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# Structural and piezoelectric properties evolution induced by cobalt doping and cobalt/niobium co-doping in BaTiO<sub>3</sub>

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## Abstract

Lead-zirconate-titanate PbZr<sub>(1-x)</sub>Ti<sub>x</sub>O<sub>3</sub> (PZT), materials for piezoelectric applications are the dominant piezoceramics since their properties are high. However PZTs need to be substituted by safer materials due to health and environmental problems of lead. In this work, the crystal structure modifications of BaTiO<sub>3</sub> induced by cobalt doping and niobium/cobalt co-doping were investigated in the range 0.1 – 25 at.%. Low Co and Co/Nb doping level significantly improve piezoelectric properties of BaTiO<sub>3</sub>. The piezoelectric constant, obtained for BaTiO<sub>3</sub> doped with 0.075 at.% of Cobalt ( $d_{33} = 200$  pC/N), is twice of that measured for pure BaTiO<sub>3</sub>. At high doping concentration, the structure of BaTi<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> and BaTi<sub>1-x</sub>Co<sub>x</sub>Nb<sub>x</sub>O<sub>3</sub> change from tetragonal to hexagonal while BaTi<sub>1-x</sub>Co<sub>x</sub>Nb<sub>2x</sub>O<sub>3</sub> remains tetragonal and gradually turns into cubic. It suggests that the ionic charge defect is balanced by oxygen vacancies formation when Ti<sup>4+</sup> are substituted by Co<sup>2+</sup>/Co<sup>3+</sup>.

## Keywords

Perovskite, barium titanate, cobalt doping, piezoelectricity

## 1. Introduction

Barium titanate  $\text{BaTiO}_3$  (BT) was one of the first materials used for the fabrication of piezoelectric devices. Nevertheless, it was quickly replaced following the discovery of lead zirconate titanate (PZT) based piezoelectric ceramics. Since several years, BT ceramics have attracted much attention again with the aim of developing lead-free piezoelectric ceramics [1]. Since BT ceramics show intrinsically lower piezoelectric performances than PZT, it is of prime importance to enhance properties via the use of dopants or innovative processing [2,3]. Many dopants have already been tested, including isovalent [4], donor or acceptor dopants [5,6]. Doping effect on structural and ferroelectric properties of  $\text{BaTiO}_3$  results to be very complex and is not yet well understood since most of time, several parameters change at the same time (nature and amount of point defects, grain size, crystal distortions...) [7].

Doping barium titanate with cobalt has been proved to lower the temperature of the ferro-paraelectric phase transition ( $T_c$ ). Cobalt was also found to be an effective dopant to flatten the dielectric constant at low temperature [8]. Cui *et al.* showed that the relative dielectric constant at Curie temperature of Co-doped  $\text{BaTiO}_3$  is higher than that of the undoped sample [9]. Cobalt was used for its magnetic properties to prepare  $\text{BaTiO}_3$ -based multiferroic materials [10]. In addition, cobalt seems also to have an effect on the processing of BT ceramics since the grain boundary mobility decreases with Co doping, due to the segregation at the grain boundaries of defects induced by doping [11]. On the other hand, pentavalent ion doped, such as  $\text{Nb}^{5+}$  on the  $\text{Ti}^{4+}$  site, could change the normally insulating behavior of  $\text{BaTiO}_3$  to semiconducting [12].

In this work, the crystal structure modifications of  $\text{BaTiO}_3$  induced by cobalt doping and cobalt/niobium co-doping were investigated. Associated ferroelectric and piezoelectric properties were also characterized for some compositions.

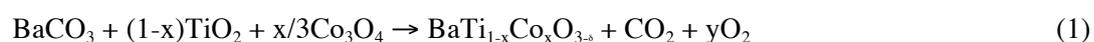
## 2. Experimental

Compounds were synthesized at 1100 °C for 2 h by conventional solid-state reaction of BaCO<sub>3</sub>, TiO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub> and Nb<sub>2</sub>O<sub>5</sub>. The reacted powder was milled and uniaxially pressed at 60 MPa before being sintered in a platinum crucible at 1350 °C for 4 h in air. Bulk density was calculated from the Archimedes method in water. X-ray diffraction measurements were taken in a Panalytical X'Pert Pro diffractometer (45 kV, 40 mA,  $\lambda_{K_{\alpha 1}}(\text{Cu}) = 1.5405 \text{ \AA}$ /forward Ge (111)). Cell parameters of samples were determined by Rietveld refinement in Le Bail mode using Fullprof software [13]. Samples were poled for electrical measurements at 150 °C by field cooling process at 600 V.mm<sup>-1</sup>. Temperature dependence of the dielectric constant was measured at 1 kHz using a HP 4192A impedance analyzer, between 20 and 177 °C. Piezoelectric constant  $d_{33}$  of the samples were measured by means of quasistatic  $d_{33}$  meter (ZJ-3A) based on Berlincourt method. The electromechanical properties of the pellets were deduced from the measurement of the complex electrical impedance around the fundamental thickness-mode resonance. A HP4294A spectrum analyzer (Agilent Technologies Inc.) and an impedance test kit were used as the experimental setup. The theoretical behavior of the electrical impedance was computed as a function of frequency for the radial and thickness-modes using a one dimensional model based on the Krimholtz–Leedom–Matthaei (KLM) equivalent electrical circuit [14,15]. A fitting process was used to deduce successively the radial and thickness-mode parameters of the pellets from the experimental data (sample's thickness  $\ll$  diameter) [16]. The radial-mode parameter  $k_p$  (planar coupling factor) was obtained and the following thickness-mode parameters were deduced: the dielectric constant at constant strain  $\epsilon_{33}^S/\epsilon_0$ , the thickness coupling factor  $k_t$ , and the electrical loss factors  $\tan \delta_e$ .

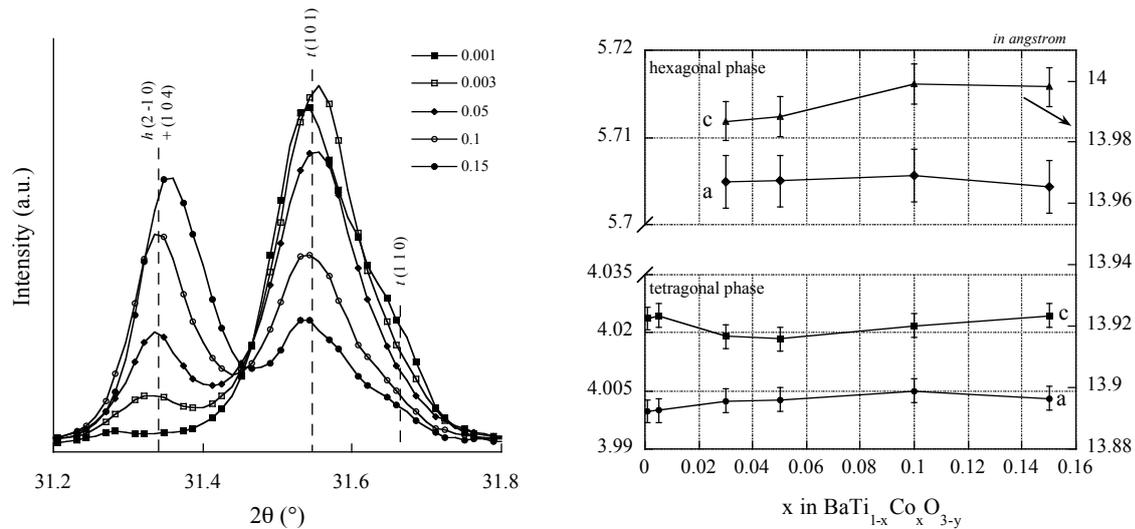
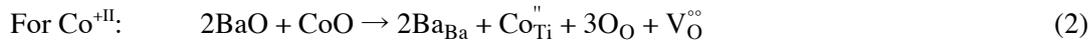
### 3. Results and discussion

#### 3.1. Structural changes induced by Co doping and Co/Nb co-doping

Considering the valencies and ionic radii of Co, Ti and Ba, one can make the assumption that Co can be introduced in the  $ABO_3$  perovskite structure on the  $B$  site. Therefore, the cobalt-doped BaTiO<sub>3</sub> powders were synthesized according to the following reaction:



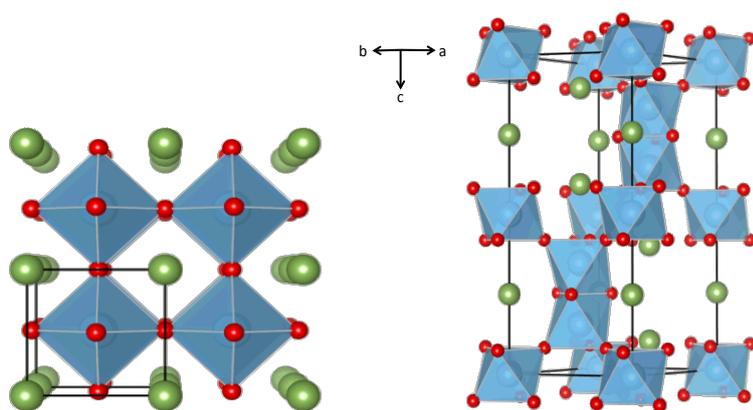
The amounts of oxygen vacancies  $\delta$  and dioxygen release  $y$  are dependant of the cobalt valence state in the final product. The formation of oxygen vacancies can be described according to the following reactions:



**Fig. 1.** XRD patterns and associated cell parameters of  $\text{BaTi}_{1-x}\text{Co}_x\text{O}_{3-y}$  compounds as a function of  $x$  ( $t$ : tetragonal phase,  $h$ : hexagonal phase).

Fig. 1 shows a zoom on XRD patterns and the associated cell parameters of the synthesized powders for different values of  $x$ . Only two phases were detected, a tetragonal ( $P4mm$ ,  $Z = 1$ ) and hexagonal ( $P6_3/mmc$ ,  $Z = 6$ ) perovskite named  $t$  and  $h$ , respectively. The amount of the hexagonal form increases with cobalt doping, while that of the tetragonal one decreases concomitantly. For both phases, cell parameters remain within the error bar. Observed for the first time in 1883 and described in details in 1948 [17], the hexagonal phase of  $\text{BaTiO}_3$  is stable above 1430 °C for undoped samples [18], but can be stabilized at room temperature by reduction of a part of  $\text{Ti}^{+IV}$  to  $\text{Ti}^{+III}$  [19] or by substituting Ti by  $d$ -blocks elements (Mn, Fe, Co...) [20,21]. In contrast of the cubic or tetragonal form of the perovskite structure in which all the  $\text{TiO}_6$  octoedra are linked by corners, in the hexagonal form, 2/3 of the  $\text{TiO}_6$  octahedra share a face to form  $\text{Ti}_2\text{O}_9$  dimers (Fig. 2). In these compounds, the presence of oxygen

vacancies are the key factor of the existence of the hexagonal form of the perovskite structure. It is well established that structure consisting of polyhedra with corner connection like tetragonal perovskite cannot accept high amount of oxygen vacancies. This can be explained by the strong coulombic repulsion between  $Ti^{+IV}$  cations that should be induced by the absence of the bridging oxygen. Keith *et al.* showed that in the hexagonal form oxygen vacancies are located between the face sharing  $TiO_6$  octahedra [22].

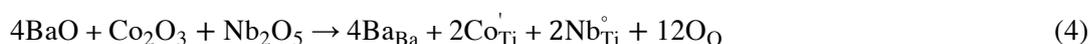


**Fig. 2.** Crystal structure of tetragonal (*t*, left) and hexagonal (*h*, right) perovskite.

For cobalt-doped  $BaTiO_3$  compounds, the formation of oxygen vacancies induced by the substitution of  $Ti^{4+}$  by  $Co^{2+}$  or  $Co^{3+}$  leads to a structural change of the perovskite structure from tetragonal to hexagonal. The chemical compositions of both phases are rather difficult to establish, but the negligible cell parameters variations of the tetragonal phase and the fact that the hexagonal one can be observed at very low doping level indicate that a major portion of the cobalt incorporates the hexagonal phase. The existence of the hexagonal form of  $BaTiO_3$  seems to be due to the presence of oxygen vacancies. This phase should therefore not be observed if the charge compensation is made by codoping with a donor element like niobium on the Ti site.

The amount of  $Nb^{+V}$  required for the charge compensation is dependent of the cobalt valence state, according to the following reactions:

For  $Co^{+III}$ ,  $Nb/Co = 1$ :



For  $Co^{+II}$ ,  $Nb/Co = 2$ :

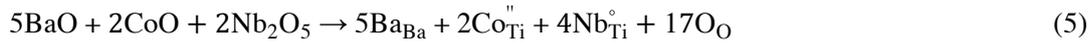
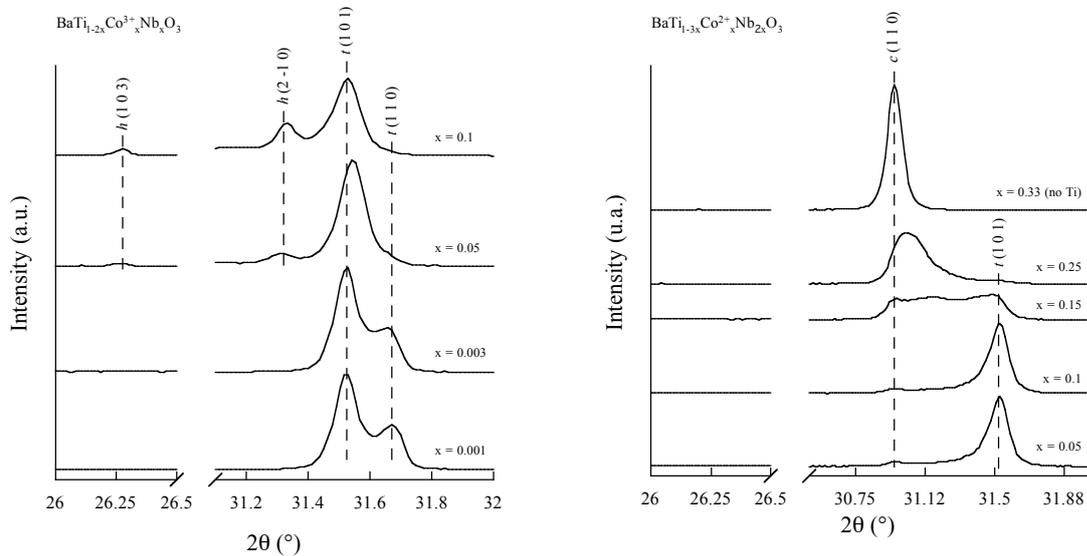


Fig. 3 shows the structural changes induced by Co/Nb codoping of  $\text{BaTiO}_3$ , observed by XRD, for the two considered valence states of cobalt. When Nb/Co = 1 ( $\text{Co}^{\text{III}}$ ), the hexagonal form of  $\text{BaTiO}_3$  can be observed since  $x = 0.005$ , suggesting the formation of oxygen vacancies in  $\text{BaTiO}_3$ , probably because there is not enough Nb to fully balance the charge defects induced by the substitution of Ti by Co. In contrast, when Nb/Co = 2 ( $\text{Co}^{\text{II}}$ ), hexagonal form was never observed. Nevertheless, the structure of  $\text{BaTiO}_3$  changes gradually from the tetragonal form to the cubic one. The broad peaks observed for intermediate values of  $x$  could be explained by composition heterogeneities within the samples.



**Fig. 3.** XRD patterns of Co/Nb substituted barium titanate.

These results suggest that, under the process conditions used in this work, the valence state of cobalt in  $\text{BaTiO}_3$  is +II. These results are in accordance with those obtained by Aguilar who characterized by EPR technique the valence state of cobalt in Co doped  $\text{BaTiO}_3$  single crystals and by Yu *et al.* [21,23] but disagree those recently obtained by Das and Roul [10].

### 3.2. Properties

Main piezoelectric properties of three samples, *i.e.* pure, cobalt doped and cobalt/niobium co-doped BaTiO<sub>3</sub>, are reported in Table 1. Because of very low resistivity and too high electrical losses, piezoelectric properties were not possible to be characterized for sample with cobalt doping level over than 0.01. Results clearly show that piezoelectric properties are significantly enhanced when BaTiO<sub>3</sub> is doped by cobalt. On the other hand, permittivity is lower and dielectric losses increase. The latter is consistent with the presence of oxygen vacancies [24]. Compared to cobalt doping, codoping with niobium does not seem to affect piezoelectric properties, but allows maintaining a good level of permittivity with low dielectric losses. As previously observed by Weill *et al.* [25], Curie temperature slightly decreases when BaTiO<sub>3</sub> is doped or codoped.

**Table 1**

Ferroelectric and piezoelectric properties of pure, Co doped and Co/Nb codoped BaTiO<sub>3</sub> ceramics

Composition	$\tau$ (%)	G ( $\mu\text{m}$ )	$k_p$ (%)	$\epsilon_{33}^S/\epsilon_0$	$\tan \delta_e$	$d_{33}$ (pC/N)	$k_t$ (%)	Tc (°C)
BaTiO <sub>3</sub>	96	>50	12	1575	0.6	70	N/D	140
BaTi <sub>0.9925</sub> Co <sub>0.0075</sub> O <sub>3</sub>	96	~50	33.6	1080	1.8	190	39	115
BaTi <sub>0.985</sub> Co <sub>0.005</sub> Nb <sub>0.01</sub> O <sub>3</sub>	96	~50	28.5	1961	0.4	200	40	114

$\tau$ : relative density, G: mean grain size,  $k_p$ : planar coupling factor,  $\epsilon_{33}^S/\epsilon_0$ : dielectric constant at constant strain;  $\tan \delta_e$ : dielectric losses,  $d_{33}$ : piezoelectric coefficient,  $k_t$ : thickness coupling factor; Tc: Curie Temperature

#### 4. Conclusions

The crystal structure modifications of BaTiO<sub>3</sub> induced by cobalt doping and niobium/cobalt co-doping were investigated. In Co doped BT samples, oxygen vacancies are responsible of the formation of the hexagonal form of BT. BT remains tetragonal or cubic for samples doped with 2 Nb for 1 Co. These results suggest that cobalt valence state in BT is +II. Low Co and Co/Nb doping level significantly improve piezoelectric properties of BaTiO<sub>3</sub>, and lead to a slight decrease of Tc.

#### Acknowledgments

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