ELSEVIER Journal of Fluorine Chemistry 73 (1995) 69–71

Ferroelectric $BaTiO_3$ ceramics sintered at low temperature with the aid of a mixture of CaF_2 and LiF

L. Benziada [a,*], J. Ravez [b]

[a] Institut de Chimie, U.S.T.H.B., B.P. 32, El-Alia, Bab-Ezzouar, Algiers, Algeria
[b] Laboratoire de Chimie du Solide du CNRS, Université Bordeaux I, 33405 Talence, France

Received 4 July 1994; accepted 18 November 1994

Abstract

A mixture of CaF_2 and LiF has been used to sinter $BaTiO_3$ at low temperature. As a result, a new solid solution has been obtained after 2 h at 930 °C. Mixing, grinding and heating were all performed in air with various starting compositions $[(1-x)BaTiO_3+xCaF_2+xLiF]$. The variation of the unit cell parameters has been determined and the sintering conditions optimized. Dielectric measurements have been performed on ceramic samples over the temperature and frequency ranges 150–450 K and 10^2–10^4 Hz, respectively. Each sample exhibited a large maximum for ϵ_r' at the Curie temperature T_C.

Keywords: Ferroelectric ceramics; Low-temperature sintering; Perovskites

1. Introduction

Ferroelectric ABO_3 perovskites are attractive materials for various applications [1,2] and solid solutions are of particular interest for the development of new ferroelectric materials. A study of $BaTiO_3$–ABF_3 systems (A = Ba, Na, K; B = Li, Mg) has allowed us to determine the influence of ABF_3 fluoride addition on the crystallographic and dielectric properties of $BaTiO_3$ [3,4]. Three oxyfluoride solid solutions have been prepared from $KNbO_3$ using the same ABF_3 additives [5]. Recently, crystallographic and dielectric studies have been performed on ceramics with the compositions $Na_{1-x}A_x(Nb_{1-x}Mg_x)O_{3-3x}F_{3x}$ (A = Na, K) [6]. The purpose of the present work was to sinter and characterize derived $BaTiO_3$ ferroelectric ceramics at low temperature using a mixture of CaF_2 and LiF.

2. Preparation of samples

$BaTiO_3$ has been synthesized previously via the reaction:

$$BaCO_3 + TiO_2 \xrightarrow{1100\,°C} BaTiO_3 + CO_2$$

Various starting compositions were prepared from a mixture of $BaTiO_3$, CaF_2 and LiF powders, i.e. $(1-x)BaTiO_3+xCaF_2+xLiF$. All weighing, mixing, grinding and heating was performed in air. The purity of the materials was checked by X-ray powder pattern analysis. The different parameters to be considered with a view to optimizing the sintering conditions are composition (x), temperature (T) and time (θ).

3. Crystallographic study

Samples obtained by heating the starting mixtures $(1-x)BaTiO_3+xCaF_2+xLiF$ at 930 ± 10 °C for 2 h were examined by X-ray powder diffractometry using monochromatic Cu $K\alpha_1$ radiation ($\lambda = 1.54051$ Å) with silicon as an internal standard. The unit cell parameters were refined using a least-squares refinement. As a result a new solid solution with a perovskite structure has been identified. This occurs in the $0 \leq x \leq 0.10$ initial composition range. The tetragonal symmetry of pure $BaTiO_3$ became cubic when more than 0.04 mol (CaF_2 + LiF) was added. The dependence of the lattice parameters on the composition is depicted in Fig. 1. Fig. 2 shows the variation in unit cell volume (V) with composition. The TiO_6 and LiF_6 octahedra in the structure are almost the same size with the increase in cation size in going from Ti^{4+} to Li^{+} being com-

---

* Corresponding author.

SSDI 0022-1139(94)03211-4

Table 1
Composition dependence of shrinkage coefficient and dielectric characteristics (1 kHz) for ceramics sintered at 930 °C for 2 h

Initial composition in mole	$\Delta\phi/\phi$	T_C (K)	ϵ'_r (at T_C)	10^3 tan δ (at T_C)
$0.975BaTiO_3+0.025CaF_2+0.025LiF$	0.080	333	2800	5
$0.95BaTiO_3+0.05CaF_2+0.05LiF$	0.117	288	3200	8
$0.925BaTiO_3+0.075CaF_2+0.075LiF$	0.129	278	2250	8
$0.90BaTiO_3+0.10CaF_2+0.10LiF$	0.131	263	2150	10

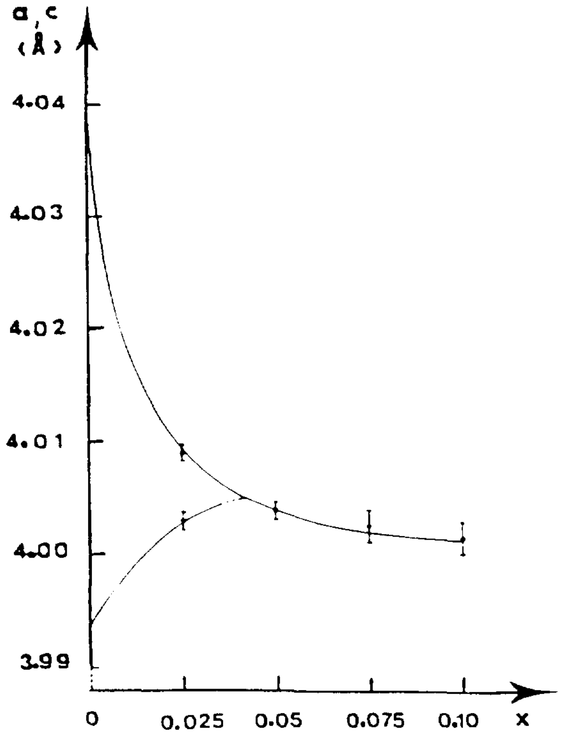

Fig. 1. Dependence of the lattice parameters (at 300 K) on the composition.

pensated by the decrease in the anion size from O^{2-} to F^- ($r_{Ti^{4+}}=0.605$ Å; $r_{Li^+}=0.74$ Å; $r_{O^{2-}}=1.40$ Å; $r_{F^-}=1.33$ Å in hexacoordination) [7]. The decrease of V with x is due to the decrease in cationic radius in going from Ba^{2+} to Ca^{2+} ($r_{Ba^{2+}}=1.60$ Å; $r_{Ca^{2+}}=1.35$ Å in 12 coordination) [7].

4. Dielectric study

Mixtures of $BaTiO_3$, CaF_2 and LiF were pressed into pellets of 13 mm diameter and ca. 1–2 mm thickness by placing the powder under a pressure of 1 tonne cm^{-2} after previous grinding in air. The various parameters used in the sintering process were as follows: (i) heating rate: 200 °C h^{-1}; (ii) sintering temperature: 800 °C, 930 °C, 1000 °C or 1100 °C; and (iii) sintering time: 2 h, 4 h or 8 h.

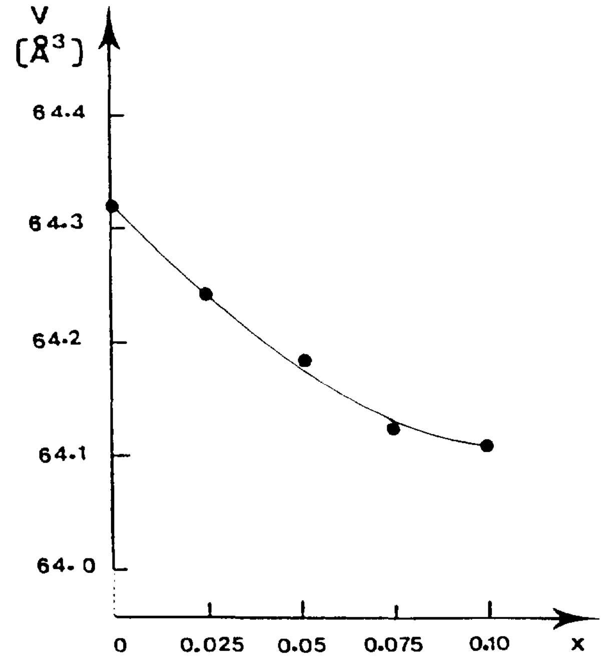

Fig. 2. Dependence of the unit cell volume (at 300 K) on the composition.

Table 2
Influence of the sintering temperature on the shrinkage coefficient and the dielectric characteristics (1 kHz) for a ceramic corresponding to $x=0.05$ and $\theta=2$ h

Sintering temperature (°C)	$\Delta\phi/\phi$	T_C (K)	ϵ'_r (at T_C)	10^3 tan δ (at T_C)
800	0.07	368	1200	2
930	0.117	288	3200	8
1000	0.125	293	3500	7
1100	0.125	273	3000	8

The influences of the various parameters are listed in Tables 1, 2 and 3. The temperature dependencies of both the permittivity (ϵ'_r) and the dielectric losses (tan δ) were measured on ceramic samples over the temperature and frequency ranges 150–450 K and 10^2–10^4 Hz, respectively. The measurements were carried out under vacuum.

Fig. 3 shows the dependence of T_C on composition. In each case, the ferroelectric phase transition was diffuse and the Curie temperature decreased with the

Table 3
Influence of the sintering time on the shrinkage coefficient and the dielectric characteristics (1 kHz) for a ceramic corresponding to $x=0.05$ sintered at 930 °C

Sintering time (h)	$\Delta\phi/\phi$	T_C (K)	ϵ'_r (at T_C)	$10^3 \tan\delta$ (at T_C)
2	0.117	288	3200	8
4	0.117	288	4500	8
8	0.128	263	3200	15

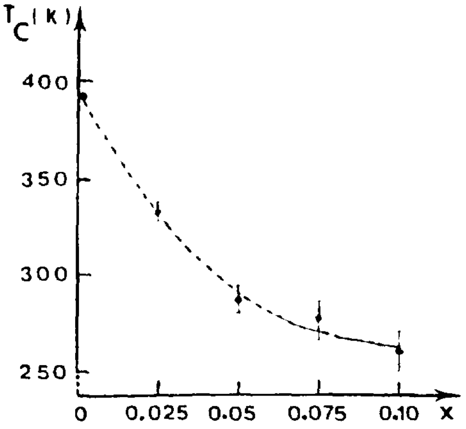

Fig. 3. Variation of T_C with composition (1 kHz).

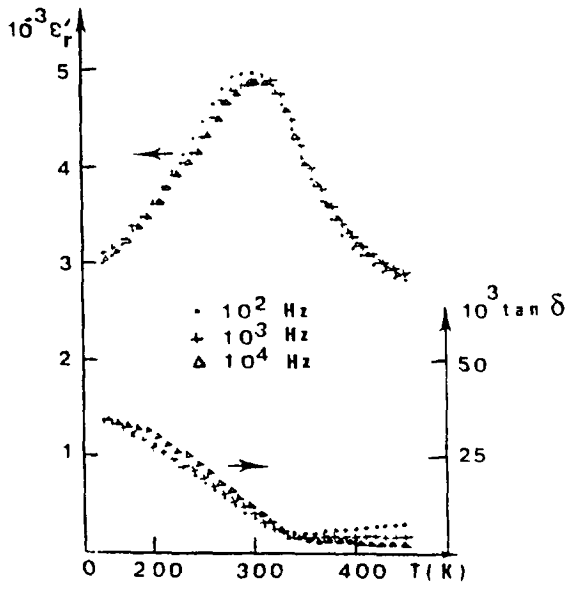

Fig. 4. Temperature dependencies of ϵ'_r and tan δ for a ceramic corresponding to $x=0.05$ sintered at 1000 °C for 4 h.

amount of fluorine present: T_C varied from 393 K ($x=0$) to 263 K ($x=0.10$). This result which is due especially to oxygen–fluorine substitution is in good agreement with our previous work on the ferroelectric oxyfluorides [3–6]. Fig. 4 shows, as an example, the temperature dependence of ϵ'_r and tan δ for a ceramic corresponding to the initial composition, i.e. ($0.95BaTiO_3+0.05CaF_2+0.05LiF$), sintered for 4 h at 1000 °C. A strong maximum in ϵ'_r (~5000) was observed at each frequency, with the variation of ϵ'_r with frequency being very weak. This result is in good agreement with a phase transition which occurs without dielectric relaxation in the frequency range investigated (10^2–10^4 Hz) [8,9]. The temperature dependence of ϵ'_r is consistent with the 'Z5U' capacitor norms (Fig. 4).

5. Conclusions

A solid solution derived from $BaTiO_3$ has been obtained. The shrinkage coefficient and the value of ϵ'_r (at T_C) were greatest when the starting mixture ($0.95BaTiO_3+0.05CaF_2+0.05LiF$) was sintered for 4 h at 1000 °C ($\Delta\phi/\phi \approx 0.141$; ϵ'_r (at T_C) ≈ 5000). Dielectric measurements performed at low frequency on the ceramic samples showed a decrease in the ferroelectric Curie temperature T_C with increasing x. The ferroelectric phase transition was very diffuse. The high values of permittivity ϵ'_r associated with the low values of tan δ and the temperature dependence of ϵ'_r give these ceramics a particular interest in the field of multilayer capacitors (Z5U).

References

[1] M.E. Lines and A.M. Glass, *Principles and Applications of Ferroelectrics and Related Materials*, Clarendon Press, Oxford, 1977.
[2] P. Günter, *Ferroelectris, 24* (1980) 35.
[3] A. Benziada-Taïbi, J. Ravez and P. Hagenmuller, *J. Fluorine Chem., 26* (1984) 395.
[4] A. Benziada, R. Von Der Mühll, J. Ravez and P. Hagenmuller, *Rev. Chim. Miner., 23* (1986) 858.
[5] L. Benziada, Z. Ladjeroud and J. Ravez, *Ferroelectrics, 124* (1991) 73.
[6] Z. Ladjeroud, L. Benziada and J. Ravez, *Ferroelectrics, 154* (1994) 207.
[7] R.D. Shannon, *Acta Crystallogr., A32* (1976) 751.
[8] G.A. Smolenski, *Seignetto Electricity and Antiseignetto Electricity*, Scientific Edition, Leningrad, 1977.
[9] L.E. Cross, *Ferroelectrics, 76* (1987) 211.