

NEW DEFECT PYROCHLORE SOLID SOLUTION IN THE $\text{KBi}_2\text{M}_5\text{O}_{16}$ – $\text{TlBi}_2\text{M}_5\text{O}_{16}$ (M=Nb, Ta) SYSTEMS

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Abstract: synthesis and caraterization of new solids solutions $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{M}_5\text{O}_{16}$ with ($0 \leq x \leq 1$; M=Nb, Ta) defect pyrochlore type.

Two solid solutions $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{M}_5\text{O}_{16}$ ($0 \leq x \leq 1$; M=Nb, Ta) were prepared using solid state reaction method and characterized by x-ray diffraction and Infrared absorption spectroscopy. All compositions were indexed in the cubic system (space group Fd3m) and showed the defect pyrochlore-type structure like oxides as $\text{ABi}_2\text{M}_5\text{O}_{16}$ (A=K, Tl; M=Nb, Ta) [1]. The cell parameter of the two defect pyrochlores solid solutions varies linearly with increasing x of compositions from $a=10.5701(1)$ Å to $a=10.5343(1)$ Å for $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{Nb}_5\text{O}_{16}$ ($0 \leq x \leq 1$) and from $a=10.5489(1)$ Å to $a=10.5144(1)$ Å for $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{Ta}_5\text{O}_{16}$ ($0 \leq x \leq 1$).

Résumé – Synthèse et caractérisation de nouvelles solutions solides $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{M}_5\text{O}_{16}$ ($0 \leq x \leq 1$; M=Nb, Ta) de type pyrochlore déficitaire. Deux solutions solides $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{M}_5\text{O}_{16}$ ($0 \leq x \leq 1$; M=Nb, Ta) ont été préparées à l'état solide et caractérisées par diffraction des rayons X et par spectroscopie d'absorption infrarouge. Toutes les compositions des solutions solides cristallisent dans le système cubique (groupe d'espace Fd3m) et appartiennent à la famille des pyrochlores déficitaires, $\text{ABi}_2\text{M}_5\text{O}_{16}$ (A=K, Tl; M=Nb, Ta) [1]. Le paramètre de maille des deux solutions solides varie linéairement avec la composition x de $a=10.5701(1)$ Å à $a=10.5343(1)$ Å pour $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{Nb}_5\text{O}_{16}$ ($0 \leq x \leq 1$) et de $a=10.5489(1)$ Å à $a=10.5144(1)$ Å pour $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{Ta}_5\text{O}_{16}$ ($0 \leq x \leq 1$).

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I. Introduction

Material pyrochlore and related phases have been characterized by many workers over the past several years, this as a result of the stability and diverse physical properties of this material. The pyrochlore structure with general formula $\text{A}_2\text{B}_2\text{O}_6\text{O}'$ [2-4] and with eight formula units per cell can be considered as interpenetrating networks completely independent B_2O_6 and $\text{A}_2\text{O}'$; this latter is not essential for the stability of the structure [5-7]. When the compounds processes a general formula $\text{A}_2\text{B}_2\text{O}_6\text{O}'$ the A cation retain the eight-fold coordination but the B cation are only in six-fold coordination. Thus the A ions are larger than the B ions in compound with this structure. The coordination polyhedra of th ions in the ideal case are $\text{AO}_6\text{O}'_2$, BO_6 , OA_2B_2 and $\text{O}'\text{A}_4$. The pyrochlore structure tolerates a high degree of non stoichiometry on the A cations and on the O' anions sites particularly for A= Tl, Pb and Bi, AB_2O_6 -type defect pyrochlores are obtain with all O' atoms missing; also this type of defect pyrochlore are known for large univalent A cations such as Rb^+ [8]. So, by removing of A and O' ions, a variety of deficient

structures can be produced with, are know to occur with the general formula $\text{A}_{2-x}\text{B}_2\text{O}_{6+y}$ [9-11] with $0 < x \leq 1$ and/or $0 \leq y < 1$.

In this work we report the preparation and characterization of a new defect pyrochlore solid solutions $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{M}_5\text{O}_{16}$ ($0 \leq x \leq 1$; M=Nb, Ta).

II. Experimental

The compounds $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{M}_5\text{O}_{16}$ ($0 \leq x \leq 1$; M=Nb, Ta) were prepared by usual solid solution from starting reagents Bi_2O_3 , Nb_2O_5 , Ta_2O_5 , K_2CO_3 and Tl_2CO_3 . Weighted quantities of the reactants were intimately mixed and ground in a agate mortar. In order to avoid a possible oxidization of Tl^+ to Tl^{3+} , all compounds were treated under nitrogen atmosphere. Three thermal processings with intermittent regrinding at 300°C (6 hours) (to provoke the departure of CO_2 and in the same time to avoid volatilization of Tl_2CO_3 [12], 800°C (12 hours) (to finish the decomposition of K_2CO_3) and $950 - 1000^\circ\text{C}$ (12 hours) were necessary to obtain the final compounds. X-ray powder diffractograms were obtained using Cu K α line of a D5000 Siemens diffractometer with Bragg-Brentano

geometry and equipped with a back monochromator. The data were recorded between 10 and 120 (2θ) in steps of 0.04° with a count time of 72 s. Temperature programmed X-ray diffraction was performed on a Siemens D5000 diffractometer fitted out with an ANTON PARR furnace (CHTK10) and a linear detector (Elphyse 14°). The powders were ground in the presence of polyvinyl alcohol and polyethylene glycol and pressed into pellets (10mm in diameter and approximately 1.4 mm thick) using an uniaxial pressure (200 MPa). Before sintering, the pellets were heated at 500°C to evaporate the binder. The morphology of sintered materials was determined by SEM. The thermal gravimetric analysis (TGA) of powder samples was carried out using a SETARAM TG with a heating rate of $10^\circ\text{C}/\text{mn}$. The IR spectra were recorded between 4000 and 400 cm^{-1} with 4 cm^{-1} resolution using a Foirier-Transformed BOMEN MX spectrometer from dics containing 2 mg of sample and 100 mg of KBr or CsCl. The densities were measured using ACCUPYC 13330 helium pycnometer.

III. Results And Discussions

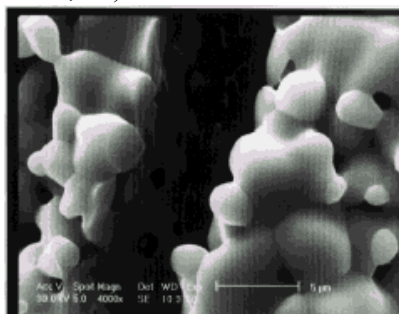
III-1. Solid solution

In order to study the dielectric properties for compounds $\text{KBi}_2\text{M}_5\text{O}_{16}$ (M = Nb, Ta) [13] we have examined the morphology of sintered pellets (*figure 1*) we note for this two compound that pellets crack in contact with air. This phenomenon could be the result of the increase of the cell volume in relation with atmospheric humidity. To solve this problem of pellets cracking we howver substitute the potassium by the thallium in the $\text{KBi}_2\text{M}_5\text{O}_{16}$ (M = Nb, Ta) for two reasons:

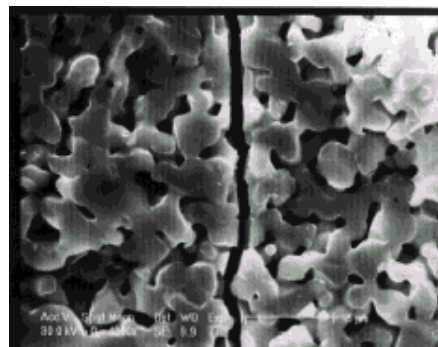
1) The size, in six-fold coordination, of thallium ion ($r\text{TI}^+(6) = 1.50\text{\AA}$) is relatively near to potassium ion ($r\text{K}^+(6) = 1.38\text{\AA}$).

2) Compounds $\text{KBi}_2\text{M}_5\text{O}_{16}$ and $\text{TlBi}_2\text{M}_5\text{O}_{16}$ (M = Nb, Ta) crystallize in the same structural type [1].

In spite of this substitution on one hand and by using of optimal conditions for sintering materials on the other hand, the pellet crack. So dielectrics properties can't be determined because all prepared pellets crack at ambient temperature. However we have identify two solid solution $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{M}_5\text{O}_{16}$ ($0 \leq x \leq 1$; M=Nb, Ta).



$\text{KBi}_2\text{Nb}_5\text{O}_{16}$



$\text{KBi}_2\text{Nb}_5\text{O}_{16}$

Figure 1. Micrographs of cracking pellets of $\text{KBi}_2\text{M}_5\text{O}_{16}$ (M=Nb,Ta).

III-2. X-ray diffraction

All compound $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{M}_5\text{O}_{16}$ ($0 \leq x \leq 1$; M=Nb, Ta) were prepared like compounds $\text{KBi}_2\text{M}_5\text{O}_{16}$ and $\text{TlBi}_2\text{M}_5\text{O}_{16}$ (M = Nb, Ta) [1]. The final products are yellow and white respectively for $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{Nb}_5\text{O}_{16}$ and $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{Ta}_5\text{O}_{16}$. *Figure 2* shows the x-ray diffraction diagrams for the two solid solutions. They characterize a continuous solid solution crystallizing in the defect pyrochlore type structure (S.G. $\text{Fd}3\text{m}$).

The parameter exhibit a quasi-linear evolution with composition x. The substitution of K^+ (1.38\AA) by TI^+ (1.50\AA) must normally induce an increasing of the cell parameter. *Figure 3* shows an evolution of the cell parameter in the inverse sense. This could be the result of the action of two antagonistic phenomena: on one hand, the substitution by a bigger size cation (increase cell parameter) and on the other hand, composition rich with thallium present a slight hydration degree (decrease cell parameter); the consequence of these two effects is an appreciable reduction of cell parameter with x compositions. No significant change in the x-ray diffraction patterns of these compositions was observed, however a slight shift in the position of peaks was detected by the mean of high temperature diffraction patterns. In *table I* we give the cell parameter of extreme compounds ($x=0$ and $x=1$) for the two solid solutions at 25°C and at 500°C . Other effects of hydration are the change in the relative intensity of (311) Bragg peaks. Indeed, when hydration degree increase, relative intensity of (311) Bragg peaks increase as can be seen in *figure 2*. This phenomenon was also observed in NH_4NbWO_6 [14].

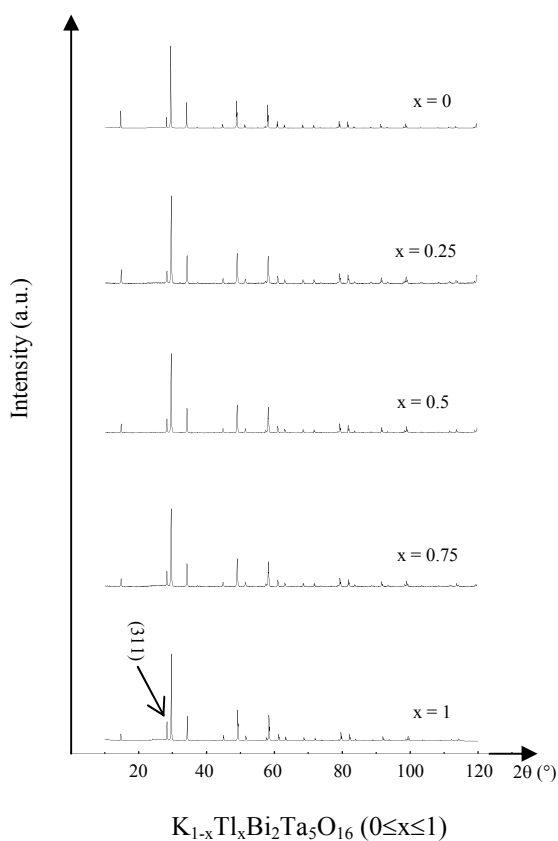
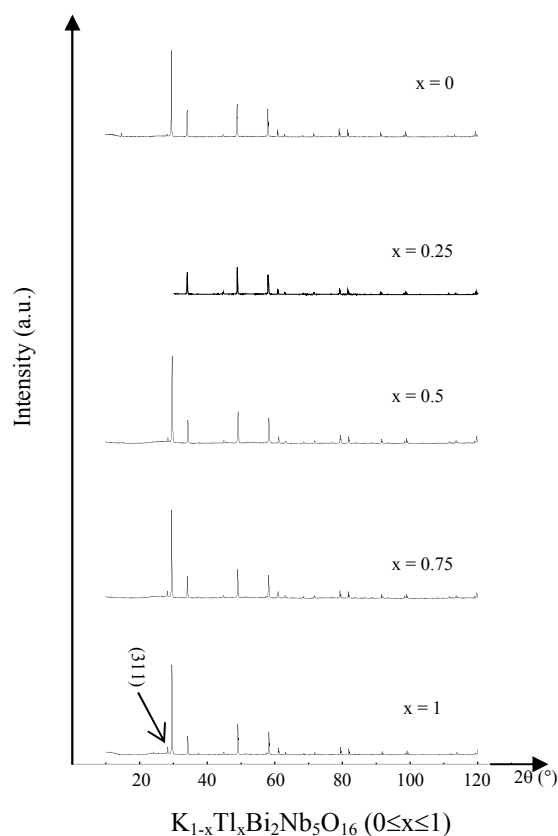


Figure 2. X-ray powder diffractograms of $K_{1-x}Tl_xBi_2M_5O_{16}$ ($0 \leq x \leq 1$; $M=Nb, Ta$)

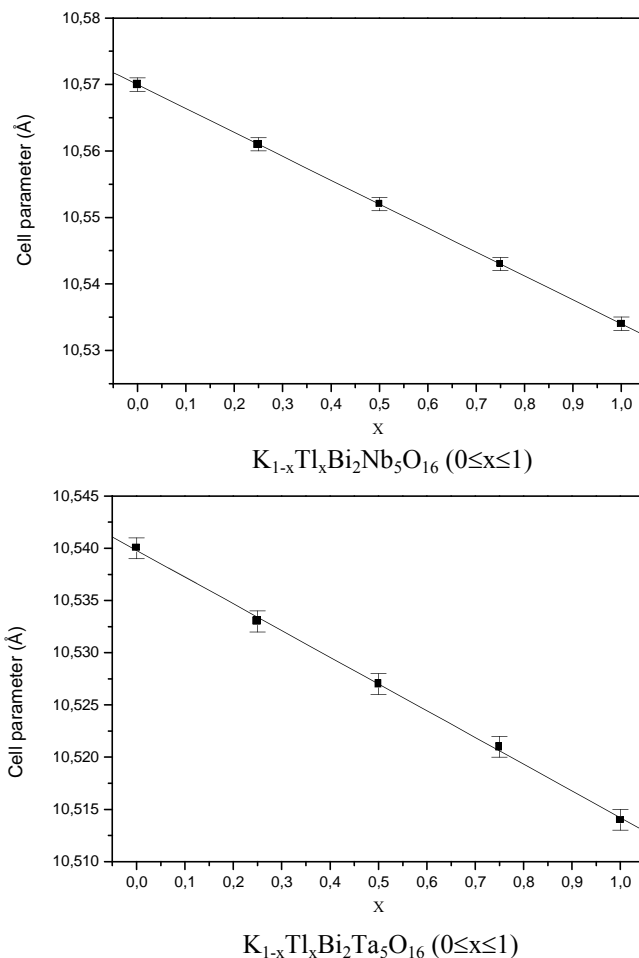


Figure 3. Cell parameter variation versus composition of $K_{1-x}Tl_xBi_2M_5O_{16}$ ($0 \leq x \leq 1$; $M=Nb, Ta$)

Tableau I. Cell parameter at 25°C and at 500°C of $ABi_2M_5O_{16}$ ($A=K, Tl$; $M=Nb, Ta$)

Compounds	Cell parameter at 25°C	Cell parameter at 500°C
$KBi_2Nb_5O_{16}$	10.5701(1)	10.5051(1)
$TlBi_2Nb_5O_{16}$	10.5343(1)	10.5093(1)
$KBi_2Ta_5O_{16}$	10.5389(1)	10.4684(1)
$TlBi_2Ta_5O_{16}$	10.5144(1)	10.4786(1)

III-3. TGA

The thermal gravimetric analysis (TGA) (*figures.4*) of the prepared powders of $K_{1-x}Tl_xBi_2M_5O_{16}$ ($0 \leq x \leq 1$; $M=Nb, Ta$) show that dehydration temperatures starts at about 50°C and are relatively low indicate the presence of water adsorbed and from 100°C to 400°C we assist to the loss of a bounded water. The effect of this insertion of water molecular is an appreciable increasing in the cell constants or cell volume. *Table II* gives the number of water moles adsorbed in each composition Compounds $KNbWO_6$

and KTaWO_6 prepared by Darriet and Al [15] are hygroscopic at ambient temperature; similar results have been obtained for other related pyrochlore such as $\text{K}_{3/2}\text{Cr}_{1/2}\text{Te}_{3/2}\text{O}_6$, $1/2\text{H}_2\text{O}$ [16, 17]. We note from $x=1$ to $x=0$, an increasing of weight losses ΔM (%) for the two solid solutions indicating that composition rich with K_2O retain atmospheric humidity more than Tl -containing pyrochlores.

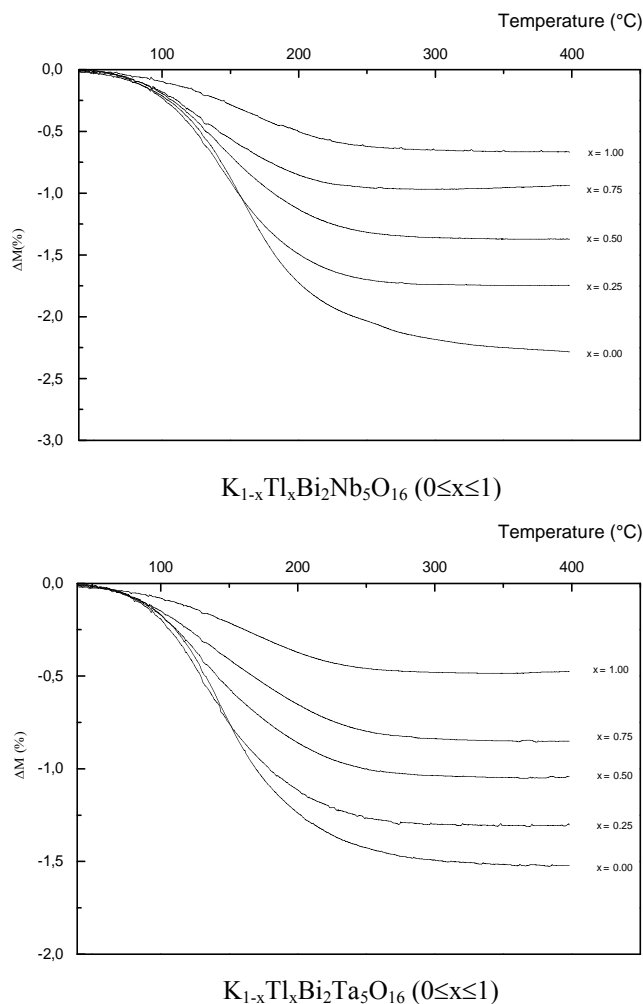


Figure 4. TGA thermograms of $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{M}_5\text{O}_{16}$ ($0 \leq x \leq 1$; $\text{M}=\text{Nb}, \text{Ta}$)

Tableau II. Weight losses ΔM (%) and number of water moles of $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{M}_5\text{O}_{16}$ ($\text{M}=\text{Nb}, \text{Ta}$)

Compositi on x	$\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{Nb}_5\text{O}_{16} \cdot n$ H_2O		$\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{Ta}_5\text{O}_{16} \cdot n$ H_2O	
	ΔM (%)	n (H_2O)	ΔM (%)	n (H_2O)
x = 0	2.27	0.61	1.51	0.55
x = 0.25	1.73	0.48	1.21	0.48
x = 0.5	1.34	0.39	1.01	0.40
x = 0.75	0.96	0.28	0.83	0.33
x = 1	0.63	0.19	0.47	0.19

III-4. Specific mass measurements

Figure 5 shows a normal evolution with composition x. This is with a good agreement with the difference of molar weight of thallium (204,37g/mol) and potassium (39,102g/mol). The effect of hydration has been masked by the great difference between molar weights.

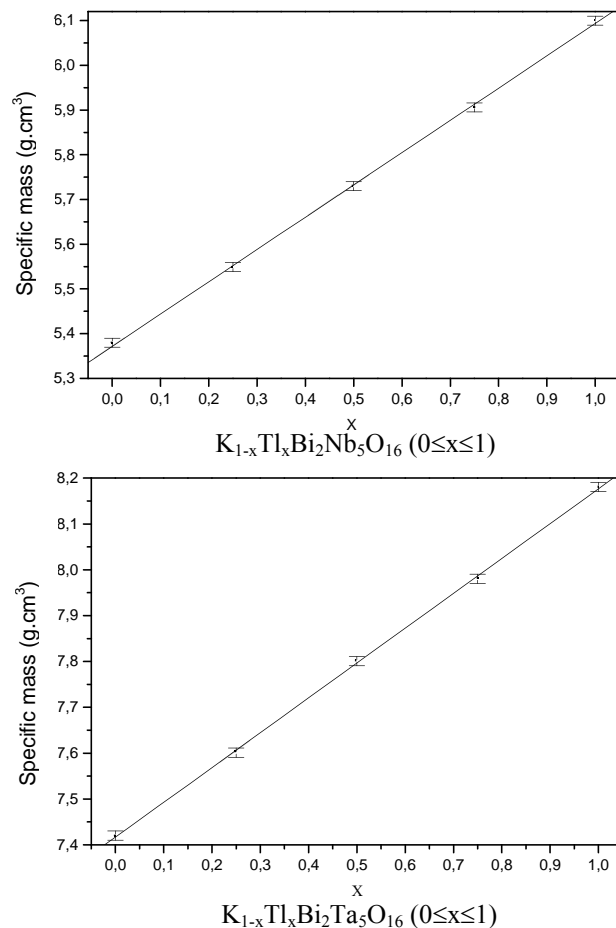


Figure 5. Variation of specific mass versus composition of $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{M}_5\text{O}_{16}$ ($0 \leq x \leq 1$; $\text{M}=\text{Nb}, \text{Ta}$)

III-5. Infrared spectroscopy

The group theoretical analysis for optical and acoustical modes from correlation method and taking account the symmetry conditions of pyrochlore structure [18] are given in table III.

IV. CONCLUSION

In this work we have determined the existence of two solid solutions $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{M}_5\text{O}_{16}$ ($0 \leq x \leq 1$ and M = Nb, Ta) inside the systems $\text{KBi}_2\text{M}_5\text{O}_{16}$ - $\text{TlBi}_2\text{M}_5\text{O}_{16}$ (M = Nb, Ta). The structure of all composition is isotypic with defect pyrochlore like $\text{ABi}_2\text{M}_5\text{O}_{16}$ (A= K, Tl and M = Nb, Ta) compounds [1]. Infrared spectra, TGA and high temperature diffraction patterns show the existence of water in all compositions of $\text{K}_{1-x}\text{Tl}_x\text{Bi}_2\text{M}_5\text{O}_{16}$ ($0 \leq x \leq 1$ and M = Nb, Ta). As a consequence hydration we note a slight increase in the unit cell volume; this phenomenon is responsible of cracking of all sintered pellets destined to dielectrics measurements.

V. REFERENCES

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