



HAL
open science

Sintering, microstructures and dielectric properties of $\text{Ba}_{1-x}\text{Pb}_x(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3-3x}\text{F}_{3x}$ ferroelectric ceramics

Laldja Taïbi-Benziadaa, Annie Simon

► **To cite this version:**

Laldja Taïbi-Benziadaa, Annie Simon. Sintering, microstructures and dielectric properties of $\text{Ba}_{1-x}\text{Pb}_x(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3-3x}\text{F}_{3x}$ ferroelectric ceramics. Central European Journal of Chemistry, 2009, 7 (2), pp.159-163. 10.2478/s11532-008-0063-y. hal-00382794

HAL Id: hal-00382794

<https://hal.science/hal-00382794>

Submitted on 5 Mar 2024

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.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Sintering, Microstructures and Dielectric Properties of $\text{Ba}_{1-x}\text{Pb}_x(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3-3x}\text{F}_{3x}$ Ferroelectric Ceramics

SSC-2008

Laldja Taïbi-Benziada^{1*}, Annie Simon²

¹ Faculty of Chemistry, USTHB, El-Alia,
16311 Bab-Ezzouar, Algeria

² ICMCB, CNRS,
33608 Pessac, France

Received 17 June 2008; Accepted 18 August 2008

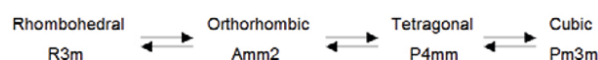
Abstract: Various compositions $(1-x)\text{BaTiO}_3 + x\text{PbF}_2 + x\text{LiF}$ were prepared, shaped to pellets then sintered at 900°C for 2 h in gold sealed tubes. The purity and the symmetry of the obtained samples were checked by X-ray diffraction. A new solid solution with $\text{Ba}_{1-x}\text{Pb}_x(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3-3x}\text{F}_{3x}$ formula occurs in the composition range $0 \leq x \leq 0.20$. SEM observations were performed on polished and fractured ceramics. The complex permittivity was measured as a function of temperature ($-120^\circ\text{C} \leq T \leq 250^\circ\text{C}$) and frequency ($50 \text{ Hz} \leq f \leq 4 \times 10^7 \text{ Hz}$). The dielectric performances are the best for ceramic $\text{Ba}_{0.97}\text{Pb}_{0.03}(\text{Ti}_{0.97}\text{Li}_{0.03})\text{O}_{2.91}\text{F}_{0.09}$. The real component ϵ' , exhibits a maximum of approximately 7500 at the ferroelectric Curie temperature $T_C \approx -18^\circ\text{C}$, the dielectric losses $\tan \delta$ value being 0.012. At room temperature, the relaxation frequency f_r is around 40 MHz for this ceramic. This novel ferroelectric oxifluoride is a promising material for applications, in particular in the field of Z5U multilayer capacitors.

Keywords: BaTiO_3 • Oxifluoride • Sintering • Dielectric properties

© Versita Warsaw and Springer-Verlag Berlin Heidelberg.

1. Introduction

The progress and success in new technologies are closely linked to the development of advanced ceramics with continuously improving performance. To fulfil severe requirements demanded by the systems miniaturization, the perovskites family ABO_3 is of great interest for manufacturing smaller and smaller electronic components [1-3]. Among these materials, BaTiO_3 related ceramics were intensively studied worldwide thanks to their various applications: capacitors, sensors, resonators, piezoelectric actuators, pyroelectric detectors, modulators, and computer memories. As example, the solid solution $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ is of particular interest for the development of small size integrated circuit memories [4]. Pure barium titanate undergoes three phase transitions [5,6]:



The first order ferroelectric-paraelectric phase transition from tetragonal to cubic structure is very sharp and occurs around 120°C, which temperature is too high for applications. On the other hand, BaTiO_3 exhibits a dielectric relaxation at high frequencies. Kersten *et al.* [7] reported the relaxation frequency f_r to be about 350 MHz in the temperature range $-75^\circ\text{C} \leq T \leq -5^\circ\text{C}$ (orthorhombic phase). At lower temperatures, f_r decreases and a value of 250 MHz was observed at -103°C (rhombohedral phase). In the tetragonal phase, f_r was found to be higher: 500 MHz at $+50^\circ\text{C}$. Similar results were obtained by Maglione *et al.* on BaTiO_3 crystals and ceramics [8,9].

The present work reports the structural and dielectric properties of BaTiO_3 based ceramics sintered at low temperature using the fluoride mixture $\text{PbF}_2 + \text{LiF}$. The main objectives are to lower simultaneously the

* E-mail: ikra@wissal.dz

Table 1. Unit cell parameters (a , c), volume (V) and c/a ratio of $\text{Ba}_{1-x}\text{Pb}_x(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3-3x}\text{F}_{3x}$ phases at room temperature.

Composition	a (Å)	c (Å)	V (Å ³)	c/a
BaTiO_3	3.998 ± 0.002	4.018 ± 0.008	64.223 ± 0.003	1.005
$\text{Ba}_{0.97}\text{Pb}_{0.03}(\text{Ti}_{0.97}\text{Li}_{0.03})\text{O}_{2.91}\text{F}_{0.09}$	4.008 ± 0.001	-	64.384 ± 0.001	1
$\text{Ba}_{0.95}\text{Pb}_{0.05}(\text{Ti}_{0.95}\text{Li}_{0.05})\text{O}_{2.85}\text{F}_{0.15}$	4.008 ± 0.001	-	64.384 ± 0.001	1
$\text{Ba}_{0.90}\text{Pb}_{0.10}(\text{Ti}_{0.90}\text{Li}_{0.10})\text{O}_{2.70}\text{F}_{0.30}$	4.007 ± 0.001	-	64.336 ± 0.001	1
$\text{Ba}_{0.85}\text{Pb}_{0.15}(\text{Ti}_{0.85}\text{Li}_{0.15})\text{O}_{2.55}\text{F}_{0.45}$	3.997 ± 0.002	4.014 ± 0.003	64.127 ± 0.002	1.004
$\text{Ba}_{0.80}\text{Pb}_{0.20}(\text{Ti}_{0.80}\text{Li}_{0.20})\text{O}_{2.40}\text{F}_{0.60}$	3.986 ± 0.001	4.035 ± 0.001	64.108 ± 0.001	1.012

Table 2. Shrinkage ($\Delta\Phi/\Phi$) and dielectric characteristics of $\text{Ba}_{1-x}\text{Pb}_x(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3-3x}\text{F}_{3x}$ ceramics sintered at 900°C for 2 h (1 kHz).

x	$\Delta\Phi/\Phi$ (%)	T_c (°C)	$\epsilon'_r(T_c)$	$\tan\delta(T_c)$ (%)	$\epsilon'_r(20^\circ\text{C})$	$\tan\delta(20^\circ\text{C})$ (%)
0	5.8	130	1000	1.5	400	2.5
0.03	16.3	-18	7500	1.2	6300	0.3
0.05	17.1	-60	4000	1	3200	0.3
0.10	14.5	-55	3250	1	2500	0.3
0.15	13.1	75	1800	0.5	1300	1.8
0.20	11.8	145	1350	1.6	300	2.2

ferroelectric and the sintering temperatures of pure barium titanate and to prepare oxifluoride ceramics $\text{Ba}_{1-x}\text{Pb}_x(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3-3x}\text{F}_{3x}$ with high permittivity, useful for manufacturing inexpensive multilayer capacitors.

2. Experimental Procedures

Powders of BaCO_3 , TiO_2 (rutile), PbF_2 and LiF with 99.99% in purity supplied by MERCK were used for the preparations. The carbonate, BaCO_3 , and the oxide, TiO_2 , were pre-heated at 300°C for 72 h in an oven to eliminate moisture. The fluorides PbF_2 and LiF were desiccated at 150°C for 2 h under vacuum to prevent their hydrolysis during sintering.

Stoichiometric BaTiO_3 was firstly synthesized by heating an equimolar mixture of BaCO_3 and TiO_2 at 1100°C for 15 hours in air atmosphere. Various compositions $(1-x)\text{BaTiO}_3 + x\text{PbF}_2 + x\text{LiF}$ were weighed, homogenized and dry-ground in a glove box. The powders thus obtained were shaped to pellets of 9 mm diameter and about 1 mm thickness by cold-pressing under a pressure of 10^8 Pa. The disks were sintered in gold sealed tubes under dry-argon in an electrical furnace outside the box.

The symmetry and the purity were investigated by X-ray diffraction (XRD) on crushed ceramics using a PHILIPS powder diffractometer with monochromatic $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.54051$ Å) at 40 kV and 30 mA. The data were recorded by step scanning of 0.02° in the 2θ range $5 - 120^\circ$ and a counting time of 0.5 s per step using silicon as an internal standard. The unit cell parameters were determined then refined by the least squares method.

The microstructure was systematically observed on polished surfaces and fractures of ceramics by scanning electron microscopy (SEM) with the aid of a PHILIPS apparatus type LX30. The operating voltage was 20 kV. The sintered samples were electroded with a silver paste to make capacitors. Dielectric measurements were then performed, first, versus temperature from -120°C to 250°C at 100 Hz, 1 kHz and 10 kHz, respectively, using a Wayne Kerr capacitance bridge B 905. In a second step, the complex permittivity was measured, at room temperature, in the frequency range 50 Hz – 40 MHz with the aid of a Hewlett Packard impedance analyser HP 4194 A. All experiments were carried out under vacuum.

3. Results and Discussion

The X-ray diffraction analysis revealed that $(1-x)\text{BaTiO}_3 + x\text{PbF}_2 + x\text{LiF}$ samples sintered at 900°C for 2 h in gold sealed tubes are homogeneous and monophasic up to $x = 0.20$. When more than 20 mol% of $(\text{PbF}_2 + \text{LiF})$ is added to BaTiO_3 , second phases are observed on the XRD patterns. Table 1 reports the variation of the unit cell parameters (a , c), the volume (V) and the ratio (c/a) with the chemical composition.

As seen in Table 1, the slight tetragonal distortion of BaTiO_3 disappears in a first time, the ratio c/a steps down to 1 and the lattice symmetry becomes cubic. In a second time, c/a steps up with increasing x and the distortion of the unit cell reappears ($x \geq 0.15$), nevertheless the volume change is not significant and the perovskite structure of pure barium titanate is maintained.

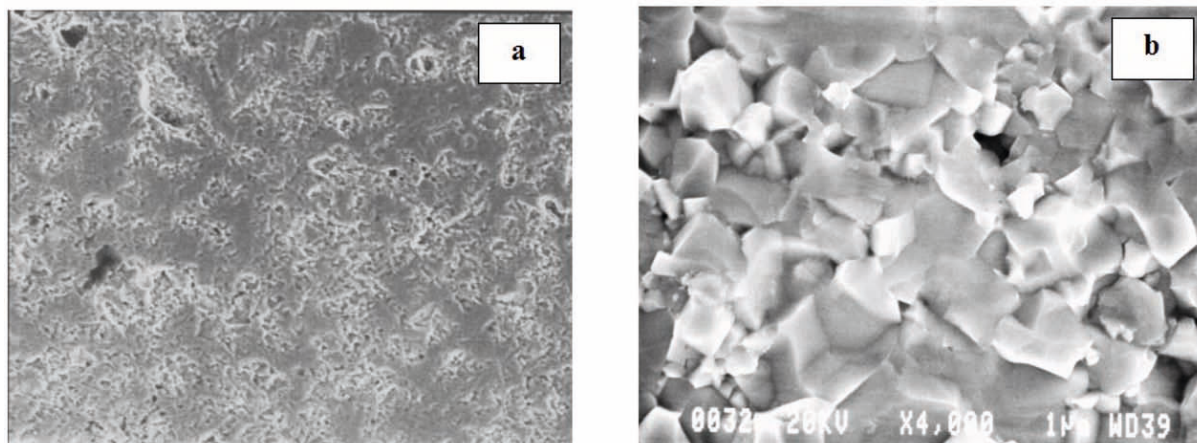


Figure 1. SEM micrographs of $\text{Ba}_{0.97}\text{Pb}_{0.03}(\text{Ti}_{0.97}\text{Li}_{0.03})\text{O}_{2.91}\text{F}_{0.09}$ ceramic: (a) surface (b) fracture.

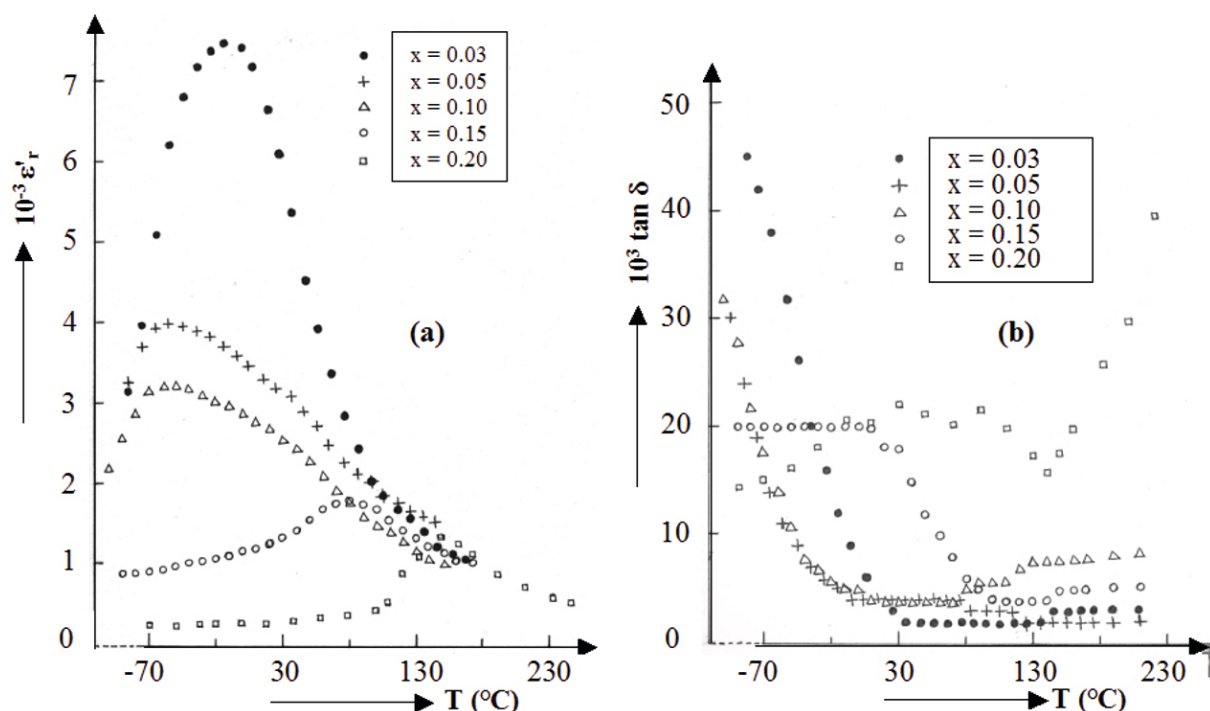


Figure 2. Temperature dependence of ϵ'_r (a) and $\tan \delta$ (b) for ceramics $\text{Ba}_{1-x}\text{Pb}_x(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3-3x}\text{F}_{3x}$ at 1 kHz.

The SEM observations show no secondary phases, neither at the grain boundaries nor at the grain surface of the ceramics. This result is in agreement with the XRD analyses. The surface and fracture micrographs of $\text{Ba}_{0.97}\text{Pb}_{0.03}(\text{Ti}_{0.97}\text{Li}_{0.03})\text{O}_{2.91}\text{F}_{0.09}$ ceramic are illustrated in Fig. 1. The grain size is not regular and homogeneous. Coarse ($\sim 6 \mu\text{m}$) and fine ($\sim 1 \mu\text{m}$) grains are detected on the fracture (Fig. 1b) and the porosity is inter-granular.

The results of the dielectric measurements performed as a function of temperature at 1 kHz on ceramics with various compositions are shown in Fig. 2 and summarized in Table 2. The permittivity exhibits a very broad maximum whose height decreases with the

increase of $\text{PbF}_2 + \text{LiF}$ content (Fig. 2a). The broadness of the ϵ'_r peak is characteristic of a diffuse phase transition with local variation of the composition either in the grain or from grain to grain. The dielectric losses $\tan \delta$ do not exceed 5% in the entire temperature range investigated (Fig. 2b).

The ferroelectric Curie temperature T_C decreases, then increases with increasing x (Table 2). These variations are ascribed to the effects of fluorine (F) and lead (Pb^{2+}) ions on the chemical bondings. The shift of T_C toward lower temperatures is attributed to diminishing covalence with F–O substitution (polarization coefficient: $\text{F}^- = 0.81 \times 10^{-24} \text{cm}^3$, $\text{O}^{2-} = 3.88 \times 10^{-24} \text{cm}^3$) whereas the

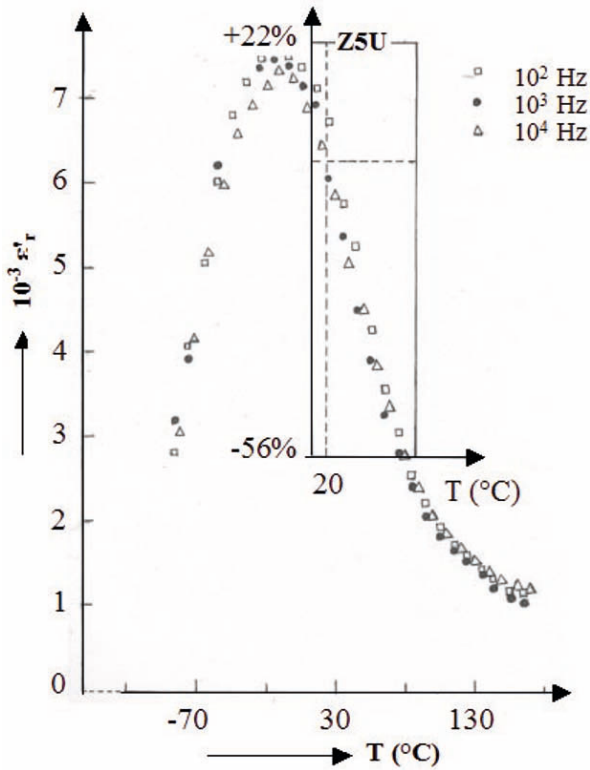


Figure 3. Variation with temperature of ϵ_r' for ceramic $\text{Ba}_{0.97}\text{Pb}_{0.03}(\text{Ti}_{0.97}\text{Li}_{0.03})\text{O}_{2.91}\text{F}_{0.09}$ at various frequencies.

increase of T_C value is due to the influence of the $6s^2$ electron pair of Pb^{2+} which induces a strong polarization in the bonds and therefore more covalence when Ba is substituted by Pb (polarization coefficient: $\text{Ba}^{2+} = 1.69 \times 10^{-24} \text{ cm}^3$, $\text{Pb}^{2+} = 3.60 \times 10^{-24} \text{ cm}^3$). All these results are in good agreement with our previous works on oxifluorides deriving from BaTiO_3 [10-13].

The shrinkage coefficient $\Delta\Phi/\Phi$ (Table 2) increases then decreases with increasing the fraction of $\text{PbF}_2 + \text{LiF}$. The shrinkage of BaTiO_3 ceramic sintered at 900°C

without additive is around 6% and jumps to more than 16% with the addition of 3 mol% of $\text{PbF}_2 + \text{LiF}$. The density reaches 96% for this sample. To get such shrinkage and density for pure barium titanate, the ceramic must be sintered at 1400°C or higher. Therefore, the fluoride mixture $\text{PbF}_2 + \text{LiF}$ is a consequent improver in the sintering process of the perovskite BaTiO_3 at low temperature.

The best dielectric characteristics are obtained for $\text{Ba}_{0.97}\text{Pb}_{0.03}(\text{Ti}_{0.97}\text{Li}_{0.03})\text{O}_{2.91}\text{F}_{0.09}$ ceramic: $\epsilon_r' \sim 7500$, $\tan \delta \sim 1.2\%$ at T_C which is around -20°C (Table 2). The temperature dependence of ϵ_r' at 100 Hz, 1 kHz and 10 kHz for this sample is depicted in Fig. 3. The values of $\epsilon_r'_{max}$ and T_C are practically independent of the frequency. This behavior is typical of a ferroelectric-paraelectric phase transition without any relaxation. Moreover, the $\epsilon_r'-T$ curves fulfil the requirements of Z5U class of capacitors ($\Delta\epsilon_r'/\epsilon_r'(20^\circ\text{C}) \leq +22\%$ at 10°C ; $\Delta\epsilon_r'/\epsilon_r'(20^\circ\text{C}) \geq -56\%$ at 85°C).

Fig. 4 reports the variation of the complex permittivity with the frequency using a logarithmic scale for the ceramic corresponding to $x = 0.03$, sintered either in a gold sealed tube (a) or in free air (b). The curves $\epsilon_r' - \log f$ and $\epsilon_r'' - \log f$ display the same profile for the two ceramics but the values are much higher for the sample sintered in a gold sealed tube. The decrease of ϵ_r' and the increase of ϵ_r'' at high frequencies are ascribed to the beginning of a dielectric relaxation which occurs not very far from 40 MHz, the limit of the setup used. This result agrees quite well with previous works on fluorinated barium titanate and can be mainly related to the simultaneous substitution Li - Ti and F - O [9,11,12].

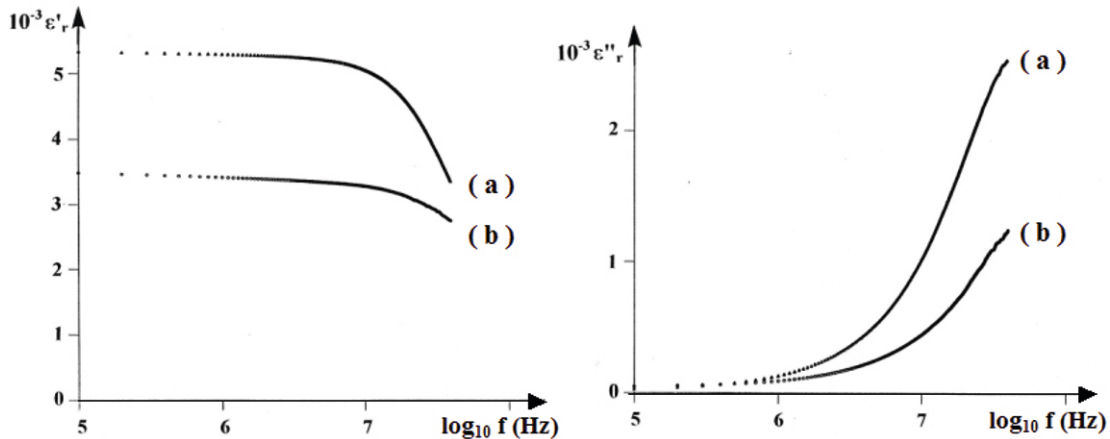


Figure 4. Frequency dependence of ϵ_r' and ϵ_r'' for ceramic $\text{Ba}_{0.97}\text{Pb}_{0.03}(\text{Ti}_{0.97}\text{Li}_{0.03})\text{O}_{2.91}\text{F}_{0.09}$ sintered at 900°C for 2 h: (a) in a gold sealed tube (b) in air atmosphere.

4. Conclusion

Barium titanate ceramics have been sintered with the aid of PbF_2 and LiF in gold sealed tubes at 900°C for 2 h. An oxifluoride solid solution $\text{Ba}_{1-x}\text{Pb}_x(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3-3x}\text{F}_{3x}$ is obtained in the composition range $0 \leq x \leq 0.20$. The additive PbF_2+LiF is a consequent improver in

the sintering process of BaTiO_3 at low temperature. Each ceramic exhibits a diffuse ferroelectric phase transition which is frequency independent. The ceramic $\text{Ba}_{0.97}\text{Pb}_{0.03}(\text{Ti}_{0.97}\text{Li}_{0.03})\text{O}_{2.91}\text{F}_{0.09}$ shows the best performance and is very promising for the manufacture of Z5U multilayer capacitors with a low factory cost.

References

- [1] C. M. Ditum, T. W. Button, J. Eur. Ceram. Soc. 23, 2693 (2003)
- [2] S. Mustofa, T. Araki, T. Furusawa, M. Nishida, T. Hino, Mater. Sci. Eng. B 103, 128 (2003)
- [3] Y. Shin, K. M. Kang, Y. G. Jung, J. G. Yeo, S. G. Lee, U. Paik, J. Eur. Ceram. Soc. 23, 1427 (2003)
- [4] J. F. Scott, Mater. Sci. Eng. B 120 (1-3), 6 (2005)
- [5] B. Matthias, A. Von Hippel, Phys. Rev. 73, 1378 (1948)
- [6] H. T. Evans, Acta Cryst. 14, 1019 (1961)
- [7] O. Kersten, A. Rost, G. Schmidt, Ferroelectrics 81, 31 (1988)
- [8] M. Maglione, R. Böhmer, A. Loidl, U.T. Höchli, Phys. Rev. B 40, 11441 (1989)
- [9] S. Kazaoui, J. Ravez, C. Elissalde, M. Maglione, Ferroelectrics 135, 85 (1992)
- [10] L. Benziada, J. Ravez, J. Fluor. Chem. 73, 69 (1995)
- [11] L. Benziada, J. Claverie, Ferroelectrics 189, 129 (1996)
- [12] L. Taïbi-Benziada, H. S. Hilal, R. Von Der Mühl, Sol. Stat. Sci. 8, 922 (2006)
- [13] M. Meyar, L. Taïbi-Benziada, J. Eur. Ceram. Soc. 27, 1097 (2007)