

## X-ray Diffraction and IR Spectroscopic Characterization of $\text{AgLn}^{\text{III}}\text{TiO}_4$ Oxides Related to the $\text{K}_2\text{NiF}_4$ Structural Type

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Uma série de óxidos ternários do tipo  $\text{AgLn}^{\text{III}}\text{TiO}_4$  (com Ln = La, Nd, Sm, Eu, Gd, Dy, Y) foi preparada e os seus parâmetros de cela unitária foram determinados por difratometria de raios X. Esses compostos são relacionados com os do tipo estrutural  $\text{K}_2\text{NiF}_4$ , com os cátions  $\text{Ag}^{\text{I}}$  e  $\text{Ln}^{\text{III}}$  distribuídos de uma maneira ordenada no sub-retículo dos íons potássio. Os espectros de absorção no infravermelho desses materiais foram registrados e são discutidos com base nas suas peculiaridades estruturais e por comparação com as de óxidos similares. Os produtos apresentam uma relação estrutural e espectroscópica forte com os materiais de partida  $\text{NaLn}^{\text{III}}\text{TiO}_4$ .

Ternary oxides of the type  $\text{AgLn}^{\text{III}}\text{TiO}_4$  (with Ln = La, Nd, Sm, Eu, Gd, Dy, Y) have been prepared and their unit cell parameters determined by X-ray powder diffractometry. They are related to the  $\text{K}_2\text{NiF}_4$  structural type, with the  $\text{Ag}^{\text{I}}$  and  $\text{Ln}^{\text{III}}$  cations distributed in an ordered way on the K-sub lattice. The infrared spectra of these materials were recorded and discussed on the basis of their structural peculiarities and by comparison with those of related oxides. They show a close relationship with the parent  $\text{NaLn}^{\text{III}}\text{TiO}_4$  materials.

**Keywords:** mixed-oxides,  $\text{K}_2\text{NiF}_4$  structure, X-ray diffraction, indexing, IR spectroscopy

### Introduction

Materials belonging to the perovskite structural type and some closely related structures present a lot of technological applications derived from their interesting physicochemical properties.<sup>1-4</sup>

We have recently investigated the spectroscopic behavior of a series of  $\text{A}_2\text{BB}'\text{O}_6$  perovskites<sup>5</sup> and of some mixed oxides of composition  $\text{AA}'\text{BO}_4$  belonging to the related  $\text{K}_2\text{NiF}_4$  structural type,<sup>6,7</sup> which meet the requirements for the deposition of superconducting films, *i.e.* they present low dielectric constants, chemical inertness, and their lattice parameters are close to that of the films to be deposited. In the last of these studies we have investigated the spectroscopic behavior of a series of ternary oxides of the type  $\text{NaLn}^{\text{III}}\text{TiO}_4$  and of two related materials, containing  $\text{La}^{\text{III}}$  or  $\text{Nd}^{\text{III}}$  in which  $\text{Na}^+$  was replaced by  $\text{Ag}^+$ .

In order to extend this investigation we have now characterized a more complete series of this type of Ag-substituted oxides.

### Experimental

#### Syntheses

Polycrystalline samples of the starting  $\text{NaLn}^{\text{III}}\text{TiO}_4$  compounds were prepared by conventional solid state reactions, following well known procedures.<sup>7-10</sup> Intimate stoichiometric mixtures of analytical grade  $\text{TiO}_2$  (anatase),  $\text{Na}_2\text{CO}_3$  and  $\text{Ln}_2\text{O}_3$  were calcined in air, in platinum crucibles. An excess of about 30% of the carbonate was used to compensate for the sodium loss due to volatilization at high temperature. During the syntheses the temperature was gradually raised up to 950-1000 °C, and then the heating was maintained for half an hour. The excess of carbonate was removed treating the final products with methanol.

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The silver compounds (with Ln = La, Nd, Sm, Eu, Gd, Dy, Y) were obtained by an ion-exchange reaction from the parent Na-compound, according to the procedure described by Toda *et al.*<sup>8</sup> The parent compound was allowed to react with molten AgNO<sub>3</sub> at 250 °C for 12 hours. The products were firstly washed with abundant distilled water and finally with diluted ammonia to eliminate Ag<sub>2</sub>O.

### Indexing

X-ray powder diagrams were recorded using a continuous step scanning procedure (step size: 0.020° (in 2θ); time *per* step: 0.5 s), with a Philips PW 3710 diffractometer and monochromatic Cu-K<sub>α</sub> radiation (λ = 1.54060 Å), using NaCl as an external calibration standard. The indexation of the diagrams and determination of the unit cell parameters were performed with a locally modified version of the program PIRUM of Werner.<sup>11</sup>

### Spectroscopic measurements

The infrared spectra were recorded with a Nicolet-Magna 550 FTIR instrument, using the KBr pellet technique. The results were also confirmed employing the Nujol-mull technique.<sup>12</sup>

## Results and Discussion

### Unit cells of the compounds

The powder diffraction patterns of all the prepared materials could be indexed on the basis of a tetragonal unit cell, confirming the K<sub>2</sub>NiF<sub>4</sub> structural type (JCPDF, No. 24-1326). In all cases, the intensity distribution of the diffraction lines closely resembles that observed for Sr<sub>2</sub>TiO<sub>4</sub> (JCPDF, No.39-1471), the oxide prototype of the K<sub>2</sub>NiF<sub>4</sub> structure.<sup>13</sup> It has been proposed that the NaLn<sup>III</sup>TiO<sub>4</sub> structures may be described as a superstructure of Sr<sub>2</sub>TiO<sub>4</sub> (or K<sub>2</sub>NiF<sub>4</sub>) consisting of single layers of TiO<sub>6</sub> octahedra that are separated in alternate layers by Na<sup>+</sup> and Ln<sup>3+</sup> cations, perpendicular to the *c* axis.<sup>14</sup> This ordering implies a change of the space group I4/mmm of K<sub>2</sub>NiF<sub>4</sub> to P4/nmm.<sup>10</sup> The charge imbalance between sodium and the lanthanide ions both located at the interlayer is compensated by a displacement of the titanium(IV) ions from the position of the regular octahedral center toward the Na<sup>+</sup> ions.<sup>8-10</sup>

According to the totally similar powder diffractograms, it becomes evident that the silver ion-exchanged compounds retain the structural characteristics of the parent phases. These compounds are probably metastable<sup>8</sup> and, therefore, the ion-

exchange reaction departing from NaLnTiO<sub>4</sub> becomes a unique synthetic route. The driving force for the reaction, in mind of the similarity in charge density between Na<sup>+</sup> and Ag<sup>+</sup> cations should be the stronger polarizing power of Ag<sup>+</sup> due to its electronic configuration.

**Table 1.** Unit cell parameters of the investigated mixed oxides of the type AgLn<sup>III</sup>TiO<sub>4</sub>

Oxide	<i>a</i> / (Å)	<i>c</i> / (Å)	<i>V</i> / (Å <sup>3</sup> )
AgLaTiO <sub>4</sub>	3.751(1)	13.290(1)	186.990(2)
AgNdTiO <sub>4</sub>	3.753(9)	13.146(1)	185.161(10)
AgSmTiO <sub>4</sub>	5.278(8)	12.813(5)	356.935(10)
AgEuTiO <sub>4</sub>	5.267(6)	12.792(7)	354.866(7)
AgGdTiO <sub>4</sub>	5.280(8)	12.842(5)	358.014(9)
AgDyTiO <sub>4</sub>	5.192(1)	12.801(6)	345.075(7)
AgYTiO <sub>4</sub>	5.229(8)	12.762(1)	348.944(8)

The determined unit cell parameters for the prepared AgLnTiO<sub>4</sub> phases are presented in Table 1. As it can be seen from these data, a relatively abrupt change in the unit cell constants occurs when going from AgNdTiO<sub>4</sub> to AgSmTiO<sub>4</sub>, whereas they are of the same order for the remaining trivalent cations. A similar change has been previously found by Toda *et al.*<sup>9</sup> in the NaLnTiO<sub>4</sub> series for which, after Ln = Sm, a pseudo-orthorhombic cell with *a* ≈ 12.5 Å and *b* ≈ *c* ≈ 5.3 Å was proposed. Notwithstanding, for this series our own results,<sup>7</sup> as well as those of Byeon *et al.*,<sup>10</sup> point to the existence of tetragonal unit cells with *a* ≈ 3.8 Å and *c* ≈ 13.0 – 12.5 Å. Attempts to index the now investigated AgLnTiO<sub>4</sub> unit cells as orthorhombic or pseudo-orthorhombic failed. Consequently, we assume that the silver-substituted materials retain the original tetragonal structure of the parent sodium compounds with an additional weak distortion of the unit cells, containing the smaller lanthanide cations. The origin of this distortion is not easy to explain but, apparently, it may be generated by a different degree of distortion of the TiO<sub>6</sub>-octahedra, and/or with the relative tilting of these building units in the different materials.<sup>9</sup> On the other hand, this distortion has no effect on the overall cationic distribution as shown by Toda and co-workers<sup>8,9</sup> and also supported by our spectroscopic measurements, analyzed in the following section.

### Infrared spectra

The infrared spectra of perovskites or of AA'BO<sub>4</sub> materials possessing the normal K<sub>2</sub>NiF<sub>4</sub> structure usually present only two strong IR bands. The higher energy band can be assigned to B-O stretchings of the BO<sub>6</sub> octahedra whereas the second one, found at lower energies, may be related to the deformational modes of these same octahedra.<sup>1,6,15</sup>

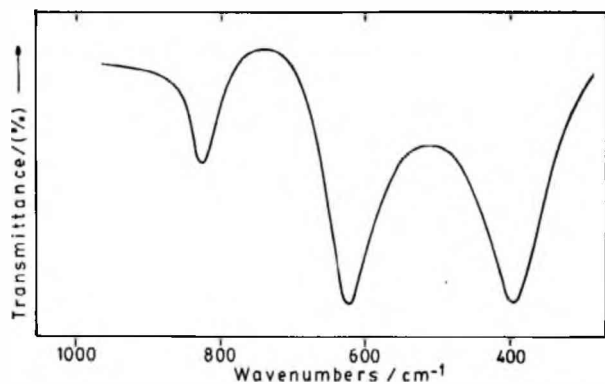


Figure 1. AgDyTiO<sub>4</sub>; FTIR spectrum in the spectral range between 1000 and 300 cm<sup>-1</sup>.

The IR spectra of the now investigated oxides are very similar. As a typical example of them, that of AgDyTiO<sub>4</sub> is presented in Figure 1. The measured band positions are shown in Table 2 and, as it can be seen, all the materials present a typical three band spectra, *i.e.* one band more than those found in the AA'BO<sub>4</sub> oxides<sup>6</sup> and in the same way as found in the previously investigated NaLnTiO<sub>4</sub> series.<sup>7</sup> This new additional, medium intensity band, is located at about 830 cm<sup>-1</sup> in most of the silver compounds.

According to the structural characteristics commented above, in the TiO<sub>6</sub> sheets the Ti-O apical bonds towards the Ag<sup>+</sup> cations are shortened due to structural compression. In agreement with this structural peculiarity, this highest energy band may be assigned in all materials to the stretching mode involving this shortened Ti-O apical bond of the TiO<sub>6</sub> polyhedra. The remaining vibrations, involving the equatorial O-atoms of these polyhedra, are expected at somewhat lower frequencies. Therefore, the two remaining strong bands can be assigned similarly as in the AA'BO<sub>4</sub> materials,<sup>6</sup> *i.e.*, the strong middle energy band (630-600 cm<sup>-1</sup>) is ascribed to the equatorial Ti-O stretchings, whereas the other strong band found at around 400 cm<sup>-1</sup> should be assigned to the deformational modes of the TiO<sub>6</sub> octahedra.

Besides, one interesting trend is clearly noticeable when the position of the first band is compared in pairs of

equivalent sodium and silver compounds. As it is also seen in Table 2, this highest energy band shows a considerable shift to lower frequencies in the case of the silver oxides suggesting an important decrease of the Ti-O bond order upon Na<sup>+</sup> substitution by Ag<sup>+</sup>. This weakening is surely induced by the higher polarizing power of the Ag<sup>+</sup> cations, which generates a certain degree of Ag-O covalent interaction. This is a well-known behaviour that has often been observed in simple silver salts and compounds.<sup>16-18</sup> Nevertheless, a final general comment upon the spectroscopic consequences of the performed ionic exchanges should be made: the comparison of the spectra of both series of materials clearly shows that the overall characteristics of the parent compound are retained in the exchanged samples, since the similarity of the spectra reveals that the same symmetry rules for the vibrating TiO<sub>6</sub> units are maintained. The additional distortion apparently generated after the Nd/Sm transition in the AgLnTiO<sub>4</sub> materials has no spectroscopic consequences, confirming the same cation ordering in the full series of investigated compounds.

In the case of the NaLn<sup>III</sup>TiO<sub>4</sub> materials with Ln<sup>III</sup> = Gd, Dy and Y, the highest energy band lies unexpectedly high (cf. Table 2). This was related to the stepwise diminution of the *c* unit-cell parameter in this series, which reinforces the strength of the shortened apical Ti-O bonds.<sup>7</sup> This effect is probably absent in the present case, due to the generation of larger unit cells for the heavier lanthanides.

## Conclusions

The unit cell parameters of a series of mixed oxides of composition AgLn<sup>III</sup>TiO<sub>4</sub>, belonging to the K<sub>2</sub>NiF<sub>4</sub> structural type, have been determined. The results confirm a close structural relationship to the parent NaLn<sup>III</sup>TiO<sub>4</sub> materials, from which they are obtained by ionic exchange in molten AgNO<sub>3</sub>. Besides, the spectroscopic study of these materials demonstrates a very close relationship between spectra and structure. In the related AA'BO<sub>4</sub> phases<sup>6</sup> in which the effect of A/A' ordering is negligible, the spectra present two strong IR bands involving the main Ti-O vibrations of the TiO<sub>6</sub> octahedra (stretching and bending vibrations of a regular TiO<sub>6</sub> moiety with six similar Ti-O bonds). The same behaviour was observed for the prototype Sr<sub>2</sub>TiO<sub>4</sub> oxide,<sup>7</sup> which presents only two strong IR bands at 576 and 362 cm<sup>-1</sup>. On the contrary, in the present group of materials as well as in the previous investigated NaLn<sup>III</sup>TiO<sub>4</sub> oxides<sup>7</sup> the shortening of one of the Ti-O bonds of the TiO<sub>6</sub> polyhedra, arising from A/A' sub lattice ordering, allows a clear separation of the Ti-O

Table 2. IR spectroscopic data of the investigated mixed oxides of the type AgLn<sup>III</sup>TiO<sub>4</sub> and comparison of its highest energy band with that in the equivalent sodium compounds

Oxide	Band positions / (cm <sup>-1</sup> )			$\nu_1$ -NaLnTiO <sub>4</sub>
AgLaTiO <sub>4</sub>	838 m	606 vs	385 vs	870 m
AgNdTiO <sub>4</sub>	818 m	605 vs	468 vs	870 m
AgSmTiO <sub>4</sub>	834 m	625 vs	433 vs	875 m
AgEuTiO <sub>4</sub>	833 m	632 vs	367 vs	878 m
AgGdTiO <sub>4</sub>	832 m	631 vs	356 vs	900 m
AgDyTiO <sub>4</sub>	833 m	618 vs	400 vs	977 m
AgYTiO <sub>4</sub>	835 m	620 vs	400 vs	980 m

Band intensities: vs: very strong; m: medium.

apical and equatorial stretching motions, generating the observed characteristic three band IR spectra.

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