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Preparation and characterisation of the $Ba(Zr,Ti)O_3$ ceramics with relaxor properties

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Abstract

$Ba(Zr_xTi_{1-x})O_3$ ceramics with $x = 0.10$, 0.15 and 0.18 were prepared via solid state reaction. For the composition $x = 0.10$, ceramics with various grain sizes in the range 0.75–3.20 μm were obtained by sintering at various temperatures 1350–1500 °C. High permittivity (above 14,000 at the transition temperature) and losses smaller than 7% for temperatures below 120 °C, together with a shift of the Curie temperature towards lower values with increasing x, are characteristic to these ceramics. A ferroelectric-relaxor crossover takes place when x increases, with intermediate character for all the compositions. For the composition $x = 0.10$, the relaxor state is favoured by reducing the grain size.

Keywords: Ferroelectric properties; $BaTiO_3$ and titanates

1. Introduction

$BaTiO_3$-based solid solutions are environment-friendly dielectrics with similar performances as many Pb-based electroceramics. Their properties can be tuned by composition and by controlling their microstructural characteristics (porosity level, grain size, secondary phases, core-shell structures, etc.). $BaZr_xTi_{1-x}O_3$ (BZT) system, one of the first $BaTiO_3$-based solid solution studied for use in applications[1,2] became again attractive: new data concerning the phase formation mechanism,[3,4] local polar characteristics,[5] and dielectric/tunability properties for microwave applications[6,7] were recently reported. The dielectric data of $BaZr_xTi_{1-x}O_3$ ceramics suggest a normal ferroelectric behaviour for compositions $0 \le x \le 0.1$, relaxor character for $0.10 \le x \le 0.42$ when the degree of diffuseness of the ferro-para phase transition is increasing with x[1,2,8] and antiferroelectric properties for Zr-rich compositions. Macroscopically, the relaxor state is characterized by a strong frequency dependence of the permittivity below the maximum permittivity temperature T_m, a shift of T_m towards higher values with increasing frequency and deviations from the Curie–Weiss law in the paraelectric phase.[9] It was found that a high substitution rate ($x > 0.35$) is necessary to induce relaxor state if using homovalent substitution only (Zr on the Ti sites).[1,8,10,11] Therefore, these compositional limits are very sensitive to the preparation method, the presence of possible secondary phases and to the microstructural characteristics.

In the present study, $BaZr_xTi_{1-x}O_3$ ceramics with $x = 0.10$, 0.15 and 0.18 prepared by solid-state reaction were investigated. For the composition $x = 0.10$, samples with grain sizes in the range 0.75–3.20 μm were obtained by sintering at temperatures in the range 1350–1500 °C for observing the effect of grain size on the relaxor behaviour.

2. Sample preparation and experimental details

$BaZr_xTi_{1-x}O_3$ (BZT) ceramics were prepared by solid-state reaction using high purity nanometric precursors of $BaCO_3$ (Solvay), TiO_2 (Toho) and ZrO_2 (Tosoh) reagents. These were dried, weighted, then wet-mixed with distilled water, dried and calcined at 1000 °C/6 h. The calcined powders were milled and compacted by cold isostatic pressing at 1500 bar and then sintered at 1500 °C/2 h. The phase purity was checked by X-ray diffraction (XRD, Philips, Model PW 1710). The microstructures were examined by scanning electronic microscopy (SEM,

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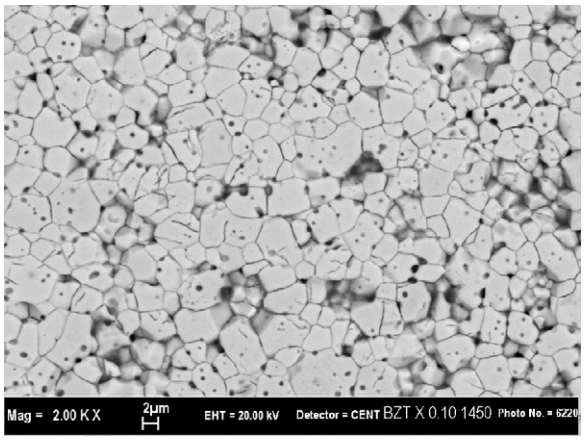

Fig. 1. Back-scattered SEM image of a polished $BaZr_{0.10}Ti_{0.90}O_3$ ceramic's surface sintered at 1450 °C/2 h.

Philips, Model 515) analysis. The apparent densities were measured by the immersion method in water (Archimedes). For the electric measurements, Ag–Pb paste was deposited on the plane-parallel polished clean surfaces of the ceramics followed by annealing in air at 500 °C/12 h. Impedance measurements were performed in the frequency domain 1 to 10^6 Hz by using an impedance analyser Solartron SI1260 in the temperature range 20–160 °C with a heating/cooling rate of 0.5 °C/min under an applied voltage of 1 V.

3. Results and discussions

The XRD data proved the BZT phase formation for all the compositions after calcination and the phase purity after sintering.[12] The SEM analysis shows a good homogeneity of the microstructures and a small degree of porosity (Fig. 1). The increasing Zr amount acts as inhibitor of the grain growth during sintering, so that a reduction of the average grain size of the BZT ceramics sintered at 1500 °C is obtained for higher x (~3.3 μm for $x = 0.10$ and ~1 μm in $x = 0.18$). The decreasing grain size with increasing x is associated with the lower grain-growth rate caused by slow diffusion of the Zr^{4+} ion, which has a larger ionic radius of 86 pm than Ti^{4+} with 74.5 pm (smaller ions lead to fast diffusion and grain growth).[12] In addition, for the composition $x = 0.10$, samples with grain sizes (GS) of: ~0.75, ~2.62 and ~3.20 μm were obtained by sintering at 1350, 1450 and 1500 °C for 2 h, respectively. A relative density above 97% was found for all the compositions with exception of the samples sintered at 1350 °C for which it was ~90%.

The temperature dependence of the permittivity and tan δ at a few frequencies obtained in $BaZr_xTi_{1-x}O_3$ ceramics with $x = 0.10$, 0.15 and 0.18 sintered at 1500 °C/2 h and in the $BaZr_{0.10}Ti_{0.90}O_3$ ceramics sintered at 1350, 1450 and 1500 °C for 2 h are shown in Figs. 2 and 3, respectively. These data demonstrate for all the ceramics relaxor properties, with a diffuse ferro-para phase transition and dispersion in the radio-frequency range in the polar phase ($T < T_m$). The temperature corresponding to the maximum permittivity T_m has a small shift of 2–5 °C when the frequency ranges from 1 to 10^5 Hz. For $T > 100$ °C, a strong increase of tan δ (Fig. 2b and 3b), particularly for high Zr content is due to a thermally activated space charge contribution (Maxwell–Wagner type) that is commonly present in systems with local compositional and electrical inhomogeneity.[13,14] This is realised by different levels of oxygen deficiency in various regions within the sample, leading to electric heterogeneity even in the single phase. In polycrystalline ceramics the grain boundaries and various defect structures play an important role in this mechanism.[15]

Relaxor behaviour is typical for higher Zr compositions (Fig. 1a). Diffuse phase transitions and small shifts of T_m towards higher values as the frequency is increasing from 1 to 10^5 Hz (72–74 °C for $x = 0.15$ and 55–58 °C for $x = 0.18$) are observed. For all the compositions the losses are below 7% in the range 40–110 °C and are rapidly increasing towards 100% above 120 °C, particularly at low frequencies (Fig. 1b). As mentioned, ferroelectric character has been reported for the composition $x = 0.10$.[1,2,8,10] However, the dispersion of permittivity in the

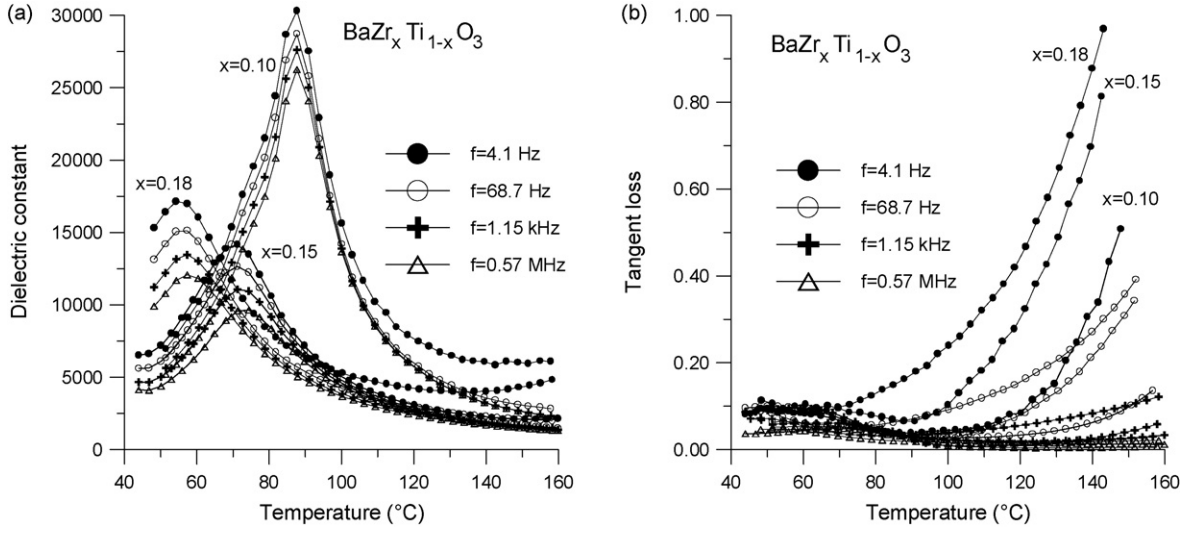

Fig. 2. Temperature and frequency dependence of the: (a) permittivity and (b) tangent loss in $BaZr_xTi_{1-x}O_3$ ceramics with $x = 0.10$, 0.15 and 0.18 sintered at 1500 °C/2 h.

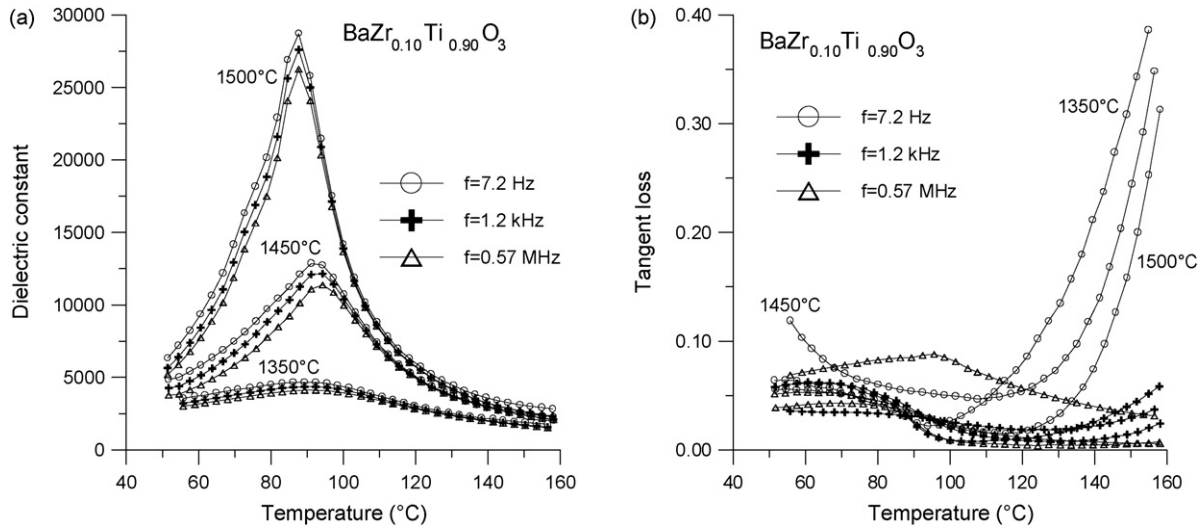

Fig. 3. Temperature and frequency dependence of the: (a) permittivity and (b) tangent loss in $BaZr_{0.10}Ti_{0.90}O_3$ ceramics sintered at 1350, 1450 and 1500 °C for 2 h.

radio-frequency range and the diffuse phase transition suggest relaxor properties for this composition. This is confirmed by the analysis with the empirical equation:

$$\varepsilon = \frac{\varepsilon_m}{1 + ((T - T_m)/\delta)^{\eta}}, \quad (1)$$

describing dielectric properties in relaxors, even in the dielectric dispersion region, with unique values of parameters δ and η for all the frequencies.[16] The coefficient η gives information on the character of the phase transition: for $\eta = 1$, normal Curie–Weiss law is obtained, $\eta = 2$ describes a full relaxor state with completely diffuse phase transition and $\eta \in (1, 2)$ a combined ferroelectric/relaxor state with a certain degree of diffuseness in the phase transition. The parameter δ indicates the temperature extension for the diffuse phase transition, which is correlated with the dielectric permittivity broadening. The values of these parameters obtained by fitting the dielectric data to Eq. (1): $\eta = 1.5$ and $\delta = 20$ °C for $x = 0.10$; $\eta = 1.65$ and $\delta = 32$ °C for $x = 0.15$ and $\eta = 1.7$ and $\delta = 36$ °C for $x = 0.15$, respectively. An increasing relaxor character and a shift of T_m towards lower values ($T_m = 92$, 73 and 58 °C at $f = 79.1$ kHz for $x = 0.10$, 0.15 and 0.18, respectively) take place with increasing Zr content, similar as reported in literature.[1,2,8,10,11]

The preliminary investigations showed that all the ceramics with $x = 0.10$ have mixed ferroelectric/relaxor properties.[12] However, the relaxor character is more evident as GS is smaller: the finest ceramic with GS = 0.75 μm has $\eta = 1.7$ and $\delta = 46$ °C by comparison with $\eta = 1.55$ and $\delta = 23$ °C for GS = 2.62 μm and $\eta = 1.5$ and $\delta = 20$ °C for GS = 3.30 μm. The relaxor properties are related to the disruption of the ferroelectric long-range order which are normally caused by chemical disorder. Usually, low substitution of Ti with Zr does not give rise to strong random fields. Therefore, the relaxor character of the present $BaZr_{0.10}Ti_{0.90}O_3$ ceramics is probably caused by contributions from grain boundaries. Compositional gradients and defects related to the ceramic grain boundaries are creating local random fields. Since a higher density of grain boundaries is present in the fine ceramics, this contribution is higher for the smaller grain sizes with corresponding enhancement of the relaxor character.

An increasing relaxor character with reducing the GS from 60 to 2 μm was also reported for the sol–gel derived $BaZr_{0.20}Ti_{0.80}O_3$ ceramics,[17] which is a composition already in the relaxor state. The results were explained as possible caused by different internal stresses existing in samples with various grain sizes. However, the composition $x = 0.10$ was reported in literature to show full ferroelectric properties.[1,2,8] In this case, the reduction of GS in the range 1–3 μm seems to play an important role in determining the relaxor properties. Further investigations on a larger range of GS (below 500 nm to above 10 μm) are expected to demonstrate the possibility of inducing the crossover ferroelectric-relaxor by reducing the GS only in this composition.

4. Conclusions

High density (~97%) $Ba(Zr_xTi_{1-x})O_3$ ceramics with $x = 0.10$, 0.15 and 0.18 and homogeneous microstructures were prepared via solid state reaction. Good dielectric properties with low losses (<7%) below 120 °C and high permittivity above 14,000 at the transition temperature were found. By increasing the Zr addition, a shift of Curie temperature towards lower values and ferroelectric-relaxor crossover takes place. For $x = 0.10$, ceramics with GS in the range of 0.75–3.20 μm were investigated. Their dielectric data show that the relaxor state seems to be favoured by the GS reduction, which contributes to enhance the local disorder. The possible effect of the GS or of other microstructural parameters in inducing relaxor effects in the BZT solid solution, as suggested by these preliminary data, is a very interesting topic to be further investigated in samples with different grain sizes (particularly at nanometric level) by a more complete study.

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