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Dielectric properties of Ba(Ti, Ce)O₃ from 10² to 10⁵ Hz in the temperature range 85–700 K

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Abstract. Ba(Ti_{1-x}Ce_x)O₃ ceramics with $x = 0.1, 0.2, 0.3, 0.33, 0.4$ and 0.5 have been synthesized by the mixed oxide method. Dielectric measurements were performed for Ba(Ti_{1-x}Ce_x)O₃ ceramics from 10² to 10⁵ Hz in the temperature range 85–700 K. The dielectric measurements confirmed that the solid solution range extends up to about $x = 0.3$. In the solid solutions, the temperature of the permittivity maximum was shifted at a rate of -7 K/mol% Ce atom and the permittivity maximum decreased with increasing Ce content. The temperature and frequency dependence of the permittivity was fitted by the Curie–Weiss law beyond the transition temperature and characterized by parameters that are used to describe relaxor behaviour.

1. Introduction

A series of dielectric ceramics with the general composition MBa₃Ti₂O_{8+δ}, which is in the BaO-rich region of the BaO–M₂O₃–TiO₂ (M = Y, Nd, Sm, etc) system, has been reported by the present authors [1, 2]. These single-phase compounds belong to the hexagonal crystal system. When M = Ce, the results of x-ray diffraction (XRD) analysis indicate that CeBa₃Ti₂O_{8+δ} belongs to the tetragonal system. In addition, it was recognized that the composition CeBa₃Ti₂O_{8+δ} was formed by a solid solution of BaTiO₃ and BaCeO₃. Based on these observations, a series of Ba(Ti_{1-x}Ce_x)O₃ ceramics was synthesized [3]. The XRD results indicate that the limit of solid solubility is about $x = 0.30$ when Ba(Ti_{1-x}Ce_x)O₃ ceramics are prepared by the mixed oxide method and that they have the perovskite crystal structure.

Preliminary dielectric measurements have also shown that the permittivity peak broadens as the Ce content is increased, resembling a system with relaxor behaviour [3]. The study of relaxor behaviour has attracted much attention not only in ferroelectric relaxors [4] but also in solid solutions such as Li-doped KTaO₃ [5] and Ca-doped SrTiO₃ [6]. Solid solutions composed of ferroelectric and non-ferroelectric materials, such as Ba(Ti, Sn)O₃ [7] and Ba(Ti, Hf)O₃ [8], were reported a long time ago. The dielectric properties of the Ba(Ti_{1-x}Ce_x)O₃ solid solutions as a function of temperature and frequency are characterized in the present paper and discussed in terms of parameters that are used to characterize relaxor systems.

2. Experimental procedure

The ceramics were prepared by the mixed oxide method. The starting materials (BaCO₃, TiO₂ and CeO₂) were weighed according to the ratio of Ba(Ti_{1-x}Ce_x)O₃ where $x = 0.1,$

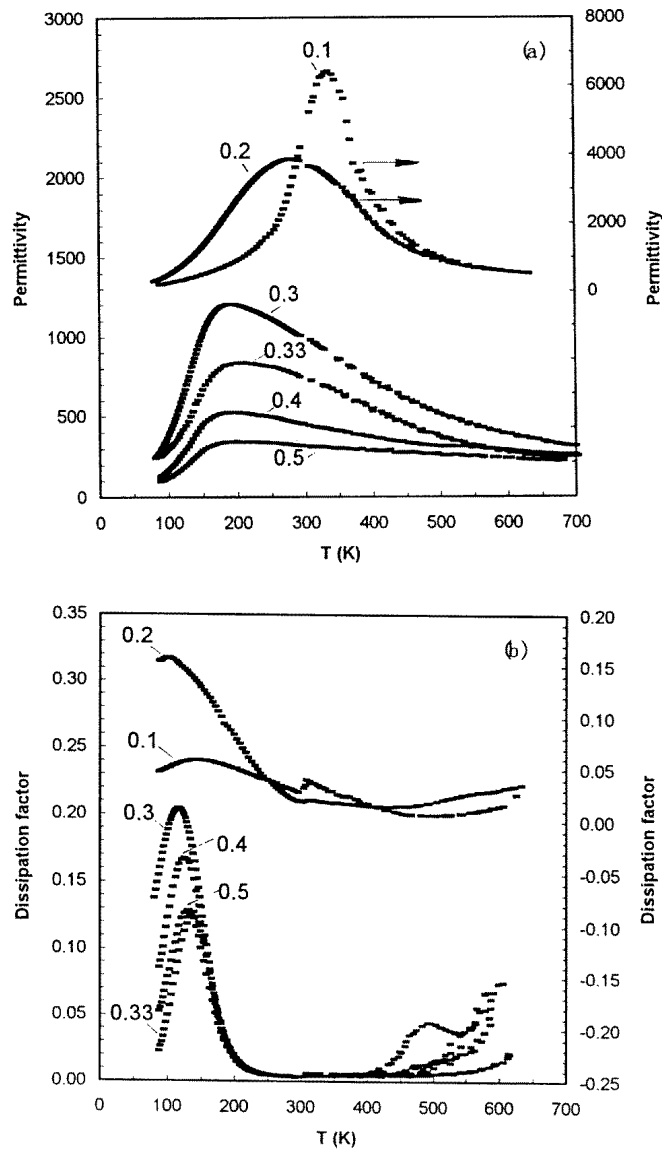


Figure 1. The temperature dependences of (a) the permittivity and (b) the dissipation factor for all the compositions at 10 kHz.

0.2, 0.3, $\frac{1}{3}$, 0.4 and 0.5, respectively. The weighed batches were wet mixed in an agate mill for 5 h. After drying and calcining at 1200 °C, the powders were isostatically pressed at 300 MPa into discs. Finally, the discs were sintered in air at 1540 °C for 6 h supported on discs with the same composition which had been sintered before.

The dielectric properties were measured with a weak applied field of 10 V cm⁻¹ by a Keithley 3330 LCZ meter and a Solartron 1260 impedance/gain-phase analyser from 85 to 700 K and from 10² to 10⁵ Hz.

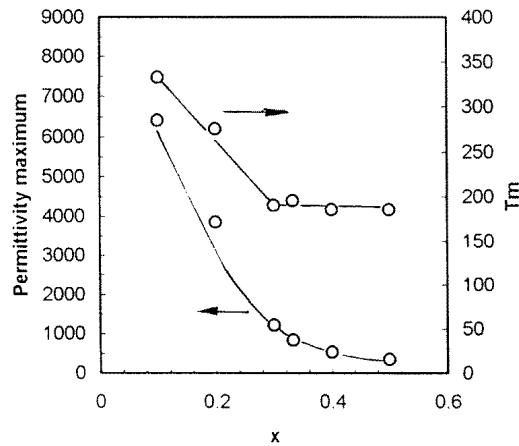


Figure 2. The compositional dependence of the permittivity maximum (ϵ_m) and the temperature at which $\epsilon(T)$ reaches a maximum (T_m) at 10 kHz.

3. Results and discussion

3.1. Dielectric properties

The temperature and frequency dependences of the dielectric properties of the $\text{Ba}(\text{Ti}_{1-x}\text{Ce}_x)\text{O}_3$ ceramics ($0.1 \leq x \leq 0.5$) were measured. The temperature dependence of the relative permittivity (ϵ) and dissipation factor of all the compositions at 10 kHz is shown in figure 1. The increase in the Ce content leads to a decrease in the permittivity maximum (ϵ_m) and to a shift to lower temperatures in the temperature T_m at which $\epsilon(T)$ reaches a maximum. The decrease in both ϵ_m and T_m in figure 1(a) is almost linear with the increase in the Ce content for $x \leq 0.3$ at 10 kHz, as shown in figure 2. The shift rate of T_m is ~ -7 K/mol% Ce atoms. This is in accordance with the solid solubility range obtained from the XRD results [3].

The variation of relative permittivity and dissipation factor as a function of temperature for $x = 0.1, 0.2$ and 0.3 , at 1, 10 and 100 kHz, is shown in figure 3. For the sample with $x = 0.1$, a permittivity peak occurred at about 320 K, almost independent of frequency. However, in the low-temperature range from 100 to 300 K, a small dielectric dispersion can be seen. For $x = 0.2$ and 0.3 , a much more obvious dielectric dispersion with frequency and temperature can be observed.

3.2. Fitting by the Curie–Weiss law

As mentioned above, the limit of the solid solubility is about $x = 0.30$ in the $\text{Ba}(\text{Ti}_{1-x}\text{Ce}_x)\text{O}_3$ system. The variation of the dielectric properties with temperature and frequency for compositions in the solid solution range is described below.

The curves of the reciprocal permittivity (at 10 kHz) versus temperature for $x = 0.1$ and 0.2 are shown in figure 4(a) and (b) respectively and fitted to the Curie–Weiss law on the high-temperature side. A Curie constant (C) and a Curie temperature (Θ) of 1.25×10^5 K and 337.5 K for $x = 0.1$ and 1.5×10^5 K and 329.6 K for $x = 0.2$ were obtained. The data are summarized in table 1. The Curie constants are similar to that of pure BaTiO_3 ceramics [9]. The deviation from the Curie–Weiss behaviour starts near 430 K for $x = 0.1$,

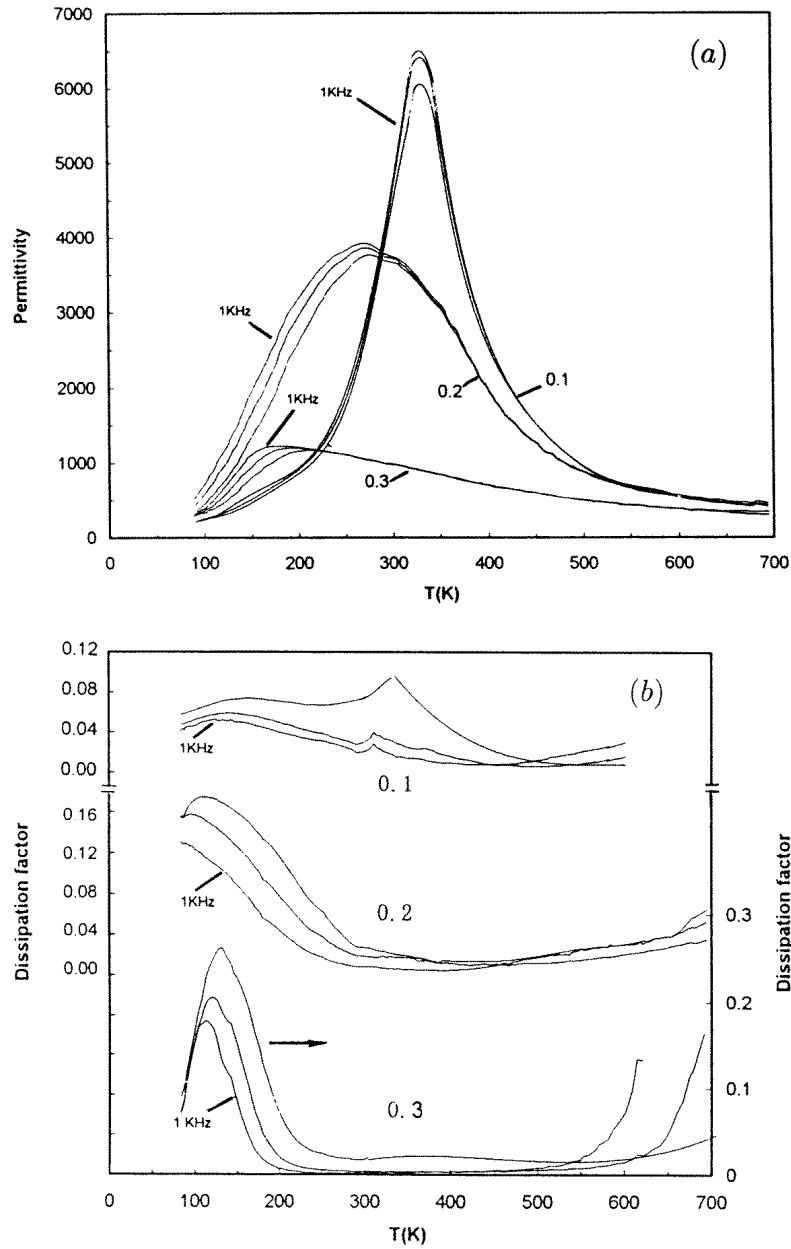


Figure 3. The variation of (a) the permittivity and (b) the dissipation factor as a function of temperature for $x = 0.1, 0.2,$ and $0.3,$ at 1, 10, and 100 kHz.

and 435 K for $x = 0.2$. ($T_{dev} - T_m$) is the temperature difference between the temperature T_{dev} at which there is a departure from the Curie–Weiss law and the temperature T_m at which the permittivity maximum occurs. From table 1, it can be seen that ($T_{dev} - T_m$) also increases with x . This implies that the temperature range which can be characterized by the Curie–Weiss law becomes narrow as the Ce content increases. Rather than following

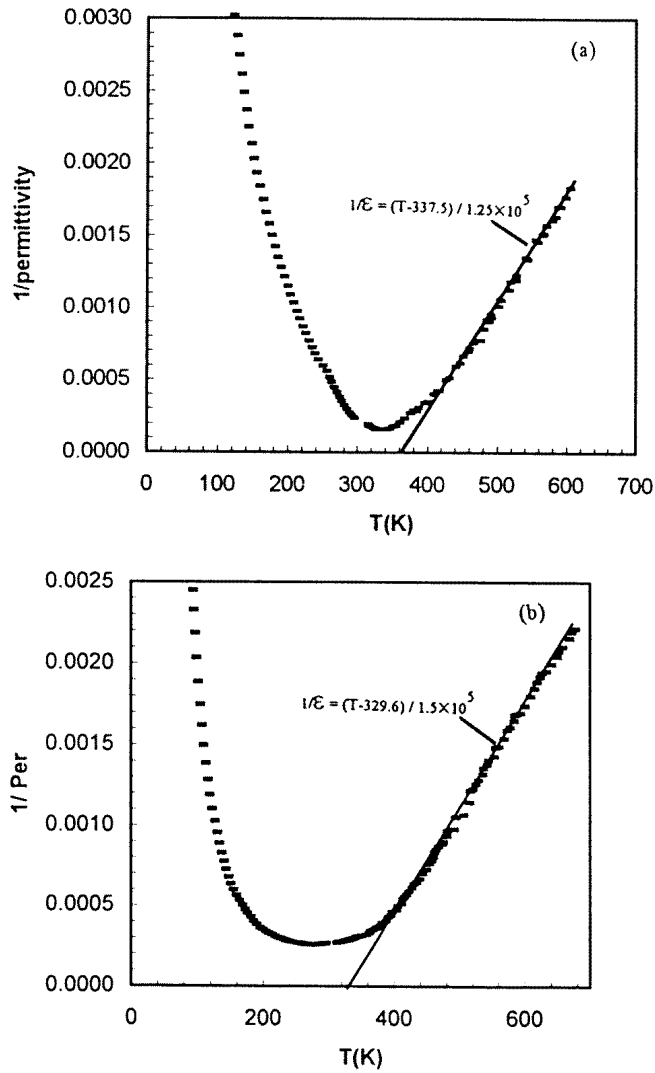


Figure 4. The curve of the inverse permittivity versus temperature at 10 kHz for (a) $x = 0.1$ and (b) $x = 0.2$: solid line, fitting curve; dots, experimental data.

the Curie–Weiss law in the range $T > T_m$, the temperature dependence of the reciprocal dielectric permittivity $1/\varepsilon(T)$ of the solid solutions with frequency dispersion exhibits a more complex behaviour. In what follows, this behaviour is characterized by using some empirical parameters that were used in previous works [10–13].

3.3. Some empirical parameters to characterize dielectric properties

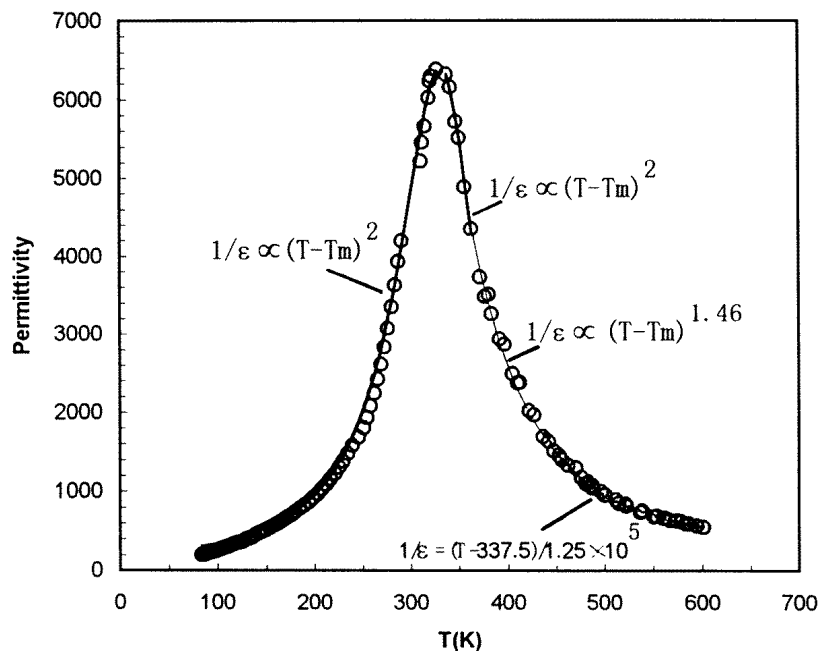
Smolenskii [10] and Kirillov *et al* [11] modelled the deviation from the Curie–Weiss law using the compositional heterogeneity model, predicting a quadratic dependence shown by

$$1/\varepsilon - 1/\varepsilon_m = (T - T_m)^2 / 2\varepsilon_m \delta^2 \quad (1)$$

Table 1. The Curie temperature Θ , Curie constant C and parameters δ , γ and ΔT for $x = 0.1$, 0.2 and 0.3.

		$x = 0.1$	$x = 0.2$	$x = 0.3$
Curie–Weiss law	Θ (K)	33.75	329.6	183.33
	C (K)	1.25×10^5	1.5×10^5	1.67×10^5
	$T_{dev} - T_m^a$ (K)	110	144	213
	ΔT (K)	~ 0	~ 10	45
	δ (K)	1.46	~ 1.7	1.73
		39.5	99.8	188

^a T_{dev} denotes the temperature deviation from the Curie–Weiss law; T_m denotes the temperature at which the permittivity maximum occurs.

**Figure 5.** The curve of permittivity versus temperature fitted by different equations in three temperature ranges, for $x = 0.1$: solid lines, fitting curves; dots, experimental data.

where ε_m is the permittivity maximum, and δ is a parameter to quantify the diffuseness of a given $\varepsilon_m(T)$ maximum.

On the other hand, an empirical expression [12, 13] was proposed to describe the phase transition diffuseness as

$$1/\varepsilon - 1/\varepsilon_m = (T - T_m)^\gamma / C_1 \quad (2)$$

where γ and C_1 are assumed to be constant, and $1 < \gamma < 2$. The limiting values $\gamma = 1$ and $\gamma = 2$ reduce the expression to the Curie–Weiss law valid for the case of a normal ferroelectric and to the quadratic dependence in equation (1) for a relaxor.

In addition, the parameter ΔT used to quantify the degree of relaxation behaviour is defined as

$$\Delta T = T \varepsilon_{m(100 \text{ Hz})} - T \varepsilon_{m(100 \text{ kHz})}. \quad (3)$$

ΔT is explicitly a measure of the degree of relaxation behaviour.

For $x = 0.1$, the best fitting was obtained by considering three temperature ranges. For $T > 430$ K, the curve can be fitted by the Curie–Weiss law. For 370 K $< T < 430$ K, it is better to fit the data to equation (2) with $\gamma = 1.46$. For $T_m < T < 370$ K, the best fitting was obtained by using equation (1). The fitting curves are illustrated in figure 5.

For the samples with high Ce contents, $x = 0.2$ and 0.3 , the fitting can be performed again, using the Curie–Weiss law, equation (1) and equation (2) in different temperature ranges. The parameters δ , γ and ΔT obtained are presented in table 1.

3.4. Discussion

It can be seen that, as the Ce content is increased, the deviation from the Curie–Weiss law and the diffuseness become more pronounced, as shown by the increase in the values of δ and γ . The increase in ΔT indicates that the relaxor behaviour also becomes more pronounced with the increase in the Ce content.

It is known that a diffuse phase transition can be observed in $BaTiO_3$ doped with different elements, substituting either the Ba site or the Ti site [7, 8, 14]. The $Ba(Ti, Sn)O_3$ [7] and $Ba(Ti, Hf)O_3$ [8] systems are those that show most similarities to the present work, such as (i) the substitution is in the Ti site, (ii) the increase of the content of the substituting element results in a shift to lower temperatures of the first permittivity peak (which arose from the ferroelectric–paraelectric phase transition at 393 K for pure $BaTiO_3$ [9]) and (iii) the permittivity peaks become more diffuse with increasing amount of the substituting element.

In addition, it should be pointed out that, for the $Ba(Ti_{1-x}Ce_x)O_3$ ceramics with $x = 0.1$, besides the permittivity peak at about 320 K, a small dispersion of the permittivity between 100 K and 300 K and dispersion of the dissipation factor peak around 150 K can be seen in figure 1. It is not certain whether this behaviour is due to the shift from the second and/or the third permittivity peaks of $BaTiO_3$ at 278 and 193 K [9]. Recently, the coexistence of low-temperature dispersion and a high-temperature sharp ferroelectric–paraelectric phase transition has been reported by Guo *et al* [15] and explained by a polarization fluctuation mechanism. Whether the present results can or cannot be explained by the same mechanism is not clear at this stage. Further work is being conducted to detect the variation of the crystal structure of the $Ba(Ti_{1-x}Ce_x)O_3$ solid solutions with the decrease in temperature to determine whether any structural phase transition occurs.

On the other hand, the variation of the dissipation factor with composition and temperature as shown in figure 1(b) is more difficult to interpret with the data available. As mentioned above, for $x = 0.1$, two peaks were observed in the dissipation factor curve. The one situated at 310 K corresponds to the ferroelectric–paraelectric phase transition observed on the dielectric permittivity curve. The origin of the one situated around 120 K has not been identified yet. With increasing Ce content ($x = 0.2$), the loss peak corresponding to the ferroelectric–paraelectric phase transition tends to become less visible although the diffuse transition can still be clearly seen on the dielectric permittivity curve. The loss peak observed at 100 K for $x = 0.2$ has probably the same origin as the loss peak observed at 150 K for $x = 0.1$. For $x = 0.3$ and above, a dissipation peak around 120 K is clearly seen and is probably related to the diffuse phase transition although a contribution from an extra phase cannot be excluded. A clear perception of the loss behaviour needs further research.

4. Conclusions

The dielectric properties were measured in the perovskite type $\text{Ba}(\text{Ti}_{1-x}\text{Ce}_x)\text{O}_3$ solid solutions. The results indicate that the Ce dopant not only shifted the first permittivity peak (corresponding to the ferroelectric–paraelectric phase transition at 393 K for pure BaTiO_3 [9]) to a lower temperature, by a shift rate of ~ -7 K/mol% Ce atoms, but also made the dielectric characteristics of the solid solutions more diffuse and dispersed. This behaviour is similar to that of other solid solutions of BaTiO_3 doped with Sn and Hf elements. The coexistence of the low-temperature dispersion and the high-temperature sharp ferroelectric–paraelectric phase transition was also observed, which needs further study.

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