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A perovskite ceramic of composition $Ba_{0.92}Ca_{0.08}(Ti_{0.75}Zr_{0.25})O_3$ with both ferroelectric and relaxor properties

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Dielectric, pyroelectric current and X-ray diffraction studies have been performed on a ceramic of composition $Ba_{0.92}Ca_{0.08}(Ti_{0.75}Zr_{0.25})O_3$ belonging to the $BaTiO_3$–$BaZrO_3$–$CaTiO_3$ ternary diagram. A spontaneous classical ferroelectric–relaxor transition was evidenced at $T = 210$ K. Such behaviour has been reported previously in other perovskite relaxors (PSN, PST, …). This lead-free ceramic is suitable for dielectric applications in capacitors and actuators because it is environmentally friendly.

Introduction

In perovskites, relaxor behaviour occurs dominantly in lead-based compositions (PMN, PSN, PST, PLZT, …), more than one type of ion occupying the equivalent six-coordination number (C.N.) crystallographic site.[1] Lead-free compositions could be of great interest for environmentally-friendly applications (dielectric for capacitors, actuators, …). Studies have been performed in particular on ceramics with $BaTiO_3$-derived compositions.[2–6]

A recent study of the $BaTiO_3$–$BaZrO_3$–$CaTiO_3$ (BT–BZ–CT) system showed the existence of three zones with different behaviours[7] (Fig. 1).

In zone I, there are three dielectric anomalies corresponding to phase transitions:

rhombohedral $T_1 \rightarrow$orthorhombic $T_2 \rightarrow$tetragonal $T_3 \rightarrow$cubic

as is the case for $BaTiO_3$.[3,5]

In zone II, there is only one phase transition:

rhombohedral $T_C \rightarrow$cubic

In zone III, there is only one broad peak of the two permittivities ε_r' and ε_r'' at T_m. The value of T_m depends on the frequency, as is the case for a ferroelectric relaxor.

In addition, for compositions corresponding to a wide boundary between zones II and III (Fig. 1), there is still a maximum of ε_r' at T_m, but in addition there is the appearance of a classical ferroelectric phase at $T < T_3$, when the temperature is $< T_m$. Such a type of transition at T_3 which occurs spontaneously (without applied electric field) was previously observed in other lead-containing relaxors: PSN, PST, PMN–PT solid solution, ….[8–10] The various kinds of transition sequences are shown on a particular composition line $Ba_{0.90}Ca_{0.10}(Ti_{1-0.90x}Zr_{0.90x})O_3$ identified in Fig. 1. The variation of the corresponding temperature *vs.* x is plotted in Fig. 2.

The aim of the present work was to study in detail the dielectric and structural properties corresponding to the temperature sequence including T_3 and T_m. Such a study was performed on a ceramic belonging to the wide boundary between zones II and III (Fig. 1). The selected composition $Ba_{0.92}Ca_{0.08}Ti_{0.75}Zr_{0.25}O_3$ is marked as point A in Fig. 1. Three methods of investigation were used: dielectric, thermocurrent and X-ray diffraction measurements.

A recent dielectric study was also performed on $(Ba_{1-x}Ca_x)(Ti_{1-y}Zr_y)O_{3-\delta}$ ceramics doped with various donors or acceptors. The authors also claimed that such compositions exhibited frequency relaxation effects similar to the relaxor effect.[11]

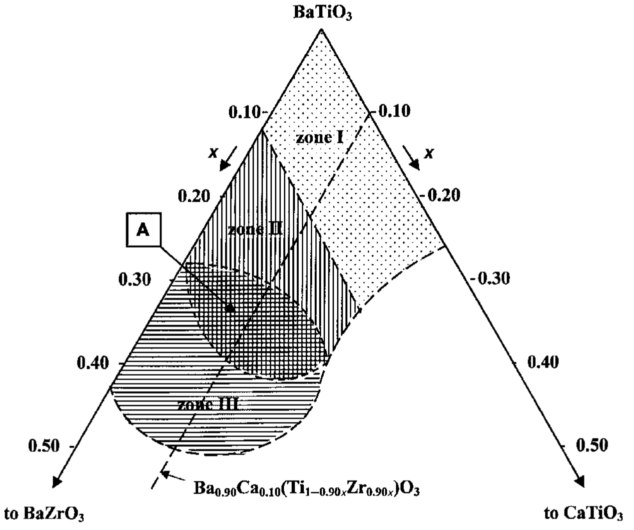

Fig. 1 Schematic representation of the $BaTiO_3$–$BaZrO_3$–$CaTiO_3$ ternary diagram.

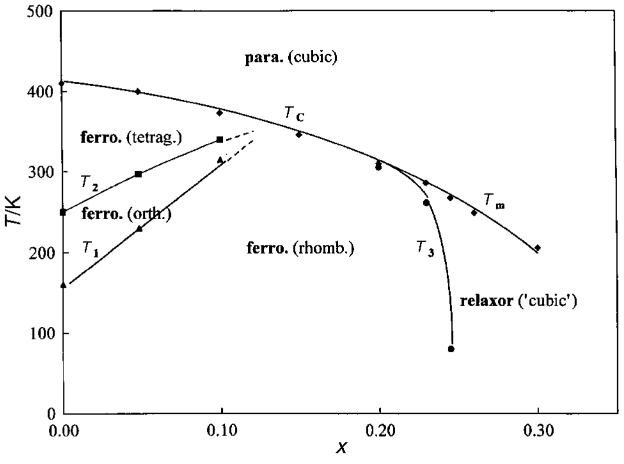

Fig. 2 Variation of transition temperatures with composition for ceramics of the $Ba_{0.90}Ca_{0.10}(Ti_{1-0.90x}Zr_{0.90x})O_3$ solid solution.

Experimental

The various compositions of the BT–BZ–CT ternary diagram were obtained from $CaCO_3$ (Cerac 99.9%), $BaCO_3$ (Cerac 99.9%), TiO_2 (Aldrich 99.99%) and ZrO_2 (Aldrich 99.99%) by solid state reaction:

$$0.08\ CaCO_3 + 0.92\ BaCO_3 + 0.75\ TiO_2 + 0.25\ ZrO_2 \rightarrow Ba_{0.92}Ca_{0.08}(Ti_{0.75}Zr_{0.25})O_3 + CO_2$$

After calcination at 1200 °C for 15 h under oxygen, pressed pellets (8 mm diameter and *ca.* 1 mm thickness) were sintered at 1400 °C for 4 h always under oxygen atmosphere.

X-Ray measurements were performed on a prototype two-axis goniometer (Bragg–Brentano geometry), using a (Cu-Kβ) rotating anode generator of 18 kW, at the Ecole Centrale, Paris (Laboratoire de Chimie-Physique du Solide).[10] A cryofurnace was used with a temperature stability of *ca.* 0.5 K.

Diameter shrinkages $\Delta\Phi/\Phi$ were systematically determined as $(\Phi_{\text{init.}} - \Phi_{\text{final}})/\Phi_{\text{init.}}$. Microstructure studies were performed by scanning electron microscopy (SEM) (JEOL JSM-840A).

Dielectric measurements were performed on ceramic disks after deposition of gold electrodes on the circular faces by cathodic sputtering. The real part of the relative permittivity ε_r' was determined under helium as a function of both temperature (77–550 K) and frequency (10^2–2×10^5 Hz) using a Wayne-Kerr 6425 component analyzer.

A pyroelectric study was performed on the same sample as that used for the dielectric study. Before measurements, it was poled using a dc electric field of 10 kV cm^{-1} from 300 to 77 K and then short-circuited for several hours. The poled ceramic specimen was put in a metal cell under dry helium and heating–cooling cycles were performed at a rate close to 4 K min^{-1}. The pyroelectric charges were measured with a 610C Keithley electrometer from 77 to 400 K. The value of the primary pyroelectric coefficient was calculated from the relation: $p(T) = i(T)/sb$ where $i(T)$ is the current, s is the surface area of an electrode and $b = dT/dt$ the heating (+) or cooling (−) rate. The thermal variation of the apparent spontaneous polarization of the sample was then calculated by integration of the thermal variation function of p *vs.* T according to the relation: $P_s(T) = \int_{+\infty}^{T} p(u)\,du$, where u is the current value of the temperature.

Results

Dielectric study

The density of the ceramic was *ca.* 98% of the calculated value with a grain size in the range 5–10 μm.

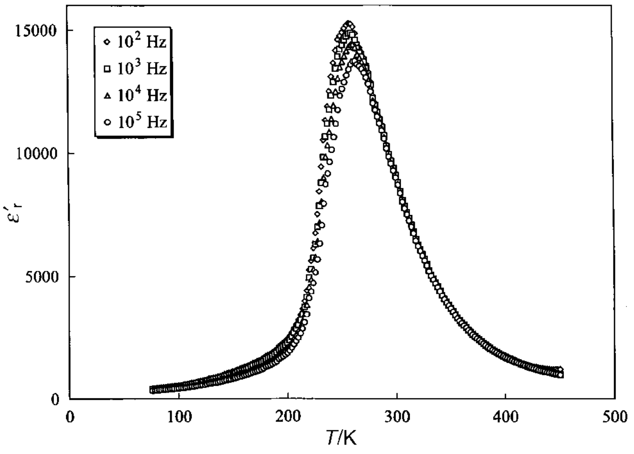

Fig. 3 Thermal variation of the real part of the permittivity ε_r' for a ceramic with composition corresponding to point A in Fig. 1.

The temperature dependence of the permittivity ε_r' showed a relatively broad maximum at $T_m \approx 255$ K at 10^3 Hz (Fig. 3). On cooling from 450 K, a frequency dispersion appeared at $T = T_m$. In addition, there was an increase in T_m when the frequency was increased. Such a behaviour is of relaxor type. However, the frequency dispersion disappeared with a further decrease in temperature to values significantly below T_m, thus implying the corresponding low temperature phase ($T < T_3 = 210$ K) to be of classical ferroelectric type. This corresponds to a sequence like that found for PSN, PST, … where there is a spontaneous (without application of an electric field) ferroelectric–relaxor transition at T_3.[8–10]

The frequency dispersion of ε_r' showed a relatively high value of ε_r'' for the relaxor phase ($T = 250$ K $< T_m$); by contrast, ε_r' did not vary with frequency and ε_r'' was very weak when $T = 300$ K $> T_m$ (Fig. 4). Deviation from the Curie–Weiss law occurred for $T_0 > T_m$ (Fig. 5).

The temperature dependence of the relative frequency dispersion $\Delta\varepsilon_r'/\varepsilon_r' = [\varepsilon_r'(10^2\ \text{Hz}) - \varepsilon_r'(10^4\ \text{Hz})]/\varepsilon_r'(10^3\ \text{Hz})$ clearly revealed a peak at a temperature close to T_m (Fig. 6). All these experiments were performed on a pristine sample and were in agreement with the above-mentioned transition sequence.

A new series of experiments was performed on the same sample but after initial poling under a dc electric field, $E = 10$ kV cm^{-1} from 300 to 70 K. The temperature dependences of ε_r' and ε_r'' were relatively close to those previously obtained without poling. However, as shown in Fig. 7,

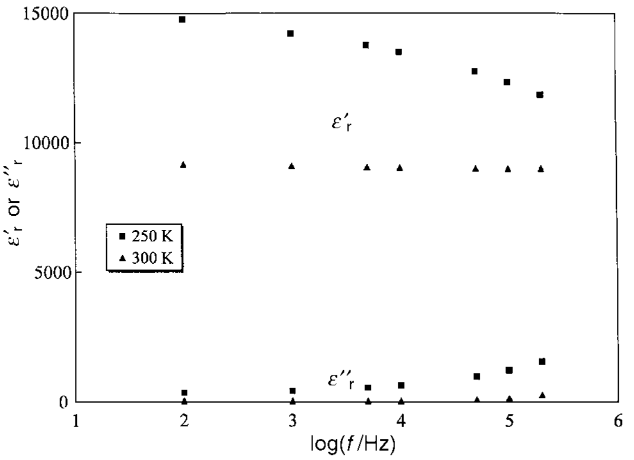

Fig. 4 Frequency dependences of the permittivities ε_r' and ε_r'' for a ceramic with composition corresponding to point A in Fig. 1.

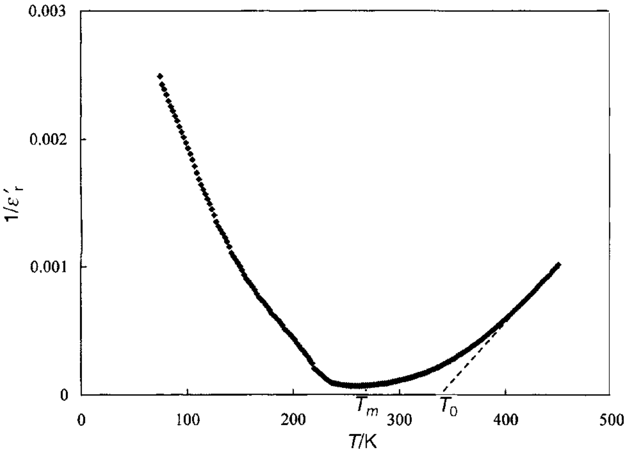

Fig. 5 Thermal variation of the inverse of the real part of the permittivity $1/\varepsilon_r'$, at 10^3 Hz for a ceramic with composition corresponding to point A in Fig. 1.

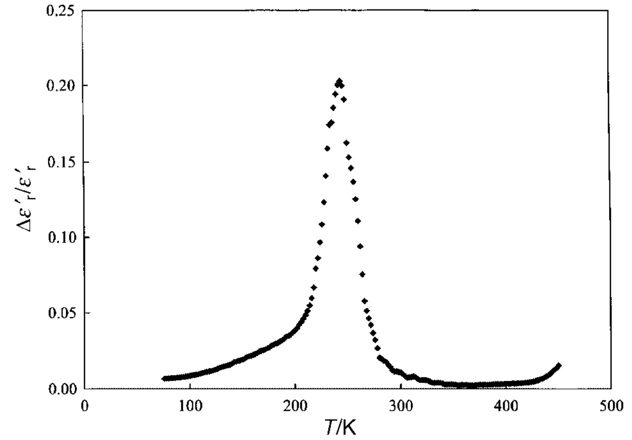

Fig. 6 Thermal variation of $\Delta\varepsilon_r'/\varepsilon_r' = [\varepsilon_r'(10^2\text{ Hz}) - \varepsilon_r'(10^4\text{ Hz})]/\varepsilon_r'(10^3\text{ Hz})$ for a ceramic with composition corresponding to point A in Fig. 1.

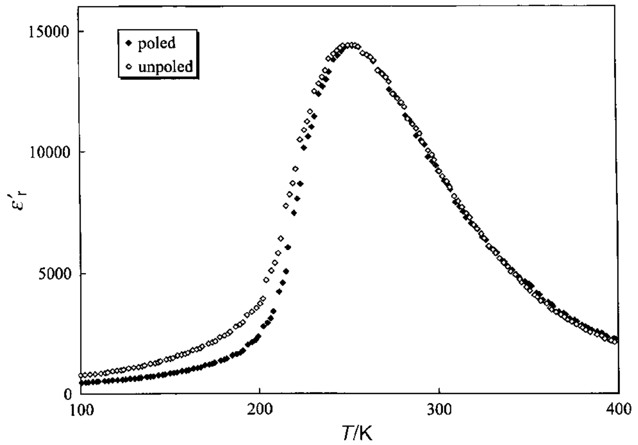

Fig. 7 Thermal variation of the real part of the permittivity ε_r' for a poled or unpoled ceramic with composition corresponding to point A in Fig. 1.

although there was a good concordance for $T > T_3$, there was a significant difference for temperatures lower than T_3, thus implying the ferroelectric phase to be more dependent on poling. Such a behaviour for $T < T_3$ is probably related to the orientation of the ferroelectric domains by the dc electric field.

Pyroelectric study

The temperature dependences of both the pyroelectric coefficient calculated on heating and the apparent spontaneous polarization are shown in Fig. 8.

The material appears to be pyroelectric from 80 to *ca.* 350 K. The sample could be polarized at 77 K. Its polarisation could also be reversed so implicating ferroelectric behaviour. A sharp peak of p close to 100 K led to an anomalous response for P_s which was further studied. In addition, numerous sudden intensity spikes were recorded between 100 and 200 K during sample heating; they could not be plotted on the calculated thermal variation of p in Fig. 8; such peaks are referred to as Barkhausen jumps and correspond to a re-orientation of the ferroelectric domains, as has been observed in a PMN–PT compound.[12] The strong and sharp current peak around 200 K which leads to a steep decrease in spontaneous polarization could be due to a decrease in the ferroelectric distortion in the lattice structure on heating. At higher temperatures, a progressive decrease in p occurred, along with a decrease in P_s with increasing temperature. This can be attributed to a complete randomization of the arrangement of the dipoles.

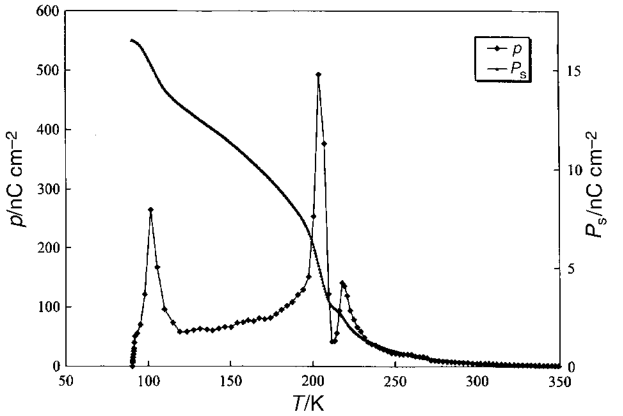

Fig. 8 Thermal variations of the pyroelectric coefficient p and spontaneous polarization P_s for a ceramic with composition corresponding to point A in Fig. 1.

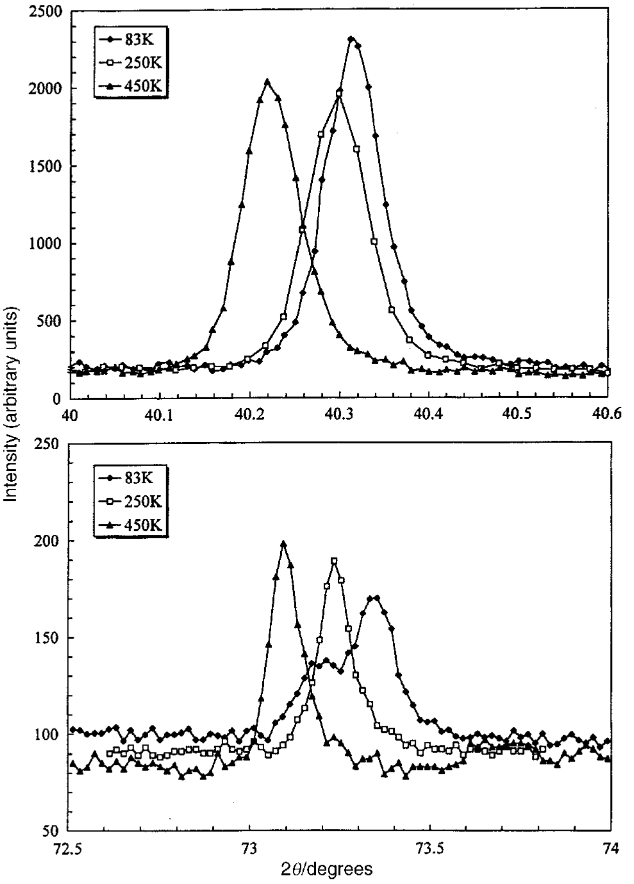

Fig. 9 The 200_c (a) and 222_c (b) cubic reflections at different temperatures. The splitting of 222_c is evident at 83 K.

X-Ray diffraction study

The cubic reflections 111_c, 200_c, 220_c, 222_c and 400_c were recorded at 450 K *i.e.* far above T_m 250 K, *i.e.* just below T_m (10^3 Hz) and at 83 K, *i.e.* below T_3.[13] At 450 K, the structure was cubic with a cell parameter $a_c = 4.050(1)$ Å. At 250 K, it was also cubic with $a_c = 4.043(1)$ Å. At 83 K, as shown in Fig. 9, the 222_c peak was split, but there was no significant increase of the full width at half maximum (FWHM) of the 200_c and 400_c reflections. These results are consistent with a rhombohedral symmetry at 83 K, a fit of all measured reflections leading to $a_r = 4.040(2)$ Å and $\alpha = 89.93(2)°$.

Discussion

Substitution of Ti by Zr in the well known classical ferroelectric $BaTiO_3$ leads to a decrease in the Curie temperature which is related to the fact the ionic radius of Zr^{4+} is greater than that of Ti^{4+}.[4,14] For instance, the value of T_C for the composition $Ba(Ti_{0.75}Zr_{0.25})O_3$ ($T_C = 280$ K) was lower than that of $BaTiO_3$ ($T_C = 395$ K). These two compositions are still of classical ferroelectric type. The dielectric study of the titanozirconate showed only one phase transition at T_C without any frequency dispersion of the permittivities ε_r' and ε_r''. The ceramic studied in the present work ($Ba_{0.92}Ca_{0.08}Ti_{0.75}Zr_{0.25}O_3$) is derived from the latter only by a partial replacement of Ba^{2+} by Ca^{2+}.

Dielectric, pyroelectric and X-ray diffraction studies demonstrated the existence of a classical ferroelectric phase with rhombohedral symmetry at low temperature, for $T < T_3 \approx 210$ K. A frequency dispersion of ε_r' and ε_r'' occurred for $T > 210$ K and a maximum of ε_r' was observed at a temperature T_m the value of which depended on frequency ($T_m = 255$ K, at 10^3 Hz). The frequency dispersion decreased strongly at a temperature just higher than T_m, but disappeared only at a temperature close to 400 K, *i.e.* at $T \approx (T_m + 150)$ K. In addition, the value of the spontaneous polarization P_s calculated by integration of the pyroelectric coefficient reached zero in the temperature range 350–400 K. These two results, associated with deviation from the Curie–Weiss law at $T \approx 400$ K imply the temperature range of the relaxor phase to be $210 \leqslant T \leqslant 400$ K.

The highest temperature phase ($T > 400$ K) is paraelectric in good agreement with the cubic symmetry determined at 450 K and with a value of P_s of zero for $T > 400$ K, thus implying this phase to be non-polar.

Relaxor behaviour is related to nanoscale composition heterogeneity. The replacement of Ti^{4+} by Zr^{4+} in $BaTiO_3$ probably causes heterogeneity which is nevertheless insufficient to lead to a relaxor phase for $Ba(Ti_{0.75}Zr_{0.25})O_3$.[7] The appearance of the relaxor phase when Ca^{2+} is substituted for Ba^{2+} is probably due to a additional local polarization resulting from displacement of Ca^{2+} from the crystallographic site also occupied by Ba^{2+}. Such a local effect would break the long-range cationic correlation. Indeed, the small size of Ca^{2+} compared to that of Ba^{2+} ($r_{Ca^{2+}} = 1.12$ Å, $r_{Ba^{2+}} = 1.42$ Å in [8 C.N.]) indicates that Ca^{2+} is off-centred and adopts an anionic environment with eight nearest neighbours and four further ones. Such an assumption is likely in view of previous work on the $BaTiO_3$–$CaTiO_3$ binary system.[15] Here the value of the Curie temperature is practically independent of the degree of calcium–barium substitution. This behaviour is related to various competing effects, one being the local dipolar moment due to the displacement of Ca^{2+} from the centre of its original perovskite 12 C.N. crystallographic site.

Conclusion

The ceramic with composition $Ba_{0.92}Ca_{0.08}(Ti_{0.75}Zr_{0.25})O_3$ inside the BT–BZ–CT ternary diagram behaves like a classical ferroelectric phase at low temperature and shows a spontaneous, classical ferroelectric–relaxor transition at *ca.* 210 K without applying an electric field. Such a transition has previously been observed in lead-containing relaxor ceramics (PSN, PST, …).[1,11] The present work shows this lead-free ceramic to be suitable for dielectric applications in capacitors and actuators because it is environmentally friendly.

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