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Study of Kβ X-ray emission spectroscopy applied to $Mn_{(2-x)}V_{(1+x)}O_4$ ($x=0$ and 1/3) oxyspinel and comparison with XANES

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ABSTRACT

Oxidation state and coordination of transition metal cations seems to be hard to assess when considering multiple cations, each one with different possible oxidation states. In fact, this is the case of the spinel-type double oxides family. High resolution Kβ X-ray fluorescence spectra were measured in $Mn_{(2-x)}V_{(1+x)}O_4$ ($x=0$ and $\frac{1}{3}$) spinels-type double oxides in order to determine the oxidation state and coordination of V and Mn cations. The relative intensity of radiative Auger effect $KM_{2,3}M_{4,5}$ to the total intensity and the integral absolute difference value were used as reference parameters for the characterization of Mn oxidation states. The coordination of Mn ions was inferred by the intensity of the $K\beta_5$ line. In the case of V compounds, it was used as the intensity of the line $K\beta'$ relative to the total area of Kβ region. The obtained results were further compared with X-ray absorption spectra analysis, showing good agreements regarding the oxidation state characterization. However, there were found some discrepancies in coordination, due to customary oversimplifications in the $K\beta_5$ line origin. The obtained results might represent valuable and useful data for chemical scopes of characterizing spinel-type oxides family.

1. Introduction

The characterization of the oxidation state and occupation sites is a challenge typically found when studying and developing new materials since magnetic and electrical properties may be determined. Moreover, it is possible to take advantage from this characterization method for appropriate description, control and prediction of materials physical properties. Particularly, the spinel-type oxides are interesting and promising materials due to potential technological applications. Actually, they are widely studied mainly motivated by diverse effects arising from different electronic correlations related to chemical composition and crystal structure. Spinel-type compounds [1–3] are considered as new research topic in the field of materials science since the discovery of the magnetoresistance effect [4]. Spinel-type oxides exhibit AB_2O_4 stoichiometry, where A and B are cations of either 2+ and 3+ charge or of 4+ and 2+ charge. This kind of materials present structures described as a densely packed oxygen array with A and B cations in tetrahedral (T) and octahedral (O) coordination, respectively. A precise knowledge about cation distribution is useful and sometimes mandatory for attaining improved understanding of the physical and magnetic properties, it is necessary to determine the oxidation states and distribution between T and O sites of Mn and V.

There are many techniques that can be used to study the cations oxidation state and distribution between T and O sites. Customary X-ray absorption fine structure (XAFS) [5] is the technique most commonly used to explore low concentrated metals or poor crystalline systems, e.g., to study the Mn coordination in doped perovskite $SrTiO_3$ [6]. X-ray diffraction anomalous fine structure is also used to obtain element-specific and site-specific information on site occupancy, local structure, and valency in epitaxial manganese ferrite thin films [7]. Okita et al. [8] employed the X-Ray Anomalous Scattering to determine the cation distribution in Mn–Zn–Fe ferrite, and Eba and Sakurai [2] reported successful determination for manganese spinels by analyzing Kβ X-ray fluorescence spectra investigating in detail ratio of intensities between $K\beta'$ satellite and $K\beta_5$ bands. Although it is known that there are also other conventional techniques for studying the chemical environment of this type of metals, it is remarkable that the obtained results were highly satisfactory, due to the high reliability of the determination of the oxidation states.

In this paper, a detailed study of high resolution Kβ X-ray emission spectra of family members spinel $Mn_{(2-x)}V_{(1+x)}O_4$ ($x=0$

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