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Dielectric characterization of $BaTiO_3$–$BaM_{1/3}N_{2/3}O_3$ systems (with M = Co, Mg and N = Nb or Ta)

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The dielectric behaviour of $(1 - x)BaTiO_3$–$x\ BaM_{1/3}N_{2/3}O_3$ systems, in which M = Co, Mg and N = Nb, Ta is described when x varies from 0 to 0.1. The evolution of the Curie temperature and of the dielectric constant, either in the ferroelectric state or in the paraelectric state are correlated to the structure and the ceramic microstructure. An observed diffuse phase transition is discussed.

1. Introduction

Additions to barium titanate and their effects on physical properties of the material are the topic of much research. It is the dielectric properties of barium titanate which give rise to this interest. The aim of these studies is to obtain a high dielectric constant with a slight variation with either the temperature and/or the applied electric field. We have previously [1] described, from a crystallographic and a morphology point of view, the behaviour of $BaTiO_3$–$BaM_{1/3}N_{2/3}O_3$ systems (with M = Co, Mg and N = Nb, Ta). It has been shown that the structure becomes cubic at room temperature when about 5 mol % of doping perovskite is added to barium titanate. The exact ratio slightly depend on the nature of the addition. On the basis of geometrical considerations we demonstrated that this evolution is faster than we could expect. The evolution of the grain size of the sintered specimens with the doping ratio were found to be discontinuous. When the doping ratio is higher than abcut 5 mol %, the ceramics are made of grains with an average diameter of 1 μm.

In this paper we investigate the dielectric properties of these compositions in relation with the crystallographic structure and the morphology.

2. Preparation

The preparation of the raw material has been described previously [1]. The ceramics are obtained from the impregnation of a barium titanate precursor: the barium and titanyl oxalate by a solution of the doping elements. The powders are pressed into pellets and sintered at a temperature between 1300 and 1400 °C for 1.5 h. The sintered pellets are about 1.5 mm in thickness and 12.5 mm in diameter and have a density higher than 92% of the theoretical density. Electrodes needed to perform dielectric measurements consist in a silver–palladium ink sintered at 700 °C. We measure the capacity and the loss angle with a general bridge device. The samples are laid in a tubular furnace so that dielectric constant and dissipation factors can be recorded in a 20 to 150 °C temperature range.

3. Results and discussion

Table I tabulates the results of our dielectric measurements. Three points have to be discussed:

1. the experimental Curie temperature,
2. the evolution of the dielectric constant (K) in the paraelectric state,
3. the evolution of the dielectric properties in the ferroelectric state.

The Curie temperature is the temperature of the highest value of the dielectric constant. It corresponds to the transition between a ferroelectric state and a paraelectric state, which for pure barium titanate leads to a structural transition from tetragonal to cubic.

The plot of the Curie temperature against the doping ratio shows a linear dependence. Furthermore, this evolution is similar to those already mentioned for the ratio c/a of the crystallographic parameters [1] as it can be seen in Fig. 1. This observation confirms the structural evolution of the modified barium titanate.

3.1. Evolution of K in the paraelectric state

In the paraelectric state, the dielectric constant of a ferroelectric compound obeys the Curie–Weiss law

$$K = C/(T - T_o)$$

in which K is the dielectric constant, C is the Curie

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TABLE I Dielectric measurements for several doped materials

Doping material	Doping ratio	K at 20 °C	DF at 20 °C (%)	T_c (°C)
	0	1 950	10	117
$BaMg_{1/3}Nb_{2/3}O_3$	1	140 000	10	117
	2	145 000	5	100
	3	190 000	30	95
	4	220 000	17	60
	5	120 000	26	35
	6	175 000	35	< 20
	7	8 000	17	< 20
	8	3 000	0.5	< 20
	9	2 000	1.5	< 20
	10	1 500	1	< 20
$BaCo_{1/3}Nb_{2/3}O_3$	1	180 000	30	102
	2	345 000	25	96
	3	650 000	15	90
	4	360 000	20	60
	5	100 000	20	35
	6	6 000	0.8	< 20
	7	3 500	14	< 20
	8	1 800	52	< 20
	9	1 700	0.6	< 20
$BaMg_{1/3}Ta_{2/3}O_3$	1	310 000	45	115
	2	160 000	50	97
	3	2 000	22	74
	4	260 000	42	50
	5	6 760	7	36
	6	1 200	7	< 20
	7	975	5	< 20
	8	1 050	2.5	< 20
	9	1 000	1.8	< 20

(K = dielectric constant, DF = dissipation factor, T_c = Curie temperature)

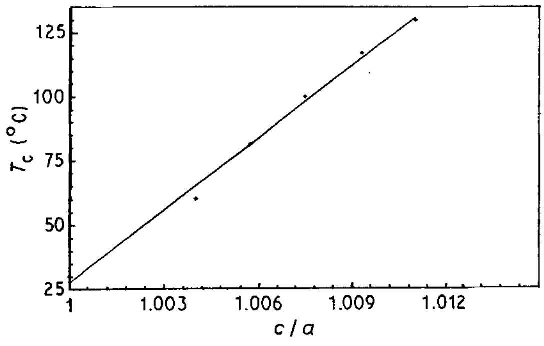

Figure 1 Linear evolution of Curie temperature plotted against doping ratio for $BaTiO_3$–$BaMg_{1/3}Nb_{2/3}O_3$. (a) $1/K = C/(T - T_m)$ and (b) $1/K \doteq 1/K_m + B(T - T_m)^2$.

TABLE II Computed values of Curie constant C and temperature T_c for the $BaTiO_3$–$BaMg_{1/3}Nb_{2/3}O_3$ and $BaTiO_3$–$BaCo_{1/3}Nb_{2/3}O_3$ systems

Doping material	Doping ratio	$C(10^{-5})$	T(°C)
$BaTiO_3$	0	1.32	122
$BaMg_{1/3}Nb_{2/3}O_3$	1	144.9	36.2
	2	151	22.8
	4	340.8	− 87.2
	5	5.52	− 1.38
	6	6.67	− 13.8
	7	3.6	− 26.6
	8	1.12	− 11.1
	9	1.02	− 26.9
	10	0.68	− 41.5
$BaCo_{1/3}Nb_{2/3}O_3$	1	17.45	108.5
	2	381	− 6.7
	3	256	67.9
	4	47.9	67.9
	5	17.7	38.5
	6	1.47	11.3
	7	1.22	− 5.6

constant and T_0 the Curie temperature. The values of C and T_0 calculated from the experimental data are listed in Table II. Let us focus attention on the Curie temperature T_0. Table III tabulates the differences between the experimental value of the temperature, T_c corresponding to the maximum of K and the computed value T_0.

From the thermodynamic theory, the Landau theory, describing the evolution of a ferroelectric crystal the temperature T_0 is the Curie temperature only when the transition between the ferroelectric and the paraelectric state is a second-order transition. The examination of Table III even if the values are to be considered with caution, since the determination of either the experimental temperature or the calculated temperature is inaccurate, let us think that the order of the transition depends on the nature of the doping perovskite. Nevertheless, thermal analysis recorded between 20 and 150 °C on doped barium titanate does not show any thermal effect occurring during the

TABLE III Differences between T_c and T_0 values of the systems $BaTiO_3$-$BaMg_{1/3}Nb_{2/3}O_3$, $BaTiO_3$-$BaCo_{1/3}Nb_{2/3}O_3$ $BaTiO_3$-$BaMg_{1/3}Ta_{2/3}O_3$ and $BaTiO_3$

Doping material	Doping ratio	$T_c - T_0$ (°C)
$BaMg_{1/3}Nb_{2/3}O_3$	1	81
	2	77
	4	147
	5	36
$BaCo_{1/3}Nb_{2/3}O_3$	1	−6
	3	22
	4	−7
	5	1

transition between the ferroelectric and the paraelectric state whatever the doping perovskite is. In addition to this contradiction the plot of $1/K$ against the temperature points out a rather important deviation from the straight line which represents the Curie–Weiss law (Fig. 2).

These two reasons:

(i) no thermal effect whatever the doping perovskite is,

(ii) deviation to the Curie–Weiss law,

conduct us to propose the second-order relation

$$1/K = 1/K_m + B(T - T_m)^2 \qquad (1)$$

to describe the evolution of the dielectric constant with temperature. In this relation K_m is the value of the maximum of the dielectric constant and T_m the corresponding temperature. Experimental data fit this relation well (Fig. 2b).

From the Clausius–Mossoti relation, which links the dielectric constant K to the polarizability

$$(K - 1)/(K - 2) = (1/3\ \varepsilon_0)(\alpha/V) \qquad (2)$$

it is possible to derive the Curie–Weiss law in considering that α and V have a linear dependence with temperature. Jonker [2] has shown that if terms of the second order were introduced to describe the variation of α and V, the Expression 1 could be derived from Relation 2 and should then be considered as an extension of the Curie–Weiss law.

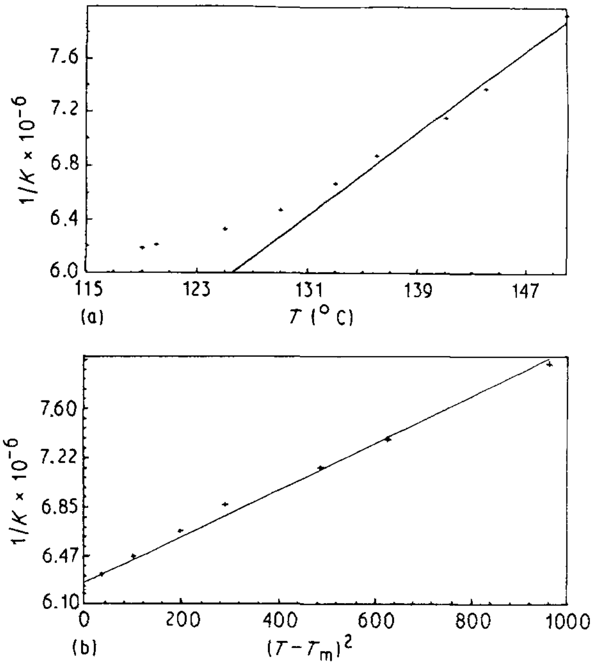

Figure 2 Evolution of $1/K$ plotted against (a) $(T - T_0)$ and (b) $(T - T_m)^2$ for the 1% $BaTiO_3$-$BaMg_{1/3}Nb_{2/3}O_3$ ceramic.

The real meaning of this relation is not yet clear. From the study of Smolensky [3] on $PbMg_{1/3}Nb_{2/3}O_3$ and $PbNi_{1/3}Nb_{2/3}O_3$ and the works of Godefroy *et al.* [4] on cobalt-modified barium titanate, it seems that local heterogeneities of the composition could be responsible for this second-order relation. These heterogeneities may create microferroelectric areas which have their own transition temperatures. This hypothesis should then explain the observed diffuse transition. An appropriate method to obtain direct evidence for these micro-areas should be high resolution electron microscopy since the X-ray diffraction is useless to prove their existence because of a too small volume of diffraction [3]. Furthermore, we can note that the presence of such a microstructure could explain the abnormal variations of the crystallographic parameters described in previous work [1].

3.2. Electrical properties in the ferroelectric state

In the ferroelectric state, i.e. for a temperature lower than T_0, the dielectric constant is important (Table I) and they show weak variation with temperature (Fig. 3).

The dissipation factors, measured under the same conditions, show important values which means that these compositions are not insulators. This analysis is confirmed by the conductivity measurements (Table IV). Under these conditions it is worth saying that the dielectric constants measured are probably not pure dielectric constants and their values are exaggerated. The conduction of our specimens can be due to the reduction during the thermal treatment of one of the elements of the composition. In the systems studied here, this element can be either the titanium or the niobium. During the cooling a partial reoxidation takes place but it is not enough to prevent the presence of a mixed valence.

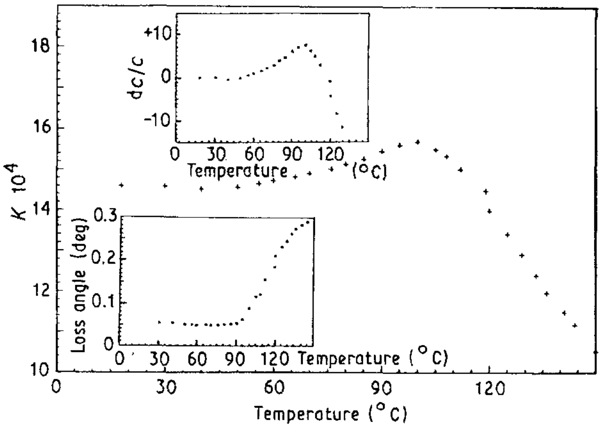

Figure 3 Dielectric constant plotted against temperature for 2% $BaTiO_3$-$BaMg_{1/3}Nb_{2/3}O_3$ ceramic.

TABLE IV Conductivity in the system $BaTiO_3$-$BaMg_{1/3}Nb_{2/3}O_3$

Doping ratio	Conductivity (Ω^{-1} cm^{-1})
0	20.6×10^{-9}
1	2380×10^{-7}
2	9932×10^{-8}
3	2743×10^{-7}
4	1353×10^{-8}
6	5745×10^{-9}
8	33×10^{-9}
9	36×10^{-9}

A clear correlation can be found between the conductivity of the specimen and the grain size measured after the thermal treatment (Fig. 4) [1]. This relation confirms our latter analysis since it is obvious that the complete reoxidation of grains of a significant size is much more difficult than the reoxidation of grains of about 1 μm.

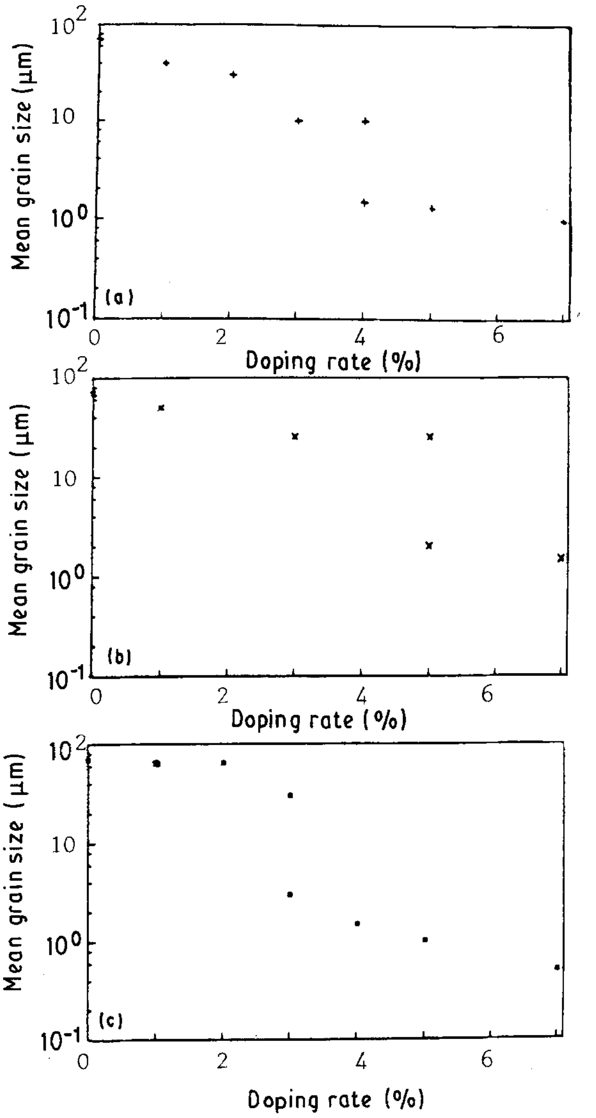

Figure 4 Evolution of the mean grain size in the sintered ceramics. (a) $BaTiO_3$-$BaMg_{1/3}Nb_{2/3}O_3$, (b) $BaTiO_3$-$BaCo_{1/3}Nb_{2/3}O_3$, (c) $BaTiO_3$-$BaMg_{1/3}Ta_{2/3}O_3$.

On both pure barium titanate and modified barium titanate, ferroelectric domains can be revealed by acid etching [5]. The comparison between the micrographs related to pure barium titanate and those related to modified barium titanate (Fig. 5) does not reveal any difference in the general organization of the ferroelectric domains. It can just be seen that the structure is less orderly in the case of doped barium titanates. These results are similar to those of Kulcsar *et al.* [6] on the compositions $BaTiO_3$-$CaTiO_3$.

4. Conclusion

During this work we tried to link the structural aspects, developed in previous work [1], to the dielectric evolution described in this paper. It has been shown that the abnormal variation of the crystallographic parameters could be correlated to the evolution of the Curie temperature and could be explained by the presence of microareas in the materials. These microareas were introduced after the analysis of the variation of the dielectric constant in the paraelectric state. The diffuse phase transition observed could be fully explained by the introduction of a second-order relation between the dielectric constant and the temperature.

The similarity pointed out in the variation of the conductivity of the specimen and of the grain size leads us to propose a mechanism to explain the apparition of conductivity in the slightly doped barium titanate.

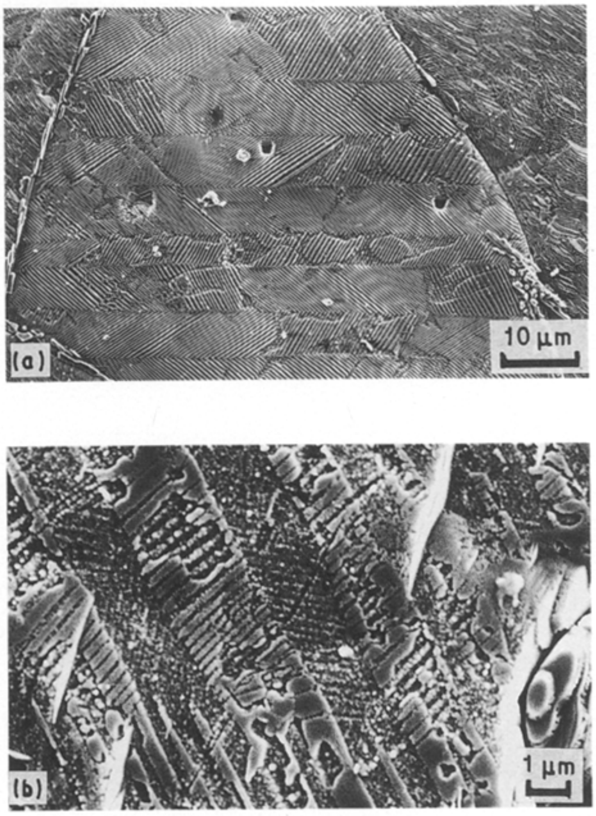

Figure 5 SEM micrographs of etched barium titanates (a) pure barium titanate, (b) 2% $BaTiO_3$-$BaMg_{1/3}Nb_{2/3}O_3$ ceramic.

It is worth mentioning that complementary analysis such as HREM or EPR is necessary to fully understand the observed phenomena.

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