaTiO_3 -type atomic displacements i.e., relative shifts of Ti and Ba from the oxygen skeleton which lead to the spontaneous (long range) polarization. We have calculated these polarizations from our structural results. The concentration and temperature evolution is in qualitative agreement with our measurements deduced from the pyroelectric current and dielectric susceptibility study: the lower the temperature, the higher the polarization, and the higher the concentration of Ba, the higher the polarization. In the $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ system, these ferroelectric shifts are incompatible with the rotation of the oxygen octahedra, at least on a long-range order: we never observed compounds which displayed both types of displacements, which can be observed, for instance, in the $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ system.³¹

However at low temperature a local (short ranged) polarization is observed for $x < x_c$; furthermore Lemanov *et al.*² reported a glassy state in this part of the phase diagram. It is

thus possible that disordered shifts with short correlation lengths exist in addition to the octahedra rotations, but we could not evidenced them from the structural refinements: in particular no strong B parameter value (which could be associated to disordered atoms shifting^{14,32}), nor diffuse scattering intensity, as classically observed in the study of relaxor compounds³² could be evidenced.

V. CONCLUSION

In their study of the $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ system (with $x \geq 0.70$), the authors of Ref. 11 proposed a picture in which the progressive introduction of Sr inside BaTiO_3 induces a progressive breaking of the ferroelectric state toward mesoscopic random-field domains and eventually to a glassy state with dipolar clusters. The existence of a glassy state was also proposed by Lemanov *et al.*² in a weak in a Ba range of concentration ($x < 0.035$). We believe that our diffraction experiments have allowed us to specify to some extent the limit of existence between the short- and long-range polarizations. From a crystallographic point of view we have shown only two concentrations ranges: a low Ba concentration range ($x < 0.094$) with a phase characterized by SrTiO_3 -like tilting of oxygen octahedra and a high concentration range with BaTiO_3 -like shifts. For $x < x_c$ the $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ compounds may be called “incipient” ferroelectric and become a “true” ferroelectric compounds for higher Ba concentrations. These results give the limit for the existence of the macroscopic or mesoscopic spontaneous polarization which is associated to the “true” ferroelectric phases.

However, many different signatures of local polar order or disorder have been evidenced by several authors and our dielectric polarization results are coherent with this large set of data, in particular the high value for γ and the existence of

strong local polarization. From this point of view the situation has some similarities with the one encountered in $\text{PbMg}_{1/3}\text{Nb}_{2/3}/\text{PbTiO}_3$ (Ref. 32) (PMN/PT) and $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (Ref. 14) (PSN) relaxors: indeed in these systems (above a critical concentration of PT in the case of PMN/PT) one deals with compounds which manifest a long-ranged polarization component associated to a ferroelectric phase but which also display a disordered (short-ranged) component along the plane perpendicular to this polarization. However as pointed out in Ref. 11 an important difference is the fact that in $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ there is a frequency dispersion of the dielectric properties which is much weaker than in relaxors and which is essentially Debye-like. Clearly further works are needed to understand the structural nature of the polar order or disorder in the $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ system. Probably an important step should be to perform studies of the temperature dependence of the nonlinear dielectric susceptibility, as performed in the $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ system.³³

Finally, we want to stress the interest of the study of such a system in the whole range of substitution. Indeed, on the one hand, when one introduces a small amount of Sr in the structure of BaTiO_3 one has the physical picture, similar to lithium or sodium inside the structure of KTaO_3 , of local dipole moments induced by off-center positions. On the other hand, introduction of a small concentration of Ba in the structure of SrTiO_3 cannot directly induce dipole moments, as Ba is a larger ion than Sr; one has to put forward the existence of quadrupole moments which are supposed to arise from elastic strains induced by ion size mismatch.² Therefore, a complete picture of the whole diagram is still lacking. We believe that regarding structural data, a further step could be achieved through an anharmonic study, as we have performed in lead perovskites;³⁴ however, this requires very high Q data collection of excellent quality.

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