JOURNAL OF MATERIALS SCIENCE 27 (1992) 2316–2320

Crystallographic study of $BaTiO_3$–$BaM_{1/3}N_{2/3}O_3$ solid solutions (M = Co or Mg and N = Nb or Ta)

F. WEILL
Laboratoire de Chimie du Solide, 351 Cours de la Libération, 33405 Talence Cedex, France

J. L. REHSPRINGER, P. POIX, C. KIPELEN, J. C. BERNIER
Groupe des Matériaux Inorganiques, IPCMS, EHICS, 1 rue Blaise Pascal, 67008 Strasbourg Cedex, France

In order to understand the effect of niobium, tantalum, cobalt and magnesium cations on the ferroelectric properties of barium titanate we study solid solutions between $BaTiO_3$ and $BaM_{1/3}N_{2/3}O_3$ perovskite compounds where $M = Co^{2+}$ or Mg^{2+} and $N = Nb^{5+}$ or Ta^{5+}. These solid solutions become cubic at room temperature for very weak additions. This result cannot be explained by geometrical consideration and suggests that an intermediate solid solution is made for weak additions.

1. Introduction

Since the discovery of the ferroelectric properties of barium titanate, this compound has been mainly used in the preparation of multi-layer capacitors. The industrial requirements, however, need physical properties that conform to standard variations with temperature, current isolation and frequency. The initial properties of barium titanate must thus be modified by incorporating many doping compounds. Most of them belong to the oxide group. Niobium oxide and tantalum oxide, transition metal oxides such as cobalt oxides, rare earth oxides and magnesium oxide are used. Such additions modify the crystallographic structure as well as the sintered grain size and/or the physical properties of barium titanate. Much work has been carried out on solid solution between barium titanate and only one oxide in order to understand its own effect on barium titanate properties.

In recent work, Chu *et al.* [1] showed that compositions containing mostly barium titanate and two different doping oxides reached a higher dielectric constant. They investigated the association of two types of cation: in the first group they used either niobium as Nb_2O_5, tantalum as Ta_2O_5 or antimony as SnO_2; in the second group the cation was cobalt as Co_3O_4 or CoO, zirconium as ZrO_2 or magnesium oxide MgO. Dielectric measurements showed a variation of the stable level of the dielectric constant with, of course, the total amount of doping oxide addition and the N/M doping ratio but also with the ratio Ba/Ti for weak variations around the unit. These different parameters also have an influence on the other characteristic physical properties related to ferroelectric properties (e.g. Curie temperature, and dC/C against temperature).

In order to explain these phenomena, it is assumed that solid solutions between barium titanate and complex perovskites can take place. A general formula such as $BaM_{1/3}N_{2/3}O_3$ can thus be given for these perovskites, with M = Co or Mg and N = Nb or Ta. In this formula, the barium is located in the twelve-fold oxygen environment while the other cation takes place at a six-fold oxygen site of the classical perovskite structure. In previous work [1] the Ba/Ti ratio and M/N ratio were modified simultaneously but independently. It is rather difficult to determine which parameters influence the ferroelectric properties. On the contrary in our study, the amount of barium cation is that necessary to obtain the doping perovskite structure $BaM_{1/3}N_{2/3}O_3$. We may then study compositions of the form

$$(1 - x)\ BaTiO_3 + x\ BaM_{1/3}N_{2/3}O_3$$

with M = Co or Mg and N = Nb or Ta. The paper deals with the crystallographic aspect of these compositions. We point out a structural evolution which does not obey the classical laws of perovskite structure.

2. Procedure

A two-step route was chosen to prepare the compositions in order to obtain the highest homogeneity and sinterability of doped powders. Firstly, the barium titanyl oxalate coprecipitation is undertaken. This preparation method is well known to lead to a high level of purity and a Ba to Ti ratio close one. The reaction

$$BaCl_2 + TiOCl_2 + 2\ C_2O_4H_2 + 4\ H_2O \rightarrow BaTiO(C_2O_4)_2\ 4\ H_2O + 4HCl$$

was described firstly by Clabaugh and Swiggard [2] and later Rehspringer [3] determined the condition needed to obtain a Ba to Ti ratio equal to one and a narrow grain size distribution. As far as pure barium titanate is concerned, narrow grain size distribution is necessary to obtain a homogeneous grain growth during the sintering process. The introduction of doping elements takes place during the second step: a suspension of barium and titanyl oxalate is realized from a solution containing the doping elements salts. The used salts are barium nitrate, magnesium or cobalt nitrates, and niobium or tantalum oxalates. A complete homogenization is achieved in rotavapour, the solvent is evaporated and a first thermal treatment, up to 700 °C is undertaken. The resulting barium titanate powder is then ground for 12 h in ethanol, dried, pressed into pellets and sintered at a temperature between 1350 and 1400 °C for 1.5 h. This way of preparation leads to sintered pellets of about 1.5 mm in thickness with densities higher than 92% of the theoretical density.

3. Measurements

We determine the ratio c/a of the crystallographic lattice from the X-ray diffractogram of 3 1 0, 1 0 3 and 3 0 1 planes using the formula

$$c/a = 3\,d\,[1\,0\,3]/(10\,d^2\,[3\,1\,0] - d^2\,[1\,0\,3])^{1/2}$$

We use a 1/100° of 2θ step and for each step the signal is measured for 100 s. To precisely measure the values of c and a we use alumina as an internal standard. The experimental position of Bragg reflections values are corrected by considering that parameters of alumina are those given by Wyckoff [9]. Measurements conditions are

step: 6/1000 of 2θ
time: 4 s.

All the X-ray experiments are done on a Siemens Kristalloflex D500 using CoK_α radiations ($K_\alpha = 0.1788/92$ nm; $K_\beta = 0.179978$ nm).

We use microprobe analysis to determine the repartition of barium and titanium in the sintered specimens and we point out the grain size evolution of the sintered specimens from scanning electron microscope (SEM) observations of polished and thermally etched surface.

4. Results

Fig. 1 shows the crystallographic evolution which is important as it can be seen. Table I tabulates the c/a ratio calculated from these data. This ratio is a linear function of the doping rate. We also found a linear dependence between the parameters a and c and the doping rate (Figs 2 and 3). No second phase can be detected by X-ray measurements but the SEM observations of polished surfaces show a variation of the composition for few grain boundaries. For a low addition ratio some grain boundaries are characterized by a Ba to Ti ratio rather different from one. We correlate the intensity of X-ray emission of $BaTiO_3$ and the grain boundary area (Fig. 4) and attribute to the grain boundary the composition $Ba_6Ti_{17}O_{40}$. No information was obtained on the repartition of Mg, Nb, or Co, mainly because the amount of those elements is too small.

The observation of thermally etched polished surface of ceramics reveals a discontinuous growth of the grain size with the doping ratio (Fig. 5). Whatever the doping perovskite is, there is, however, always a doping amount for which two very different grain sizes are observed as illustrated in Fig. 5. For higher doping

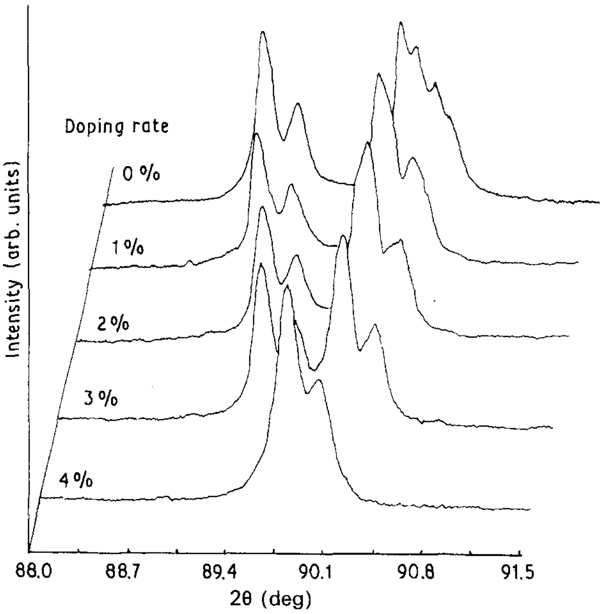

Figure 1 Evolution of the diffractogram of the 3 10–1 0 3 and 3 0 1 planes of $(1-x)\,BaTiO_3 + x\,BaMg_{1/3}Nb_{2/3}O_3$ when x varies from 0 to 0.04.

TABLE I Evolution of c/a ratio with the doping ratio in the systems $BaTiO_3$–$BaMg_{1/3}Nb_{2/3}$ and $BaTiO_3$–$BaCo_{1/3}Nb_{2/3}O_3$

Doping ratio (%)	c/a	
	$BaTiO_3$–$BaMg_{1/3}Nb_{2/3}$	$BaTiO_3$–$BaCo_{1/3}Nb_{2/3}O_3$
0	1.012	1.012
1	1.009	1.008
2	1.008	1.007
3	1.005	1.007
4	1.003	1.004
5	1.000	1.002
6	1.000	1.000

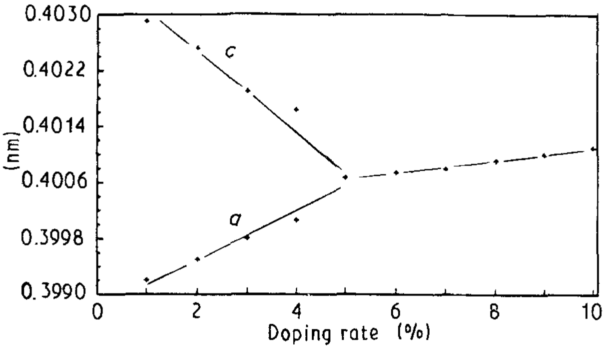

Figure 2 Evolution of the parameters a and c of $(1-x)BaTiO_3 + x\,BaMg_{1/3}Nb_{2/3}O_3$ with x.

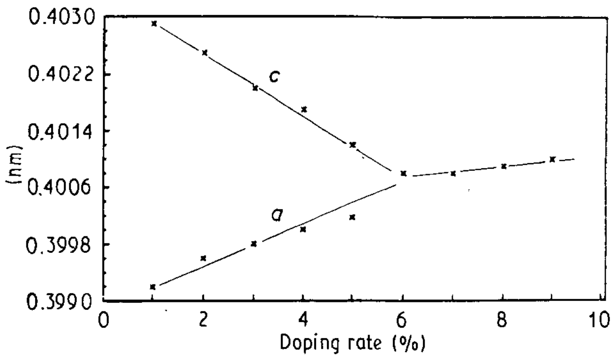

Figure 3 Evolution of the parameters a and c of $(1-x)\mathrm{BaTiO_3} + x\ \mathrm{BaCo_{1/3}Nb_{2/3}O_3}$ with x.

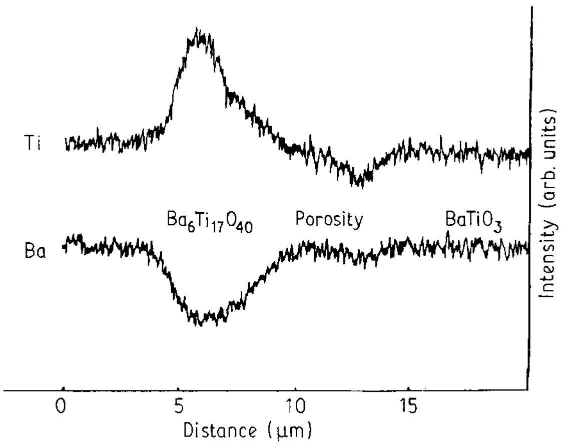

Figure 4 Compared X-ray emission from bulk and grain boundary of the composition $\mathrm{BaTiO_3}$ + 1% $\mathrm{BaMg_{1/3}Nb_{2/3}O_3}$.

ratio the ceramic is made up only of small grains (average diameter 1 µm).

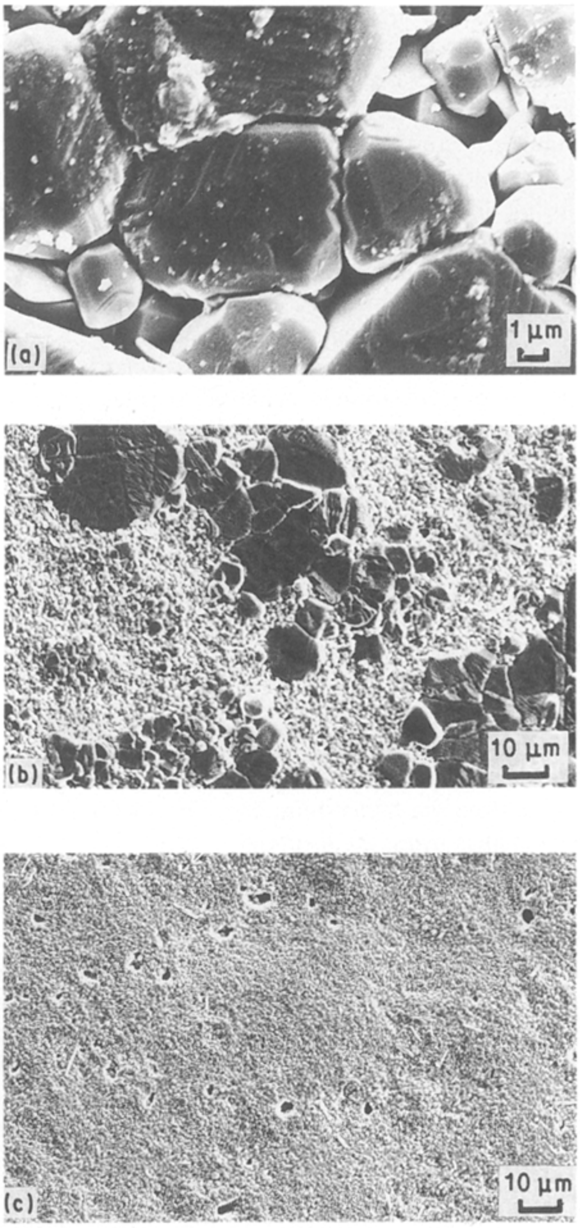

Figure 5 Evolution of grain size plotted against the doping ratio and the doping perovskite. (a) $\mathrm{BaTiO_3}$ + 3% $\mathrm{BaMg_{1/3}\ Nb_{2/3}O_3}$. (b) $\mathrm{BaTiO_3}$ + 4% $\mathrm{BaMg_{1/3}\ Nb_{2/3}O_3}$. (c) $\mathrm{BaTiO_3}$ + 5% $\mathrm{BaMg_{1/3}Nb_{2/3}O_3}$.

5. Discussion

From a crystallographic point of view, a very fast evolution of the symmetry with the doping ratio characterizes all the studied compositions. In the perovskite structure, the Goldschmidt factor can be used as an indicator of the distortion of the ideal cubic structure [4]. Poix [5] developed the concept of characteristic metal–oxygen distance and using this concept, the Goldschmidt factor, t, can be calculated using

$$t = \theta/\sqrt{2}\beta$$

where θ (β) is the characteristic distance of the cation in 12-fold (six) oxygen environment. Table II [5] tabulates the characteristic distances used. Fig. 6 shows the theoretical Goldschmidt factor evolution of some barium titanate-base compositions.

TABLE II Metal–oxygen distances used to compute the Goldschmidt factors (after Poix [5])

Cation	Metal–oxygen distance
Ba^{2+}	2.886
Sr^{2+}	2.775
Ti^{4+}	1.944
Nb^{5+}	2.012
Mg^{2+}	2.106
Co^{2+}	2.126

We notice the theoretical evolutions of the Goldschmidt factor corresponding to our compositions are very close to those calculated for the $\mathrm{BaTiO_3}$–$\mathrm{SrTiO_3}$ system. In this system about 30% of strontium titanate in barium titanate is necessary to obtain a cubic lattice at room temperature [6]. The structural evolution recorded of the systems $\mathrm{BaTiO_3}$–$\mathrm{BaMg_{1/3}Nb_{2/3}}$ and $\mathrm{BaTiO_3}$–$\mathrm{BaCo_{1/3}Nb_{2/3}O_3}$ shows, however, that the lattice becomes cubic when 5 or 6% of complex perovskite is added to barium titanate. This observed structural evolution is very close to that pointed out by Subbarao and Shirane in the system $\mathrm{BaTiO_3}$–$\mathrm{Ba_{1/2}NbO_3}$ [7] even though the theoretical variation of the Goldschmidt factor is rather different. It is then obvious that the geometrical considerations

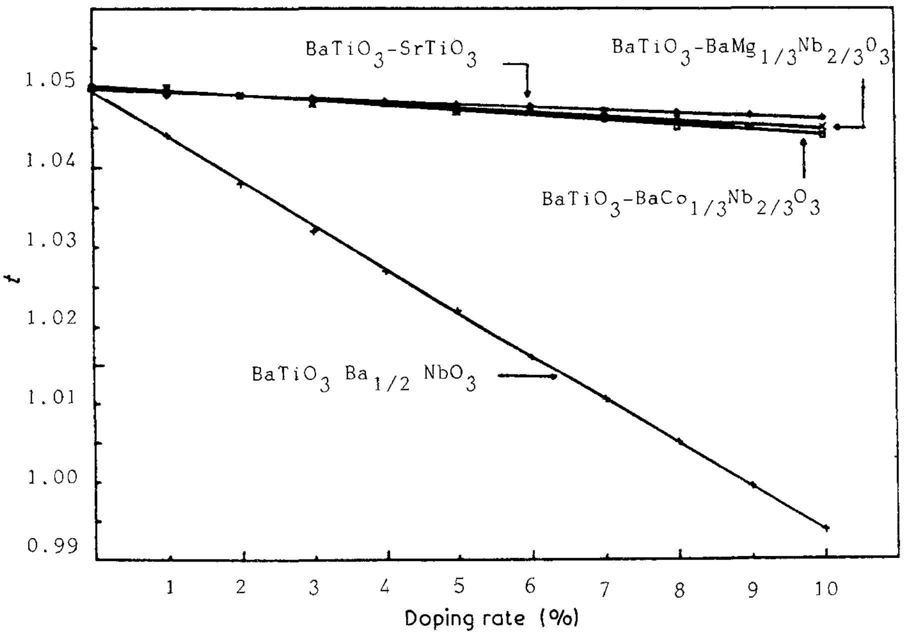

Figure 6 Variation of the Goldschmidt factor plotted against the composition and the doping ratio.

cannot explain this considerable crystallographic evolution of the studied systems.

At room temperature, cubic barium titanate has been obtained for only fine grain ceramics. If, however, we compare the evolution of the crystallographic structure and of the average grain size against the doping ratio we do not find any correlation. The crystal lattice varies linearly while the grain size development is discontinuous.

The niobium cation is probably responsible for the discontinuity of the grain size evolution. Buessem and coworkers [8] have shown that the diffusion of niobium in barium titanate is low and inhibits the grain growth. Our preparation consists of coating the barium and titanyl oxalate with the doping salts. We can assume that the increase of the doping ratio and hence of the niobium content leads to the grain size decrease but we cannot find any explanation for the jump of grain size near the structural transformation between quadratic and cubic structural change. In fact, before it reaches the cubic structure, we notice that the solid solution does not follow the relation

$$1.207a = \theta + \beta$$

which links for a perovskite structure the metal oxygen distance of the cation in a six-fold environment, β, in a twelve-fold environment, θ, and the equivalent parameter, a. Once the structure is cubic the relation written above fits the evolution of the parameter well (see Appendix). This observation means that the solid solution which is obtained when the structure is tetragonal does not correspond to the general formula chosen: $(1-x)$ $BaTiO_3 + x\ BaM_{1/3}N_{2/3}O_3$. On the other hand, this formula represents properly the composition when the structure is cubic.

The substitution of niobium by tantalum leads to rather close results: the only difference is a faster evolution of both crystallographic parameters and the grain size. The structure becomes cubic for about 3% of $BaMg_{1/3}Ta_{2/3}O_3$ in $BaTiO_3$, and the finest grain size appears in the sintered ceramic for 3% of addition. Nevertheless we notice that a composition containing 3% of doping perovskite is unstable: the same composition after firing to apparently the same temperature appears sometimes to have a cubic structure and sometimes a tetragonal structure. This is probably due to the higher acidity of tantalum.

6. Conclusion

The compositions corresponding to the general formula

$$(1-x)\ BaTiO_3 + x\ BaM_{1/3}N_{2/3}O_3$$

(with M = Mg, Co and N = Nb, Ta) show a very fast structural evolution. On the basis of parameter measurements, it has been shown that the cubic–tetragonal transformation is depressed by the addition of $BaM_{1/3}N_{2/3}O_3$. This evolution, similar to those previously described when niobium barium vacancy perovskite is added to $BaTiO_3$, is faster than expected if we only consider geometrical data or the grain size of the ceramic. We assume that before the cubic transformation the barium titanate interacts with the doping perovskite leading to a solid solution which the formula is not, up to now, clearly established. It is only after the structure becomes cubic, that the general formula $(1-x)$ $BaTiO_3 + x\ BaM_{1/3}N_{2/3}O_3$ seems to be valid as far as the evolution of structure is concerned.

Further investigation should try to determine the nature of the compound which has the tetragonal structure.

Appendix

In developing the concept of "Characteristic distance", Poix [4] showed it is possible to calculate an equivalent parameter for every perovskite. The developed theory considers the distance between an anion and a cation: "the characteristic distance" only depends on:

(i) the nature of both the anion and the cation,
(ii) the valency of the cation,
(iii) the nature of the cation site.

Using these characteristic distances, the parameter of a perovskite can be calculated with the formula

$$1.207a = \theta + \beta$$

where a is the equivalent parameter, θ the characteristic distance of the cation in the 12-fold oxygen environment, β the characteristic distance of the cation in the six-fold oxygen environment.

When many cations occupy one site, as for instance in $BaMg_{1/3}Nb_{2/3}O_3$, the general formula is still valid. The characteristic distance related to the six fold environment is then the average of the characteristic distance of each cation.

The parameter of the latter compound can be calculated, using the equation

$$1.207\,a = \theta\mathrm{Ba} + (1/3\ \beta\ \mathrm{Mg} + 2/3\ \beta\ \mathrm{Nb})$$

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Received 17 October 1990
and accepted 25 March 1991