Comparative Structural and Spectroscopic Characterization of $M^I Ln^{III} TiO_4$ Ion-exchanged Phases, with M^I: Na, H, K

Araceli Elisabet Lavat[*] and Claudia Cecilia Wagner

CIFICEN (Centre of Investigations in Physics and Engineering of the Centre of Buenos Aires Province), CONICET-UNCPBA (National Council of Scientific and Technical Research, Faculty of Engineering, National University of the Centre of Buenos Aires Province), Olavarría B7400 JWI, Argentina

Abstract: In this paper, a comparative study of the XRD characterization and FTIR spectroscopic behavior of some $M^I Ln^{III} TiO_4$ phases with M^I: Na, H, K and Ln^{III}, the trivalent lanthanides elements: Sm, Eu, Er and Yb is reported. The H and K- oxides were obtained by ion-exchange from $NaLnTiO_4$. These ternary oxides belong to the K_2NiF_4 structural type, with the M^I and Ln^{III} cations distributed in an ordered way on the K-sub lattice. The FTIR spectra of the materials were analyzed by comparison with structurally related materials. A close relationship with the parent $NaLnTiO_4$ was found.

Key words: $NaLnTiO_4$, ion-exchange, X-ray characterization, FTIR spectra

1. Introduction

Transition metal oxides belonging to the perovskite structural type and some closely related structures display a wide variety of interesting properties, including HTSC (High Temperature Superconductivity), colossal magneto resistance, ferroelectricity and catalytic activity, depending on the stoichiometry and combination of A- and B- site cations [1].

Layered perovskite can be described as crystalline structure formed by 2-dimensional perovskite slabs interleaved with cations or cationic structural units. Among them, there are the oxides that adopt the K_2NiF_4 structure, the first member of the R-P (ruddlesden-popper) series ($A_{n+1}B_nO_{3n+1}$), which have been studied for some time for their catalytic and electrocatalytic properties. In addition, substituted phases of $La_2Cu_{4\pm\delta}O_4$, the well-known HTSC belonging to K_2NiF_4 structural type, have been identified as new highly conductimetric noxious gas sensors, with great potential for miniaturization of devices [2].

On the other hand, layered materials represent an interesting opportunity to develop new materials with a tailored nano-design for environmental protection, selective oxidation and refinery/biorefinery. Starting from the beginning of the petrochemical industry, layered materials have been used as catalysts. The main area of interest on layered perovskite-type catalysts is their performances in the photochemical splitting of water, but these materials show an interesting behavior also in the combined removal of NO_x, low temperature oxidation of CO and CH_4 oxidative coupling [3].

In recent years, there has been a permanent interest in the development of novel layered perovskite compounds obtained by soft chemistry procedures with specific properties. *Chemie-douce* as soft chemistry route involves the low-temperature modification of existing solid structure to form new solids that retain many of the structural features of the precursor phase [4].

In this way, a variety of metastable solids that do

---

*Corresponding author: Araceli Elisabet Lavat, Ph.D., research fields: chemistry and ceramics.

not form using conventional solid-state reaction routes can be obtained. New materials as layered perovskite known to show a wide variety of interesting chemical and physical properties such as ion-exchange and intercalating photocatalysis, ferromagnetism and giant magneto resistences have been obtained by soft-chemistry [5].

$NaLnTiO_4$ (Ln = lanthanide) R-P phases consists of an ordered array of Na^{1+} and Ln^{3+} cations in alternate layers due to their similar sizes and different charges undergo ion-exchange reactions. The $KLnTiO_4$ mixed oxides due to the larger size of K^{1+} cation, these titanates are unstable at the high temperature of synthesis. However, the synthesis of these compounds is feasible using $HLnTiO_4$ as a template by reaction with hot KOH aqueous solution [4]. Novel $NaLnTiO_4$ synthesized by ion-exchange reactions displays a higher ionic conduction than the parent $NaLnTiO_4$ due to the higher polarizability of Ag^+ cations [6, 7]. Furthermore, in the last decade, based on the reactivity of $NaLnTiO_4$, many novels layered- perovskites have been reported via topochemical routes. Ion exchange reactions resulted in the formation of new compounds by exchange of other cations besides monovalent K, H, or Ag, like divalent and transition metal R-P oxides [8].

New series of layered perovskite titanates have been developed as new semiconductor photocatalyst for efficient water splitting [9]. Zr- substituted $KLaTiO_4$ has been applied for photocatalytic water splitting under UV light irradiation [10] and Nitrogen doped $K_2La_2Ti_3O_{10-x}N_x$ photocatalyst have shown significant higher visible-light photocatalytic activity than pure TiO_2 in organic dyes solution under visible light irradiation [11]. Protonated forms of layered perovskite compounds have attracted considerable attention because of the proton conduction and Brönsted acidity, which bring intercalation compounds with a variety of organic bases. Moreover, H^+ conduction has appeared, or photocatalytic property has been improved by the protonation [12, 13]. More recently the photocatalytic activity of $HLnTiO_4$ and its

dehydration products has been demonstrated [14].

In view of the technological importance of this type of materials, particularly in the area of photocatalysis, it seems interesting to investigate the physico-chemical properties of them. Further studies are needed to improve the understanding of the relationship between catalytic performance and structural peculiarities. In this paper, a comparative study of the FTIR spectroscopic behavior of some $M^I Ln^{III} TiO_4$ phases with M^I: Na, H, K and Ln^{III}, the trivalent lanthanides elements: Sm, Eu, Er and Yb is reported in order to contribute to a better physico-chemical characterization of this type of materials.

2. Experiments

The preparation of the starting oxides $NaLnTiO_4$ was carried out by solid state reaction. The reacting stoichiometric mixture of analytical grade TiO_2 (anatase), Na_2CO_3 and Ln_2O_3 (Ln = Sm, Eu, Er, Yb) were calcined in air, in Pt crucibles with intermediate grindings. An excess of about 30% of Na_2CO_3 was used to compensate for the sodium loss due to volatilization at high temperature. During the synthesis the temperature was gradually raised up to 950-1,000 °C, and then the heating was maintained for half an hour. The excess of carbonate was removed treating the final products with methanol.

The $HLnTiO_4$ phases were obtained by an ion-exchange reaction from the parent Na-compounds using HNO_3. For this purpose, initial Na-containing oxides were ground, suspended in 0.1 M HNO_3 solution and stirred at 25 °C during 48 h. The as-prepared H-containing phases were centrifuged, washed with distilled water and dried at room temperature [1].

$KLnTiO_4$ phases were synthesized by stirring 1 g of $KLnTiO_4$ in 100 ml of 1 M KOH for 3 days at 60 °C. The powders were dried at 500 °C for 12 h prior to analysis.

The synthesized mixed oxides were studied by

Comparative Structural and Spectroscopic Characterization of $M^I Ln^{III} TiO_4$
Ion-exchanged Phases, with M^I: Na, H, K

3

X-ray diffraction and FTIR analysis. X-ray diffraction patterns were obtained using a Philips PW 3710 diffractometer and monochromatic CuKα radiation. The infrared spectra were recorded on a Nicolet-Magna 550 FT-IR instrument, using the KBr pellet technique. Unit cell parameters were obtained with a minimum squared procedure and refined with a locally modified version of the Werner PIRUM programme [15].

3. Results and Discussions

3.1 Structural Features and Characterization

In the mixed oxides $A_2 BO_4$ and $AA'BO_4$ belonging to the K_2NiF_4 structural type A ions are definitely larger than B ions. The smaller BO_6 polyhedra by sharing corners in the *a-b* plane generate the perovskite-like array. These layers are intercalated with AO rock salt-type layers along the *c* direction and also A sites can be statistically occupied by two different elements labelled A and A' [16]. According to Blasse, who was the first in reporting the crystal features, $M^I Ln^{III} TiO_4$ oxo-metallates can be described as a superstructure of the related $Sr_2 TiO_4$, the oxidic prototype of K_2NiF_4 lattice, which consists of pillared TiO_6 octahedral sheets interleaved by M^I and Ln^{3+} cations along [001]. According to this structural description in the TiO_6 sheets the Ti-O apical bonds located towards the monovalent M^+ cations should be shortened by compression (in order to compensate the charge misbalance between $(M^I_2 O_2)^{2-}$ and $(Ln^{III}_2 O_2)^{2+}$ sheets. In the perovskite-derived layered structure with general formula $AA'BO_4$ R-P phases the difference in the ionic radius between the A or A' and B cations is an important factor determining the ordering in this structural type [17]. This ordering implies a change of the space group *I*4/mmm of K_2NiF_4 to *P*4/nmm due to the charge imbalance between M^I.

The X-ray powder diagrams of all the materials synthesized clearly confirm the presence of the layered perovskite structural type since the XRD

pattern of the samples could be indexed based on the tetragonal K_2NiF_4 lattice, which crystallizes in D_{4h}^{17}-*I*4/mmm space group with Z = 2 (PDF#211276). The typical pattern of each substituted $M^I Ln^{III} TiO_4$ phases with M^I: Na, H, K shown in Fig. 1 are similar confirming the isomorphic substitution by the incorporation of the H^+ and K^+ cations in the Na^+ in the departing $Na^I Ln^{III} TiO_4$ crystal network. In addition, the intensities distribution of the diffraction peaks resemble those observed for the parent compound $Sr_2 TiO_4$ (JCPDF (Joint Committee on Powder Diffraction Standards), No. 39-1,471). From the similarity of the XRD patterns of the three series of oxides it is evident that H and K ion-exchanged phases retain the structural features of the Na parent compounds.

The calculated unit cell parameters are shown in Table 1 for the three families of materials. According to the data of this table, some structural relationship can be observed and the dependence of the parameters with the crystal radii of cations will be discussed.

Based on the ionic arrangement described, the variation of a cell dimension is mainly influenced by the size of the AA'combination of cations. As it can be seen, the parameters *a* vary slightly in the three series of titanates phases whereas the *c* cell dimensions
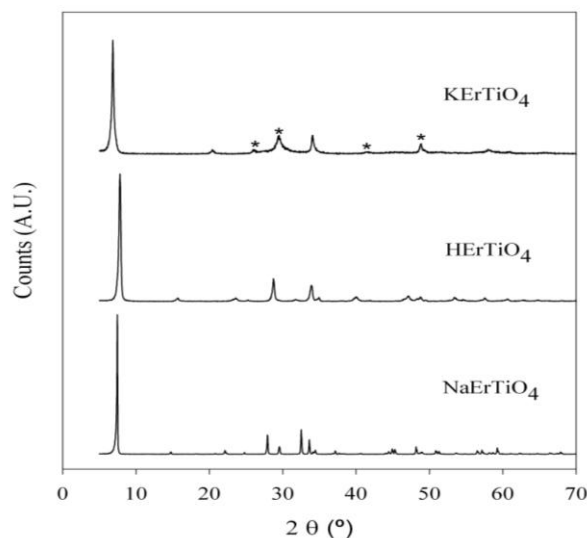

Fig. 1   XRD patterns of $M^I Ln^{III} TiO_4$.

Table 1   Unit cell parameters of $M^{I}Ln^{III}TiO_4$ oxides.

Compounds	a (Å)	c (Å)	c/a
$NaYbTiO_4$	3.782 (3)	12.005 (0)	3.174 (2)
$HYbTiO_4$	3.676 (6)	11.405 (2)	3.102 (1)
$KYbTiO_4$	3.754 (4)	13.080 (1)	3.483 (9)
$NaErTiO_4$	3.775 (6)	12.116 (4)	3.209 (1)
$HErTiO_4$	3.683 (1)	11.406 (7)	3.097 (0)
$KErTiO_4$	3.799 (0)	12.936 (1)	3.405 (1)
$NaEuTiO_4$	3.756 (9)	12.518 (1)	3.332 (0)
$HEuTiO_4$	3.685 (3)	11.851 (7)	3.215 (9)
$NaSmTiO_4$	3.752 (0)	12.602 (0)	3.358 (7)
$HSmTiO_4$	3.685 (7)	11.963 (3)	3.245 (9)
$KSmTiO_4$	3.753 (3)	13.043 (4)	3.475 (2)

are more dependent on the size of AA' cations combination. In most of the investigated compounds the c/a ratio is close to the reported value 3.3 for the isostructural oxides, particularly Sr_2TiO_4 prototype [7].

For a fixed Lanthanide, the comparison of the cell parameter variations with M^{I} ion sizes shows, according to Table 1, that both a and c parameters and more markedly c are influenced by the size of the monovalent interleaving cations following the sequence H < < Na < K, in good agreement with the monovalent cation radii.

On the other hand, for each individual series of $M^{I}Ln^{III}TiO_4$ phases keeping fixed the M^{I} cations Na, H, K; the dependence with the lanthanide sizes was analyzed. The change of the lanthanide cation has a negligible effect on a cell parameter which increases slightly from Yb to Sm. Moreover, the most significant change is the increase in the value of c cell dimensions according to Yb < Er < Eu < Sm. In Na and H-containing phases, the values of the parameter c show a linear dependence with the ionic radii, with the exception of the oxide $HYbTiO_4$ which is larger than expected. Both tendencies are compatible with the structural features of these families of mixed layered oxides with an ordered distribution of M^{I} and Ln^{III} cations in the same crystal sites. In the case of $KLn TiO_4$ the values of the parameter c are close and a clear trend was not observed.

3.2 Spectroscopic Behaviour

The FTIR spectra of the precursor $NaLn^{III}TiO_4$ oxides have been published and now the H- and K-containing materials obtained by topochemical reaction from Na-precursor were interpreted based on the IR assignment of these materials and also the isostructural AA' BO_4 spectra, previously reported and compared to Sr_2TiO_4 spectrum [7]. According to factor group analysis, 7 IR bands are expected for a unit cell with D_{4h}^{17} symmetry to which A_2BO_4 and AA' BO_4 belong. There are A_{2u} modes and four are E_u modes. The A_u modes involve stretching A-O motions of translatory type and A-O-A linkages involving the apical O of the sheets; and also the bending mode of equatorial O of the BO_6 units; whereas the four E_u modes are described as the bending movements of A-O bonds of translatory type and also of the A-O-B bonds containing apical O of BO_6 polyhedra, as well as the stretching and bending motions of BO_6 units involving B-O equatorial linkages.

Based on the structural details described in the previous section, in the $M^{I}Ln^{III}TiO_4$ the TiO_6 octahedra are mostly shortened along c-axis due to the compression of interlaying cations and consequently 4 longer basal Ti-O distances and 2 shorter apical ones are generated. Regarding BO_6 stretching vibrations, the highest frequency band v_1 can be assigned to Ti-O apical bond stretching which is the strongest Ti-O bond and the strong middle energy band v_2 may be attributed to Ti-O equatorial stretching vibrations, whereas the bending counterpart of the same polyhedra v_3 should be expected in the low energy region.

The spectra of $M^{I}Ln^{III}$-titanates investigated are very similar and some representative examples of the three families containing M^{I}: Na, H, K are shown in Fig. 2. As it can be seen, although 7 bands are predicted according to factor group analysis for I4/mmm, the spectral patterns consist of 2 or 3 strong bands, some of them splitted or with shoulders, in the middle and low energy region.
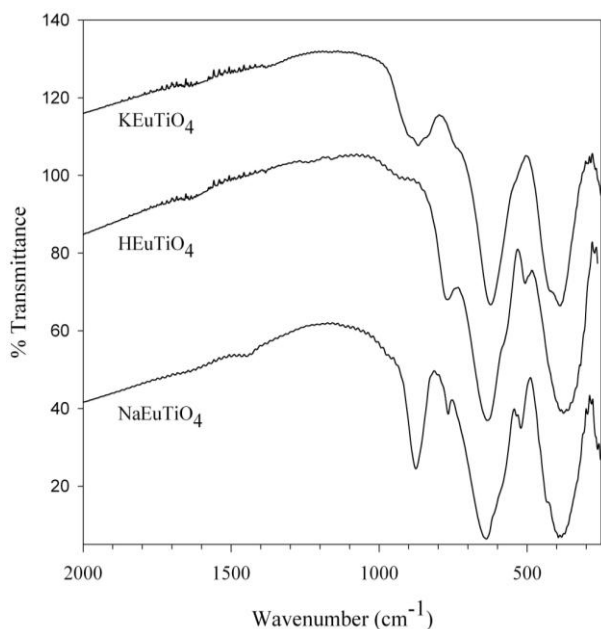
**Comparative Structural and Spectroscopic Characterization of M^{I}Ln^{III}TiO$_4$
Ion-exchanged Phases, with M^I: Na, H, K**

5

Fig. 2   FTIR spectrum of of M^{I}EuTiO$_4$.

Table 2   Band positions in cm^{-1}.

Oxides	v_1	v_2	v_3
NaYbTiO$_4$	872 Vs	754 m, 634 Vs, 596 m	548 w, 484 m, 395 Vs
HYbTiO$_4$		759 sh, 607 Vs,	551 sh, 480 m, 391 Vs
KYbTiO$_4$	869 Vs	750 sh, 603 Vs	555 w, 475 Vw, 384 Vs
NaErTiO$_4$	875 Vs	759 m, 638 Vs, 592 m	544 w, 471 m, 387 Vs
HErTiO$_4$	918 sh	763 m, 616 Vs	466 m, 385 Vs
KErTiO$_4$	957 Vs	668 w, 601 Vs	530 w, 470 m, 419 Vs
NaEuTiO$_4$	877 Vs	768 m, 641 Vs	522 m, 385 Vs
HEuTiO$_4$		771 w, 635 Vs	507 m, 374 Vs
KEuTiO$_4$	869 m	624 Vs	391 Vs
NaSmTiO$_4$	870 Vs	767 m, 639 Vs, 580 sh	380 Vs
HSmTiO$_4$		758 sh, 630 Vs	376 Vs
KSmTiO$_4$	898 sh 63 Vs	617 Vs	418 sh, 381 Vs

Vs: very strong; m: medium; w: weak; Vw: very weak; sh: shoulder.

The spectral pattern of Na and K-containing compounds are very much alike since these show a typical three band spectra. However, in H-compounds some differences are noticeable mainly because the highest band v_1 is absent or appears slightly as a shoulder resembling the spectrum of Sr$_2$TiO$_4$.

The band positions measured are detailed in Table 2.

Some correlations were found for the Ti-O stretching motions when the pairs of equivalent Na and K compounds are compared. Both v_1 and v_2 bands, involving apical and equatorial Ti-O stretching, respectively, show a shift towards lower frequencies in the case of K compounds suggesting a decrease in the bond strength of Ti-O upon substitution of interlaying Na$^+$ by bigger K$^+$ cations, in accordance with the ionic sizes and cell parameters. The ordering for M^I/Ln^{III} allows a clear separation of the Ti-O apical and equatorial stretching vibrations sublattices. When the same bands are compared as a function of the Ln interlaying cations sizes present in the cells no important shifts are noticeable. Hence, the variation of the Ti-O strength seems to be more influenced by M^I than by Ln^{III} interlaying cations.

On the other hand, the presence the characteristic intense band near 900 cm^{-1} of parent NaLn^{III}TiO$_4$ assigned to the symmetric stretching of Ti-O apical bonds was not observed for proton-exchanged derivatives. Such a change is probably the result of the change of Ti-O-Na$^+$ ionic bond by covalent Ti-O-H bonds due to the polarizing effect of H$^+$ in HLn^{III}TiO$_4$ oxides.

4. Conclusions

These results demonstrate that IR spectra are sensitive to the structural modifications occurred when the M^I cations are exchanged and this spectroscopic behaviour can be interpreted based on the structural features of these characteristic layered compounds. In Na and K compounds, a three band spectrum is obtained with two separated vibrations, a higher frequency one involving Ti-O apical and a lower frequency band related to equatorial stretching. These features allow distinguishing between both bonds, being possible to notice the shortening of Ti-O apical bond closer to the interlaying cations by its higher frequency which is a consequence of the M^I/Ln^{III} ordering. A marked shift towards lower energy is observed when K is occupying the interlaying site.

Based on band shift, the presence of the alkaline M^I cations seems to influence more markedly on the Ti-O apical and equatorial bond strength. On the contrary, the gradual change in the Ln sizes does not seem to cause a marked change on the same bonds. The presence of a single band assigned to Ti-O apical stretching, similar to the prototype Sr_2TiO_4, suggests the covalency of Ti-O-H bonds.

Acknowledgments

References

[1] Schaak, R., and Mallouk, T. 2001. "$KLnTiO_4$ (Ln = La, Nd, Sm, Eu, Gd, Dy) : A New Series of Ruddlesden-popper Phases Synthesized by Ion-Exchange of $HLnTiO_4$." *J. Solid St. Chem. 161*: 225-32.

[2] Edwin, S. R. E., Pratt, K., Skinner, S., Parkin, I., and Kilner, J. 2006. "High Conductivity $La_{2-x}Sr_xCu_{1-y}$ (Mg, Al)$_y$O$_4$ Solid State Metal Oxide Gas Sensors with the K_2NiF_4 Structure." *Chem. Mater.* 18: 3351-5.

[3] Centi, G., and Perathone, S. 2008. "Catalysis by Layered Materials: A Review." *Micropor. Mesopor. Mater.* 107: 3-15.

[4] Schaak, R., and Mallouk, T. 2002. "Perovskites by Design: A Toolbox of Solid-State Reactions." *Chem. Mater* 14: 1455-71.

[5] Baszczuk, A. 2006. "Synthesis and Crystal Structure of Two Novel Layered Compounds Ba_3InBiO_{7-x} and Ba_4InBiO_{8-x} and their Water Containing Derivatives." *J. Alloys Compd.* 414: 287-92.

[6] Toda, K., Kurita, S., and Sato, M. 1995. "Synthesis and Ionic Conductivity of Novel Layered Perovskite Compounds, $AgLaTiO_4$ and $AgEuTiO_4$." *Sol. State Ionics* 81: 267-71.

[7] Lavat, A., and Baran, E. 2006. "IR-spectroscopic Characterization of $NaLn^{III}TiO_4$ and $AgLn^{III}TiO_4$ Oxides Related to the K_2NiF_4 Structural Type." *J. Alloys Compd.*

419: 334-6.

[8] Neiner, D., Golub, V., and Wiley, J. 2004. "Synthesis and Characterization of the New Layered Perovskite, $Na_{0.10}(VO)_{0.45}LaTiO_4 \cdot nH_2O$." *Mater. Res. Bull.* 39: 1385-92.

[9] Li, Y., Chen, G., Zhang, H., and Lv, Z. 2010. "Band Structure and Photocatalytic Activities for H_2 Production of $ABi_2Nb_2O_9$ (A = Ca, Sr, Ba)." *Int. J. Hydrogen Energy* 35: 2652-6.

[10] Reddy, V., Hwang, D., and Lee, J. 2003. "Effect of Zr Substitution for Ti in $KLaTiO_4$ for Photocatalytic Water Splitting." *Catal. Lett.* 90: 39-43.

[11] Li, Z., Wang, Y., Liu, J., Chen, G., Li, Y., and Zhou, Ch. 2009. "Photocatalytic Hydrogen Production from Aqueous Methanol Solutions under Visible Light over $Na(Bi_xTa_{1-x})O_3$ Solid-solution." *Int. J. Hydrogen Energy* 34: 147-52.

[12] Nishimoto, S., Matsuda, M., and Miyake, M. 2005. "Novel Protonated and Hydrated Image Ruddlesden-popper Phases, $H_xNa_{1-x}LaTiO_4 \cdot yH_2O$, Formed by Ion-Exchange/Intercalation Reaction." *J. Solid St. Chem.* 178: 811-8.

[13] Nishimoto, S., Matsuda, M., Miyake, M., Harji S., Hoshikawa, A., Kamiyama, T., Ishigaki, T., and Miyake, M. 2006. "Structural Change in a Series of Protonated Layered Perovskite Compounds, $HLnTiO_4$ (Ln = La, Nd and Y)." *J. Solid St. Chem.* 179: 1892-7.

[14] Silyukov, O., Abdulaeva, L., Burovikhina, A., Rodionov, I., and Zvereva, I. 2015. "Phase Transformations during $HLnTiO_4$ (Ln = La, Nd) Thermolysis and Photocatalytic Activity of Obtained Compounds." *J. Solid St. Chem.* 226: 101-6.

[15] Werner, P. E. 1969. "Fortran Program for Least-squares Refinement of Crystal Structure Cell Dimensions." *Ark. Kemi.* 31: 513-6.

[16] Müller-Buschbaum, H. 2003. "The Crystal of AM_2O_4 Oxometallates." *J. Alloys Compd.* 349: 49-104.

[17] Byeon, S., Park, K., and Itoh, M. 1996. "Structure and Ionic Conductivity of $NaLnTiO_4$; Comparison with those of $Na_2Ln_2Ti_3O_{10}$ (Ln = La, Nd, Sm, and Gd)." *J. Solid St. Chem.* 121: 430-6.