

Dielectric ferroelectric and piezoelectric properties of $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ ceramic

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Abstract

The present work concerns the preparation, dielectric, ferroelectric and piezoelectric characterizations of the lead-free ceramic composition $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$. This lead-free composition could be of great interest for environment friendly applications (dielectric for capacitors, actuators, etc.). This ceramic was prepared using the conventional mixed-oxide technique. The temperature dependence of the dielectric constant of this composition $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ was investigated. The rhombohedral–orthorhombic and orthorhombic–quadratic perovskite transitions are characterized by two weak peaks but the tetragonal–cubic ferroelectric–paraelectric one is characterized by a pronounced peak with weak frequency dispersion. Excellent dielectric properties have been obtained for this composition. A ϵ'_r value at 1 kHz reaches of about as 9700 was observed. The polarization versus electric field hysteresis measurements showed a well-defined hysteresis loop with a remanent polarization of $1.05 \mu\text{C}/\text{cm}^2$ with a coercive field of 0.85 kV/cm at room temperature. $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ exhibits an important value of d_{31} coefficient which reaches as high as 90 pC N^{-1} . From these results, we can consider this composition is of great interest for applications.

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1. Introduction

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 [1,2]. Much attention has been given to the interests of perovskite compounds with disordered cation (complex perovskite-type) [3].

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 [4–7].

Due to their technological applications, compounds exhibiting high piezoelectric and electromechanical coupling constants have attracted the interest of many material science researches in

the past few years. Coupled mixed perovskite have been widely used compound in piezoelectric and electromechanical devices. Such as $\text{Pb}(\text{Ti}, \text{Zr})\text{O}_3$ (PZT), $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMN-PT) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PZN-PT). The lead-based complex perovskite with chemical formula $\text{Pb}(\text{B}'_x\text{B}''_{1-x})\text{O}_3$ have attracted much attention due to industrial and academic interest [6,7]. 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 [8]. 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 [9]. Onada et al. [10] and Endo et al. [11], respectively, investigated the effects of mixed Ba/Sr and Zn/Co sites in BZN and highlighted the versatility and tuning capabilities of the BZN system.

Recent work by Reaney [12] based on analysis of the tolerance factor suggested that the Zn/Co route would give the best opportunity for a high Q_m , temperature stabilized material. They suggested a reduction of the range of ionic radii in the crystal structure would help to reduce the lattice strain. This reduction

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in strain is likely to help lower the dielectric loss of the sintered ceramic. Several authors discuss the importance of B-site ordering for optimising the electrical properties of BZN type ceramics [11,12].

The present study concerns compositions relatively close to that of BaTiO_3 ; $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$. This lead-free ceramic $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ was investigated by X-ray analysis, the dielectric constant study, E – P hysteresis measurements and piezoelectric characterization.

2. Experimental

Ceramic sample with the chemical formula of $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ was prepared using a conventional solid-state reaction method by reacting the stoichiometric proportions of high purity (up 99%) BaCO_3 , ZnO , Nb_2O_5 and TiO_2 powders. The mixture was ball-milled, dried and then calcined at 1100°C for 15 h 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 $\text{Mo K}\alpha$ radiation ($\lambda = 0.710690 \text{ \AA}$) in the angle range $5^\circ \leq 2\theta \leq 60^\circ$ with 10 s 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. For piezoelectric measurements, the ceramic was checked at 280 K by applying a dc electric field of 20 kV/cm for 5 min. Piezoelectric properties were measured by the resonance–antiresonance method based on of IRE Standards [13] using an impedance analyzer (HP 4194A).

3. X-ray diffraction analysis

Fig. 1 shows the X-ray diffraction pattern of the $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ sample taken at room temperature which reveals that the ceramic was 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]. Good agreement between the observed and calculated interplaner spacing suggests that the compound has a tetragonal structure at room temperature with a space group $P4/mmm$, $a = b = 4.0062(9) \text{ \AA}$ and $c = 4.0091(9) \text{ \AA}$; $\alpha = \beta = \gamma = 90^\circ$.

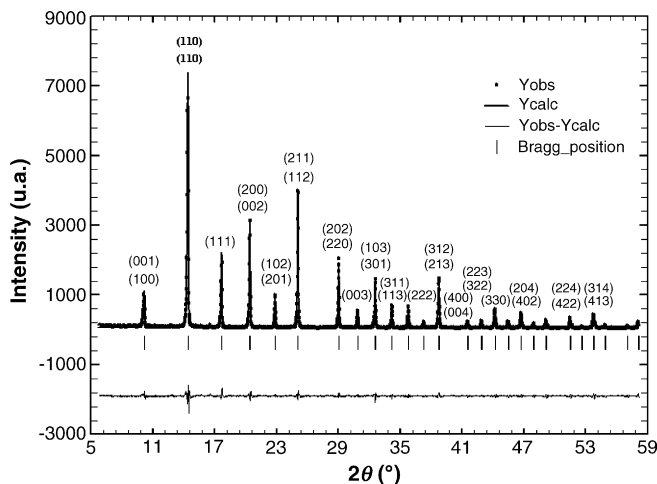


Fig. 1. X-ray diffraction pattern for $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ ceramic.

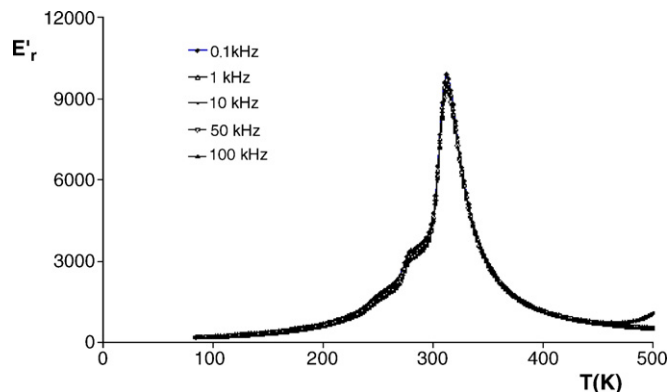


Fig. 2. Temperature dependence of the permittivity ϵ'_r for $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$.

4. Dielectric measurements

Before measurements, the samples were first heated at 473 K for 4 h under vacuum (this heat treatment was used to eliminate, as much as possible, the water content in the ceramic pores). The temperature dependence of the real ϵ'_r and imaginary ϵ''_r parts of the permittivity at several selected measurements frequencies (100 – 10^5 Hz) of $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ sample is shown in Figs. 2 and 3, respectively. Three anomalies related to the phase transitions (rhombohedral–orthorhombic at T_2 , orthorhombic–tetragonal at T_1 and tetragonal–cubic at T_C) for BaTiO_3 have been observed at $T_C = 312 \text{ K}$, $T_1 = 282 \text{ K}$ and $T_2 = 258 \text{ K}$. The values of T_C , T_1 and T_2 were independent of frequency.

Fig. 4 depicts the variation of $1/\epsilon'_r$ against temperature at 10^3 Hz . The Curie–Weiss relation, $\epsilon'_r = C/(T - T_0)$, holds at $T \geq 312 \text{ K}$ where C is the Curie constant and T_0 is the Curie temperature. T_0 of 383 K and C of $1.56 \times 10^5 \text{ K}$ have been obtained for a pure BaTiO_3 crystal [15]. For $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$, the ϵ'_r was fitted to the Curie–Weiss law. The fitting parameters are $C = 1.05 \times 10^5 \text{ K}$ and $T_0 = 314 \text{ K}$ nearly equal to T_C at 1 kHz . In Landau's theory of phase transition [16], a first-order transition takes place when $T_C > T_0$, and a second order in the case of $T_C = T_0$. Therefore, for the composition $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$, the second order ferroelectric paraelectric transition occurs

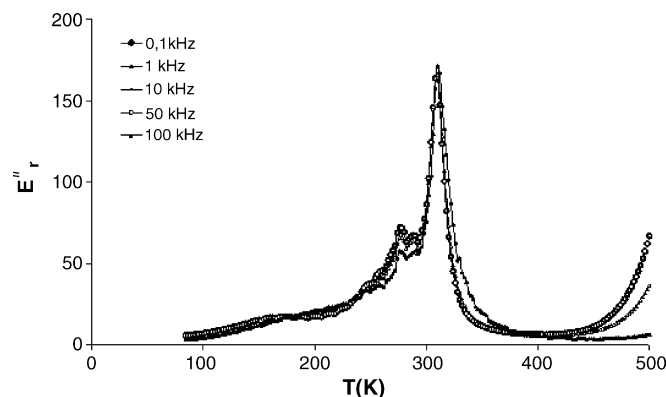


Fig. 3. Temperature dependence of the imaginary part ϵ''_r of the permittivity.

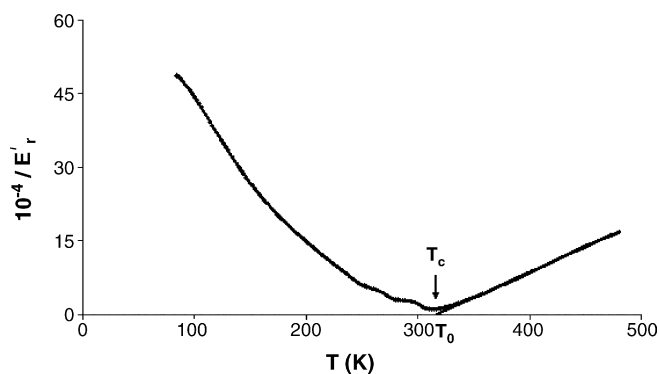


Fig. 4. The variation of $1/\epsilon'_r$ against temperature for $x=0.025$.

as well as for BZT in which the composition is very close to BaTiO_3 [16,17]. All these physical properties show that $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ compound is a classical ferroelectric.

In addition, comparing dielectric properties of BaTiO_3 which is characterized by $\epsilon'_{\text{rm}} \approx 9000$ and $T_C \approx 400$ K [18] to our specimen $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ (Fig. 2), we note that substituting Ti by Zn and Nb, the Curie temperature T_C decreases to room temperature ($T_C = 312$ K at 1 kHz) and ϵ'_{rm} increases to 9700. This is an important result in ferroelectric perovskite materials.

5. Ferroelectric study

The polarization hysteresis loops measured at different temperatures are shown in Fig. 5. At the temperature far below $T_C = 312$ K, a non-linear P - E loops are observed, which is a typical normal ferroelectric characteristic. At $T > T_C$, a linear P - E behaviour is present, implying micro-polar clusters and then characterize the paraelectric phase.

The temperature dependence of the remanent polarization and the coercive field are shown in Figs. 6 and 7. With increasing temperature, P_r and the coercive field decrease simultaneously. A remanent polarization of $1.05 \mu\text{C}/\text{cm}^2$ and a coercive field of 0.85 kV/cm at 290 K were obtained. These values are so smaller than those obtained in BaTiO_3 which are, respectively, $P_r \approx 26 \mu\text{C}/\text{cm}^2$ and $E_C \approx 1.2$ kV/cm [19].

These parameters can be interesting for many applications, added to piezoelectric results which show important evolution from that obtained in BaTiO_3 and derived solutions.

The polarization behaviour shows that $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ ceramic could be promising for room temperature ferroelectric and piezoelectric applications.

6. Piezoelectric studies

The spectrum of excited mechanical vibrations as a function of frequency in the range 10^2 to 4×10^7 Hz was determined by measuring the electrical impedance of the samples prepared in disc shapes to determine the piezoelectric d_{31} coefficient.

For the measurement of the mechanical quality factor Q_m , the resonator is characterized in the IEEE International standards

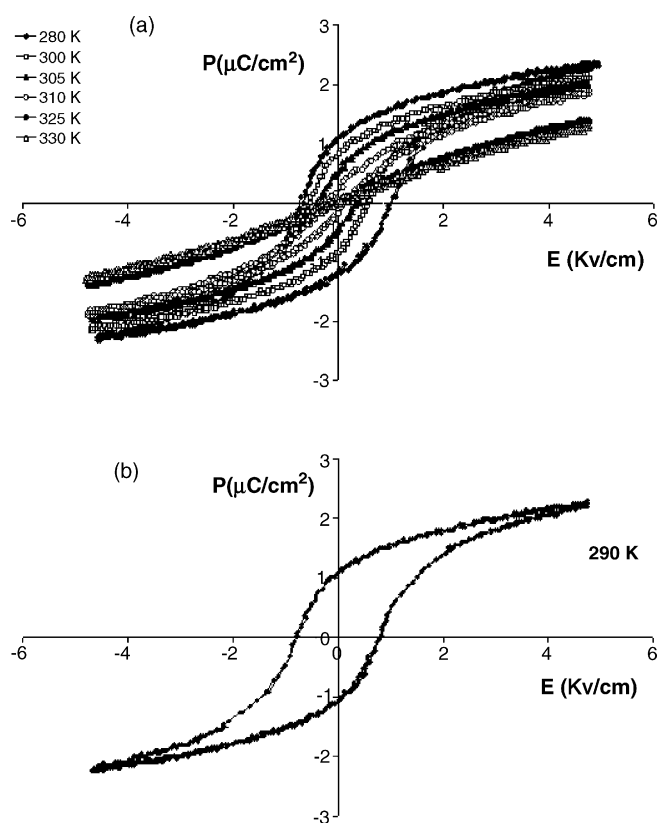


Fig. 5. (a) P - E hysteresis loops of $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ ceramic at different temperature. (b) P - E hysteresis loops of $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ ceramic at $T = 290$ K.

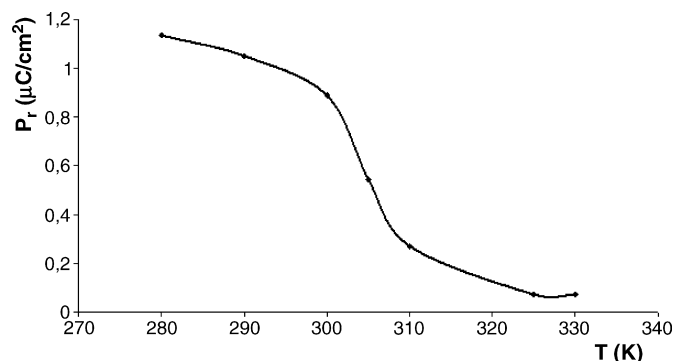


Fig. 6. Temperature dependence of the remanent polarization.

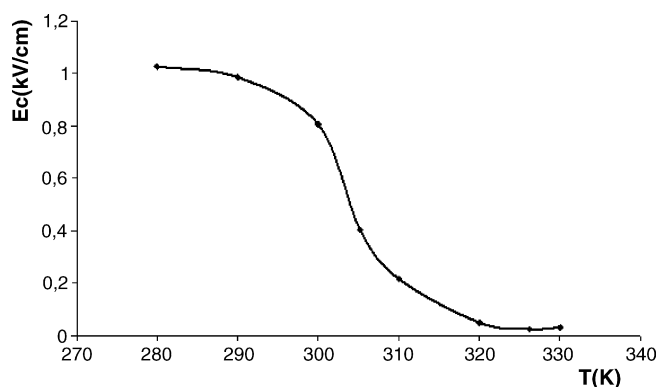


Fig. 7. Temperature dependence of the coercive field.

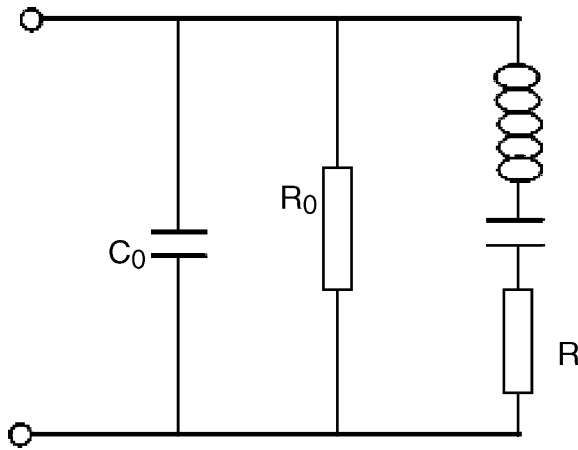


Fig. 8. Equivalent circuit (RLC).

[20] by a lumped-parameter equivalent circuit (RLC) (Fig. 8), where the motional resistance R accounts for the mechanical dissipation.

The motional branch (RLC) quality factor Q_m is thus defined as

$$Q_m = \frac{(L/C)^{1/2}}{R}$$

From the input impedance expression of the RLC equivalent circuit, and with the assumptions: minimum impedance $|Z_m| \approx 1/G_{\max} = R$; $1/\omega C_0 \gg R$, Mason and Fair [21] proposed the following expression for Q_m :

$$Q_m = \frac{f_s^2 / (f_p^2 - f_s^2)}{2\pi f_s C_0 R} \approx \frac{1}{4\pi R C_0 (f_p - f_s)}$$

where f_s is the resonant frequency and f_p is the antiresonant frequency.

Piezoelectric measurements were performed at 280 K on the ceramic with composition $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$. The sample (7.19 mm diameter and 0.89 mm thickness) was first poled using a dc electric field of 1.5 kV/mm at 280 K for 5 min and then short-circuited for some hours at the same temperature in order to eliminate any residual space charge. The evolution of admittance and susceptance versus frequency is plotted in Fig. 9. The value of the characteristic elements of the equivalent

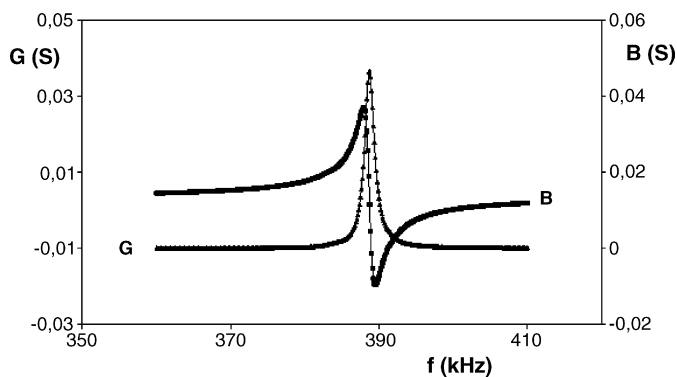


Fig. 9. Admittance G and susceptance B vs. frequency for $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ ceramic around the main radial piezoelectric resonance.

Table 1

Piezoelectric characteristics of $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ ceramic at 280 K

Radial resonance frequency, f_r (kHz)	399.662
Young's modulus, $1/s_{11}$ (N m^{-2})	80.67
Speed of sound, v (m s^{-1})	4418.39
Planar coupling factor, k_p	0.258
Mechanical quality factor, Q_m	240.65
Piezoelectric coefficient, d_{31} (pC N^{-1})	90.517

lent circuit of the piezoelectric sample is obtained by fitting the admittance circle $B = f(G)$ and the curves $G(f)$ and $B(f)$ [22]. The piezoelectric coefficients d_{31} , K_p , Q_m and k_{31} were calculated from IRE standards [23]. The results are reported in Table 1. The value obtained for the d_{31} transverse piezoelectric coefficient is 90.517 pC N^{-1} . This piezoelectric coefficient is comparable to the values obtained in some ceramic such as $\text{KTa}_{0.6}\text{Nb}_{0.4}\text{O}_3$ ($d_{31} = 18$) [24] and $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ($d_{31} = 14$) [25]. The d_{31} values make $\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ ceramic of great interest for many applications.

7. Conclusion

$\text{BaTi}_{0.975}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.025}\text{O}_3$ ceramic with perovskite structure was prepared by a conventional ceramic fabrication technique. These structural, dielectric and piezoelectric properties were investigated. The X-ray diffraction study shows that the compound exists in a single phase at room temperature with a tetragonal symmetry. Dielectric permittivity was measured in the temperature and frequency range, respectively, 80–500 K and 0.1–200 kHz. Substituting Ti by Zn and Nb induce a decrease of T_C to room temperature and increase of ϵ'_r . A P_r of $1.05 \mu\text{C/cm}^2$ and E_C of 0.85 kV/cm were obtained at $T = 290 \text{ K}$. These results make this composition suitable for diverse applications.

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References

- [1] A. Aydi, H. Khemakhem, C. Boudaya, R. Von Der Muhll, A. Simon, Solid State Sci. 6 (2004) 333.
- [2] H. Khemakhem, A. Simon, R. Von Der Muhll, J. Ravez, J. Phys. Condens. Mater. 12 (2000) 5951.
- [3] K. Uchino, Ferroelectrics 151 (1994) 321.
- [4] F. Bahri, H. Khemakhem, M. Gargouri, A. Simon, R. Von Der Muhll, J. Ravez, Solid State Sci. 5 (2003) 1235.
- [5] N. Abdelmoula, H. Khemakhem, A. Simon, R. Von Der Muhll, J. Alloys Compd. 417 (2006) 264.
- [6] J.C. Burfoot, G.W. Taylor, Polar Dielectrics and Their Applications, Macmillan, London, 1979.
- [7] M.E. Lines, A.M. Glass, Principles and Applications of Ferroelectrics and Related Materials, Gharendon, Oxford, 1977.
- [8] C.A. Randall, A.S. Bhalla, Nanostructural-properties relation in complex lead perovskites, Jpn. J. Appl. Phys. 29 (1990) 327.
- [9] OKI Electric Ind. Co. Ltd., Patent JPO5298922A2 (November 1993).
- [10] M. Onoda, K. Kuwata, K. Toyama, S. Nomura, Jpn. J. Appl. Phys. 21 (1987) 1707.

- [11] K. Endo, K. Fujimoto, K. Murakawa, *J. Am. Ceram. Soc.* 70 (9) (1987) 215.
- [12] I.M. Reaney, American Ceram. Soc. Meeting, May, 2002, Abstract AMA.1-B-01-2002.
- [13] IRE Standard on piezoelectric crystals: measurements of piezoelectric ceramics, *Proc. IRE* 49 (1961) 1161.
- [14] T. Roismel, Program Fullprof, Laboratoire de Chimie du Solide Inorganique et moléculaire 4MR6511, CNRS-Université de Rennes, version 3.70, May 2004;
J. Rodriguez-Carvajal, Laboratoire Brillouin (CEA-CNRS), LLB-LCSIM, March 2005.
- [15] W.J. Mertz, *Phys. Rev.* 91 (1953) 513.
- [16] J. Ravez, C. Broustera, A. Simon, *J. Mater. Chem.* 9 (1999) 1609.
- [17] Ph. Sciau, G. Galvarin, J. Ravez, *Solid State Commun.* 113 (2000) 77.
- [18] W.J. Merz, *Phys. Rev.* 76 (8) (1949) 1221.
- [19] H.H. Wieder, *Phys. Rev.* 99 (1955) 4.
- [20] Standards on piezoelectricity, ANSI/IEEE std 176 (1987).
- [21] W.P. Mason, I.E. Fair, *Proc. IRE* 465 (1942) 921.
- [22] D. Berlincourt, D. Curran, H. Jaffe, in: W.P. Mason (Ed.), *Physical Acoustics*, vol. 1, Academic Press, London, 1964, p. 169.
- [23] I.R.E. Standards on piezoelectrics, *Proc. IRE* 49 (1961) 1161.
- [24] B. Jaffe, W.R. Cook, H. Jaffe, *Piezoelectric Ceramics*, Academic Press, London, 1971, p. 115.
- [25] R. Von Der Muhll, H. Khemakhem, J. Ravez, *Ann. Chim. Sci. Mater.* 22 (1997) 725.