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Electronic structure and polaronic excitation in $FeVO_4$

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We investigated the electronic properties of $FeVO_4$ films using optical, valence band x-ray photoelectron, and infrared spectroscopies. These studies show that $FeVO_4$ is a direct bandgap system with a 2.7 eV gap with the Fermi level in the middle of the valence band maximum and conduction band minimum. A polaronic excitation is also observed in the middle infrared, indicating the importance of charge-lattice coupling in this multiferroic material. Fits to a model for the optical response of large polarons yield a binding energy of approximately 130 meV. © *2011 American Institute of Physics*. [doi:10.1063/1.3646402]

Understanding the electronic structure of transition metal oxides has been an on-going theme in condensed matter physics research.[1,2] This is because fundamental studies of electronic structure impact our understanding of charge-lattice-spin coupling in electronically soft materials[3] and are also relevant for applications like light harvesting, where the band gap match to the solar spectrum is critical. Many strongly correlated electron systems with significant charge-lattice coupling show polaronic excitations, which have dramatic effects on the optical and electrical properties of these materials. Polaron formation depends strongly on the nature of the electron-phonon interactions. Large polarons typically form when long-range Coulombic interactions between an electron and ions dominate the behaviour, whereas small polarons arise when short-range interactions are most significant.[4] Large and small polarons are known to have distinct spectral signatures[5] although both provide characteristic peaks in the infrared spectrum.

$FeVO_4$ is a transition metal oxide that has been studied primarily for potential applications in catalysis[6] and electrochemistry.[7] Recently, this system has been found to develop multiferroic order at low temperatures, stimulating additional interest in the physical properties.[8–11] $FeVO_4$ is an n-type semiconductor,[12,13] where the electrical transport is attributed to oxygen non-stoichiometry and thermally activated hopping of electrons.[12,13] More recent experiments revealed evidence for hopping conduction in $FeVO_4$ nanoparticles, with an activation energy of 0.28 eV.[14] Spectral studies on $FeVO_4$ films suggest that the optical response in this system is determined mainly by the electronic transitions involving the vanadium site, while combined cyclic voltammetry and optical spectroscopy show electrochromic behavior.[15] Diffuse reflectance spectroscopy measurements on iron vanadate find two broad charge transfer bands near 37 000 and 30 000 cm^{-1} corresponding to oxygen *p* to metal *d* transitions and two lower energy *d*-*d* transitions at 20 500 and 16 500 cm^{-1}.[16]

There is particular interest in understanding the electronic and optical properties of multiferroic materials. These systems typically exhibit large spin-charge-lattice coupling, which can lead to novel properties and interesting new functionalities. A number of proposed applications for multiferroics, including photovoltaics and magneto-optical devices, depend strongly on the electronic structure and optical response. This important interplay among different materials properties is highlighted by recent studies suggesting that a Zener polaron instability may induce multiferroic order in manganites.[17] Determining the electronic and optical properties of multiferroic $FeVO_4$, particularly with the identification of a polaron excitation, will help to elucidate the nature of the charge-lattice coupling in this system and, more generally, in related multiferroic materials.

Single phase $FeVO_4$ thin films were synthesized by rf magnetron sputter deposition using a target pressed from a ceramic sample prepared by a solid state reaction.[8,11] The $FeVO_4$ thin films used in this investigation were deposited on two-side-polished c-axis (0001) oriented sapphire substrates for optical studies and on an insulating Si substrate for infrared investigations. These as-deposited samples were amorphous but crystallized in the correct structure on air annealing at 700 °C for 4 h, producing polycrystalline yellowish $FeVO_4$ films. A Rigaku RU200 powder x-ray diffractometer was used for structural characterization together with a Hitachi scanning electron microscope (SEM) to estimate the thickness of the thin films from a cross-sectional image. Elemental analysis of the samples was carried out using x-ray photoelectron spectroscopy (XPS). Optical transmittance and reflectance (in the range of middle infrared to near ultraviolet) and valence band x-ray photoelectron spectroscopy (VB-XPS) were employed to investigate the optical and electronic properties of the $FeVO_4$ system. The absorption coefficient $\alpha(E)$ and the optical conductivity $\sigma_1(\omega)$ were calculated from combined transmittance and reflectance measurements,[18,19] as appropriate.

Figure 1(a) displays a representative θ–2θ x-ray diffraction (XRD) pattern for a $FeVO_4$ thin film prepared on sapphire. The peaks are fully indexed to a polycrystalline $FeVO_4$ triclinic structure with $P\bar{1}$ space group.[20] The film thickness is estimated to be ~200 nm using an SEM micrograph (not shown), in good agreement with interference fringes in the reflectance spectrum.

Narrow scan XPS spectra of iron, vanadium, and oxygen for the ceramic $FeVO_4$ sample used to press the sputtering target are plotted in Figs. 1(b) and 1(c). The pure Fe 2P doublet consists of $2P_{3/2}$, which shows a peak at 711.4 eV, and $2P_{1/2}$, with a peak at 724.7 eV, is ascribed to $Fe2P_{3/2}$–O and

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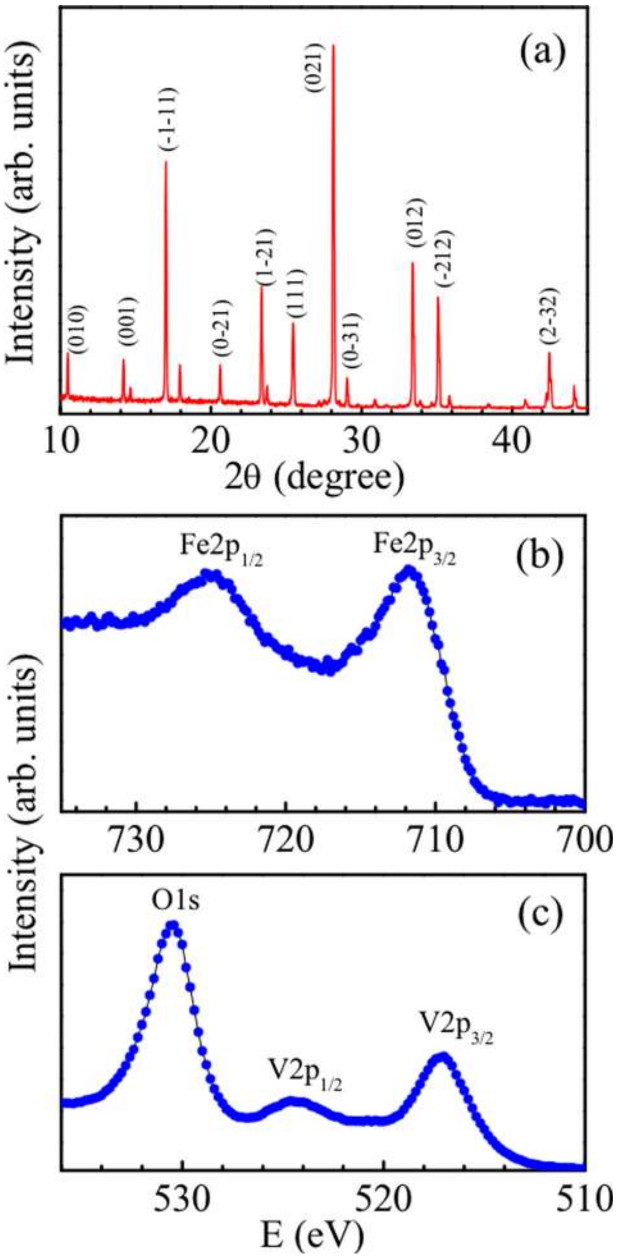

FIG. 1. (Color online) (a) θ–2θ x-ray diffraction pattern of $FeVO_4$, (b) XPS elemental spectrum of Fe for a $FeVO_4$ ceramic, and (c) XPS elemental spectrum of V and O for a $FeVO_4$ ceramic.

$Fe2P_{1/2}$–O bonds confirming the 3+ valence state for Fe. The vanadium 2P doublet, shown in Fig. 1(c), consists of $V2P_{3/2}$ and $V2P_{1/2}$ at 517.1 and 524.2 eV, respectively. The spin-orbit splitting for the V 2P doublet is 7.1 eV, in line with the value for ΔV_{2P} of 7.5 eV for V_2O_5, confirming the 5+ oxidation state of vanadium.[21] The narrow scan O1s XPS spectrum shown in Fig. 1(c) in conjunction with the V XPS spectrum consists of O1s peak at ~530.5 eV, indicating that O is in the 2− valence state in $FeVO_4$. The elemental composition was estimated using the standard expression, correcting for the different elemental sensitivities and subtracting an estimate of the background.[22] The calculated atomic percent ratio for Fe:V:O is 17.7%:18.1%:64.2%. These values are in good agreement with the expected stoichiometry as well as the elemental composition determined by energy dispersive x-ray spectroscopy (not shown).

The inset of Fig. 2(a) displays the absorption coefficient of a $FeVO_4$ thin film on sapphire as a function of energy (E). As shown in the main panel, a plot $(\alpha * E)^2$ versus E was used to determine the size and nature of the charge gap. $(\alpha * E)^2$ versus E displays a sharp and linear rise above the absorption onset, indicative of direct gap behavior. A straight line fit yielded $E_g \sim 2.7$ eV, as indicated by the open square in Fig. 2(a). The valence band XPS spectrum of $FeVO_4$ (Fig. 2(b) provided additional insight into the electronic structure. Extrapolating the leading edge of the valence band spectrum to zero, as indicated by the dashed line, it can be seen that the energy of the uppermost valence band falls at 1.35 eV below the Fermi energy (E_F). The Fermi energy, therefore, lies in the middle of the charge gap between the valence and conduction bands, consistent with intrinsic insulating behaviour in $FeVO_4$. A schematic diagram of the electronic energy levels is shown in the inset to Fig. 2(b).

One indicator of strong charge-lattice coupling in complex oxides is the polaron, the signature of which is commonly observed in the infrared. Considering the importance of charge-lattice-spin mixing in $FeVO_4$ and other oxide-based multiferroics, it is of great interest to investigate these polaronic excitations. Figure 2(c) displays the optical conductivity $(\sigma_1(\omega))$ of $FeVO_4$. We selected this optical constant (rather than α(E) as in previous discussion) because it provides the most natural connection to various charge defect models. The broad peak centered near 2000 cm^{-1} (~250 meV) is assigned as a polaronic excitation in this system. The sharp, low-energy excitations are lattice vibrations. The shape of the polaronic peak in $\sigma_1(\omega)$ depends upon the degree of electron localization, with different spectral curves for large and small polarons.[5] In Fig. 2(c), we fit the optical conductivity using functional forms suitable for both large (blue dashed line) and small (green dotted lines) polarons. The optical conductivity in the large polaron model is expressed as[5]

$$\sigma(\omega) = n_p \frac{64}{3} \frac{e^2}{m} \frac{1}{\omega} \frac{(k(\omega)R)^3}{[1 + (k(\omega)R)^2]^4},$$

where $k(\omega) = \sqrt{2m\hbar(\omega - \omega_0)}/\hbar$, ω_0 is the temperature-dependent threshold frequency for the absorption, R is the radius of the hydrogenic ground state of the polaron, n_p is the density of polarons, and m is the effective mass of the free-carrier states at the band minimum. The experimental data are most closely fit by the large polaron curve, mainly due to the superior match of the sharp drop-off on the higher energy side of the band. The threshold absorption energy used in this fit is ~132 meV, which compares well with the roughly 120 meV binding energy found for large polarons in $La_{2/3}Sr_{1/3}MnO_3$.[5]

To summarize, we investigated the electronic structure of $FeVO_4$ thin films using a variety of spectroscopic techniques. The optical absorption studies, taken together with valence band XPS spectroscopy, show that $FeVO_4$ is a direct bandgap system ($E_g \sim 2.7$ eV), with the Fermi level lying halfway in between the conduction and valence bands. This demonstrates that $FeVO_4$ should be a good insulator intrinsically, which is important for potential multiferroic applications. There is clear evidence for a large polaron excitation

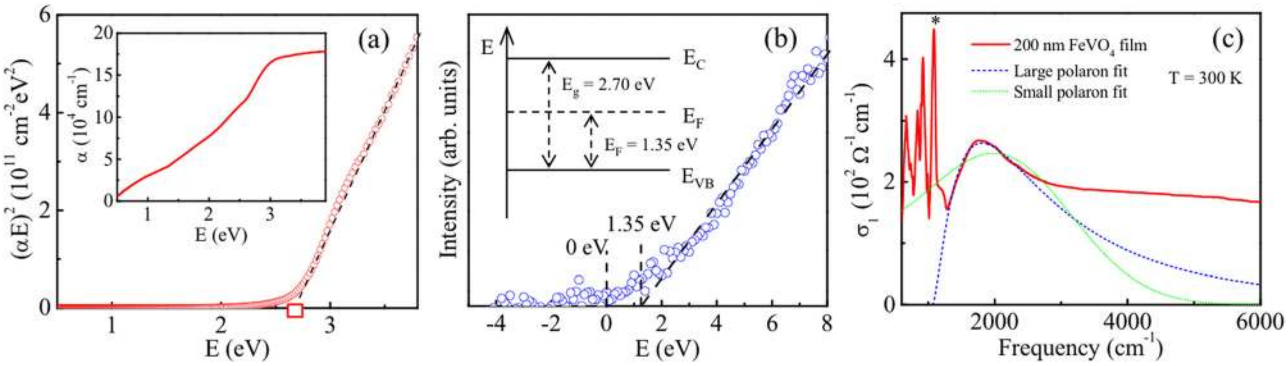

FIG. 2. (Color online) (a) $(\alpha * E)^2$ versus energy for band gap determination in $FeVO_4$. The dashed line is a guide to the eye, and the open box indicates the ∼2.7 eV bandgap. Inset: absorption as a function of energy. (b) Valence band XPS spectrum for $FeVO_4$. The dashed line is a guide to the eye. Inset: schematic energy diagram. (c) Optical conductivity spectrum of $FeVO_4$. The blue dashed line shows our best fit to a large polaron model, whereas the dotted green line shows our best fit to a small polaron model. The sharp features at lower frequency are the normal modes of vibration. The peak marked with a "*" corresponds to a signature of the Si substrate.

in the infrared, with an ∼132 meV binding energy. As $FeVO_4$ has already been shown to exhibit considerable spin-lattice coupling,[8] the behavior of this polaron at high magnetic fields or through the low temperature multiferroic transition will provide important insight into spin-charge-lattice coupling in complex oxides.

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