

The Calcium Thallate $\text{Ca}_3\text{Tl}_2\text{O}_6$, Third Member of the Series $\text{Ca}_n\text{Tl}_2\text{O}_{n+3}$

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A new calcium thallate, $\text{Ca}_3\text{Tl}_2\text{O}_6$ has been synthesized. It crystallizes in the space group $Pbam$ with $a = 11.248(2)$ Å, $b = 16.513(2)$ Å, and $c = 3.3329(3)$ Å. The ab initio determination of its structure from powder X-ray data shows that it consists of zigzag rock-salt-type layers $[\text{Ca}_4\text{Tl}_4\text{O}_{14}]_\infty$ parallel to (010), built up from quadruple ribbons of TlO_6 octahedra running along c , interconnected with single and double ribbons of CaO_6 octahedra. Along b , these rock-salt-type layers share the corners of their octahedra forming tunnels approximately similar to those observed in CaTi_2O_4 , where calcium ions are located with a monocapped trigonal prismatic coordination. This oxide represents the third member of the series $\text{Ca}_n\text{Tl}_2\text{O}_{n+3}$; its relationships with the two $n = 1$ and 2 members CaTi_2O_4 and $\text{Ca}_2\text{Tl}_2\text{O}_5$, that correspond to a chemical twinning of the rock salt structure, are discussed. In fact $\text{Ca}_3\text{Tl}_2\text{O}_6$ is isostructural with $\text{Ca}_3\text{In}_2\text{O}_6$. © 1995 Academic Press, Inc.

INTRODUCTION

After the discovery of superconductivity in thallium cuprates at high temperature (1), several studies have shown that trivalent thallium was a potential candidate to generate a large series of layered copper oxides (see for review Ref. (2)). However, as yet, the chemistry of Tl(III) oxides has not been extensively studied, so that very few data are available for understanding the behavior of Tl(III) in such complex systems from the chemical as well as from the physical point of view. The pseudobinary systems $\text{Tl}_2\text{O}_3\text{--AO}$, with $A = \text{Ca, Sr, Ba}$, that are involved in the synthesis of such oxides, are themselves as yet not well known. Only one barium thallate, $\text{Ba}_2\text{Tl}_2\text{O}_5$ (3), and two strontium thallates, $\text{Sr}_4\text{Tl}_2\text{O}_7$ (4) and SrTl_2O_4 (5), have been obtained up to now. Recently, the exploration of the system $\text{CaO--Tl}_2\text{O}_3$ allowed two new phases to be isolated, CaTi_2O_4 and $\text{Ca}_2\text{Tl}_2\text{O}_5$, that correspond to the two first members of a series of oxides $\text{Ca}_n\text{Tl}_2\text{O}_{n+3}$ (6), characterized by a chemical twinning of the rock salt structure. We report here on the third member of this series, $\text{Ca}_3\text{Tl}_2\text{O}_6$, that also exhibits rock-salt-type layers, but differs from the two first members.

EXPERIMENTAL

The oxide $\text{Ca}_3\text{Tl}_2\text{O}_6$ has been prepared from an intimate mixture of Tl_2O_3 and CaO in stoichiometric molar ratios. Various conditions of synthesis were investigated. The best results were obtained by heating the mixture at 700°C for 10 hr in a sealed silica tube, in order to avoid thallium losses, using an alumina crucible as a support. The sample was finally air quenched down to room temperature.

The powder X-ray pattern was registered with a Bragg–Brentano diffractometer, the details of the data collection are presented in Table 1. The X-ray pattern was used to refine the structure with the profile computer program FULLPROF (8).

The electron diffraction study of the microcrystals was performed with a JEOL 200CX electron microscope fitted with an eucentric goniometer ($\pm 60^\circ$). The microanalysis (EDS) was made with a KEVEX analyzer.

RESULTS AND DISCUSSION

For the above experimental conditions, an almost pure phase could be obtained in the form of a well-crystallized orange powder. The EDS analysis was performed on more than 30 microcrystals and gave an atomic ratio $\text{Ca/Tl} \approx 1.3$, close to the nominal composition $\text{Ca}_3\text{Tl}_2\text{O}_6$. Nevertheless, besides the latter, one always observed another phase that was identified as a new thallium oxycarbonate $\text{Ca}_4\text{Tl}_2\text{O}_6\text{CO}_3$ and whose structure is reported elsewhere (7). It is not known whether the oxycarbonate results from the exposure of $\text{Ca}_3\text{Tl}_2\text{O}_6$ to atmosphere, or from the presence of traces of calcium carbonate in the starting calcium oxide; nevertheless the high stability of $\text{Ca}_4\text{Tl}_2\text{O}_6\text{CO}_3$ suggests that it is formed at high temperature due to the presence of CaCO_3 traces.

The electron diffraction patterns of this new oxide (Fig. 1) allowed one to conclude it is an orthorhombic cell, with the reflection conditions $h0l$, $h = 2n$ and $0kl$, $k = 2n$, leading to the space group $Pbam$. Note that the weak $h00$ and $0k0$ reflections with $n = 2n + 1$ and $k = 2n + 1$ are

TABLE 1
Rietveld Refinement Data for $\text{Ca}_3\text{Tl}_2\text{O}_6$

Diffractometer	Philips PW 3710
Radiation	$\text{CuK}\alpha$, equipped with a secondary graphite monochromator
2θ range [°]	8–120
Step scan increment [° 2θ]	0.02
Count time [sec/step]	15
Peak shape	Pseudo-Voigt
Number of observations	5601
Number of reflexions	1108
Number of refined structural parameters	30
Number of profile parameters	8
R_i	4.84
R_p	8.92
R_{wp}	12.1
R_{exp}	6.19
χ^2	3.79

observed in the [001] ED patterns (Fig. 1b), due to multiple diffraction effects. The X-ray pattern (Fig. 2), could then be indexed on the basis of this orthorhombic cell with the following parameters: $a = 11.248(2)$ Å, $b = 16.513(2)$ Å, $c = 3.3329(3)$ Å.

The ab initio resolution of the structure was carried out by the heavy atom method. The integrated intensities were extracted from the powder X-ray data corresponding to $8^\circ \leq 2\theta \leq 55^\circ$ by a full pattern decomposition method with the FULLPROF program. As for CaTi_2O_4 (6), the resolution of the Patterson function allowed the "Tl–Tl" peaks to be easily identified, and in a second step allows the calcium atoms to be localized, confirming the composition " Ca_3Tl_2 ." The oxygen sites were located after subsequent cycles of refinement and difference Fourier syntheses. The refinement of the structure was then carried out, with the FULLPROF program, introducing the oxy-

carbonate $\text{Ca}_4\text{Tl}_2\text{O}_6\text{CO}_3$ (7) as an impurity in the calculations.

The integrated peak intensities of $\text{Ca}_4\text{Tl}_2\text{O}_6\text{CO}_3$ were extracted from the powder X-ray pattern of pure $\text{Ca}_4\text{Tl}_2\text{O}_6\text{CO}_3$, by a full pattern decomposition method in the range $8^\circ \leq 2\theta \leq 120^\circ$. During the refinement the relative intensities were fixed and only three variable parameters, a , c , and the scale factor, were refined, ($P4/mmm$, $a = 3.38$ Å, $c = 9.10$ Å).

The positional parameters of all the atoms were first refined for the metallic atoms and for the oxygen atoms successively. The occupancy factors and thermal factors of the metallic atoms were then refined successively. The refinement of B(Tl₁) tends toward a small negative value, which has no physical meaning. Thus we have arbitrarily fixed B(Tl₁) at 0.1 Å²; this value did not lead to a significant change in the reliability factor. The B factor of all the oxygen atoms were arbitrarily fixed at 1 Å², due to their low atomic diffusion factor.

In these conditions the reliability factor was lowered to $R_i = 4.84\%$ for the atomic coordinates listed in Table 2. The ordering between thallium and calcium is remarkable. Two 4(g) sites, labeled Tl₁ and Tl₂ are fully occupied by thallium, and one 4(h) site labeled Ca₃ is fully occupied by calcium. The two other 4(h) sites, Ca₁ and Ca₂, are found to be mainly occupied by calcium (90%) with a presence of thallium (10%). The ability of thallium to occupy octahedral calcium sites is not unusual since it has previously been observed for $\text{Ca}_2\text{Tl}_2\text{O}_5$ (6). Nevertheless, this partial occupation by thallium cannot be considered as significant especially if one takes into account the difficulty of the resolution due to the presence of a secondary phase. Thus, the chemical formula deduced from these refinements, $\text{Ca}_{2.8}\text{Tl}_{2.2}\text{O}_6$ (i.e., $\text{Ca}_{2.75}\text{Tl}_{2.16}\text{O}_6$) is in perfect agreement with the EDS analysis $\text{Ca}/\text{Tl} \approx 1.3$. We can also conclude to a small deviation from the ideal formulation $\text{Ca}_3\text{Tl}_2\text{O}_6$ in the form $\text{Ca}_{3-x}\text{Tl}_{2+x'}\text{O}_6$. This difference with

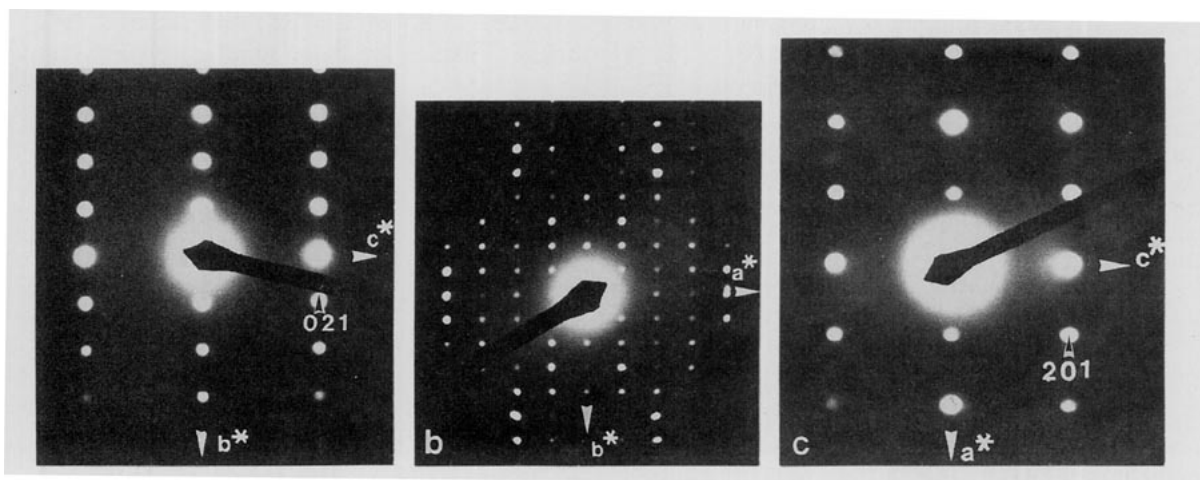


FIG. 1. (a) [100], (b) [001], and (c) [010] ED patterns of $\text{Ca}_3\text{Tl}_2\text{O}_6$.

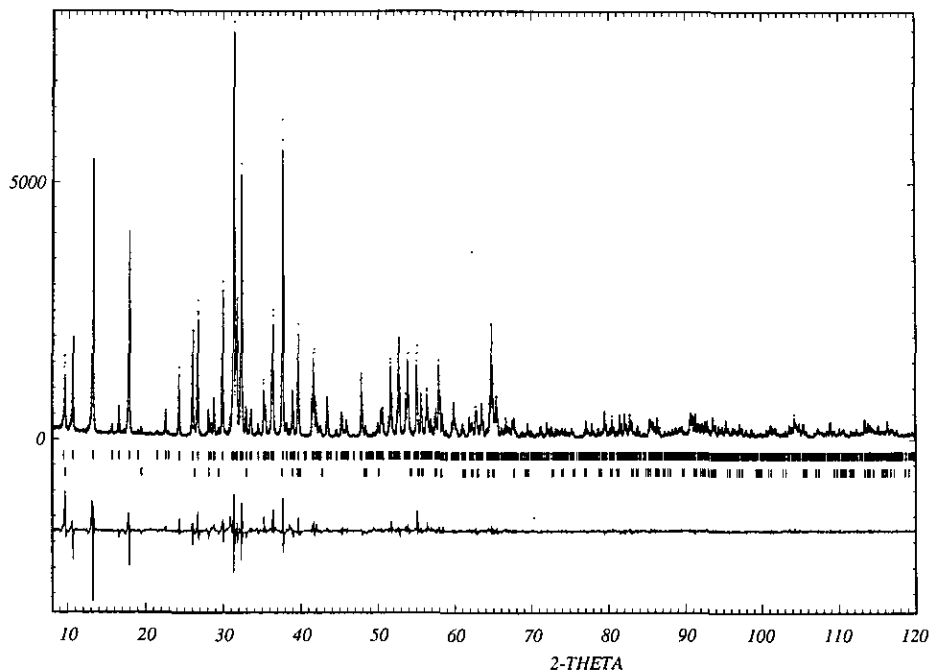


FIG. 2. Final profile refinement of $\text{Ca}_3\text{Ti}_2\text{O}_6$; observed (point), calculated (line), and difference (lower) profiles are shown.

the nominal composition $\text{Ca}_3\text{Ti}_2\text{O}_6$ can be explained by the presence of $\text{Ca}_4\text{Ti}_2\text{O}_6\text{CO}_3$, which is calcium rich.

The projection of this structure onto the (001) plane (Fig. 3) shows that it is very similar to those of $\text{Ca}_3\text{In}_2\text{O}_6$ and $\text{SrCa}_2\text{In}_2\text{O}_6$ described by Müller-Buschbaum *et al.* (9, 10). One indeed recognizes similar ribbons of edge-sharing TlO_6 and CaO_6 octahedra linked themselves through their

apices. Nevertheless $\text{Ca}_3\text{Ti}_2\text{O}_6$ differs from the indium compounds by the ordered arrangement of the TlO_6 and CaO_6 octahedra, whereas indium and calcium are distrib-

TABLE 2

Crystallographic Parameters of $\text{Ca}_3\text{Ti}_2\text{O}_6$ Space Group: $Pb3m$; $Z = 4$ Cell parameters: $a = 11.248(2) \text{ \AA}$, $b = 16.513(2) \text{ \AA}$, and $c = 3.3329(3) \text{ \AA}$

Atom	Site	x	y	z	Occupation	B (\AA^2)
Tl ₁	4g	0.1346(2)	0.04572(3)	0.0	1	0.1(a)
Tl ₂	4g	0.0852(2)	0.6491(1)	0.0	1	0.5(1)
Ca ₁	4h	0.1703(5)	0.2264(3)	0.5	0.90(5)	0.4(2)
Tl ₃	4h	0.1703(5)	0.2264(3)	0.5	0.10(5)	
Ca ₂	4h	0.1349(5)	0.4592(4)	0.5	0.90(5)	0.4(2)
Tl ₄	4h	0.1349(5)	0.4592(4)	0.5	0.10(5)	
Ca ₃	4h	0.3936(6)	0.3548(5)	0.5	1	0.7(2)
O ₁	4g	0.053(2)	0.157(2)	0.0	1	1 ^a
O ₂	2c	0.5	0.0	0.0	1	1 ^a
O ₃	4g	0.275(2)	0.429(1)	0.0	1	1 ^a
O ₄	2b	0.0	0.0	0.5	1	1 ^a
O ₅	4h	0.289(2)	0.091(2)	0.5	1	1 ^a
O ₆	4h	0.046(2)	0.332(1)	0.5	1	1 ^a
O ₇	4g	0.305(2)	0.263(2)	0.0	1	1 ^a

^a B factors for Tl₁ and oxygen are arbitrary fixed at 0.1 and 1 \AA^2 respectively.

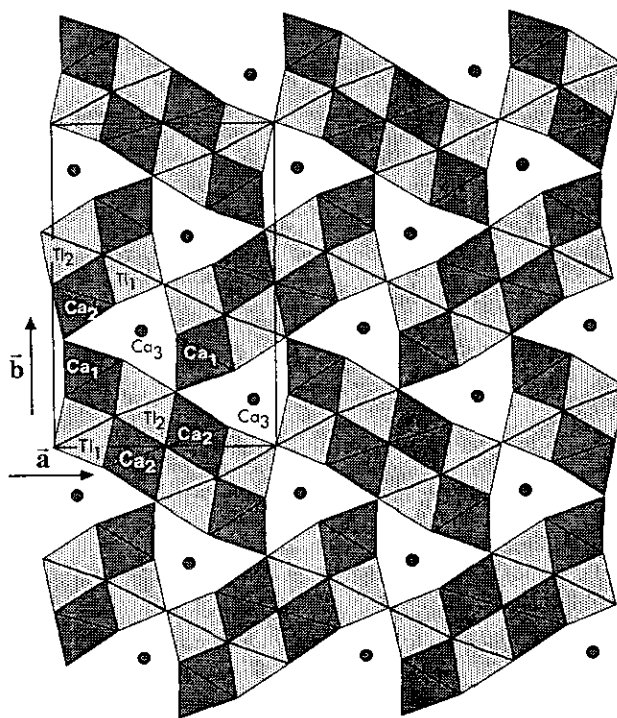


FIG. 3. Projection of the $\text{Ca}_3\text{Ti}_2\text{O}_6$ structure onto the (001) plane; the thallium octahedra (clear) and the calcium octahedra (dark) are shifted $c/2$ with respect to each other.

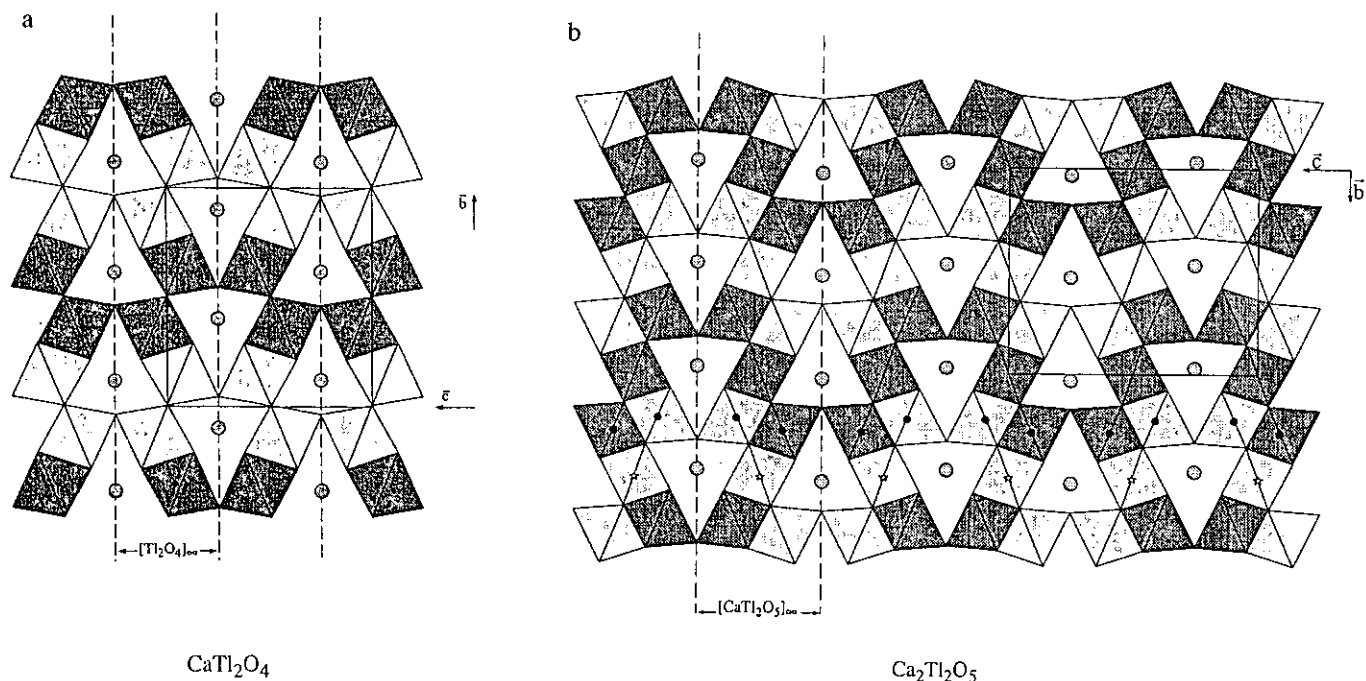


FIG. 4. (a) Projection of the CaTi_2O_4 structure onto the (001) plane; dark and clear octahedra are shifted $c/2$. (b) Projection of the $\text{Ca}_2\text{Ti}_2\text{O}_5$ structure onto the (001) plane; dark and clear octahedra are shifted of $c/2$.

uted at random in $\text{Ca}_3\text{In}_2\text{O}_6$ and $\text{SrCa}_2\text{In}_2\text{O}_6$. This different behavior may be due to the experimental conditions especially the temperature close to 700°C for the Tl-phase, instead of 1400°C for the In compounds.

This structure is also closely related to those of CaTi_2O_4 (6) (Fig. 4a) and $\text{Ca}_2\text{Ti}_2\text{O}_5$ (6) (Fig. 4b). Like the latter it exhibits zigzag rock salt layers of edge-sharing TlO_6 and CaO_6 octahedra forming approximately similar tunnels running along c where the calcium ions are located. Such layers (Fig. 5), that can be formulated $[\text{Ca}_4\text{Tl}_4\text{O}_{14}]_\infty$, are paralleled to the (010) plane, i.e., to the $(113)_{\text{RS}}$ plane of the rock salt structure, as in $\text{Ca}_2\text{Ti}_2\text{O}_5$ and CaTi_2O_4 . But the mechanism of the assemblage is quite different; here the layers are shifted $(a/2 - b/6)$ (Fig. 5) with respect to their ideal structure (Fig. 6) derived directly from $\text{Ca}_2\text{Ti}_2\text{O}_5$ and CaTi_2O_4 . As a result the rows of prismatic tunnels zigzag along a . In fact, each $[\text{Ca}_4\text{Tl}_4\text{O}_{14}]_\infty$ layer can be described as being built up from infinite ribbons of edge-sharing TlO_6 octahedra running along c that are four octahedra wide along $[3\bar{1}0]$ or $[3\bar{1}0]$ (clear octahedra). These thallium ribbons located at $z = 0$ share the edges of their octahedra with calcium ribbons running also along c , but shifted $c/2$. The CaO_6 octahedra form in fact two kinds of ribbons (dark octahedra), single and double rutile ribbons. Two successive $[\text{Ca}_4\text{Tl}_4\text{O}_{14}]_\infty$ rock salt layers (Fig. 5) share the corners of their octahedra in such a way that one CaO_6 octahedron of one layer (Ca_1) shares one apex with two adjacent octahedra TlO_6 (Tl_2) and CaO_6 (Ca_2), of the next layer; as a result the oxygen

atoms that are shared by two successive rock salt layers are linked to four cations (2Tl, 1Ca1, 1Ca2). Thus two successive rock salt layers $[\text{Ca}_4\text{Tl}_4\text{O}_{14}]_\infty$ form the framework $[\text{Ca}_4\text{Tl}_4\text{O}_{12}]_\infty$ (Fig. 5).

TABLE 3
Interatomic Distance for $\text{Ca}_3\text{Ti}_2\text{O}_6$
(in Å)

$\text{Tl}_1\text{-O}_1$	2.06(3)	×1
$\text{Tl}_1\text{-O}_3$	2.16(2)	×1
$\text{Tl}_1\text{-O}_4$	2.37(1)	×2
$\text{Tl}_1\text{-O}_5$	2.45(2)	×2
$\text{Tl}_2\text{-O}_2$	2.64(2)	×1
$\text{Tl}_2\text{-O}_5$	2.45(2)	×2
$\text{Tl}_2\text{-O}_6$	2.45(1)	×2
$\text{Tl}_2\text{-O}_7$	2.25(2)	×1
$(\text{Ca}_1, \text{Tl}_3)\text{-O}_1$	2.41(2)	×2
$(\text{Ca}_1, \text{Tl}_3)\text{-O}_5$	2.55(2)	×1
$(\text{Ca}_1, \text{Tl}_3)\text{-O}_6$	2.24(2)	×1
$(\text{Ca}_1, \text{Tl}_3)\text{-O}_7$	2.33(2)	×2
$(\text{Ca}_2, \text{Tl}_4)\text{-O}_2$	2.35(4)	×2
$(\text{Ca}_2, \text{Tl}_4)\text{-O}_3$	2.38(2)	×2
$(\text{Ca}_2, \text{Tl}_4)\text{-O}_5$	2.38(2)	×1
$(\text{Ca}_2, \text{Tl}_4)\text{-O}_6$	2.32(2)	×1
$\text{Ca}_3\text{-O}_1$	2.46(2)	×2
$\text{Ca}_3\text{-O}_3$	2.43(2)	×2
$\text{Ca}_3\text{-O}_4$	2.681(8)	×1
$\text{Ca}_3\text{-O}_7$	2.46(2)	×2

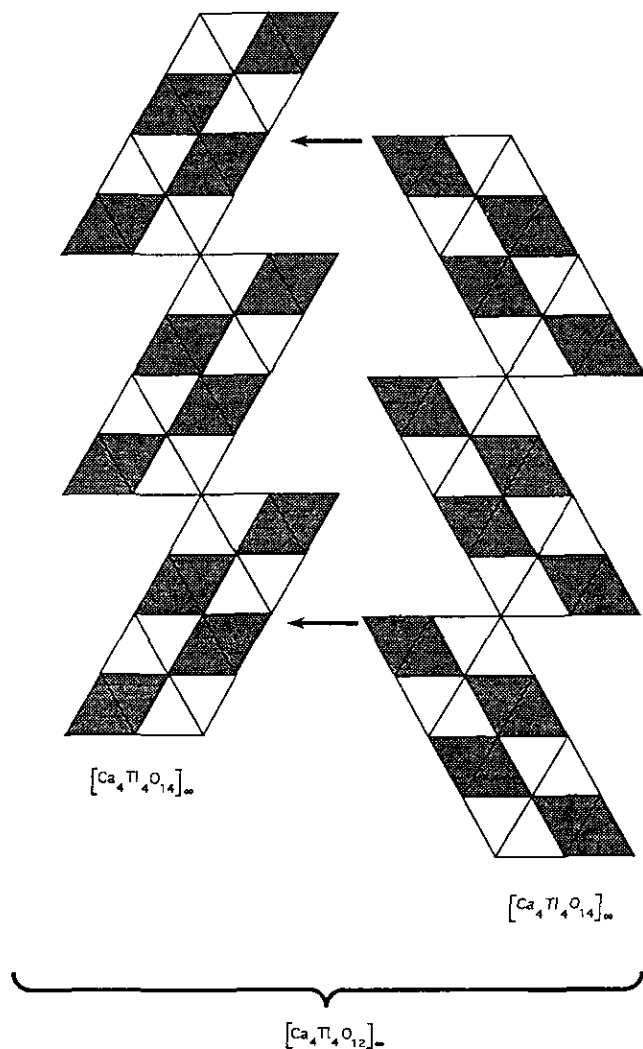


FIG. 5. Assemblage of two $[Ca_4Ti_4O_{14}]_x$ layers to form the framework $[Ca_4Ti_4O_{12}]_x$.

Thus $Ca_3Ti_2O_6$ can be considered from its structural relationships and from its chemical formula as the $n = 3$ member of the series $Ca_nTi_2O_{n+3}$, $CaTi_2O_4$ and $Ca_2Ti_2O_5$ corresponding to $n = 1$ and 2 respectively. Nevertheless in spite of this similarity it does not exhibit the hypothetical structure (Fig. 6) that would be obtained from the extrapolation of the two first members of this series (Fig. 4a and 4b). Clearly $Ca_3Ti_2O_6$ does not correspond to a chemical twinning of the rock salt structure in contrast with the two other members of the series, $CaTi_2O_4$ and $Ca_2Ti_2O_5$. Consequently the tunnels formed at the junction between two rock salt layers are different. In the three structures the tunnels are built up of six rows of octahedra running along c (Fig. 7), five of them being oriented in a similar manner. $Ca_3Ti_2O_6$ tunnels (Fig. 7a) differ from the tunnels of the other structures (Fig. 7b and 7c) by the orientation of the row of CaO_6 octahedra (Ca_1) that

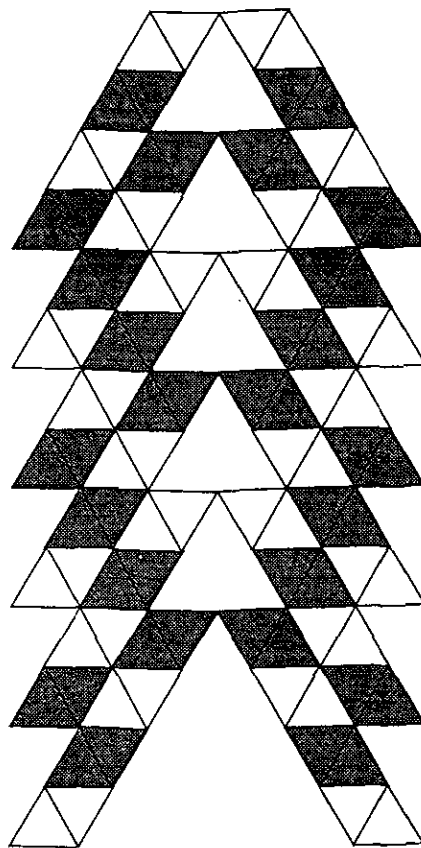


FIG. 6. Ideal structure of the hypothetical member $n = 3$ of the series $Ca_nTi_2O_{n+3}$: $Ca_3Ti_2O_6$, built up of infinite $[Ca_2Ti_2O_6]_x$ layers.

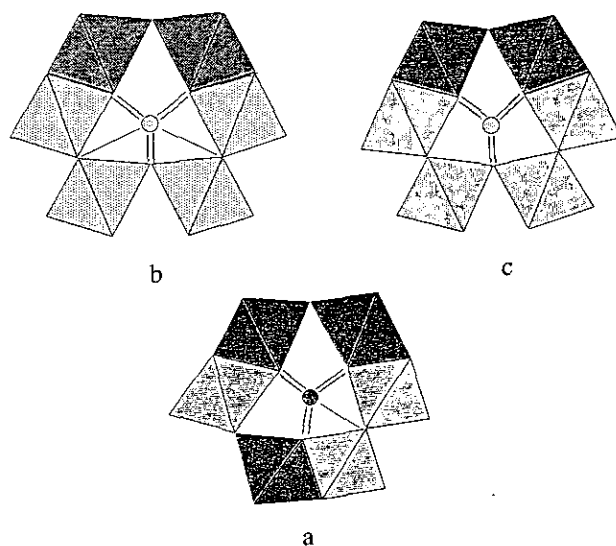


FIG. 7. (a) Projection of the ideal pentagonal tunnel of $Ca_3Ti_2O_6$ structure onto the (001) plane, dark and clear octahedra are shifted $c/2$. (b) Projection of the ideal pentagonal tunnel of $CaTi_2O_4$ and (c) $Ca_2Ti_2O_5$ structures onto the (001) plane; dark and clear octahedra are shifted $c/2$.

is moreover translated $c/2$ with respect to the latter. Nevertheless, the coordination of the calcium ions is similar in the two structures, corresponding to a monocapped trigonal prism CaO_7 for (Ca_3) in $\text{Ca}_3\text{Tl}_2\text{O}_6$ (Fig. 7a), to a bicapped trigonal prism CaO_8 in CaTl_2O_4 (6) (Fig. 7b), and to a pure trigonal prism CaO_6 in $\text{Ca}_2\text{Tl}_2\text{O}_5$ (6) (Fig. 7c).

The interatomic distances (Table 3) are similar to those observed for $\text{Ca}_2\text{Tl}_2\text{O}_5$ and CaTl_2O_4 . The (Tl_1) octahedra exhibit Tl–O distances ranging from 2.06 to 2.45 Å, close to those observed in CaTl_2O_4 and $\text{Ca}_2\text{Tl}_2\text{O}_5$. The (Tl_2) octahedra are more distorted: one Tl–O distance is indeed abnormally long: 2.64 Å, compared to the five other distances ranging from 2.25 to 2.45 Å. The CaO_6 octahedra are rather regular with Ca–O distances ranging from 2.24 to 2.55 Å for (Ca_1) and from 2.35 to 2.38 Å for (Ca_2) . The six Ca–O distances that form the CaO_6 trigonal prism for (Ca_3) are close to those obtained for CaTl_2O_4 and $\text{Ca}_2\text{Tl}_2\text{O}_5$, ranging from 2.43 to 2.46 Å instead of 2.32–2.39 Å for CaTl_2O_4 and 2.27–2.51 Å for $\text{Ca}_2\text{Tl}_2\text{O}_5$; the seventh oxygen is located at a shorter distance from calcium: 2.68 Å instead of 2.87 Å for CaTl_2O_4 and 3.07 Å for $\text{Ca}_2\text{Tl}_2\text{O}_5$.

CONCLUDING REMARKS

The synthesis of $\text{Ca}_3\text{Tl}_2\text{O}_6$ confirms the great ability of the Ca–Tl–O system to form rock-salt-type derived phases. The close relationships between this phase and

the two thallates CaTl_2O_4 and $\text{Ca}_2\text{Tl}_2\text{O}_5$ suggest that other members of the series may exist. A systematic exploration of this system, varying the experimental conditions, will be performed.

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