The influence of charge transfers effects in monazite-type LaVO_4 and perovskite-type LaVO_3 prepared by sol-gel acrylamide polymerization.

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Abstract

Core-hole spectroscopy such as X-ray absorption spectroscopy (XAS) is useful to determine the electronic structure of strongly correlated and strongly hybridized compounds such as vanadates. Monazite-type LaVO_4 and perovskite-type LaVO_3 are good candidates to elucidate the electronic structure through the vanadium $L_{2,3}$ edge. LaVO_4 was prepared by sol-gel acrylamide polymerization and solid-state reaction. LaVO_3 was obtained by reduction of LaVO_4 using Zr as gatherer. Monoclinic crystal phase for LaVO_4 and orthorhombic crystal phase for LaVO_3 were confirmed by the Rietveld refinement of X-ray diffraction patterns. XAS comparison between Vanadium $L_{2,3}$ edge confirms the presence of V^{5+} for the monazite and V^{3+} for the orthorhombic perovskite. Multiplet calculations including crystal field and charge transfer effects (CTM) were performed in order to elucidate the tetragonal (D_{4h} symmetry) parameters Dq , Ds and Dt , the charge transfer energy Δ , and d-d Coulomb repulsion energy U parameters. CTM confirms for LaVO_3 the strong V 3d – O 2p hybridization with a significant contribution of covalent character due to the delocalization of 3d electrons. For LaVO_4 this work suggest the reclassification of this band insulator as charge transfer insulator that shows a significant contribution of ionic character.

Introduction

Lanthanum vanadates such as LaVO_4 and LaVO_3 are interesting compounds for the scientific community. Both compounds have a wide range of applications. LaVO_4 is useful for catalysis for example in the vapor phase dehydrogenation of parafins, propane, butane and ethyl benzene [1,2]. This compound has also optical application in polarizers [3], as a laser host material [4], and as a phosphor [5]. The interest in the LaVO_3 is it presents unusual electric and magnetic properties [6]. LaVO_4 crystallizes either in the tetragonal phase (t- LaVO_4) with the zircon structure or in the monoclinic phase with monazite structure (m- LaVO_4). Bulk LaVO_4 normally crystallizes in the monazite type due to the higher oxygen coordination number (Fig. 1a). This compound is isostructural to CePO_4 with space group $\text{C}_{2h}^5 \text{P}2_1/\text{n}$, No. 14, with lattice parameters: $a = 7.0434(5) \text{ \AA}$; $b = 7.2793(7) \text{ \AA}$; $c = 6.7211(6) \text{ \AA}$ and $\beta = 104.864(1)^\circ$ [7-9]. LaVO_4 is considered as band insulator with a V $3d^0$ electronic configuration. Sun et al. suggest [10] that this compound has an indirect band gap energy around 3.4 eV. In this context, the literature on electronic structure of m- LaVO_4 is scarce. On other hand, LaVO_3 normally crystallizes as an orthorhombic perovskite with space group $\text{D}_{2h}^{16} \text{Pnma}$ (Fig. 1b), No. 62, having lattice parameters $a = 5.5470(2) \text{ \AA}$, $b = 7.8401(5) \text{ \AA}$ and $c = 5.5595(4) \text{ \AA}$. It is isostructural with GdFeO_3 , in which all V sites are equivalent and VO_6 octahedra are regular [11]. The orthorhombic perovskite LaVO_3 is considered as a Mott-Hubbard insulator with band gap around 1.3 eV [12].

Soft X-ray absorption spectroscopy (XAS); as a core level spectroscopy, is a powerful tool to study strong correlated systems in particular early transition metal systems [13, 14]. XAS is a first-order optical process where a single photon participates in the process [14, 15]. This spectroscopy penetrate solids a few micrometers, but the main detection technique is total

electron yield (TEY), where the electrons have an escape depth of only a few nanometers [16]. XAS in the vicinity of the $L_{2,3}$ edge (from transitions from the $2p_{3/2}$, L_3 edge, and $2p_{1/2}$, L_2 edge) of the transition metal oxides gives information about the unoccupied states of 3d symmetry which is of predominantly metal 3d character hybridized with a significant amount of O 2p character [17, 18]. In recent years, it has also become apparent that analysis of the intensity distribution and energy can allow the determination of the oxidation state of the atom undergoing excitation.

By comparing XAS data at the $L_{2,3}$ of transition metal compounds with an atomic multiplet calculation, one can obtain important information on the electronic states of these materials [14]. This calculation takes into account the interplay between intra-atomic multiplet coupling and interatomic hybridization [19]. The physical parameters that one can obtain are the: the on-site d-d Coulomb repulsion energy U_{dd} between two 3d electrons; the charge-transfer energy Δ required to transfer an electron from a ligand valence orbital (O 2p) to the transition metal 3 d shell; and the ligand p to metal d hopping energy t [20]. Zaanen, Sawatzky and Allen (ZSA) [20] proposed a diagram based on these parameters in which the transition metal compounds can be classified as charge transfer ($\Delta < U_{dd}$) or Mott-Hubbard systems ($U_{dd} < \Delta$), see Fig. 2 a and b. In addition, the covalency between transition metal 3 d and ligand valence states (O 2p) that promotes a delocalization of the transition metal 3d electrons can be determined by this calculation. Also, the Coulomb energy U_{dd} between 3d electrons on the same site stabilizes the ionic (i.e. local) character of the electronic structure [22].

On the other hand, XAS-TEY data for oxyanions shows that the intrinsic width of the L_2 edge is considerably broader than that of the L_3 [18, 14 23-25]. Owing to the existence of an extra Coster-Kronig decay channel in which the $2p_{1/2}$ core-hole state decays via production of a $2p_{3/2}$ core hole and the simultaneous ejection of a d electron [18, 26]. The purpose of this

work is to investigate the influence of charge transfer effects on the Vanadium $L_{2,3}$ edge in the monoclinic monazite- LaVO_4 compound. We prepared this compound by the sol-gel acrylamide polymerization route (SGAP) and solid-state reaction (SSR). We performed X-ray absorption spectroscopy in order to elucidate the electronic structure through the vanadium $L_{2,3}$ edge. The multiplet calculation was used to propose a valence state and symmetry and to determine the crystal field parameters (D_{4h} symmetry): Dq , Ds and Dt ; the charge transfer parameters such as d-d Coulomb repulsion energy U , the charge-transfer energy Δ . The vanadium pentoxide, V_2O_5 and the orthorhombic perovskite- LaVO_3 were used as a reference compounds to validate their insulator classification.

Experimental Procedure

The V_2O_5 (CERAC, 99.9%) was a commercial powder. The LaVO_4 sample was prepared by SGAP in order to optimize the synthesis conditions, thermal treatments that reduce the temperature of crystal formation and to improve the homogeneous shape and size particle distribution in the nanometer range [27]. For a comparative evaluation, LaVO_4 was also prepared by solid-state reaction (SSR). LaVO_3 was obtained by the reduction of, LaVO_4 using Zr rod (Aldrich, 99%) as a gatherer [27].

Crystalline phases were identified by X-ray diffraction (XRD), using a Bruker-AXS D8-Advance with Vantec-1 detector diffractometer with λ (CuK) = 1.5406 Å radiation. XRD patterns were collected at room temperature in a 10–70° range with a $2\theta^\circ$ step size of 0.02° and time per step of 10 s. Lattice constants and other structural parameters of both monoclinic monazite- LaVO_4 and orthorhombic perovskite- LaVO_3 phases were determined by refinement with the Rietveld technique using Fullprof98 [28]. The refinement involved the

following parameters: scale factor, zero displacement correction, unit cell parameters, peak profile parameters using a pseudo-Voigt function, and overall temperature factor.

X-ray absorption spectroscopy and X-ray emission spectroscopy took place at beam line 8.0.1 of the Advanced Light Source in Berkeley. Details of the beam line can be found elsewhere [29]. The radiation is produced in a 5.0 period undulator. It is monochromatized by one of three gold-coated spherical gratings and then it is focused onto the sample. The x-ray absorption signal is monitored by the total sample current. This results in total electron yield (TEY) spectra. **The TEY spectra presented here are not representative of the bulk of the samples.** The monochromator energy is calibrated by comparing our V_2O_5 TEY spectrum with those reported in the literature [30].

Calculations to determine the physical parameters: the d-d Coulomb repulsion energy U_{dd} , the charge-transfer energy Δ , and the ligand p to metal d hopping energy t , the Vanadium valence state and symmetry were performed using the CTM4XAS charge-transfer multiplet software [31]. This semi-empirical program is based on a Hartree–Fock method corrected for correlation effects to solve the atomic Hamiltonian [32–34]. It includes the core and valence spin-orbit coupling, the core-valence two-electron integrals (multiplet effects) and the effects of strong correlations within the charge-transfer model [33]. To simulate the experimental data, the Slater integrals have been reduced to 0.8 of Hartree-Fock value. The individual Lorentzian peak broadening (the lifetime of the transition) is broadened by 0.2 eV similar to other reported values [35]. Instrumental broadening was taken into account by an additional Gaussian broadening of 0.4 eV.

Results and Discussion

Fig. 3 (a and b) shows the PDF card and XRD pattern for LaVO_4 compound after the heat treatment at 400 °C during 12 h prepared by SGAP. Similar results for the sample prepared by solid-state reaction were obtained. The single-phase pattern show reflections related to the monoclinic monazite- LaVO_4 crystal phase. Fig. 3 (c and d) shows the PDF card and XRD pattern for LaVO_3 compound obtained after the heat treatment at 850 °C during 15 days. The refinement of XRD pattern for LaVO_3 compound confirms that it has an orthorhombic phase with space group Pnma , No.62. The resulting lattice parameters for both compounds and the reliability parameters for the Rietveld refinements are summarized in Table 1. These results are in agreement with the values reported in the literature [7, 9].

The XAS at the V 2p and O 1s edges, measured in TEY mode for the monoclinic monazite- LaVO_4 compound prepared by SGAP, is shown in Fig. 4 (a). The same TEY spectrum was found for the LaVO_4 sample prepared by SSR (not shown). Both spectra were normalized and calibrated respect to the reference TEY- V_2O_5 , which is in agreement with the profile reported in the literature [30]. The TEY- LaVO_4 spectrum at the V 2p edge shows the spin orbit interaction splits the spectrum into the L_3 and L_2 components. The L_3 component of the spectrum show two peaks. The first one arises at 517.1 eV, reflecting the empty V 3d states with a t_{2g} symmetry. The following peak is located at 519.2 eV. This transition corresponds to excitation into a 3d orbital with e_g symmetry. The distortion symmetry of the VO_4 from perfect O_h symmetry to D_{4h} symmetry, causes the splitting of the e_g transition into two components. The L_2 region shows two lines located at 525.5 eV and 525.9 eV. In comparison to the features in the L_3 region, the features are significantly broadened and the t_{2g} and e_g components exhibit stronger overlap. Our experimental results are in agreements with the previously reported in the literature [23-25].

Fig. 4 (b) shows the TEY spectrum at the vanadium $L_{2,3}$ edge of LaVO_3 . This profile splits into L_3 and L_2 components due to the spin orbit interaction. In the L_3 component of the spectrum, one shoulder and the main peak can be identified. The first one arises at 515.3 eV. The following peak is located at 517.3 eV. The L_2 region is characterized by two lines located at 523.6 eV and 524.4 eV. These results are in agreement with those obtained by EELS [36] **and by XAS-TEY [37, 38].**

For the monoclinic monazite- LaVO_4 (V^{5+} , $3d^0$) compound, the D_{4h} crystal field parameters (Dq , Dt , and Ds), the charge transfer parameters such as charge transfer energy Δ , the d-d Coulomb repulsion energy U_{dd} and the configuration mixing strength were considered. These parameters, are listed in Table 2.

According to the literature in the calculation, we consider that the charge transfer energy Δ is around energy band gap ~ 3.4 eV and to provide a best fit to the experimental data U_{dd} was considered around 3.7 eV. These results suggest that the increase in U_{dd} allows explaining the charge-transfer transitions in this insulating compound.

The calculation indicates that each of these peaks is split further in D_{4h} symmetry. Between 520 and 530 eV one finds a very broad L_2 edge with no apparent structure. In the calculated absorption spectrum we indicate by a vertical line the position and relative intensity of each transition from the ground state. We then perform the convolution of these lines with Lorentzian functions to simulate the broadening due to the 2p core hole lifetime. This is the first indication of a fast CK decay [19] in LaVO_4 compound because we had to increase this Lorentzian broadening from the expected 0.12 eV (HWHM) for L_3 to 0.69 eV for L_2 . LaVO_4 compound is not the only case, this broadening has also been observed in vanadium $L_{2,3}$ edge by XAS for zircon- YVO_4 compound [26]. Similar values were found for the sample prepared by SSR. One can observe that the spectral weight has a significant contribution of the $3d^0$

configuration respect to the $3d^1\bar{L}$ state configuration. This result confirms that the V 3d–O 2p ionic character plays a dominant role in the LaVO_4 compound.

Fig. 3(b) shows also the comparison between V-2p spectrum of the orthorhombic perovskite LaVO_3 compound with the multiplet calculation using V^{3+} that gives the best approximation to the experimental profile. The D_{4h} crystal field parameters, the charge transfer energy, Δ and the d-d energy U are listed in Table 2. In order to obtain a good agreement between experiment and calculation, the crystal field parameter was 1.8 eV [39] the dd Coulomb repulsion energy, U_{dd} is considered around the band gap energy value = 1.1 eV and the charge transfer energy, $\Delta = 3.8$ eV [39]. The increase in Δ confirms the Mott-Hubbard transitions in this insulating compound. The L_2 edge is less broad and the L_3 edge is very broad respect to LaVO_4 spectrum, which suggest the delocalization of the d electrons gives rise to a broad spectrum. The spectral weight has significant contribution of the V- $3d^2$ configuration respect to the $3d^3$ state configuration. The present result suggest that the V-2p spectra, the d electrons are more delocalized in LaVO_3 respect to the LaVO_4 and suggest also a possible covalent character in V-O bonds. In addition, one can observe how the influence of multiplet effects plays a dominant role in the LaVO_3 (V- $3d^2$) compound.

Conclusions

Soft X-ray absorption spectroscopy (XAS) as a powerful tool to elucidate the electronic structure was performed through the vanadium $L_{2,3}$ edge of strong correlated compound such as LaVO_4 and LaVO_3 . Monazite-monoclinic LaVO_4 was prepared by SGAP and SSR. The orthorhombic perovskite LaVO_3 was obtained by the reduction of LaVO_4 . The Rietveld

refinement confirms the crystal structures of both vanadates. The interpretation of XAS results was performed by multiplet calculation including crystal field effects in order to elucidate Dq , Ds and Dt parameters in D_{4h} symmetry. In our interpretation, both compounds have an important contribution of charge transfer effects. The charge transfer parameters of Δ and U support that $LaVO_3$ is located in the intermediate between charge transfer regime and the Mott-Hubbard regimen due to the strong V 3d – O 2p hybridization with a significant contribution of covalent character due to the delocalization of 3d electrons. Our results for the band insulator $LaVO_4$ suggest that it can be considered in the charge transfer regime that shows a significant contribution of ionic character.

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Captions

Fig. 1. A polyhedral schematic representation of (a) monoclinic monazite-type crystal structure of LaVO_4 . (b) orthorhombic-type crystal structure of perovskite- LaVO_3 .

Fig. 2. Schematic representation of (a) Mott-Hubbard insulator. (b) Charge transfer insulator.

Fig. 3. (a) Standard XRD card (JCPDS No. 50-0367). (b) X-ray powder diffraction data for the monoclinic monazite- LaVO_4 prepared by SGAP and heated at 1000 °C during 12 h. (c) Standard XRD card (JCPDS No. 89-1673). (d) X-ray powder diffraction data for the orthorhombic perovskite- LaVO_3 . Panel (c) and (d) show the observed intensity (Y_{obs}), the calculated intensity (Y_{calc}), the difference between observed and calculated intensities ($Y_{\text{obs}} - Y_{\text{calc}}$) and the vertical lines represents the Bragg positions.

Fig. 4. Comparison between the experimental TEY spectrum (dots) and the result of the charge transfer multiplet calculation (solid line). (a) Powders of monoclinic monazite- LaVO_4 compound prepared by SGAP. (b) Powders of orthorhombic perovskite- LaVO_3 compound prepared by SSR. The vertical lines give the position of the transitions in the multiplet calculation, which are then convoluted with broadening functions. The values for the core-hole widths (HWHM) used in the calculations are at the top of spectrum.

Table 1. Unit-Cell parameters, volume and reliable parameters after the Rietveld refinement of XRPD of the monoclinic monazite-LaVO₄ and the orthorhombic perovskite-LaVO₃, respectively.

	LaVO ₄	LaVO ₃
	P 2 ₁ /n	P n m a
a (Å)	7.041(9)	5.548(9)
b (Å)	7.278(1)	7.848(5)
c (Å)	6.719(2)	5.558(1)
V (Å ³)	332.81(6)	241.99(1)
R _p (%)	16.8	14.5
R _{wp} (%)	17.9	16.6
R _{wp} (expected)(%)	18.7	11.4
χ^2	1.7	1.6

Table 2. The crystal field (D_{4h}) parameters and charge transfer parameters used in the multiplet calculation.

	LaVO ₄	LaVO ₃
	V ⁵⁺	V ³⁺
Dq (eV)	1.4	1.8
Ds (eV)	0.01	0.01
Dt (eV)	0.16	0.5
Δ (eV)	3.4	3.8
U _{dd} (eV)	3.7	1.1
U _{pd} (eV)	4.7	3.1
d ⁰ (%)	67	--
d ¹ <u>L</u> (%)	33	--
d ² (%)	--	71
d ³ (%)	--	29
Slater-Condon	80	80
(% of atomic)		