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Surface characterisation of spinels with Ti(IV) distributed in tetrahedral and octahedral sites☆

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Abstract

The differences of the binding energy of the Ti $2p_{3/2}$ electron obtained by X-ray photoelectron spectroscopy (XPS) in ternary spinels such as $LiFeTiO_4$, $LiMnTiO_4$ and $LiCrTiO_4$ have been studied. X-ray diffraction patterns for these spinels and neutron powder diffraction data for $LiFeTiO_4$, $LiMnTiO_4$ and $LiCrTiO_4$ reveal that Fe(III) is in octahedral and tetrahedral sites, and Cr(III) and Mn(III) are exclusively in octahedral sites. However, Ti(IV) cations are distributed 100% in octahedral sites for $LiFeTiO_4$, 66% in octahedral sites and 34% in tetrahedral sites for $LiMnTiO_4$, and 88% in octahedral sites and 12% in tetrahedral sites for $LiCrTiO_4$. XPS studies confirm the oxidation state of the cations Fe(III), Cr(III), Mn(III) and Ti(IV); and using high resolution XPS (5.85 eV pass energy) it is possible to decompose the Ti $2p_{3/2}$ signal in two peaks at 458.0 eV (68%) and at 458.7 eV (32%) assigned to octahedral and tetrahedral Ti(IV), respectively for $LiMnTiO_4$. In the case of $LiCrTiO_4$, the Ti $2p_{3/2}$ signal could be decomposed in two peaks at 458.4 eV (87%) and 459.3 eV (13%) with a similar assignation than that observed for $LiMnTiO_4$. A single Ti $2p_{3/2}$ peak at 458.1 eV and corresponding to octahedral Ti(IV) was observed for $LiFeTiO_4$.

Keywords: XPS; Spinels; Titanium(IV); Iron(III); Manganese(III); Chromium(III)

1. Introduction

The general chemical formula for the spinel-type materials is AB_2O_4. The spinel structure consists of a face-centered cubic array of O^{2-} ions in which the A ions reside in one-eighth of the tetrahedral holes and the B ions inhabit half the octahedral holes. Cation sites preferences in spinels are well documented [1,2] and some studies [3,4] have recently reported the interest for understanding the cation distribution in more complex systems such as ternary spinels which are useful models in solid state chemistry. $LiFeTiO_4$, $LiMnTiO_4$ and $LiCrTiO_4$ are ternary spinels whose structures have been elucidated [5–7] by X-ray diffraction powder diffraction (XRD) and by neutron powder diffraction in the case of $LiMnTiO_4$ and $LiCrTiO_4$. In the $LiFeTiO_4$ spinel, Fe(III) ions are distributed in octahedral (46%) and tetrahedral sites (54%), however, in the case of $LiMnTiO_4$ and $LiCrTiO_4$ spinels, Cr(III) and Mn(III) are exclusively in octahedral sites. Ti(IV) cations are distributed 100% in octahedral sites for $LiFeTiO_4$, 68% in octahedral sites and 32% in tetrahedral sites for $LiMnTiO_4$, and 88% in octahedral sites and 12% in tetrahedral sites for $LiCrTiO_4$.

The binding energy (BE) and the Auger parameter (α') are the most widely used magnitudes for the characterisation by X-ray photoelectron spectroscopy (XPS) of the chemical state of an element and sometimes its coordination array. For example, the BE of Ni $2p_{3/2}$ for tetrahedral coordinated Ni(II) in NiO is higher than that observed for octahedral coordinated Ni(II) [8]. In general, any change in the ionic character of a bond affects the BE of the electrons on the considered atom, and in XPS examination for a complex oxide, all of the elements involved (e.g. A and B cations and O in the present work) show BEs that should be shifted as compared to those produced by either of the simple oxide. As the interatomic distances vary in spinel-type structures due to different cation distribution, it naturally affects the BEs of the electrons of the ions. We have a unique opportunity of studying by XPS three complex oxides. Two of them with a simultaneous presence of tetrahedral coordinated titanium(IV) and octahedral one with different cation distribution. In this paper the

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☆Dedicated to Professor M. Gaitán on the occasion of his 70th birthday.

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use of XPS is proposed as a complementary technique to assess the chemical state of the metal ions and the cation distribution in ternary spinels.

2. Materials and methods

Polycrystalline samples of $LiFeTiO_4$, $LiMnTiO_4$ and $LiCrTiO_4$ were prepared and characterised by XRD and neutron diffraction as described elsewhere [5–7]. Chemical analyses were performed by ICP technique and the results are in good agreement with the proposed stoichiometry.

2.1. XPS measurements

X-ray photoelectron spectra were obtained using a Physical Electronics PHI 5700 spectrometer with a non monochromatic MgKα radiation (300 W, 15 kV, $h\nu = 1253.6$ eV) as excitation source. High-resolution spectra were recorded at 45° take-off-angle by a concentric hemispherical analyzer operating in the constant pass energy mode at 5.85 eV, using a 720-μm diameter analysis area. Under these conditions the Au $4f_{7/2}$ line was recorded with 1.16 eV FWHM at a binding energy of 84.0 eV. The spectrometer energy scale was calibrated using Cu $2p_{3/2}$, Ag $3d_{5/2}$ and Au $4f_{7/2}$ photoelectron lines at 932.7, 368.3 and 84.0 eV, respectively. Charge referencing was done against adventitious hydrocarbon (C 1s 284.8 eV). Powdered solids were mounted on a sample holder without adhesive tape and kept overnight at high vacuum in the preparation chamber before they were transferred to the analysis chamber of the spectrometer for analysis. $LiMnTiO_4$ and $LiCrTiO_4$ were also studied after heating at 110°C in the preparation chamber in order to avoid the possible interference of surface water. Each region was scanned several sweeps up to a good signal-to-noise ratio was observed. Survey spectra in the range 0–1200 eV were recorded at 187.85 eV of pass energy. The pressure in the analysis chamber was maintained lower than $2 \cdot 10^{-7}$ Pa. PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss–Lorentz curves in order to determinate more accurately the binding energy of the different element core levels. The accuracy of BE values was within ±0.1 eV. Atomic concentration percentages of O, Ti, Fe, Cr, Mn and Li of spinels were determined taking into account the corresponding area sensitivity factor [9] for the different measured spectral regions. In some cases, these atomic concentrations were not reported due to the existence of two or more signals at the same region.

3. Results and discussion

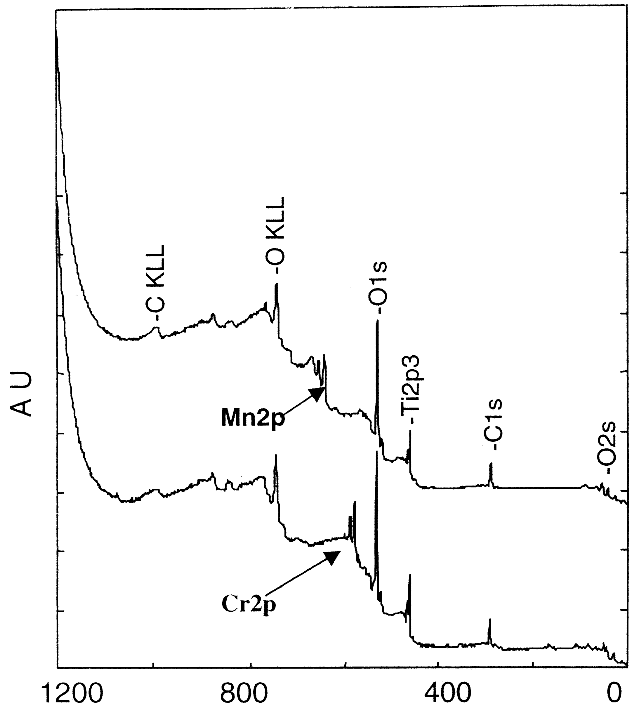

Fig. 1. Survey spectra of $LiMnTiO_4$ and $LiCrTiO_4$.

The survey XPS spectra of $LiMnTiO_4$ and $LiCrTiO_4$ are shown in Fig. 1. No impurity of other elements than adventitious carbon was observed. Moreover, C 1s spectra of the studied spinels show a single photoelectron peak without significant shoulders or bands at higher BE (not shown here) that should correspond to C bonded to O. This means that O 1s signals for both spinels do not have appreciable contributions from adventitious impurities. Table 1 reports the BEs values for O 1s, Ti $2p_{3/2}$, Li 1s, Fe $2p_{3/2}$, Mn $2p_{3/2}$ and Cr $2p_{3/2}$ photoelectron lines of the studied solids. When two or more different contributions to a photoelectron signal were observed, the percentage of their areas, determined by curve fitting, are indicated between brackets. The found BEs for Ti $2p_{3/2}$ (457.9–458.4 eV), Fe $2p_{3/2}$ (710.7 eV), Mn $2p_{3/2}$ (642.4–642.8 eV) and Cr $2p_{3/2}$ (576.6–576.9 eV) indicate that the oxidation state of the cations are Ti(IV) [10], Fe(III) [9], Mn(III) [11] and Cr(III) [12]. The Ti 2p signal of the $LiFeTiO_4$ spinel shows a single Ti $2p_{3/2}$ peak centered at 458.1 eV and a doublet Ti $2p_{1/2}$ at 463.9 eV. However, the Ti 2p signal (both Ti $2p_{3/2}$ and Ti $2p_{1/2}$) of the $LiMnTiO_4$ and $LiCrTiO_4$ spinels is asymmetric (see Fig. 2), and was decomposed in two contributions at 458.0 eV (68%) and 458.7 eV (32%) for $LiMnTiO_4$ (sample heated at 110°C), and at 458.4 eV (87%) and 459.3 eV (13%) for $LiCrTiO_4$ (sample heated at 110°C). In both cases, the peak at lower BE corresponds to octahedral coordinated Ti(IV) and the second one at higher BE to tetrahedral coordinated Ti(IV). The Ti(IV) distribution matches the cation distribution calculated from XRD and neutron powder diffraction data very well [5–7]. The observed BE Ti $2p_{3/2}$ values of the

Table 1
BEs values of O 1s, Ti $2p_{3/2}$, Li 1s, Mn $2p_{3/2}$ and Cr $2p_{3/2}$ core electron lines for $LiFeTiO_4$, $LiMnTiO_4$ and $LiCrTiO_4$

Sample	BE (eV)			
	O 1s	Ti $2p_{3/2}$	Fe $2p_{3/2}$/Mn $2p_{3/2}$/Cr $2p_{3/2}$	Li 1s
$LiFeTiO_4$	529.7 (76%) 531.6 (18%) 532.8 (6%)	458.1	710.7	54.8
$LiMnTiO_4$	530.2 (84%) 532.1 (16%)	457.9 (69%) 458.7 (31%)	642.8	54.3
$LiMnTiO_4$ 110°C	529.8 (79%) 531.2 (13%) 532.3 (8%)	458.0 (68%) 458.7 (32%)	642.4	53.6
$LiCrTiO_4$	529.8 (80%) 531.8 (20%)	458.3 (88%) 459.5 (12%)	576.6	53.4
$LiCrTiO_4$ 110°C	530.2 (66%) 531.6 (21%) 532.6 (13%)	458.4 (87%) 459.3 (13%)	576.9	53.4

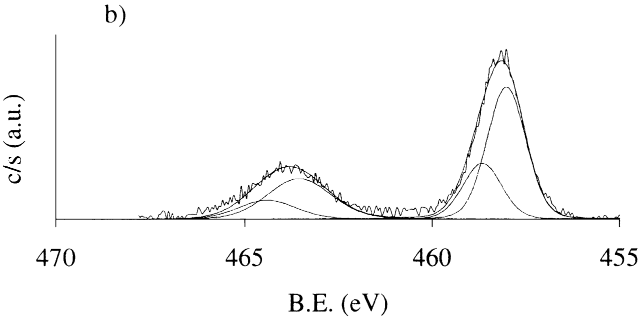

Fig. 2. Ti 2p core level spectrum for $LiMnTiO_4$ heated at 110°C.

octahedral coordinated Ti(IV) for the studied spinels are near to those observed for some perovskite titanates such as $PbTiO_3$ and $BaTiO_3$ (458.3 eV) [10] and lower than those reported for supported TiO_2 catalysts [13,14]. However, the BE values assigned to the tetrahedral coordinated Ti(IV) are in the same range of the supported TiO_2 catalysts [14]. The Auger parameter of Ti ($\alpha' =$ BE of the Ti $2p_{3/2}$ peak + KE of the Ti $L_3M_{23}V$ Auger peak) has been calculated for the studied spinels. The $L_3M_{23}V$ Auger peak is slightly sharp for the $LiFeTiO_4$ spinel, but this peak shows a considerable broadening for the $LiMnTiO_4$ and $LiCrTiO_4$ spinels (see Fig. 3). This broadening is a consequence of the coexistence of Ti(IV) with two different coordinations. However, it was not possible to decompose this Auger signal. This fact impedes to calculate the Auger parameter for tetrahedral coordinated Ti(IV) and the corresponding Wagner plot was not used to picture the dependence of the local electronic structure on the atomic environment [15]. The KE of the $L_3M_{23}V$ Auger peak is centered at 413.9 eV for $LiFeTiO_4$, 413.7 eV for $LiMnTiO_4$ and 413.7 eV for $LiCrTiO_4$. The calculated α' values are 872.0, 871.7 and 872.1 eV for $LiFeTiO_4$, $LiMnTiO_4$ and $LiCrTiO_4$, respectively. These values correspond to the octahedral coordinated Ti(IV), and are lower than those observed in the case of crystals of TiO_2 anatase (872.9 eV) and TiO_2 rutile (873.2 eV), and similar to powdered TiO_2 prepared from the hydrolysis of titanium tetraisopropoxide (872.1 eV) [16].

The bond distances M–O and M–M in $LiMnTiO_4$ and $LiCrTiO_4$, calculated from crystallographic data, are reported in Table 2. M–O distances are very similar to the 2.00 Å expected from the Shannon and Prewitt ionic radii [17]. The Ti 2p (Ti $2p_{3/2}$ and Ti $2p_{1/2}$) signal was decomposed in two contributions for the $LiMnTiO_4$ and $LiCrTiO_4$ spinels as explained above. The assignation of the contribution at high BE to tetrahedral coordinated

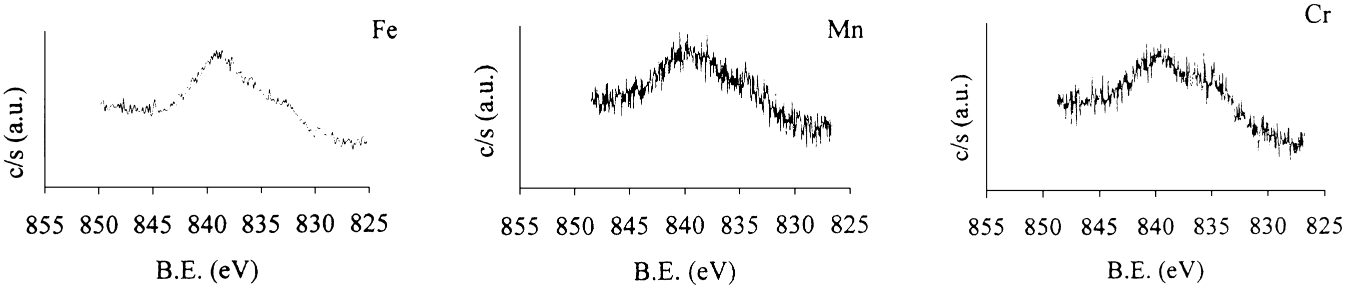

Fig. 3. Ti $L_3M_{23}V$ Auger signal for $LiMnTiO_4$ and $LiCrTiO_4$ heated at 110°C, and $LiFeTiO_4$.

Table 2
Bond distances Ti–O and Ti–M in $LiMnTiO_4$ and $LiCrTiO_4$

Sample	Bond distance (Å)			
	M_{oct}–O	M_{tet}–O	M_{oct}–M_{oct}	M_{tet}–M_{tet}
$LiMnTiO_4$	1.999	1.996	2.959	3.470
$LiCrTiO_4$	2.001	1.943	2.941	3.448

Ti(IV) was done taking into account the different calculated values of the Madelung potentials [15].

The O 1s signal for the three spinels was also decomposed in two or three contributions. The existence of two peaks of O^{2-} in the $CuCr_2O_4$ spinel at 529.4 and 531.2 eV was reported by Severino et al. [18]. Zomorrodian et al. [19] attributed a significant O 1s line broadening for $PbTiO_3$ to the existence of two BE at 529.8 and 531.1 eV which is due to the hybridisation of the Ti 3d states with O 2p. Such hybridisation of the density of states of Ti and O in a crystal affects the length of the oxygen bond, resulting in a different binding energy for the oxygen in the crystal as compared to the BE of the oxygen in the original species, TiO_2, and PbO. In our case, TiO_2, Cr_2O_3, Mn_2O_3, and Li_2O present a single an symmetric O 1s signal. The studied spinels have asymmetric O1 s signals that can be decomposed into two contributions in the case of the samples $LiMnTiO_4$ and $LiCrTiO_4$, and into three contributions in the case of the samples heated at 110°C and $LiFeTiO_{4,}$ as reported in Table 1, and shown in Fig. 4 for the $LiMnTiO_4$ spinel. The main contribution in all O 1s core level spectra appears between 529.7 and 530.2 eV. These values are near to those reported for other titanates [19]. The origin of the second contribution between 531.2 and 531.6 eV was explained above. The third weak contribution appears, upon heating at 110°C the samples $LiMnTiO_4$ and $LiCrTiO_4$; at high BE and may be assigned to the existence of surface OH acidic groups.

Table 3 shows the surface chemical composition (in atomic ratio) determined by XPS for the spinels. The observed O/Ti ratio is in all cases higher than the theoretical value of 4.00. However, if the ratio is recalculated only taking into account the area of the O 1s peak at 529.7 –530.2 eV (O*/Ti ratio in Table 3) the observed values are more near to 4.00. The corresponding Ti/M(III) and Ti/Li ratios are near to the theoretical value of 1.00, except in the case of the $LiMnTiO_4$ spinel heated at 110°C.

In conclusion, XPS analysis can supply useful information concerning the chemical state of the elements of spinels, in particular Ti(IV) and sometimes its coordination array. But new studies using reference substances with tetrahedral coordinated Ti(IV) will be considered in the near future.

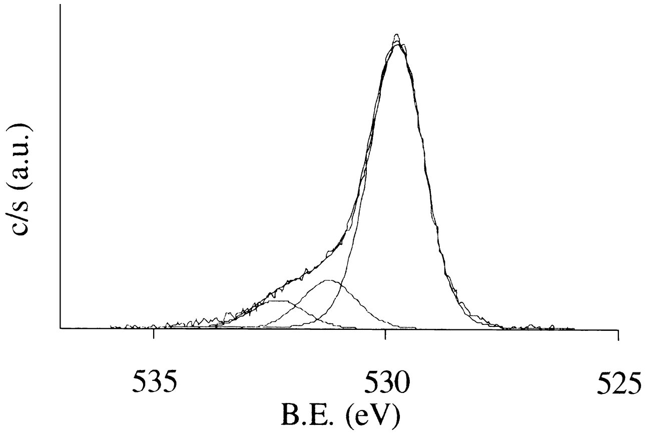

Fig. 4. O 1s core level spectrum for $LiMnTiO_4$.

Table 3
Surface composition (in atomic ratio) for $LiFeTiO_4$, $LiMnTiO_4$ and $LiCrTiO_4$

Sample	O/Ti	O*/Ti[a]	Ti/M(III)	Ti/Li
$LiFeTiO_4$	4.36	3.31	–	–
$LiMnTiO_4$	5.17	4.34	0.94	0.91
$LiMnTiO_4$ 110°C	5.35	4.23	0.82	0.89
$LiCrTiO_4$	5.21	4.17	0.98	1.03
$LiCrTiO_4$ 110°C	6.12	4.04	1.03	0.98

[a] O*/Ti is calculated taking into account the area of the O 1s at 529.7–530.2 eV.

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