

# Influence Of The Ti/Al Substitution On Ba/La Cationic Order In The $\text{Ba}_{6-x-y}\text{La}_{8+2/3x+y}\text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$ Solid Solution

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The study of the Ba/La order in the  $\text{Ba}_{6-x-y}\text{La}_{8+2/3x+y}\text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$  solid-solution was performed by X-ray diffraction on powders and single-crystals. The crystal structure of these phases belongs to the tetragonal tungsten bronze type, build on the basis of (3x3)  $\text{TiO}_6$  octahedron more than (2X2) (space group Pnma,  $a \approx 22.4\text{\AA}$ ,  $b \approx 7.7\text{\AA}$ ,  $c \approx 12.2\text{\AA}$ ). Two structural models were built, corresponding to two different orders within the structure. The model I, of formula  $[\text{Ba}_4]_{\text{A2}} [\text{Ba}_{2-z}\text{La}_{2x/3+y+q} \text{q}']_{\text{A1'}} [\text{La}_{8-q} \text{q}]_{\text{A1}} \text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$ , corresponds to a model associated to infinite perovskite rows parallels to Oy axis, build on the basis of (3X3)  $\text{TiO}_6$  octahedron. The model II, with formula  $[\text{Ba}_{6-z} \text{z-2}]_{\text{A2}} [\text{La}_{8+2x/3+y} \text{2-(2x/3)-y}]_{\text{A1'}} \text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$ , can be described on the basis of three perovskite octahedron layers parallels to xOz plane.

## I. Introduction

The use of dielectric materials for hyperfrequency resonators was proposed in 1939 by Richtmyer, and the first practical use of such materials, based upon titanium dioxide, appeared around 1960-1970. The use of dielectric materials more than resonant cavities is interesting because of a decrease by a  $1/\sqrt{\epsilon_r}$  factor ( $\epsilon_r$  : relative permittivity) of the size of such devices, which is of considerable interest in order to reduce the size of such systems.

The selection of the materials for hyper frequency devices is based upon three parameters:

- High dielectric constant,

- Low dielectric losses ( $\tan\delta$ ), which means a quality factor  $Q=1/\tan\delta$  as high as possible, in order to minimize the energy losses at high frequency.

- High stability of the resonant frequency with temperature variations, 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.

Recently, some compositions belonging to the  $\text{BaO-Ln}_2\text{O}_3\text{-TiO}_2$  system ( $\text{Ln} = \text{Sm}$  et  $\text{Nd}$ ) were studied, particularly those of the solid-solution  $\text{Ba}_6\text{-xLn}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \dots$ ).<sup>(1,2,3,4,5)</sup>

Three crystallographic sites were evidenced<sup>(6)</sup>, the tetragonal sites A1 and A1' and the pentagonal one A2 (figure 1).

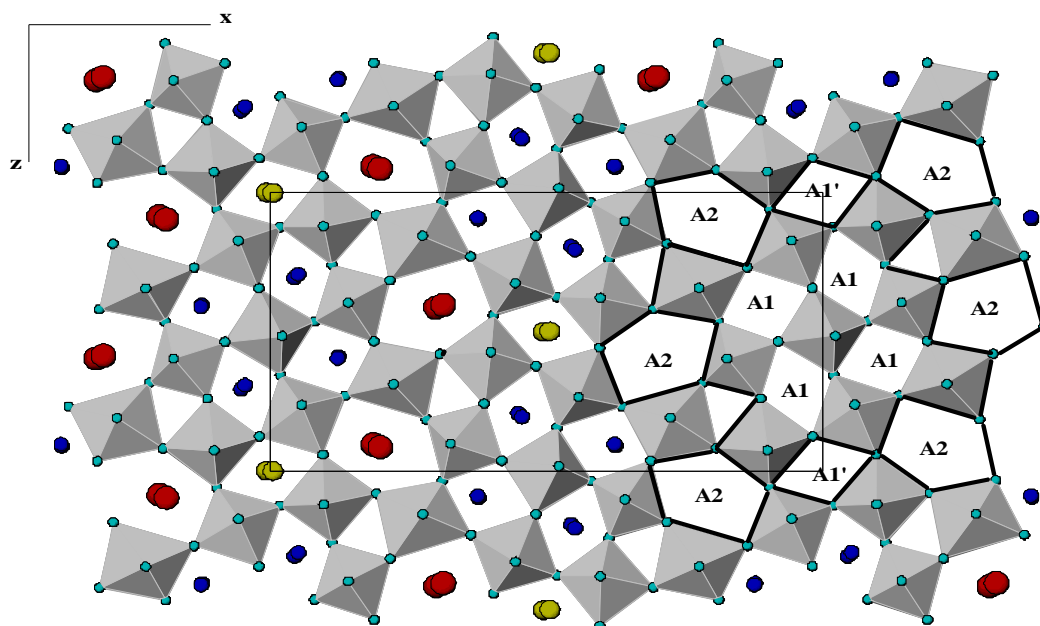


Figure 1 : General view of the cationic sites A1, A1' et A2

The aim of the present work is to study by X-ray diffraction on single-crystals and powders, the  $\text{Ba}_{6-x-y}\text{La}_{8+2x/3+y}\text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$  solid-solution, which can be considered as deriving from  $\text{Ba}_{6-x}\text{La}_{8+2/3x}\text{Ti}_{18}\text{O}_{54}$  by the substitution of aluminum by titanium, and particularly to evidence for the influence of this substitution on the Ba/La cationic order within the structure.

## II. Elaboration and characterization

The raw materials used for the powder synthesis and ceramic elaboration are commercial products of purity 99% or higher : titanium dioxide ( $\text{TiO}_2$ ), lanthanum oxide ( $\text{La}_2\text{O}_3$ ), barium carbonate ( $\text{BaCO}_3$ ) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ). Before use, the lanthanum oxide was heated at  $800^\circ\text{C}$  for 30minutes, in order to remove any water and carbon dioxide.

These precursors were weighed according to the desired stoichiometry and mixed for about 45 minutes using acetone as a liquid media. Then, the powders were calcined for 12 hours at  $1350^\circ\text{C}$  in platinum crucibles. These powders were systematically weighed before and after calcinations: as the departure of  $\text{CO}_2$  by thermal decomposition of the carbonate can be calculated, this allowed to check for a total reaction. For some of the compositions, single-crystals were elaborated by heating the obtained powders for a few hours at  $1500^\circ\text{C}$ , which is slightly lower than the melting temperature, and then by cooling these materials with a slow cooling rate ( $0.5^\circ\text{C}/\text{mn}$ ) for a tenth of degrees, followed by a normal cooling rate down to room temperature.

X-ray diffraction diagrams were recorded using respectively for powders a  $\theta/2\theta$  diffractometer (SIEMENS D5000) using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) and fitted with a rear monochromator (graphite) and for single-crystals an automatic four circles

diffractometer (P4 Siemens) using  $\text{Mo K}\alpha_1$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ).

## III. Results and discussion

The compositional domain of the  $\text{Ba}_{6-x-y}\text{La}_{8+2x/3+y}\text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$  solid-solution was determined by progressive substitution of Ti by Al for different x values ( $x = 0, 0.5, 1, 1.5, 2, 2.5$  et 3). The limits of the solid solution are represented figure 2 within the pseudo ternary  $\text{BaTiO}_3\text{-LaAlO}_3\text{-La}_2\text{Ti}_2\text{O}_7$ . For each value of x, when the y value is increased, the point representing the chemical composition moves in a parallel direction with the pseudo binary system  $\text{BaTiO}_3\text{-LaAlO}_3$ , the sum (Ba+La) remaining constant.

All the samples for which the theoretical chemical composition is located outside the domain (y greater than the maximum value) are composed of three different phases: the limit of the solid solution,  $\text{LaAlO}_3$  and  $\text{La}_2\text{Ti}_2\text{O}_7$ .

The maximum number y of aluminium ions per unit formula, which is maximum for  $x = 0$ , decrease regularly with increasing x and becomes 0 for  $x = 3$  (figure 2). The limit of the domain corresponds to the line of composition  $\text{Ba}_{3+y/2}\text{La}_{10}\text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$  ( $0 \leq y \leq 2$ ) joining the two extreme compositions  $\text{Ba}_4\text{La}_{10}\text{Ti}_{16}\text{Al}_2\text{O}_{54}$  ( $x=0$  et  $y=2$ ) et  $\text{Ba}_3\text{La}_{10}\text{Ti}_{18}\text{O}_{54}$  ( $x=3$  et  $y=0$ ).

The two other limits for the domain of solid-solution are those corresponding to:

- the « pure » solid-solution  $\text{Ba}_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$  ( $0 \leq x \leq 3$ ),
  - the particular solid-solution corresponding to  $x=0$ , of global composition  $\text{Ba}_{6-y}\text{La}_{8+y}\text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$  ( $0 \leq y \leq 2$ ).
- The double substitution, required for charge balance, is limited by a maximum number of 10 lanthanum ( $\text{La}^{3+}$ ) ions by formula unit.

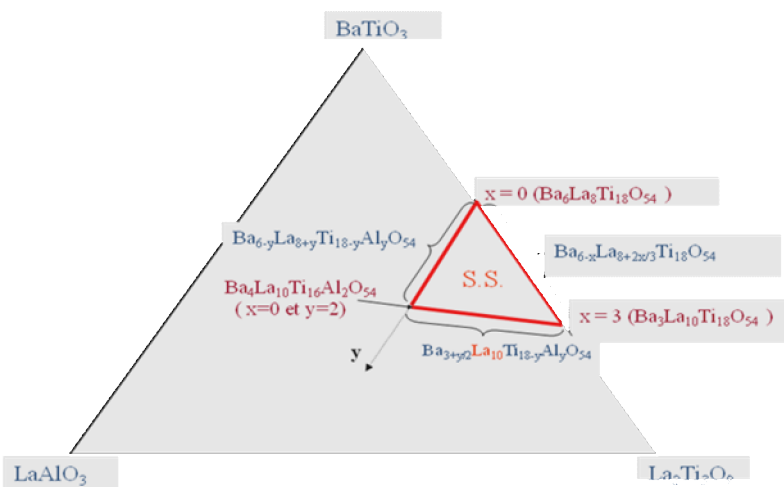


Figure 2: Limits of the solid-solution in the ternary system  $\text{BaTiO}_3\text{-LaAlO}_3\text{-La}_2\text{Ti}_2\text{O}_7$

The evolution of lattice parameters within the  $\text{Ba}_{6-x-y}\text{La}_{8+2x/3+y}\text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$  solid-solution was determined by two different ways:

- As a function of  $x$  for constant values of  $y$ ,
- As a function of  $y$  for constant values of  $x$ .

•  $\text{Ba}_{5.5-x}\text{La}_{8.5+2x/3}\text{Ti}_{17.5}\text{Al}_{0.5}\text{O}_{54}$  composition ( $y=0.5$ ) (line I)

For these compositions, the extent of the domain is limited to  $0 \leq x \leq 2.25$ .

Two different ranges can be observed, which are separated by the dotted line in figure 3:

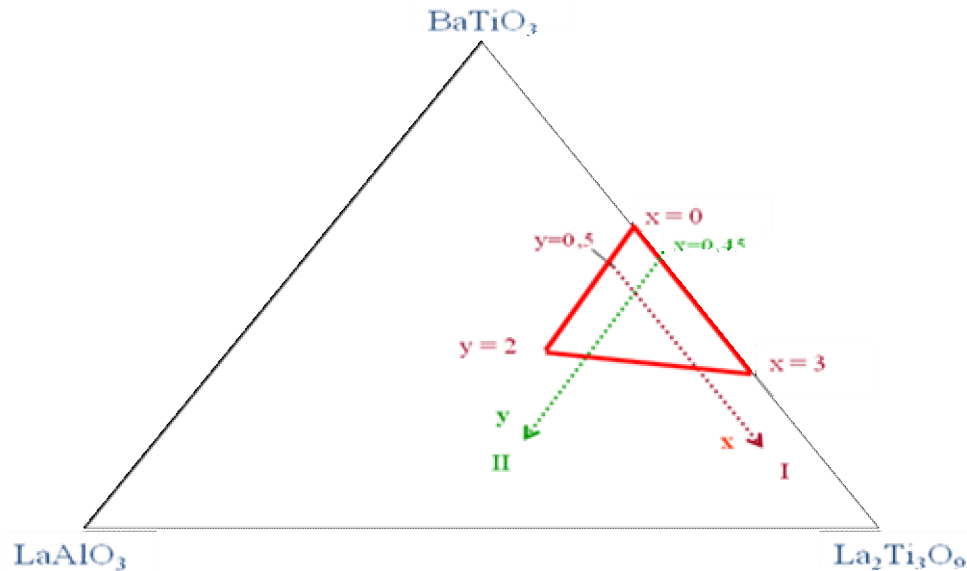


Figure 3 : Representation of the different domains studied and associated limits

Domain I :  $0 \leq x \leq 1.5$ :

All the lattice parameters  $a$ ,  $b$  and  $c$  decrease linearly with increasing values of  $x$ .

For the particular value  $x=1.5$  ( $\text{Ba}_4\text{La}_{9.5}\text{Ti}_{17.5}\text{Al}_{0.5}\text{O}_{54}$ ), the cuboctahedral cavities are occupied only by the lanthanum ions. When  $x$  is decreased, the A(2) sites are occupied by an increasing number of barium ions, which are larger than lanthanum ions ( $r_{\text{Ba}^{2+}}=1.60\text{\AA}$ ,  $r_{\text{La}^{3+}}=1.34\text{\AA}$ ); then, the three dimensional network of octahedron, of global composition  $(\text{BO}_3)_n$  ( $\text{B}=\text{Ti}$  et  $\text{Al}$ ), is progressively enlarged and this fact implies a general increase of  $V$ ,  $a$ ,  $b$  et  $c$ .

Domain II :  $1.5 \leq x \leq 2.25$  :

For increasing  $x$  values, the evolution of the lattice parameters is located within the experimental error. As a consequence, the cell volume remains quasi constant (figure 4-a).

For the entire domain, the structure is ordered but includes vacancies; the barium ions are only located in the pentagonal tunnels.

For increasing values of  $x$ , there is only a slight change of the positions and the number of cationic vacancies. As a matter of fact, taking into account the similar weight of Ba and La, the molar weight of the solid-solution doesn't change significantly: 3584.42g for  $x=1.5$  and 3550.87g pour  $x=2.25$ . As a consequence, the cell volume and the lattice parameters remain quasi constants.

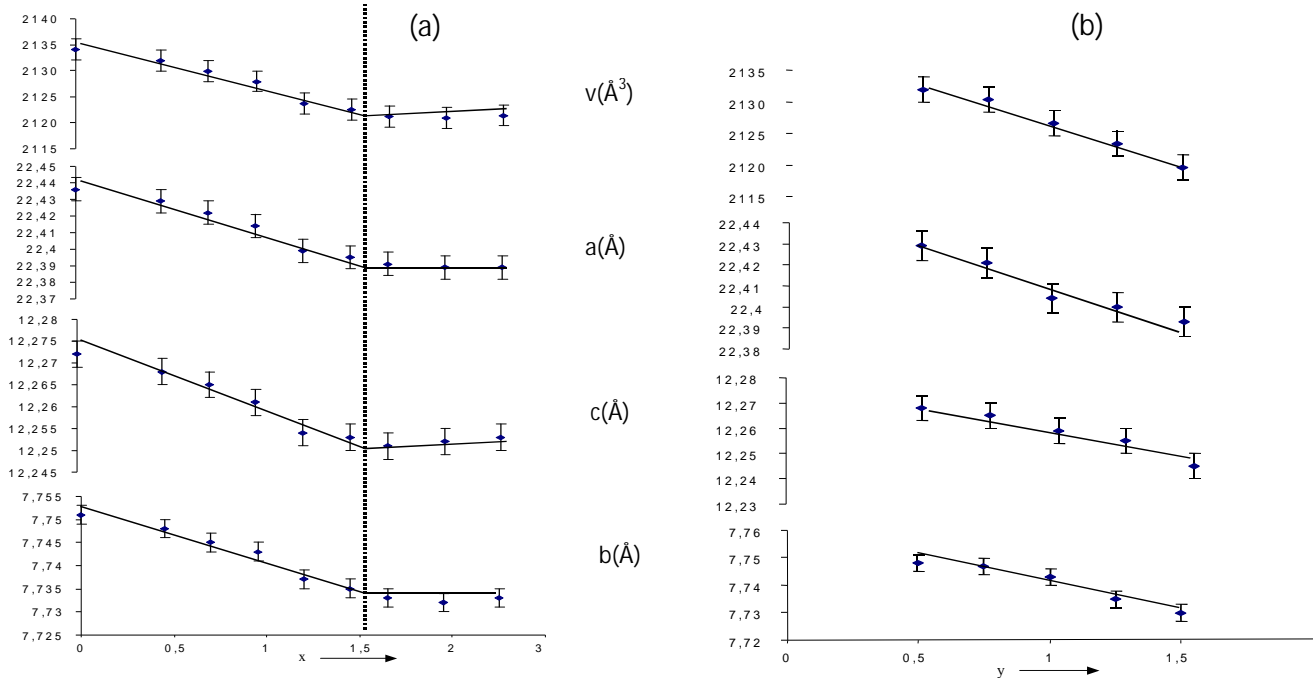


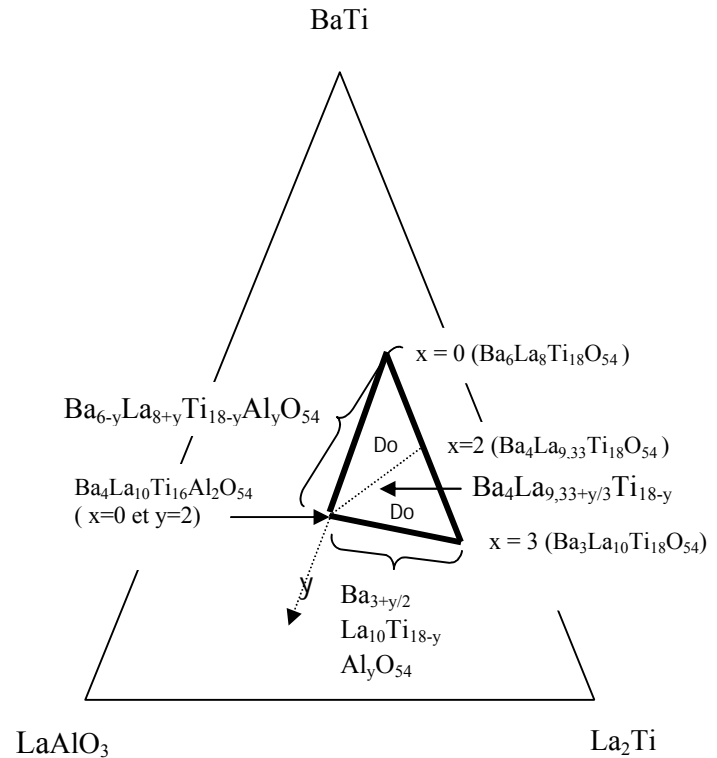
Figure 4 : Evolution of the a, b, and c lattice parameters and of the cell volume as a function of the y composition, between  $y=0.5$  and  $y=1.5$  ( $x=0.45$ )-  $\text{Ba}_{5.55-y}\text{La}_{8.3+y}\text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$ , (b). As a function of the x composition, between  $x=0$  et  $x=2.25$  ( $y=0.5$ )  $\text{Ba}_{5.5-x}\text{La}_{8.5+2x/3}\text{Ti}_{17.5}\text{Al}_{0.5}\text{O}_{54}$  (a)

•  $\text{Ba}_{5.55-y}\text{La}_{8.3+y}\text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$  ( $x=0.45$ ) Composition (line II)

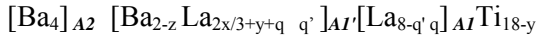
The evolution of the lattice parameters for different values of y ( $0 \leq y \leq 1.7$ ) and those of the cell volume are represented **figure 4-b**. For increasing values of x, all the lattice parameters, and so also the cell volume V, regularly decrease. This evolution logically represents the reduction of the volume of the three-dimensional network of  $[\text{BO}_6]$  octahedron, due to the decrease of the volume of the  $[\text{Ti}/\text{AlO}_6]$  octahedron for  $\text{Ti}^{4+} \rightarrow \text{Al}^{3+}$  increasing substitution ( $r_{\text{Al}^{3+}}=0.535 \text{ \AA}$  and  $r_{\text{Ti}^{4+}}=0.605 \text{ \AA}$ ). In addition, the simultaneous substitution of  $\text{Ba}^{2+}$  by  $\text{La}^{3+}$  emphasizes the decrease of the cell volume ( $r_{\text{Ba}^{2+}}=1.60 \text{ \AA}$  and  $r_{\text{La}^{3+}}=1.34 \text{ \AA}$ ).

From a structural point of view, the decrease of the lattice parameters with increasing values of x is correlated to the decrease of the Ba/La ratio in the A(2) sites of the structure. As a consequence, the evolution encountered here has the same origin as the one observed for the domain I of the  $\text{Ba}_{6-x}\text{La}_{8+2x/3}\text{Ti}_{18}\text{O}_{54}$  solid solution <sup>(7)</sup>.

As a general rule, for the  $\text{Ba}_{6-x-y}\text{La}_{8+2x/3+y}\text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$  solid-solution ( $0 \leq x \leq 3$ ;  $0 \leq y \leq 2$ ), the Ba/La ratio simultaneously changes as a function of both x and y. The compositional domain of stability of this  $\text{Ba}_{6-x-y}\text{La}_{8+2x/3+y}\text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$  solid-solution, represented figure 5, can be divided in two different domains for which the Ba/La order corresponds to two structural formulas.



\* **The structural formula I** can be used when the barium content is between 4 and 6, which means  $0 \leq x+y < 2$  (with  $0 \leq y \leq 2$ ). Taking into account the  $Ti^{4+} \rightarrow Al^{3+}$  substitution and considering the new variable quantity  $z=x+y$ , this formula can be written:

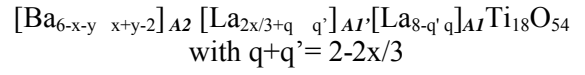


Structural formula I  
(domain I)

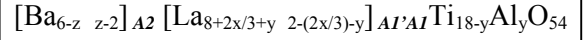
It corresponds to the cationic order existing for the compositions belonging to the triangular domain I (fig. 5), excepted for the compositions located at the right size of the line drawn between  $x=2$  and  $y=2$  delimitating the two domains.

\* **The structural formula II** is usable when the  $A1'$  are totally occupied by La, which means for all the other part of the compositional domain of stability (triangular domain II), delimited by the three segments of compositions  $Ba_4La_{9.33+y/3}Ti_{18-y}Al_yO_{18}$  ( $0 \leq y \leq 2$ ),  $Ba_{6-x}La_{8+2x/3}Ti_{18}O_{54}$  ( $2 \leq x \leq 3$ ) et  $Ba_{3+y/2}La_{10}Ti_{18-y}Al_yO_{54}$  ( $0 \leq y \leq 2$ ). The last one corresponds to the limits of compositional stability for the substitution  $Ti^{4+} \rightarrow Al^{3+}$  for which  $y=(6-2x)/3$ .

It could be written:



or



Structural formula II  
(domain II)

The two domains I and II respectively corresponds to two different structural models I and II:

- For the **Structural model I** (figure 6): the cationic order within the structure corresponds to a  $A1/A1'/A2$  type, for which the  $A1$  site is occupied by lanthanum, the  $A1'$  is a mixed site and the  $A2$  site is occupied only by barium.

- For the **Structural model II** (figure 7): the lanthanum ions are located inside the perovskite layers and the barium ions into the structural defects, similarly to the model I.

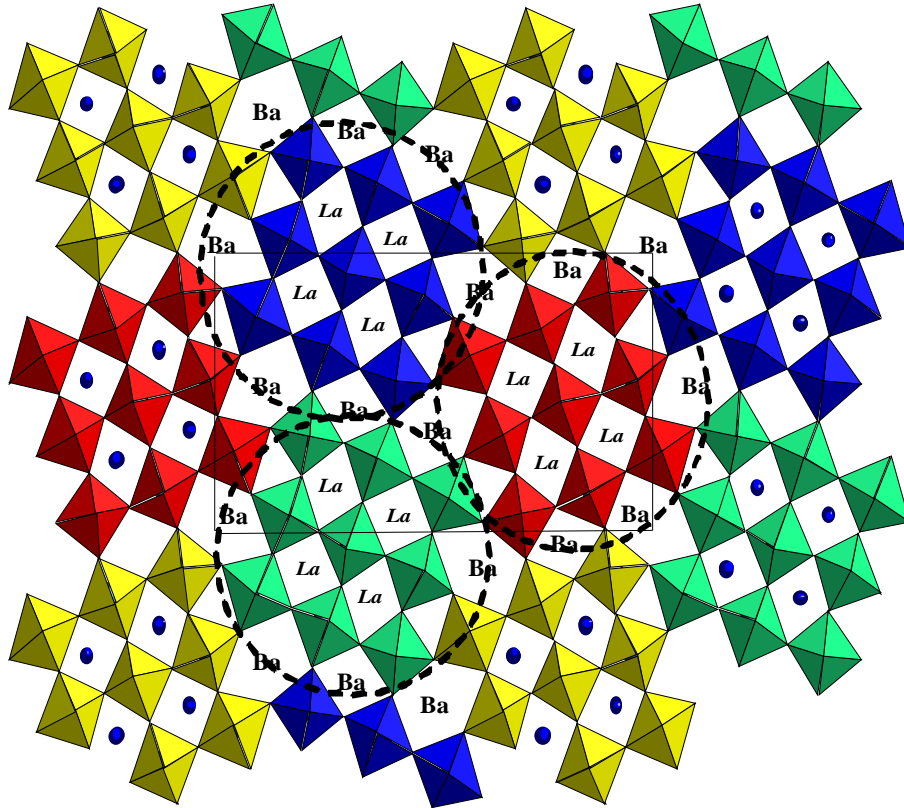


Figure 6 : crystal structure for Structural model I



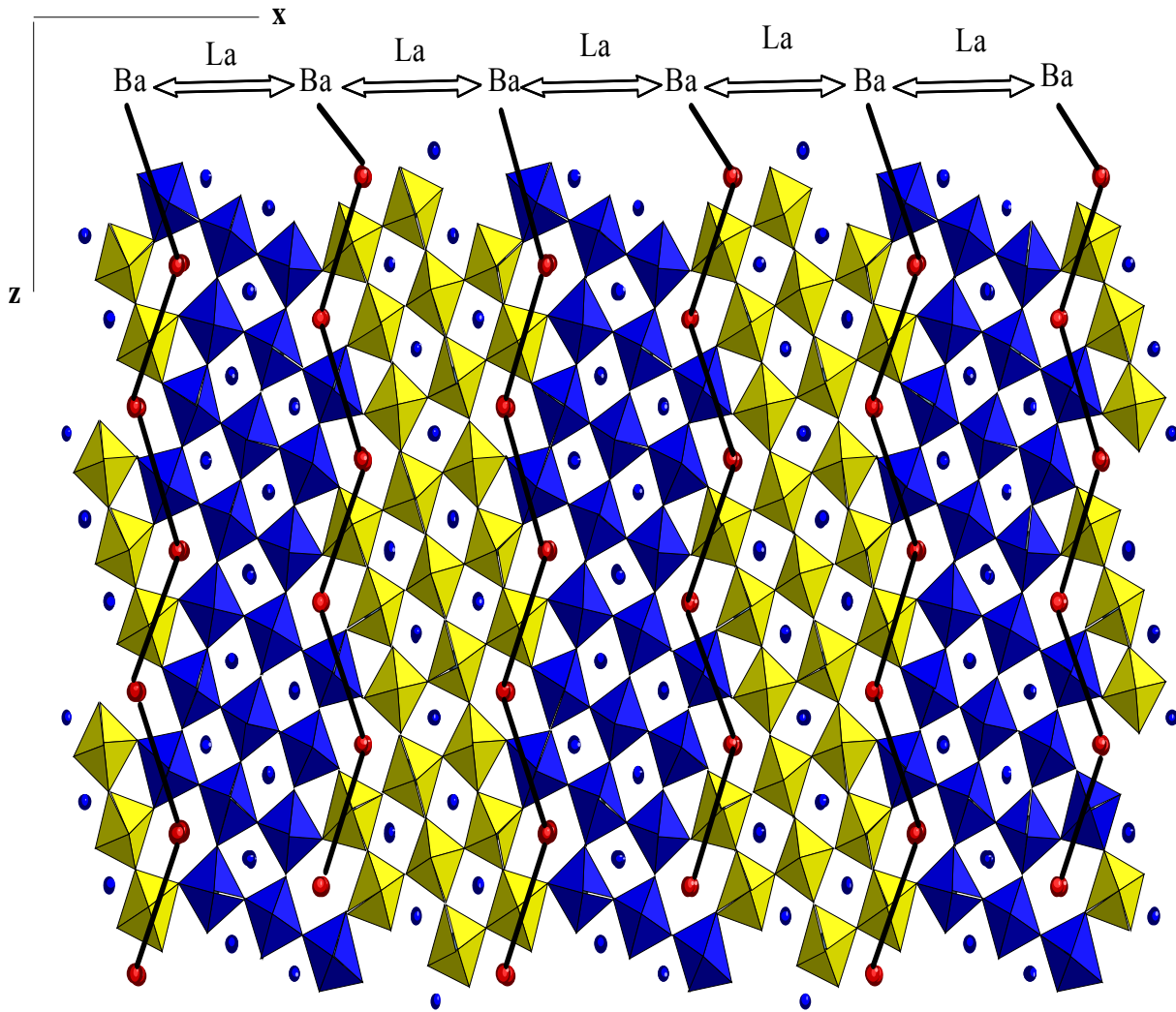


Figure 7 : crystal structure for Structural model II

#### IV. Conclusion

The structural study of the  $\text{Ba}_{6-x-y}\text{La}_{8+2x/3+y}\text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$  solid solution was undertaken in order to determine the role of the Ti/Al substitution on the Ba/La cationic distribution within the structure. The structural studies performed on single-crystals allowed to analyze the cationic environment and to obtain information about the cationic distribution of barium and lanthanum ions. The stability domain of the  $\text{Ba}_{6-x-y}\text{La}_{8+2x/3+y}\text{Ti}_{18-y}\text{Al}_y\text{O}_{54}$  solid solution was determined more precisely. For each value of  $x$  corresponds a maximum value of  $y$  ( $y_{\text{max}}$ ) for which all the tetragonal sites are fully occupied by lanthanum ions. Aluminum contents higher than  $y_{\text{max}}$  would correspond to a substitution of lanthanum by barium in the pentagonal tunnels. All the structural studies performed before demonstrated that this substitution is not possible. Two structural models were build, which correspond to two different orders in a structural point of view. The structural model I,

with formula  $[\text{Ba}_4]_{\text{A}2} [\text{Ba}_{2-z} \text{La}_{2x/3+y+q} \text{q}']_{\text{A}1'} [\text{La}_{8-q'}]_{\text{A}1} \text{Ti}_{18-y} \text{Al}_y \text{O}_{54}$ , corresponds to the occurrence of infinite perovskite rows parallels to the Oy axis, build on the basis of  $(3 \times 3)$   $\text{TiO}_6$  octahedron. The structural model II, with formula  $[\text{Ba}_{6-z} \text{La}_{2x/3+y} \text{La}_{2-(2x/3)-y}]_{\text{A}2} [\text{La}_{8+2x/3+y} \text{La}_{2-(2x/3)-y}]_{\text{A}1'} \text{Ti}_{18-y} \text{Al}_y \text{O}_{54}$  can be described using perovskite layers (three octahedron thickness) parallel to the xOz plane.

The evolution of the lattice parameters as a function of the composition allowed to evidence for two different domains, separated by a composition corresponding to a perfect Ba/La order. They correspond to the two structural models.

For the structural model I, the cationic order is of  $\text{A}2/\text{A}1'/\text{A}1$  type, for which the  $\text{A}1'$  is mixed.

For the structural model II, the lanthanum ions are located into the perovskite layers and the barium ions are, as for structural model I, located into the structural defects.

## V. References

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