

Study of the Incommensurability of $(\text{La}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$ and $(\text{Nd}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$, Members $n = 6$ of the $A_nB_nO_{3n+2}$ Family: Interpretation of the Lattice Modulation Using a Four-Dimensional Space

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$(\text{La}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$ and $(\text{Nd}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$, members $n = 6$ of the $A_nB_nO_{3n+2}$ family can be prepared in an incommensurate form, the thermal stability of which was studied by X-ray diffraction. The lattice modulation observed is a displacive type. We interpreted that by means of a four-dimensional space. © 1986 Academic Press, Inc.

1. Introduction

The $A_nB_nO_{3n+2}$ phases we investigated in the $Ln_2\text{Ti}_2\text{O}_7\text{-CaTiO}_3$ ($Ln = \text{La}, \text{Nd}$) and $\text{Ca}_2\text{Nb}_2\text{O}_7\text{-CaTiO}_3$ systems were reported in previous papers (1, 2). Their structure is derived from a perovskite structure (p) by periodic crystallographic shears delimiting structural slabs n octahedra in width. Among these different phases, only those with $n = 6$, $(\text{La}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$ and $(\text{Nd}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$, were obtained in an incommensurate form and that after melting, by means of an image furnace, and quenching at room temperature.

The thermal stability of these new modulated structures was studied. Their X-ray diffraction patterns depicted with a four-dimensional space have allowed us to pro-

pose an interpretation of the observed lattice modulation.

2. Experimental Techniques

Single crystals were isolated after crushing melted specimens into fragments in an agate mortar. Their X-ray diffraction patterns were taken with a precession camera equipped with a heating device using hot gas. The temperature range was 100–1000°C and the accuracy about 1°C (heating rate: 2000°C/hr) (19).

For each experiment, the crystal sample was held 1 hr at the experimental temperature and then the corresponding diffraction photograph was taken at the same temperature.

In addition, powder samples of these two

phases were observed in μ -DTA from room temperature to 1400°C.

3. Description of the Diffraction Patterns

The test for second harmonic generation on powder samples of $(\text{La}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$ and $(\text{Nd}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$, prepared as described, showed that they are noncentrosymmetric at room temperature. Their single-crystal patterns exhibit a set of reflections which can be expressed by the formula

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}^*,$$

h, k, l , and m being integers.

The main reflections ($m = 0$) are intense and located at orthorhombic lattice points. They characterize the basic structure (BS) and they satisfy the reflection conditions expected from the space group $Cmc2_1$.

The satellite reflections ($m = \pm 1$) show a

weaker intensity. They are derived from the preceding positions by the $\mathbf{q}^* = q\mathbf{a}^*$ wave vector and are in zig-zag lines along the $[010]^*$ direction. They are characteristic of the lattice modulation occurring in the basic structure (Fig. 1). The value of q is irrational and close to 0.49.

In the case of the lanthanum compound, diffuse streaks linking the satellite spots are observed (Fig. 2).

These different observations are to be compared with those of Yamamoto relating to the term $n = 4$, $\text{Sr}_2\text{Nb}_2\text{O}_7$ (3).

4. Thermal Stability

4.1. $(\text{La}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$ Compound

Our observations are as follows.

—Up to 300°C, diffraction patterns were the same as those taken at room tempera-

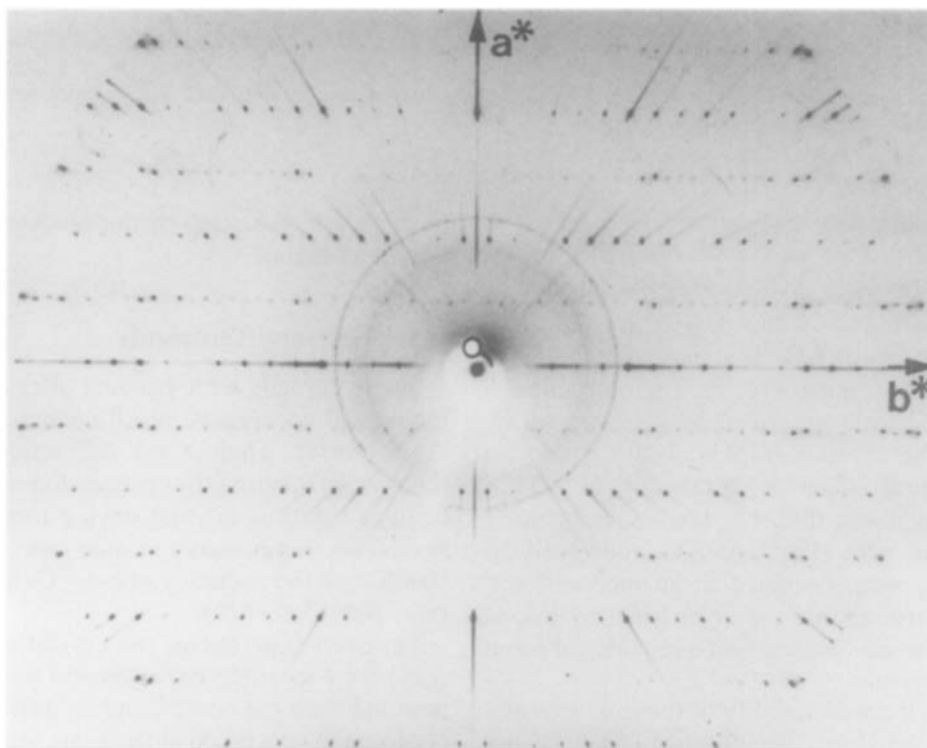


FIG. 1. Precession photograph of $(\text{Nd}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$: reciprocal plane $hk0$; λ , $\text{MoK}\alpha$; room temperature; exposure time, 16 hr.

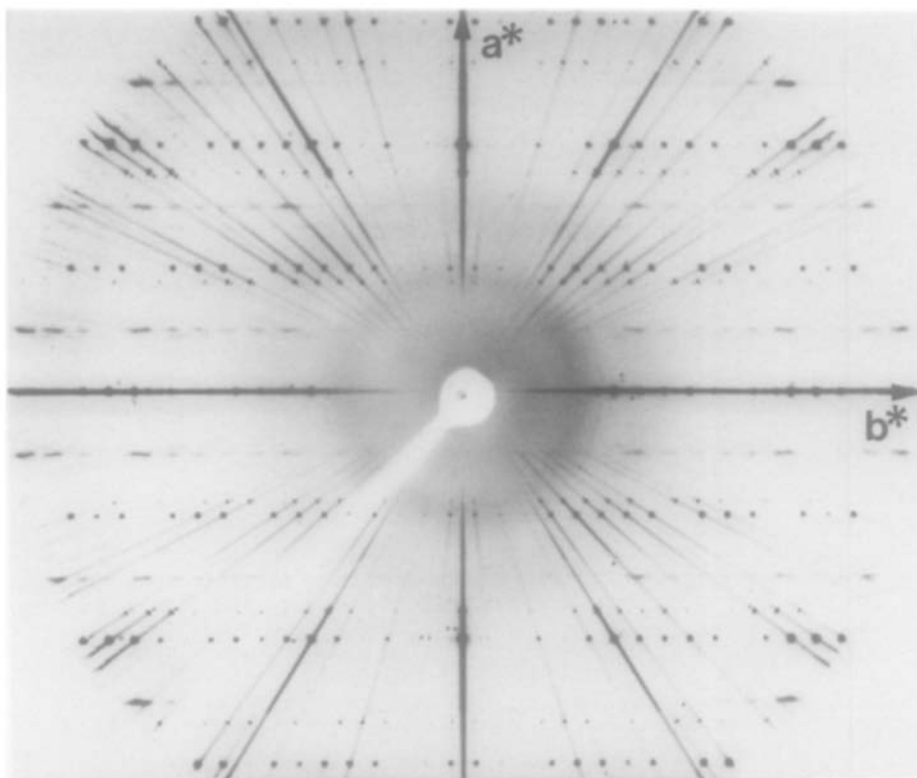


FIG. 2. $(\text{La}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$: diffuse streaks between satellite spots. Reciprocal plane $hk0$, unfiltered Mo radiation, room temperature, exposure time 40 hr.

ture. The satellite reflections are linked by diffuse streaks.

—Above 300°C , a gradual stretch of the satellite reflections is observed as well as a decrease of their intensity and of the intensity of the streaks that link them, when temperature is increasing.

When compared with the works of Schneck and Denoyer upon a barium sodium niobate (4), our observations suggest that the transition has already occurred and that we are in presence of a soft mode.

—At 450°C , only diffuse scattering remains on the X-ray diffraction patterns. The latter vanishes completely when the temperature rises to 550°C . Then, the observed photograph is similar to that of the BS (Fig. 3).

When returning to room temperature, the modulated structure reappears. The intensity condenses at the satellite reflection positions and a simultaneous reappearance of the diffuse streaks linking these satellite spots occurs. If these streaks have the same origin as those investigated in $\text{Sr}_2\text{Nb}_2\text{O}_7$ compound, they are related to faults having an effect upon the modulation as shown by Yamamoto (5).

A photograph of the $(\text{La}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$ compound, taken at -100°C , is similar to the room-temperature one.

4.2. $(\text{Nd}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$ Compound

The results of experiments are as follows.

—Between room temperature and 850°C ,

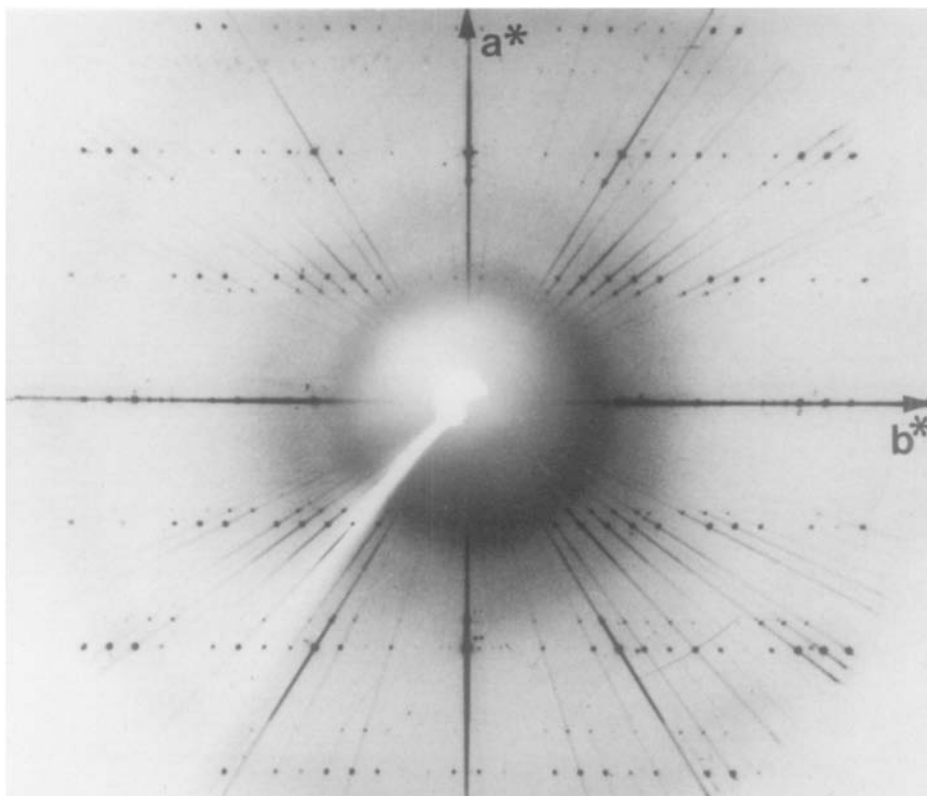


FIG. 3. $(\text{La}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$: vanishing of the modulation. Reciprocal plane $hk0$, unfiltered Mo radiation, temperature 550°C , exposure time 48 hr.

the diffraction photographs show no change.

—Above 850°C , a decrease of the satellite reflection intensity is observed together with the appearance of weak diffuse streaks like those observed with the lanthanum compound at room temperature.

—At 1000°C , the incommensurate form has disappeared from the precession photograph and is replaced by a monoclinic form (space group $P112_1$) isomorphic with those observed for the term $n = 6$, $\text{Ca}_6(\text{Nb}_4\text{Ti}_2)\text{O}_{20}$ (1). This transition is irreversible.

Annealings at temperatures higher than 1000°C , followed by a rapid quenching, have shown that the monoclinic form is sta-

ble up to 1350°C . Above this temperature, the incommensurate form obtained by melting and quenching reappears.

These different observations show that the monoclinic form is the stable one for this compound between room temperature and 1350°C and that the modulated form, at room temperature, is in a metastable state, its domain of stability being set above 1350°C .

This incommensurate form can be either stable until melting point or change into BS before melting. We cannot give precise details about that fact because we could not obtain single-crystal photographs at such high temperatures.

For $(\text{Nd}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$ and $(\text{La}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$,

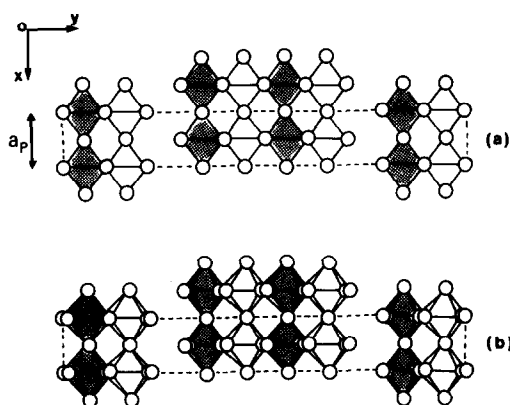


FIG. 4. Oxygen octahedra disposition in single layers: orthorhombic symmetry. (a) Space group $Cmc2_1$, (b) space group $Cmc2_1$.

μ -DTA graphs did not reveal any signal between room temperature and 1400°C .

For these two compounds—and that in the limits of accuracy of our measurements—no variation of q coefficient occurred within the explored domain of temperature.

5. Interpretation of the Modulation by Means of a Four-Dimensional Space

This structural study of $A_nB_nO_{3n+2}$ phases suggests that the observed modulation is of a displacive type because of the natural disposition of the perovskite structure of the slabs to be distorted.

The octahedra layers constituting the structural slabs of $A_nB_nO_{3n+2}$ can be as follows.

—Either of a single type (6–8). In this case, the observed symmetry is orthorhombic and the possible space groups are $Cmcm$ (Fig. 4a) and $Cmc2_1$ (Fig. 4b). The base plane of the oxygen octahedra is perpendicular to the $[100]$ direction.

—Or of two types X and Y (9–12). The structural slabs can take two types of disposition, the first is consistent with an orthorhombic symmetry (space group $Pbn2_1$), the second with a monoclinic symmetry (space group $P112_1$) (Fig. 5).

In comparison with the single slab, these two dispositions are differentiated by a displacement of cations and a rotation of the

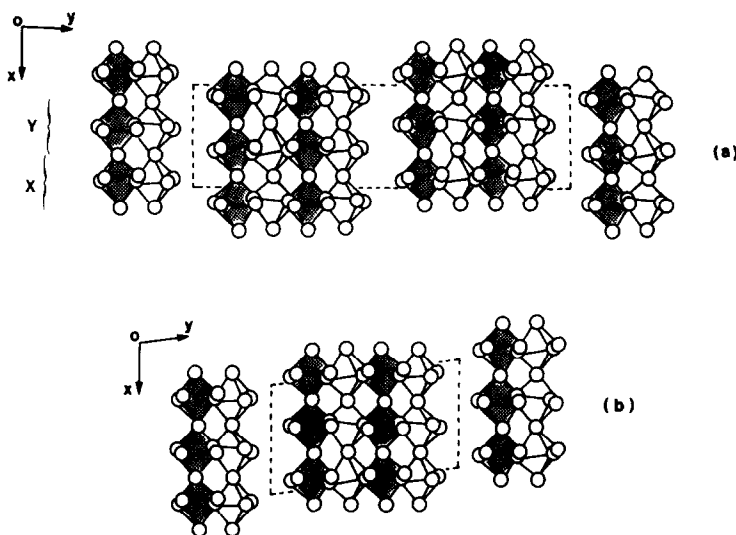


FIG. 5. Oxygen octahedra disposition with two types of layers. (a) Orthorhombic symmetry (space group $Pbn2_1$), (b) monoclinic symmetry (space group $P112_1$).

oxygen octahedra around [010]* direction. The differences between *X* and *Y* layers are due in particular to the sense of this rotation.

In a 3-dimensional space (E^3), the investigated modulated structure is not a true periodic structure. However, if depicted using a 4-dimensional space (E^4), it becomes periodic.

In such a depiction, as well described by de Wolff (13), the whole set of spots observed on the diffraction patterns may be expressed by the relation

$$\mathbf{H}_{\text{dim.4}} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m(\mathbf{e}_4 + \mathbf{q}^*)$$

in which \mathbf{e}_4 is the unit vector orthogonal to space E^3 ; \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* are the reciprocal vectors of the BS; and $\mathbf{q}^* = q\mathbf{a}^*$.

In the superspace E^4 , the reciprocal lattice of the modulated crystal is defined by the four vectors \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* , and $\mathbf{e}_4 + \mathbf{q}^*$.

Under these conditions, the observed reflection conditions of the set of spots (main + satellites) are

$$\begin{array}{|c|c|} \hline \begin{array}{c} 1 \text{ in } E^4 \\ | \\ 1 \\ | \\ 1 \\ | \\ 1 \\ | \\ 1 \end{array} & \begin{array}{c} 2 \text{ in } E^4 \\ | \\ \bar{1} \\ | \\ 1 \\ | \\ 1 \\ | \\ \bar{1} \end{array} \\ \hline 1 \text{ in } E^3 & m \text{ in } E^3 \end{array} \quad \begin{array}{|c|c|} \hline \begin{array}{c} m \text{ in } E^4 \\ | \\ 1 \\ | \\ \bar{1} \\ | \\ 1 \\ | \\ 1 \end{array} & \begin{array}{c} \bar{1}_3 \text{ in } E^4 \\ | \\ \bar{1} \\ | \\ \bar{1} \\ | \\ 1 \\ | \\ \bar{1} \end{array} \\ \hline m \text{ in } E^3 & 2 \text{ in } E^3 \end{array}$$

The names given to these symmetry operations in E^4 are according to Weigel *et al.* (15). When referring to the classification established by these same authors for crystallographic point groups of a 4-dimensional Euclidean E^4 space it results that, in E^4 , the crystal belongs to the point-symmetry group written as $2/m$.

The reflection condition $l + m = 2n$ ob-

$$hk\ell m \quad h + k = 2n$$

$$h0\ell m \quad l + m = 2n.$$

The reciprocal lattice of the crystal being known in E^4 , the direct lattice is easily obtained. It is expressed by four vectors $\mathbf{a}' = \mathbf{a} - q\mathbf{e}_4$, \mathbf{b} , \mathbf{c} , and \mathbf{e}_4 . \mathbf{a} , \mathbf{b} , \mathbf{c} are the direct vectors of the BS.

The reflection condition $h + k = 2n$, corresponding to $hk\ell m$ reflections, shows that the face (*xy*) is centered.

These relations show that the crystal belongs to system 4 of family IV and to Bravais type 9 (face $S(1 - 2)$ centered), according to the Wondratschek *et al.* classification (14).

The $mm2$ orientation symmetry of the BS being of order 4, the point-symmetry group for the crystal in E^4 must also be of order 4. Consequently, among eight generators defined by Wondratschek *et al.* for the holohedry of family IV, only four must be selected. The latter allow one to find the point-symmetry operations of the BS again if returning in E^3 space.

In the *x*, *y*, *z*, *t* basis, they are represented by the four matrices

served for $h0\ell m$ reflections induces that the *m* hyperplane is a mirror with glide

$$\frac{\mathbf{c} + \mathbf{e}_4}{2}$$

and that it is the same for $\bar{1}_3$ inversion. Thus, the superspace group of the crystal can be written as

$$S(1 - 2)/m_{\frac{c+e_4}{2}}$$

(or $P_{\bar{1}s\bar{1}}^{Cmc2_1}$ with De Wolff notation (16)).

Its operations modulo the translations $S(1 - 2)$ are the following ones.

$1 \text{ in } E^4$	$2 \text{ in } E^4$	$m_{\frac{c+e_4}{2}} \text{ in } E^4$	$\bar{1}_{3\frac{c+e_4}{2}} \text{ in } E^4$
$\begin{array}{cccc c} 1 & & & & 0 \\ & 1 & & & 0 \\ & & 1 & & 0 \\ & & & 1 & 0 \\ \hline 0 & 0 & 0 & 0 & 1 \end{array}$	$\begin{array}{cccc c} \bar{1} & & & & 0 \\ & 1 & & & 0 \\ & & 1 & & 0 \\ & & & \bar{1} & 0 \\ \hline 0 & 0 & 0 & 0 & 1 \end{array}$	$\begin{array}{cccc c} 1 & & & & 0 \\ & \bar{1} & & & 0 \\ & & 1 & & \frac{1}{2} \\ & & & 1 & \frac{1}{2} \\ \hline 0 & 0 & 0 & 0 & 1 \end{array}$	$\begin{array}{cccc c} \bar{1} & & & & 0 \\ & \bar{1} & & & 0 \\ & & 1 & & \frac{1}{2} \\ & & & \bar{1} & \frac{1}{2} \\ \hline 0 & 0 & 0 & 0 & 1 \end{array}$
$1 \text{ in } E^3$	$m \text{ in } E^3$	$c \text{ in } E^3$	$2_1 \text{ in } E^3$

This gives the following Wyckoff general positions

$$\begin{array}{cccc} x & y & z & t \\ \bar{x} & y & z & \bar{t} \\ x & \bar{y} & z + \frac{1}{2} & t + \frac{1}{2} \\ \bar{x} & \bar{y} & z + \frac{1}{2} & \bar{t} + \frac{1}{2} \end{array}$$

The structural study of the $A_n B_n O_{3n+2}$ phases belonging to the same $Cmc2_1$ space group as the BS shows that, in the latter, all the atoms are in special position, i.e., in m mirror. It follows that, in E^4 space, the atoms are also in special positions in (yz) plane. These Wyckoff special positions can be written as

$$\begin{array}{cccc} (0000), (\frac{1}{2}\frac{1}{2}00) + \\ 0 & y & z & 0 \\ 0 & \bar{y} & z + \frac{1}{2} & \frac{1}{2} \end{array}$$

For the studied modulated structure, the zero values of x and t require that the string corresponding to each independent atom passes through the origin.

For a displacive-type modulation, de Wolff has shown that the coordinates of an atom in E^4 are function of one variable τ and can be expressed by

$$\begin{cases} x = \hat{x} + u(\tau) \\ y = \hat{y} + v(\tau) \\ z = \hat{z} + w(\tau) \end{cases}$$

\hat{x} , \hat{y} , and \hat{z} are the coordinates of the atom in the BS and u , v , w the coordinates of the modulation.

The variable τ is the fourth coordinate t of the average position P_0 of the P atom considered:

$$\tau = t(P_0).$$

In the case of the harmonic approximation, very appropriate to the sample studied here because of the absence of satellites of order superior to one on the patterns, u_i , v_i , and w_i displacements of any independent atom of the n th unit cell of the BS can be given by the relation (17)

$$\begin{cases} u_i(\tau) = U_i \sin 2\pi q\tau = U_i \sin 2\pi q(\hat{x}_i + n) \\ v_i(\tau) = V_i \cos 2\pi q\tau = V_i \cos 2\pi q(\hat{x}_i + n) \\ w_i(\tau) = W_i \cos 2\pi q\tau = W_i \cos 2\pi q(\hat{x}_i + n) \end{cases}$$

U_i , V_i , and W_i corresponding to maxima amplitudes of the displacements along Ox , Oy , and Oz . In the case studied $q\hat{x}_i = 0$.

From the Wyckoff positions expressed in

E^4 space, one may deduce the Wyckoff "modulated" positions in E^3 . For the unit cell $n = 0$ they can be written as

$$\begin{aligned} & (000), (\frac{1}{2}\frac{1}{2}0) + \\ & u(0); \hat{y} + v(0); \hat{z} + w(0) \\ & u(\frac{1}{2}); -\hat{y} - v(\frac{1}{2}); \hat{z} + \frac{1}{2} + w(\frac{1}{2}) \end{aligned}$$

The knowledge of the Wyckoff "modulated" positions allows one to find the phase difference between the displacements of atoms related by the symmetry operations of the BS.

For the first atom $\tau = 0$ and for the second one, related to the latter by c mirror in the BS, $\tau = 1/2$.

Our conclusions are reported in Table I.

Along [100] direction, the phase difference from a BS unit cell to the following one is equal to 0.98π .

We have seen that the BS, where the modulation occurs, belongs to the $Cmc2_1$ space group. Consequently, it consists of oxygen octahedra layers of one type, the base planes of the latter being all perpendicular to the [100] direction.

To find the possibilities of displacement of the BS independent atoms, we compared the structures of two orthorhombic forms identified for the term $n = 4$, $Ca_2Nb_2O_7$ (8, 9). The one is isostructural with the BS, the other belongs to $Pbn2_1$ and is constituted of X - and Y -type octahedra layers.

The displacements of atoms are preferentially along the Oz direction for cations, the

TABLE I
PHASE DIFFERENCE BETWEEN THE ATOM
DISPLACEMENTS

Atoms related by the c mirror			Atoms related by the C lattice translation		
Ox	Oy	Oz	Ox	Oy	Oz
π	0	π	0.49π	0.49π	0.49π

TABLE II
PHASE DIFFERENCE BETWEEN OCTAHEDRA
ROTATIONS

Independent octahedra	Octahedra related by the c mirror	Octahedra related by the C lattice translation
1-2 $\# \pi$	1-6 π	1-1' 0.49π
1-3 $\# 0$	2-5 π	2-2' 0.49π
2-3 $\# \pi$	3-4 π	3-3' 0.49π

Ox direction for oxygen ions of the base plane of the octahedra, and the Oz direction for oxygen ions on both sides of each base plane. Inside X and Y layers, rotations of two octahedra sharing a same corner are closely related in amplitude but are in an opposite sense.

The latter data, associated with those concerning the different phases between the atoms related by the symmetry operations of $Cmc2_1$ group, led us to fix the phase difference exhibited by the rotations of the 12 octahedra of the BS unit cell. Among the latter, only three are independent. Our conclusions are reported in Table II and illustrated in Fig. 6. The BS unit cell is drawn on this figure so that the amplitude of displacement is a maximum for half of the atoms and practically zero for the other half.

This depiction of the modulated structure of $(La_4Ca_2)Ti_6O_{20}$ and $(Nd_4Ca_2)Ti_6O_{20}$ compounds leads to results similar to Yamamoto's ones upon term $n = 4$, $Sr_2Nb_2O_7$, obtained by different ways (18).

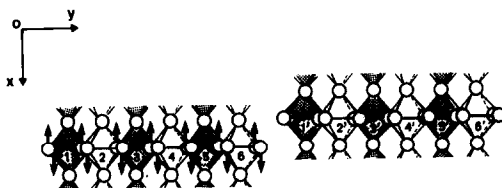


FIG. 6. Displacement along Ox of the base plane of oxygen ion octahedra in a unit cell of the basic structure.

6. Conclusion

Our X-ray diffraction study has allowed us to determine the stability versus temperature of the investigated incommensurate form of the two terms $n = 6$, $(\text{La}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$ and $(\text{Nd}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$.

In order to explain the observed modulation, we made use of a 4-dimensional space. In this space, the modulated structure of the two considered terms $n = 6$ becomes a true periodic structure. Thus we established: the reflection conditions consistent with the set of reflections; the point-symmetry group and the superspace group of the crystal; the Wyckoff positions in E^4 and consequently the "modulated" Wyckoff positions in E^3 . From "modulated" Wyckoff positions in E^3 were deduced the phase differences between the displacements of atoms related by the BS symmetry operations.

The deformation study of the perovskite structure of the slabs in the other $A_nB_nO_{3n+2}$ phases has allowed us to predict the displacement possibilities of each independent atom.

The refinement of the modulated structure of $(\text{Nd}_4\text{Ca}_2)\text{Ti}_6\text{O}_{20}$ compound will soon be completed.

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