Structural study of the $Ba_{6-x-y}La_{8+2/3x+y}Ti_{18-y}Al_y O_{54}$ solid-solution

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Abstract

The study of the Ba/La order in the $Ba_{6-x-y}La_{8+2/3x+y}$ Ti_{18-y} Al_y O_{54} solid-solution was performed by X-ray diffraction on single-crystals. The crystal structure of these phases belongs to the tetragonal tungsten bronze type, build on the basis of (3x3) TiO_6 octahedron more than (2X2) (space group Pnma, a≈22.4Å, b≈7.7 Å, c≈12.2 Å). The substitution of titanium by aluminum within the Ba_{6-x} $La_{8+2/3x}$ Ti_{18} O_{54} solid-solution concerns preferentially the two crystallographic sites Ti(1) and Ti(3) of the structural model.

Keywords: Perovskite, Tetragonal tungsten bronze, Dielectric materials.

1- Introduction

The recent progress in microwave integrated systems for telecommunication makes necessary the development of a larger number of hyperfrequency devices such as filters and resonators. The use of dielectric materials for hyperfrequency resonators was proposed by in 1939 by Ritchmyer. Dielectric resonators provide many advantages mainly due to their small size (small value of $1/\sqrt{\varepsilon}_r$ factor, ε_r : relative permittivity) and to their high thermal stability measured by the temperature coefficient $\tau_f=(1/f).(df/dT)$ which must be, for most of the case, as close as possible of 0 ppm/°C, and very low dielectric losses (tanδ), which means a quality factor Q=1/ tanδ as high as possible, in order to minimize the energy losses at high temperature.
Ceramic materials belonging to the Ba_{6-x} $La_{8+2/3x}$ $Ti_{18}O_{54}$ solid-solution present interesting dielectric properties. They present high dielectric constant and low dielectric losses, associated to a temperature coefficient at the resonance frequency close to zero [1,2,3,4,5]. The aim of the present work is to study, by X-ray diffraction performed on single-crystals, the solid-solution Ba_{6-x} $La_{8+2/3x}$ Ti_{18} O_{54}, which derived of Ba_{6-x} $La_{8+2/3x}$ Ti_{18} O_{54} by an aluminum / titanium substitution.

2- Elaboration of the crystals

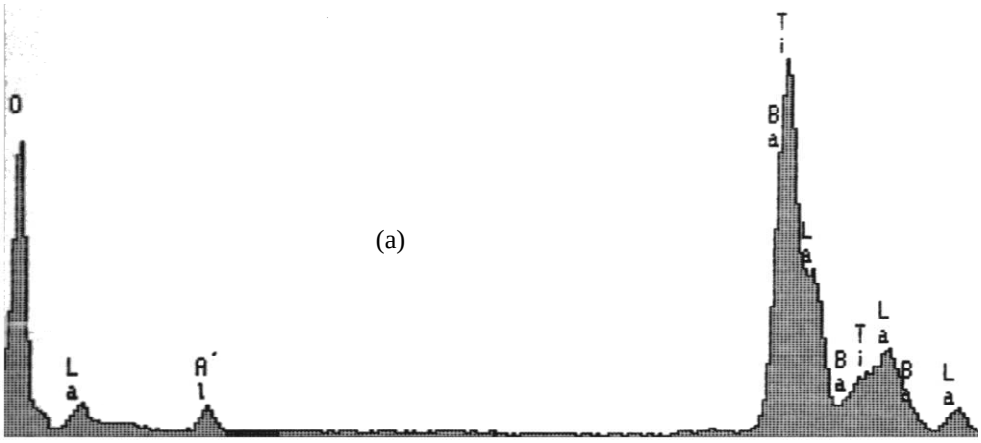
Single-crystals were elaborated using $BaCO_3$, La_2O_3 and TiO_2 at temperature ranging from 1500 to 1600°C. The occurrence of aluminum in the composition of the crystals results from diffusion of aluminum arising from the alumina crucibles used for the synthesis. The obtaining of single-crystals presenting sufficient quality and size allowed the structural determination of some phase using single-crystal X-ray diffraction. The diffracted intensities were recorded using an automatic four circles diffractometer (P4 Siemens) using molybdenum $K_{\alpha 1}$ radiation (λ = 0.71073 Å).

3. Results and discussion

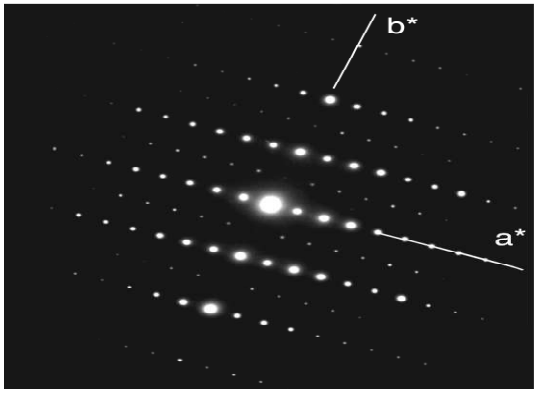
The structural determination of the three single-crystals studied here was performed using the Shelx 97 program. After refinement of different parameters (fractional coordinates of the ions and occupancies), the R_1 reliability factor was greater than 5% because the aluminum, which substitutes titanium, wasn't considerate.

At this step of the refinement, we checked for the chemical composition by transmission electron microscopy using local analysis by energy dispersive X-ray spectrometry (EDX). The powdered sample, for which the single-crystal was obtained, was crushed and deposited on a carbon membrane. An important number of crystallites belonging to the $Ba_{6-x}La_{8+2x/3}Ti_{18}O_{54}$ phase were characterized by electron diffraction and their chemical composition was then studied using a focused electron beam. The results are highly reproducible and for example, an analysis obtained for one of these crystals is represented in figure 1. This analysis revealed unambiguously the occurrence of a low content of aluminum within the crystalline lattice (fig. 1.a).

In order to precise the relative concentrations of the chemical elements, a semi-quantitative approach was performed, using a program based on the approximation of thin films and allowed to determine the apparent concentrations of the different cations for the known oxygen stoichiometry of this phase. They lead to the approximated formula $Ba_{4,3}La_{9,4}Ti_{16,4}Al_{1,4}O_{54}$.



(a)



(b)

Figure 1 : Chemical analysis of a $Ba_{6-x}La_{8+2x/3}Ti_{18}O_{54}$ (x=1.5) powder
(a)- Results of the chemical analysis performed on several crystals
(b)- Selected Area diffraction diagram of one of the crystals

The introduction of Al/Ti into the Ti(1) and Ti(3) sites of the structure (figure 2.b) decreased the the R_1 and WR2 reliability factors for the three compositions. After refinement of the Al/Ti ration for these two sites considering a full occupancy of all the Ti sites and of the A sites (figure 2.a) [6,7] , the R_1 and WR_2 reliability factors converged to a correct value of 0.0239 and 0.0565 respectively for a satisfactory merit factor S=1.04.

Table 1 includes all the crystallographic parameters of the three single-crystals, together with the acquisition conditions of the diffracted intensities and the refinement parameters.

Table 1: crystallographic parameters of the three single-crystals, together with the acquisition conditions of the diffracted intensities and the refinement parameters for the three compositions x=0, x=1.5 and x=3.

Chemical formula	$Ba_{10,5}La_{17,5}Ti_{34,5}Al_{1,5}O_{108}$ x=0	$Ba_{9,5}La_{18}Ti_{35}AlO_{108}$ x=1.5	$Ba_{8,5}La_{19}Ti_{34}Al_2O_{108}$ x=3
Temperature (K)	293	293	293
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal System	orthorhombic	orthorhombic	orthorhombic
Space Group	Pnma	Pnma	Pnma
Lattice parameters (nm) And angles (°)	a=2.2429(4) α = 90 b=0.7725(2) β = 90 c=1.2261(2) γ = 90	a=2.2447(4) α = 90 b=0.7728(2) β = 90 c=1.2258(2) γ = 90	a=2.2430(4) α = 90 b=0.7725(2) β = 90 c=1.2258(2) γ = 90
Volume (nm3)	2.1244(8)	2.1264(8)	2.1240(8)
Z	1	1	1
Calculated density (mg/m3)	5.745	5.635	5.536
Absorption coefficient (mm-1)	16.612	16.213	15.848
F(000)	3253	3199	3145
Crystal size (mm3)	0.28x0.05x0.08	0.05x0.05x0.5	0.28x0.04x0.02
2Θ limits (°)	2.46 to 29.99	2.46 to 30	2.46 to 30.01
Limits of the acquisition	-1<h<17 et –1<k<10 and –17<l<1	-31<h<1 and –1<k<10 and –1<l<17	-1<h<31 and –1<k<10 and –1<l<17
Number of measured reflexion	2927	4207	3993
Number of independant measured reflexions	2322 [R(int)=0.0403]	3297 [R(int)=0.0403]	2990 [R(int)=0.1099]
Refinement méthod	Linear regression on F2	Linear regression on F2	Linear regression on F2
Data/ restriction / parameters	2322 /2 /232	3297 /2 /241	2990 /1 /229
Figure of merit (S)	1.052	1.040	1.083
R [I > 2 sigma (I)]	R1= 0.0383 et WR2= 0.0943	R1= 0.0239 et WR2= 0.0565	R1= 0.0407 et WR2= 0.0919
R (without reject)	R1= 0.0501 et WR2= 0.1026	R1= 0.0347 et WR2= 0.0613	R1= 0.0710 et WR2= 0.1047
Extinction coefficient	0.00117(7)	0.00041(3)	0.00015(5)

The chemical synthesis of the three single-crystals is supposed to be as following:

- $1,09x(\mathbf{Ba_{12}La_{16}Ti_{36}O_{108}})+0,75Al_2O_3 \longrightarrow \mathbf{Ba_{10,5}La_{17,5}Ti_{34,5}Al_{1,5}O_{108}}+2,625BaO+4,875TiO_2$
- $1,05x(\mathbf{Ba_9La_{18}Ti_{36}O_{108}})+0,5Al_2O_3 \longrightarrow \mathbf{Ba_{9,5}La_{18}Ti_{35}AlO_{108}}+0,5La_2O_3+3TiO_2$
- $1,42x(\mathbf{Ba_6La_{20}Ti_{36}O_{108}})+Al_2O_3 \longrightarrow \mathbf{Ba_{8,5}La_{19}Ti_{34}Al_2O_{108}}+4,65La_2O_3+3TiO_2$

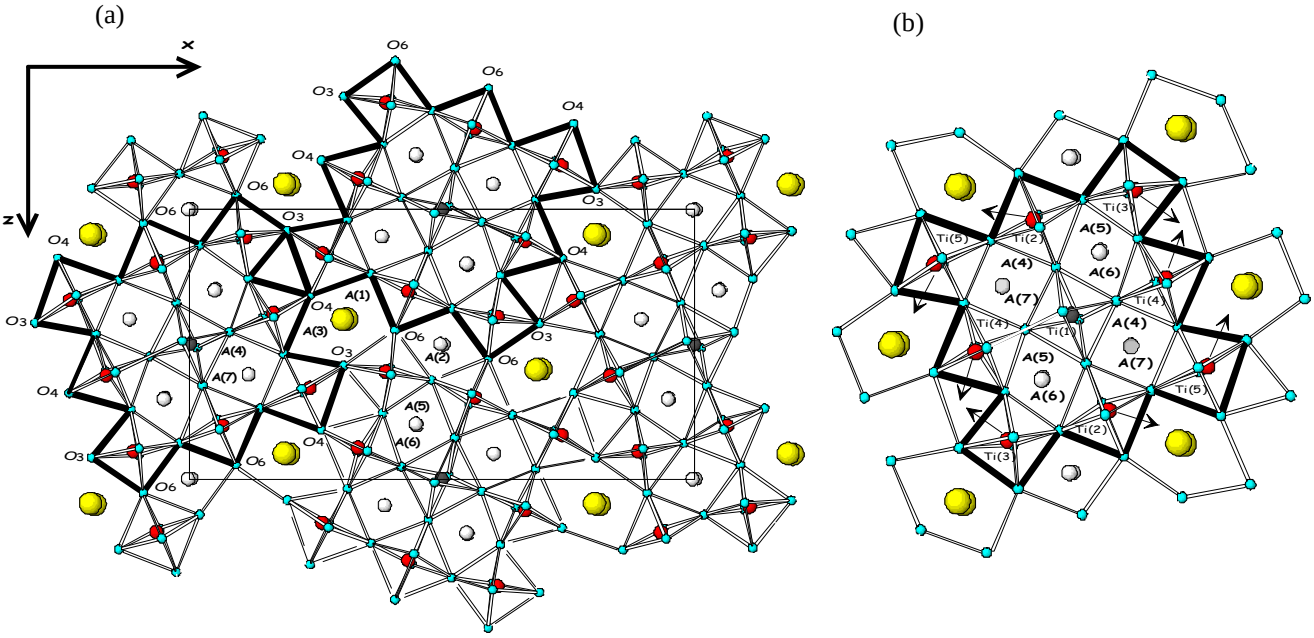


Figure 2 : (a) $Ba_{4,75}La_9Ti_{17,5}Al_{0,5}O_{54}$ – projection on the (xOz) plane

(b) Positions of the cations in a perovskite bloc

4. Conclusion

The substitution of aluminum for titanium within the Ba_{6-x} $La_{8+2/3x}$ Ti_{18} O_{54} solid-solution corresponds preferentially to the two crystallographic sites Ti(1) et Ti(3). The analysis of the cationic environments revealed that the Ti1-O and Ti3-O mean distances are the shortest ones: **<Ti(1)-O>=1.94 Å**, <Ti(2)-O>=1.96 Å, **<Ti(3)-O>=1.95 Å**, <Ti(4)-O>=1.96 Å et <Ti(5)-O>=2,01Å. As a consequence, the [Ti(1)O6] et [Ti(3)O6] octaedra can easily be occupied by Al^{3+} which possesses smaller ionic radius (0.535 Å) than the one of Ti^{4+} (0.605 Å).

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