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

M.A. Arillo\textsuperscript{a}, M.L. López\textsuperscript{a}, C. Pico\textsuperscript{a}, M.L. Veiga\textsuperscript{a}, A. Jiménez-López\textsuperscript{b}, E. Rodríguez-Castellón\textsuperscript{b,*}

\textsuperscript{a}Departamento de Química Inorgánica I, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain
\textsuperscript{b}Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, 29071 Málaga, Spain

Abstract

The differences of the binding energy of the Ti 2p\textsubscript{3/2} electron obtained by X-ray photoelectron spectroscopy (XPS) in ternary spinels such as LiFeTi\textsubscript{4}O\textsubscript{4}, LiMnTi\textsubscript{4}O\textsubscript{4} and LiCrTi\textsubscript{4}O\textsubscript{4} have been studied. X-ray diffraction patterns for these spinels and neutron powder diffraction data for LiFeTi\textsubscript{4}O\textsubscript{4}, LiMnTi\textsubscript{4}O\textsubscript{4} and LiCrTi\textsubscript{4}O\textsubscript{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 LiFeTi\textsubscript{4}O\textsubscript{4}, 66% in octahedral sites and 34% in tetrahedral sites for LiMnTi\textsubscript{4}O\textsubscript{4}, and 88% in octahedral sites and 12% in tetrahedral sites for LiCrTi\textsubscript{4}O\textsubscript{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\textsubscript{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 LiMnTi\textsubscript{4}O\textsubscript{4}. In the case of LiCrTi\textsubscript{4}O\textsubscript{4}, the Ti 2p\textsubscript{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 LiMnTi\textsubscript{4}O\textsubscript{4}. A single Ti 2p\textsubscript{3/2} peak at 458.1 eV and corresponding to octahedral Ti(IV) was observed for LiFeTi\textsubscript{4}O\textsubscript{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\textsubscript{2}O\textsubscript{4}. The spinel structure consists of a face-centered cubic array of O\textsuperscript{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\textsubscript{4}, LiMnTiO\textsubscript{4} and LiCrTiO\textsubscript{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\textsubscript{4} and LiCrTiO\textsubscript{4}. In the LiFeTiO\textsubscript{4} spinel, Fe(III) ions are distributed in octahedral (46%) and tetrahedral sites (54%), however, in the case of LiMnTiO\textsubscript{4} and LiCrTiO\textsubscript{4} spinels, Cr(III) and Mn(III) are exclusively in octahedral sites.

*Corresponding author.
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, $hν = 1253.6$ 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 $2 \times 10^{-7}$ Pa. PHI ACCESS ESCA-V 6.0 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 determine 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

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(II) [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, Li 1s, Mn 2p, and Cr 2p core electron lines for LiFeTiO$_4$, LiMnTiO$_4$ and LiCrTiO$_4$

<table>
<thead>
<tr>
<th>Sample</th>
<th>BE (eV)</th>
<th>Ti 2p$_{3/2}$</th>
<th>Fe 2p$<em>{3/2}$/Mn 2p$</em>{3/2}$/Cr 2p$_{1/2}$</th>
<th>Li 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFeTiO$_4$</td>
<td>529.7 (76%)</td>
<td>458.1</td>
<td>710.7</td>
<td>54.8</td>
</tr>
<tr>
<td></td>
<td>531.6 (18%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>532.8 (6%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiMnTiO$_4$</td>
<td>530.2 (84%)</td>
<td>457.9 (69%)</td>
<td>642.8</td>
<td>54.3</td>
</tr>
<tr>
<td></td>
<td>532.1 (16%)</td>
<td>458.7 (31%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiMnTiO$_4$</td>
<td>529.8 (79%)</td>
<td>458.0 (68%)</td>
<td>642.4</td>
<td>53.6</td>
</tr>
<tr>
<td>110°C</td>
<td>531.2 (13%)</td>
<td>458.7 (32%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>532.3 (8%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiCrTiO$_4$</td>
<td>529.8 (80%)</td>
<td>458.3 (88%)</td>
<td>576.6</td>
<td>53.4</td>
</tr>
<tr>
<td></td>
<td>531.8 (20%)</td>
<td>459.5 (12%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiCrTiO$_4$</td>
<td>530.2 (66%)</td>
<td>458.4 (87%)</td>
<td>576.9</td>
<td>53.4</td>
</tr>
<tr>
<td>110°C</td>
<td>531.6 (21%)</td>
<td>459.3 (13%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>532.6 (13%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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$_3$M$_{23}$V Auger peak) has been calculated for the studied spinels. The L$_3$M$_{23}$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$_3$M$_{23}$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 $\alpha'$ 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 assignment of the contribution at high BE to tetrahedral coordinated
Table 2
Bond distances Ti–O and Ti–M in LiMnTiO₄ and LiCrTiO₄

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bond distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M₁ Ti-O</td>
</tr>
<tr>
<td>LiMnTiO₄</td>
<td>1.999</td>
</tr>
<tr>
<td>LiCrTiO₄</td>
<td>2.001</td>
</tr>
</tbody>
</table>

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 O²⁻ in the CuCr₂O₄ 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 PbTiO₂ 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, TiO₂, and PbO. In our case, TiO₂, Cr₂O₃, MnO₂, and Li₂O 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 LiMnTiO₄ and LiCrTiO₄, and into three contributions in the case of the samples heated at 110°C and LiFeTiO₄ as reported in Table 1, and shown in Fig. 4 for the LiMnTiO₄ 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 LiMnTiO₄ and LiCrTiO₄; 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 LiMnTiO₄ 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.

References