



HAL
open science

Modulation relaxor behaviour by chemical substitution in the system $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}(\text{Zn}_{1/3}\text{Nb}_{2/3})_y\text{O}_3$

L. Khemakhem, A. Maalej, A. Kabadou, A. Ben Salah, Annie Simon, Mario
Maglione

► **To cite this version:**

L. Khemakhem, A. Maalej, A. Kabadou, A. Ben Salah, Annie Simon, et al.. Modulation relaxor behaviour by chemical substitution in the system $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}(\text{Zn}_{1/3}\text{Nb}_{2/3})_y\text{O}_3$. *Ferroelectrics*, 2008, 371 (1), pp.82-88. 10.1080/00150190802394939 . hal-00348535

HAL Id: hal-00348535

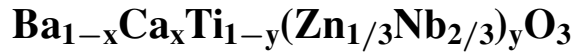
<https://hal.science/hal-00348535>

Submitted on 13 May 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Modulation of Relaxor Behaviour by Chemical Substitution in the System



L. KHEMAKHEM,^{1,*} A. MAALEJ,² A. KABADOU,¹
A. BEN SALAH,¹ A. SIMON,³ AND M. MAGLIONE³

¹Laboratoire des Sciences des Matériaux et Environnement, Faculté des Sciences de Sfax, B.P. 802, 3018 Sfax, Tunisie

²Laboratoire des Matériaux Ferroélectriques, Faculté des Sciences de Sfax B.P. 802, 3018 Sfax, Tunisie

³Institut de Chimie de la Matière Condensée de Bordeaux 87, Avenue du Dr. A. Schweitzer, 33608 Pessac, France

This paper reports the structural and dielectric properties of $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}(\text{Zn}_{1/3}\text{Nb}_{2/3})_y\text{O}_3$ ceramics with y is fixed to 0.2 and $x = 0.2$ and 0.3. Single-phase solid solutions of the simples were determined by X-ray diffraction. For the solid solution, $\text{BaTi}_{1-y}(\text{Zn}_{1/3}\text{Nb}_{2/3})_y\text{O}_3$, the evolution of dielectric behaviour from a sharp ferroelectric peak (for $y < 0.075$) and to ferroelectric relaxor (for $0.075 < y < 0.2$) was observed with increasing of Zn and Nb concentration but in this case the temperature of the maximum of dielectric permittivity T_m and ΔT_m are lowers. To modulate this relaxor character we have substitute the Ba by Ca to increase T_m and ΔT_m .

Keywords Dielectric; ferroelectric; relaxors and modulation

1. Introduction

The recent discovery on the very high piezoelectric and electro-strictive strain properties in lead-based relaxor ferroelectric single crystals [1–4] has stimulated a renewed interest in searching for high strain behaviour in environmentally friendly lead-free materials. BaTiO_3 (BT), is one end member of the industrially interesting solid-solution series. The materials with a perovskite structure of general formula ABO_3 where A is a mono or divalent ion, B is a tri, tetra or pentavalent ion have been found to be very useful and interesting for different solid-state devices [5–6]. Much attention has been given to the interests of perovskite compounds with disordered cations (complex perovskite-type) [7].

Lead-free compositions could be of great interest for environmentally friendly applications. BaTiO_3 , one of the displacive-type ferroelectric materials, is a typical ABO_3 type simple perovskite oxide. Substitution of other ions for host cations at A or B site in BaTiO_3 leads to remarkable changes in various characteristics [8–11].

*Corresponding author. E-mail: khemakhemh@yahoo.fr

However, lead is a toxic element and with increasing demands of the environment protection, lead-free materials are highly desirable. Their dielectric behaviour is dependent on the chemical composition and statistical distribution of B-site cations in the perovskite lattice [12]. In recent years there has been considerable interest in the development of a $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BZN) based system [13]. Onada et al. [14] and Endo et al. [15] respectively investigated the effects of mixed Ba/Sr and Zn/Co sites in BZN and high lighted the versatility and tuning capabilities of the BZN system.

In our last works, we have studied the system $\text{BaTi}_{1-y}(\text{Zn}_{1/3}\text{Nb}_{2/3})_y\text{O}_3$ (BTZN) to characterize the relaxor behaviour. In the present work, and to modulate the relaxor character in the region ($0.075 < y < 0.2$), we have study the Ca ion modified BTZN and we have choose the composition $y = 0.2$ because it have the lowest T_m .

2. Experimental

Ceramic sample with the chemical formula of $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}(\text{Zn}_{1/3}\text{Nb}_{2/3})_y\text{O}_3$ (BTZN) was prepared using a conventional solid state reaction method by reacting the stoichiometric proportions of high purity (up 99%) BaCO_3 , CaCO_3 , ZnO , Nb_2O_5 and TiO_2 powders. The mixture was ball-milled, dried and then calcined at 1100°C for 15h under oxygen atmosphere and cooled to room temperature. The calcined pellets were reground, pressed and sintered at 1300°C for 2 h.

X-ray diffraction analysis at room temperature was carried out on a Phillips diffractometer using MoK_α radiation ($\lambda = 0.710690 \text{ \AA}$) in the angle range $5 \leq 2\theta \leq 60^\circ$ with 10s counting time for each step of 0.02 in order to determine the structure for this ceramic composition. The dielectric measurements were performed under dry helium on ceramic disc, after deposition of gold electrodes on the circular faces by cathodic sputtering, using a Wayne Kerr 6425 component analyzer.

3. X-ray Diffraction Analysis

Figs. 1 and 2, show the X-ray diffraction pattern of some compositions of the system $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{0.8}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.2}\text{O}_3$ with $x = 0.2$ and 0.3 taken at room temperature which reveal that ceramics are single phased. All the reflection peaks of the X-ray profile were indexed, and lattice parameters were determined using a global profile-matching method with the fullprof software [14]. In table 1, we present all crystallographic parameters.

4. Dielectric Studies

Before measurements, the samples were first heated at 473K for 4h under vacuum (This heat treatment was used to eliminate, as much as possible, the water content in the ceramic pores). The evolution of the real (ϵ'_r) part of the complex permittivity for $\text{BaTi}_{1-y}(\text{Zn}_{1/3}\text{Nb}_{2/3})_y\text{O}_3$ ceramics sample as a function of both temperature and frequency shows three different dielectric behaviours.

For $0 \leq y \leq 0.05$, the sample is of normal ferroelectric behaviour. We note that there is no significant frequency dispersion for $T < T_c$.

For $0.075 \leq y \leq 0.2$ and $0.75 \leq y \leq 0.975$, there is only one broad peak in the thermal evolution of ϵ'_r at T_m . A frequency dispersion occurs for $T < T_m$ with a shift of T_m with frequency [16]. This frequency dispersion is the highest at $y = 0.95$. In the region $0.075 \leq y \leq 0.2$, the relaxor character is not pronounced T_m and ΔT_m are lowers and the lowest T_m is for the composition $y = 0.2$ (Fig. 3). So that, we have consider this composition as

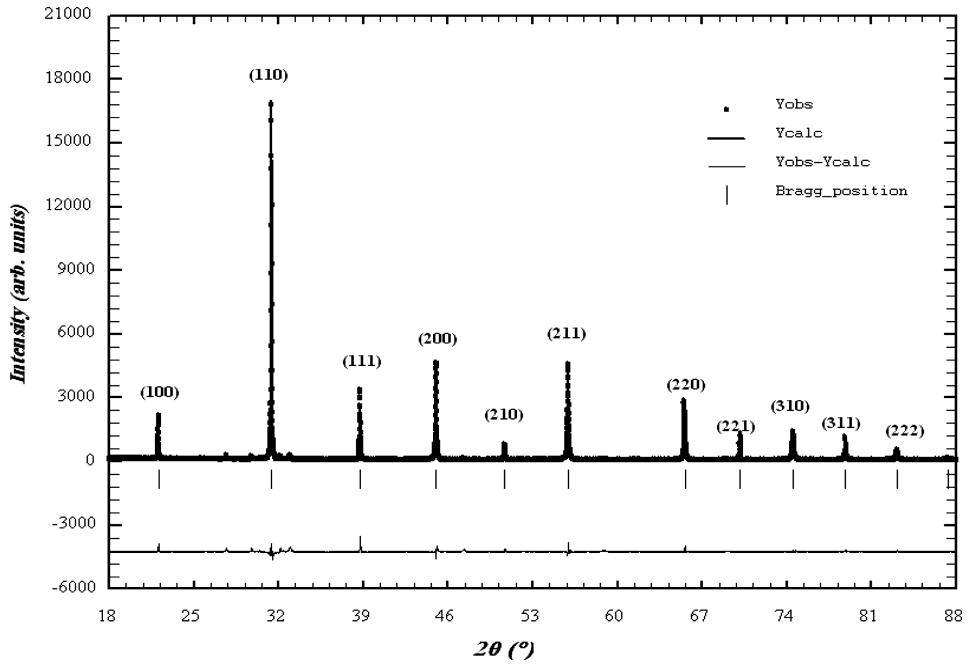


Figure 1. X-ray spectrum for the composition $x = 0.2$ of $\text{Ba}_{1-x}\text{Ca}_x(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.2}\text{Ti}_{0.8}\text{O}_3$ solid solution at room temperature.

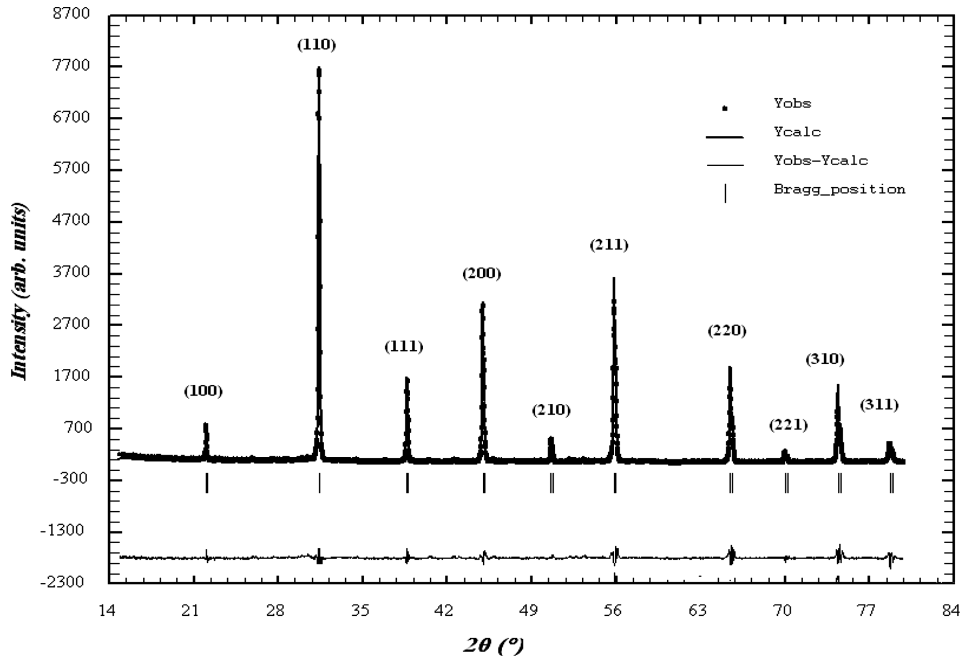


Figure 2. X-ray spectrum for the composition $x = 0.3$ of $\text{Ba}_{1-x}\text{Ca}_x(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.2}\text{Ti}_{0.8}\text{O}_3$ solid solution at room temperature.

Table 1

Crystallographic parameters of the compositions $x = 0.2$ and $x = 0.3$ of the solid solution $Ba_{1-x}Ca_x(Zn_{1/3}Nb_{2/3})_{0.2}Ti_{0.8}O_3$

x	structure	a = b = c(Å)
0,2	cubic	4,0720(2)
0,3	cubic	4,0232(2)

reference in the present study. To modulate this behaviour we have substitute Ba^{2+} by Ca^{2+} in the system $Ba_{1-x}Ca_xTi_{0.8}(Zn_{1/3}Nb_{2/3})_{0.2}O_3$ (BTZN). Figs. 4 and 5 show the temperature dependencies of the real part of permittivity ϵ'_r at different frequencies of samples with compositions $x = 0.2$ and $x = 0.3$ respectively. Diffuse transition with frequency dispersion above and around the ϵ'_r peak were observed. The temperature and frequency variations of ϵ'_r were also specific: the temperature T_m of ϵ'_r maximum was shifted to higher values on increasing frequency. The evolution of the frequency dispersion was here characterized by an increase in ϵ'_r when frequency increased. This shows that these compositions are of a relaxor type. We remark that T_m presents an evolution to higher temperatures. This behaviour can be considered as important for applications.

The relaxor characteristics for these compositions are reported in Table 2 as the T_m shift, $\Delta T_m = T_m(10^5 \text{ Hz}) - T_m(10^2 \text{ Hz})$ and the frequency relative dispersion $\Delta \epsilon'_r / \epsilon'_r = \epsilon'_r(10^2 \text{ Hz}) - \epsilon'_r(10^5 \text{ Hz}) / \epsilon'_r(10^2 \text{ Hz})$.

It can be noted that the partial substitution of Ba^{2+} by Ca^{2+} in $Ba_{1-x}Ca_xTi_{1-y}(Zn_{1/3}Nb_{2/3})_yO_3$ has considerable effects: apparition of the relaxor behaviour and increase of T_m .

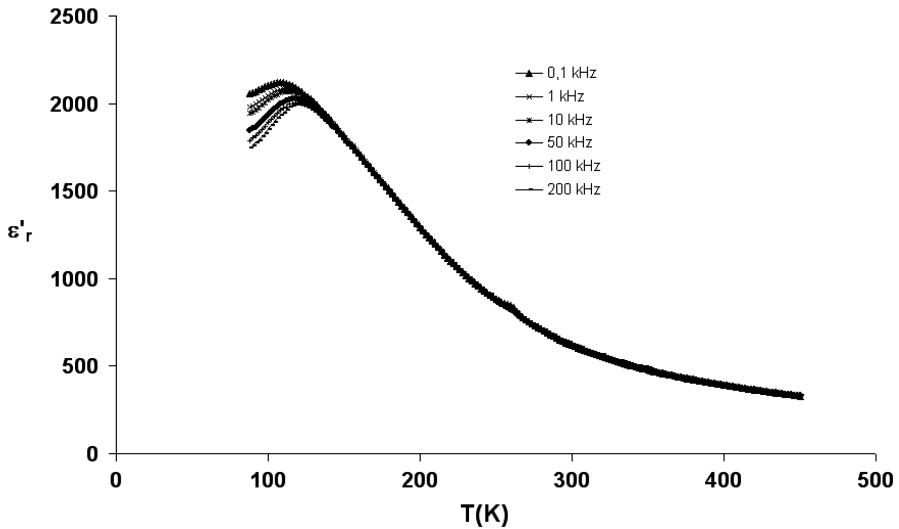


Figure 3. The real part of permittivity evolution as a function of temperature and frequency for $Ba_{1-x}Ca_x(Zn_{1/3}Nb_{2/3})_{0.2}Ti_{0.8}O_3(x = 0)$.

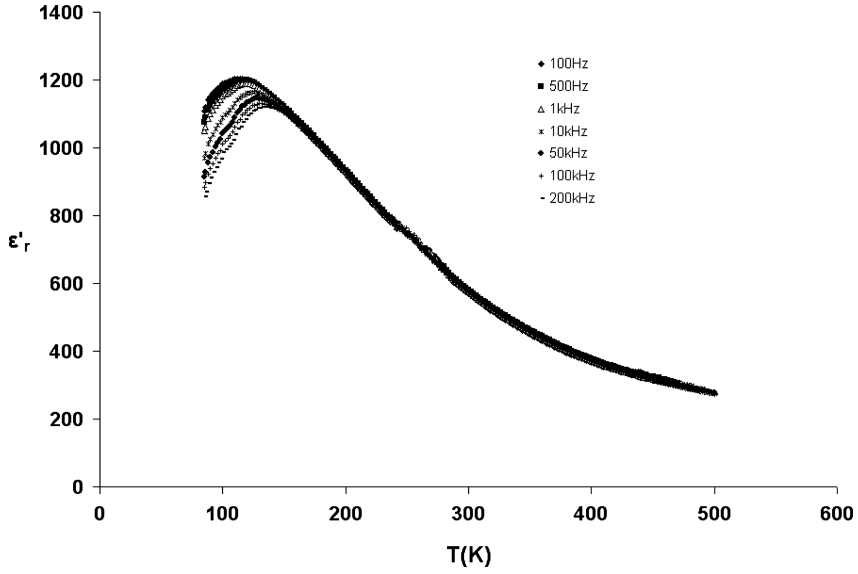


Figure 4. The real part of permittivity evolution as a function of temperature and frequency for $\text{Ba}_{1-x}\text{Ca}_x(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.2}\text{Ti}_{0.8}\text{O}_3$ ($x = 0.2$).

The degree of disorder of the $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}(\text{Zn}_{1/3}\text{Nb}_{2/3})_y\text{O}_3$ was evaluated using an empirical formula developed by Uchino and Nomura [17]:

$$\frac{1}{\varepsilon'_r} - \frac{1}{\varepsilon'_{r\max}} = \frac{(T - T\varepsilon'_{r\max})^\gamma}{c'}$$

where C is a constant and γ is a measure of diffuseness; γ value is between 1 and 2.

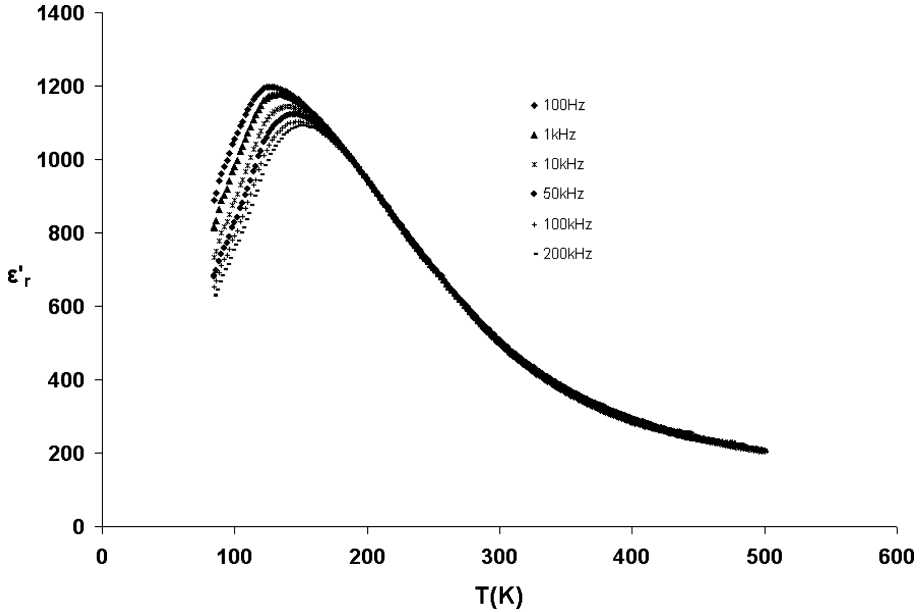


Figure 5. The real part of permittivity evolution as a function of temperature and frequency for $\text{Ba}_{1-x}\text{Ca}_x(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.2}\text{Ti}_{0.8}\text{O}_3$ ($x = 0.3$).

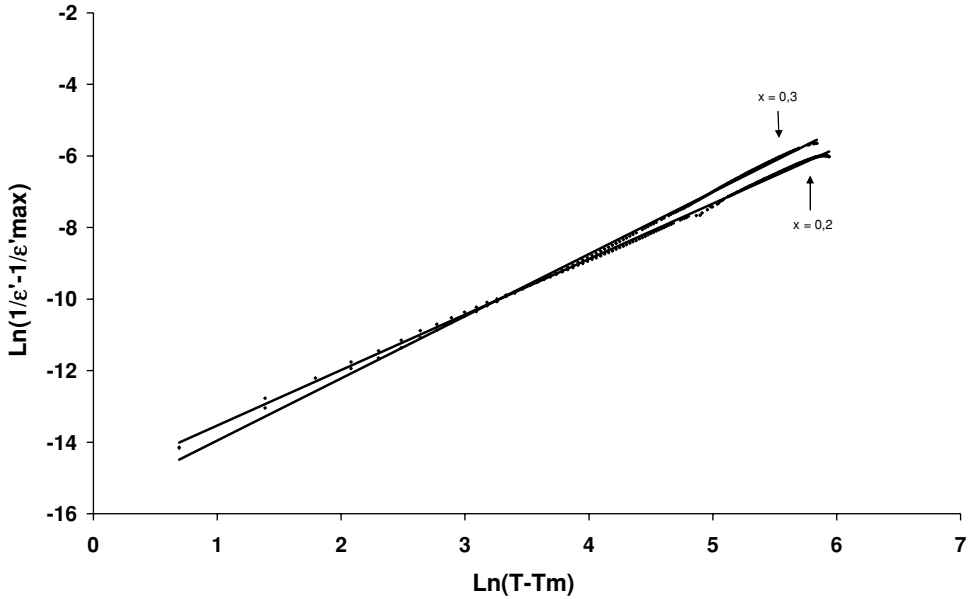


Figure 6. Variation of $\text{Ln}(1/\varepsilon' - 1/\varepsilon'_{\text{max}})$ as a function of $\text{Ln}(T-T_m)$ for $x = 0.2$ and $x = 0.3$.

The parameters γ give information on the character of the phase transition and only depending on the composition of the specimens. The limiting value $\gamma = 1$ and $\gamma = 2$ reduce the equation to Curie-weiss law for the case of normal ferroelectric and for ideal relaxor ferroelectric respectively [18].

The logarithmic plots related to this equation for all doped compositions ($x = 0.2$ and $x = 0.3$) are shown in Fig. 6.

The slope of the fitting is used to determine the value of γ at 10 kHz. These parameters are $\gamma = 1.909$ and $\gamma = 1.9175$ respectively for $x = 0.2$ and $x = 0.3$.

5. Conclusion

Ceramic samples of calcium Ca doped barium Ba with general composition $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}(\text{Zn}_{1/3}\text{Nb}_{2/3})_y\text{O}_3$ have been elaborated by solid state reaction method. It was shown by X-ray diffraction at room temperature that the structure of the compounds is of perovskite type. Dielectric measurements on the two compositions show that the phase

Table 2
Values of T_m , ΔT_m and $\Delta\varepsilon'_r/\varepsilon'_r$ characteristics of the relaxor behavior of some $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}(\text{Zn}_{1/3}\text{Nb}_{2/3})_y\text{O}_3$ ceramics with various compositions

x	T_m (K) at 1kHz	ΔT_m (K)	$\Delta\varepsilon'_r/\varepsilon'_r$
0	112	12	0.05700
0,2	118	40	0.05833
0,3	134	42	0.01837

transition becomes diffuse and characterizes a relaxor behaviour. The amelioration in the relaxor character introduced by the substitution of barium by calcium represents the originality of this study. This result can be considered as important for applications.

Acknowledgment

The authors would kindly like to thank Dr. Regnault von der Muhll for his technical helps.

References

1. J. Kuwata, K. Uchino, and S. Nomura, Dielectric and Piezoelectric Properties of $0.91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.09\text{PbTiO}_3$ Single Crystals. *Jpn. J. Phys. Part I*, **21**, 1298–1302 (1982).
2. S. E. Park and T. R. Shrout, Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals. *J. Appl. Phys.* **82**, 1804–1811 (1997).
3. D. S. Paik, S. E. Park, S. Wada, S. F. Liu, and T. R. Shrout, *E*-field induced phase transition in 001-oriented rhombohedral $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.08\text{PbTiO}_3$ crystals. *J. Appl. Phys.* **85**, 1080–1083 (1999).
4. S. F. Liu, S. E. Park, T. R. Shrout, and L. E. Cross, Electric field dependence of piezoelectric properties for rhombohedral $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.045\text{PbTiO}_3$ single crystals. *J. Appl. Phys.* **85**, 2810 (1999).
5. A. Aydi, C. Boudaya, H. Khemakhem, R. Von Der Muhll, and A. Simon, New ferroelectric and relaxor ceramics in the mixed oxide system $\text{NaNbO}_3\text{-BaSnO}_3$. *Solid State Sci.* **6**, 333–337 (2004).
6. H. Khemakhem, A. Simon, R. Von Der Muhll, and J. Ravez, Relaxor or classical ferroelectric behavior in ceramics with composition $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_{1-x}\text{Nb}_x\text{O}_3$. *J. Phys. Condens. Mat.* **12**, 5951–5959 (2000).
7. K. Uchino, Relaxor ferroelectric devices. *Ferroelectrics* **151**, 321–330 (1994).
8. F. Bahri, H. Khemakhem, M. Gargouri, A. Simon, R. Von Der Muhll, and J. Ravez, Dielectric and Raman studies on the solid solution $(1-x)\text{BaTiO}_3/x\text{NaNbO}_3$ ceramics. *Solid State Sci.* **5**, 1235 (2003).
9. N. Abdelmoula, H. Khemakhem, A. Simon, and R. Von Der Muhll, Structural and dielectric studies of relaxor ferroelectric $\text{Ba}_{1-x}\text{La}_{x(1-y)/2}\text{Eu}_{xy/2}\text{Na}_{x/2}\text{TiO}_3$ ceramics. *J. Alloy. Compd.* **417**, 264–268 (2006).
10. J. C. Burfoot and G. W. Taylor, Polar dielectrics and their applications. Macmillan, London, 1979.
11. M. E. Lines and A. M. Glass, Principles and applications of ferroelectrics and related Materials. Gharendon, Oxford, 1977.
12. C. A. Randall and A. S. Bhalla, Nanostructural-properties relation in complex lead perovskites. *Jpn. J. Appl. Phys.* **29**, 327–333 (1990).
13. M. R. Varma and M. T. Sebastian, Effect of dopants on microwave dielectric properties of $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics. *J. Euro. Ceramic Soc.* **27**, 2827–2833 (2007).
14. M. Onada, K. Kuwata, K. Toyama, and S. Nomura, $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-Sr}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ Solid Solution Ceramics with Temperature-Stable High Dielectric Constant and Low Microwave Loss. *Jpn. J. Appl. Phys.* **21**, 1707–1710 (1987).
15. K. Endo, K. Fujimoto, and K. Murakawa, Dielectric Properties of Ceramics in $\text{Ba}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ Solid Solution. *J. Am. Ceram Soc.* **70**, 215–218 (1987).
16. L. Khemakhem, A. Kabadou, A. Maalej, A. Ben Salah, A. Simon, and M. Maglione, New relaxor ceramic with composition $\text{BaTi}_{1-x}(\text{Zn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$. Journal of alloys and compounds (in press).
17. K. Uchino, S. Nomura, Critical exponents of the dielectric constants in diffused-phase-transition crystals. *Ferroelectrics Lett.* **44**, 55–61 (1982).
18. D. Viehland, M. Wuttig, L. E. Cross, The glassy behavior of relaxor ferroelectrics. *Ferroelectrics* **120**, 71–77 (1991).