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Photoemission and Photoaborption Investigation of the Electronic Structure of Ytterbium Doped Strontium Fluoroapatite

A. J. Nelson, T. van Buuren, C. Bostedt, K. I. Schaffers, L. Terminello

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

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PHOTOEMISSION AND PHOTOABSORPTION INVESTIGATION OF THE ELECTRONIC STRUCTURE OF YTTERBIUM DOPED STRONTIUM FLUOROAPATITE

A. J. Nelson, T. van Buuren, C. Bostedt, K. I. Schaffers, and Lou Terminello
Lawrence Livermore National Laboratory, Livermore, CA 94550 USA

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X-ray photoemission and x-ray photoabsorption were used to study the composition and the electronic structure of ytterbium doped strontium fluoroapatite (Yb:S-FAP). High resolution photoemission measurements on the valence band electronic structure was used to evaluate the density of occupied states of this fluoroapatite. Element specific density of unoccupied electronic states in Yb:S-FAP were probed by x-ray absorption spectroscopy (XAS) at the Yb 4d ($N_{4,5}$-edge), Sr 3d ($M_{4,5}$-edge), P 2p ($L_{2,3}$-edge), F 1s and O 1s (K-edges) absorption edges. These results provide the first measurements of the electronic structure and surface chemistry of this material.

1. Introduction

Host materials doped with the Yb^{3+} ion have sparked a great deal of interest in the last several years for their use as diode-pumped solid-state lasers. Crystals of Yb Doped Strontium Fluoroapatite [Yb:S-FAP or Yb^{3+}:$Sr_5(PO_4)_3F$] are currently being studied for use in an average power 100 J, 10Hz, diode pumped laser operating at 1047 nm.[1] The Yb^{3+} dopant is a $4f^{13}$ ion and possesses only two relevant electronic states derived from the single 4f hole - the $^2F_{7/2}$ ground-state and the $^2F_{5/2}$ excited-state. An anomalous absorption has been observed in some Yb:S-FAP crystals that is thought to be related to the crystallographic site occupied by the Yb.

S-FAP has the hexagonal crystal structure shown in Figure 1(a), space group $P6_3/m$, a = 9.7078 Å and c = 7.2819 Å.[2] The unit cell contains two formula units. There are 6 PO_4 groups with their central P ions at the hexagonal corners on the reflection planes and the F ions are centered on the hexagonal faces. The ten divalent Sr^{2+} ions occupy two different crystallographic sites in the unit cell [Fig. 1(b)].[2,3] Site I has trigonal symmetry with four Sr^{2+} ions occupying a nine-coordinated oxygen polyhedron. Site II has six Sr^{2+} ions surrounded by six oxygen and one fluorine. The trivalent Yb dopant has a strong tendency to occupy the lower symmetry site II. The charge compensation mechanism for rare earth doping at site II involves substitution of the F^- with an O^{2-}, i.e. Sr^{2+}-F^- is replaced by Yb^{3+}-O^{2-}. The aforementioned anomalous absorption has been attributed to Yb^{3+} on a second site in the crystal.

This paper presents results from an x-ray photoemission (XPS) and x-ray photoabsorption (XAS) investigation of the composition and the electronic structure of ytterbium doped strontium fluoroapatite (Yb:S-FAP). Core-level spectroscopy and results for the occupied states in the valence band and unoccupied states in the conduction band reveal chemical differences associated with anomalous optical absorption.

2. Experimental

Crystals of Yb:S-FAP are grown in an inert atmosphere by the Czochralski (CZ) method. $SrHPO_4$, $SrCO_3$, SrF_2 and Yb_2O_3 powders are mixed and inductively heated to prepare the melt. Crystal growth runs were initiated with oriented single crystal seeds having the desired orientation, and with a pull rate of ~0.5 mm/hr and a rotation rate of ~20 rpm. Yb^{3+} doping concentration is ~1-2 x 10^{19} cm^{-3}.

The Yb:S-FAP samples examined were CZ171218, which exhibited anomalous optical absorption, and C200115, an optically ‘clean’ sample.

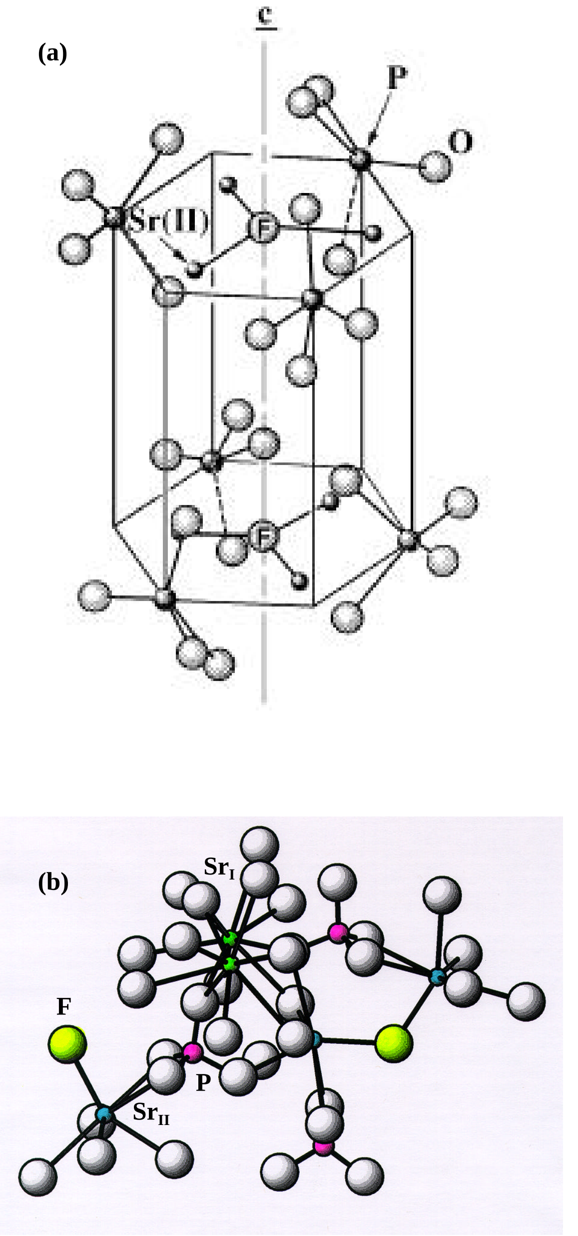

Figure 1. (a) Crystal structure of $Sr_5(PO_4)_3F$ and (b) the two Sr^{2+} sites for Yb-doping in the crystal.

Analytical results for these samples were compared to determine compositional and electronic differences. The starting compounds were also analyzed by XPS and XAS to provide a basis for quantitative analysis. The $SrHPO_4$, $SrCO_3$, SrF_2, Yb_2O_3 and YbF_3 powders were used as received and pressed into In foil for analysis.

XPS spectra were obtained using a focused monochromatic Al Kα x-ray (1486.7 eV) source for excitation and a spherical section analyzer. XAS analysis was performed at beamline 8.2 at the Stanford Synchrotron Radiation Laboratory (SSRL) by scanning the photon energy of the incoming monochromatic synchrotron radiation through the Yb 4d ($N_{4,5}$-edge), Sr 3d ($M_{4,5}$-edge), P 2p ($L_{2,3}$-edge), F 1s and O 1s (K-edges) core-level edges while monitoring the total electron yield (TEY, surface sensitive, 50-100Å).

3. Results and Discussion

The valence band (VB) spectra for the Yb:S-FAP crystals and model compounds are presented in Figure 2. The valence band for Yb:S-FAP is composed of overlapping P 3p, O 2p, and F 2p states. The localized Yb $4f^{13}$ states lie below the upper part of the O 2p density of states,[4-6] as can be seen in the expanded VB maximum region for the Yb_2O_3 model compound.

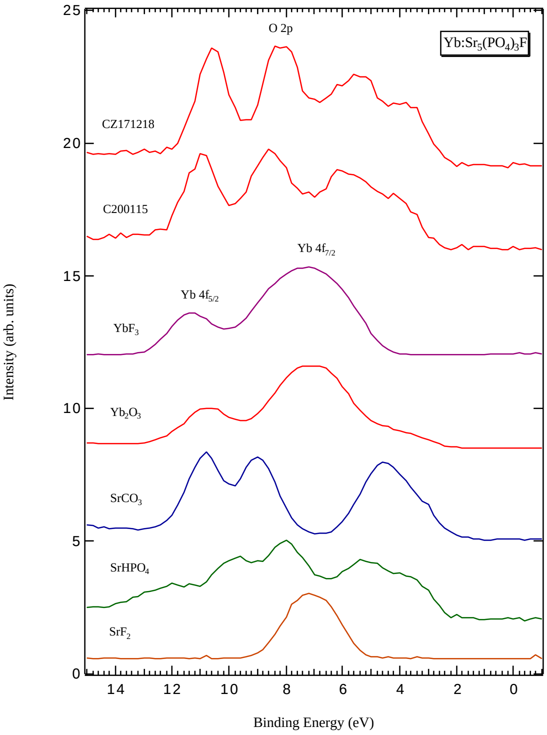

Figure 2. VB region for the Yb:S-FAP crystals and model compounds.

In addition, note the broadened peaks in the expanded VB maximum region for the YbF_3 model compound that is due to the overlapping F 2p valence band. Visual inspection of the expanded VB maximum region shows a similarity between the spectra of $SrHPO_4$ and the Yb:S-FAP crystals, indicating that P and O p-states dominate the valence band. The feature at ~9 eV is assigned to O 2p and the feature at ~11 eV is assigned to O-H bonding.[4-6]

The XAS technique probes empty or unfilled electronic states and provides information on the local chemical environment. Transitions between the initial state ($4d^{10}5s^25p^64f^N$, N = 13 for Yb^{+3}) and a series of final states ($4d^95s^25p^64f^{N+1}$) yields numerous features at the Yb $N_{4,5}$-edge that can provide structural information. For 4d X-ray absorption, the dipole allowed transitions are 4d → 4f and 4d→ 5p, with transitions to the 4f states dominant. The dipole forbidden 5p → 4f transition ($4d^{10}5p^64f^N \rightarrow 4d^95p^64f^{N+1} \rightarrow 4d^{10}5p^54f^{N+1}$) becomes weakly dipole-allowed due to spin-orbit interaction and manifests itself as pre-threshold features,[7] and is of course absent in the divalent $4f^{14}$ (Yb^{2+}) case. Enhancement of these transitions has been noted when valence electrons associated with oxygen bonding contribute.[5] The nature of the crystal field splitting in the $^2F_{7/2}$ and $^2F_{5/2}$ electronic states derived from the single 4f hole are affected by the symmetry of the two distinct crystallographic sites.

Figure 3 presents the Yb 4d core-level XAS of the Yb:S-FAP crystals and model compounds. The spectra have been normalized to the same edge-jump.[8] The spectra for the Yb_2O_3, clean Yb:S-FAP and to some extent the YbF_3, exhibit a sharp feature ~1 eV FWHM at the absorption edge. This feature is absent in the anomalous Yb:S-FAP spectrum. Also note the lower energy separation and edge shift in the spectrum for the crystal with the anomalous absorption, thus indicating differences in the chemical environment of the Yb ion and associated changes in crystal field splitting. Also note that the pre-edge features (separated by 4 eV) are only present in the spectrum of the clean crystal. The enhancement of these features occurs when valence electrons associated with oxygen bonding contribute and thus are probably due to Yb^{3+}-O^{2-} complexes. The absence of these features and the edge shift in the spectrum for the Yb:S-FAP crystal exhibiting the anomalous absorption would seem to indicate incomplete replacement of Sr^{2+}-F^- by Yb^{3+}-O^{2-} at site II.

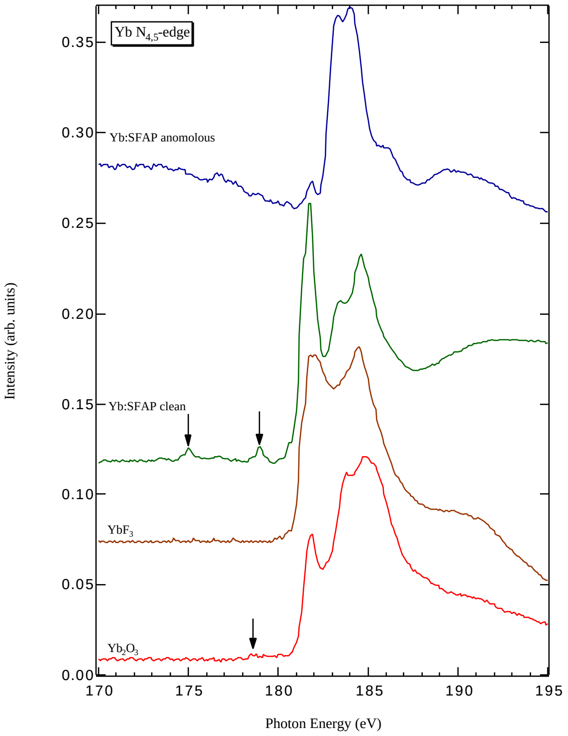

Figure 3. Yb $N_{4,5}$-edge photoabsorption spectra for the Yb:S-FAP crystals and Yb model compounds.

The overlapping Sr $M_{4,5}$-edge and P $L_{2,3}$-edge photoabsorption spectra for the Yb:S-FAP crystals and the $SrHPO_4$ model compound are shown in Figure 4. The weak dipole allowed Sr 3d → 4p transition has a lower energy than the P 2p → 3d transition. The spectrum for the $SrHPO_4$ represents the standard for Sr-O and $–PO_4$ bonding. Comparing the spectrum for the clean Yb:S-FAP crystal indicates similar Sr-O and $–PO_4$ bonding, however the anomalous crystal has a much more intense Sr $M_{4,5}$-edge signal.

Figure 5 presents the O K-edge photoabsorption spectra for the Yb:S-FAP crystals and the oxide model compounds. Again we see distinct similarities between the spectrum for $SrHPO_4$ and the Yb:S-FAP crystals. The presence of the π^* feature at ~530 eV indicates residual carbonaceous contamination. The major peak centered at 537 eV is

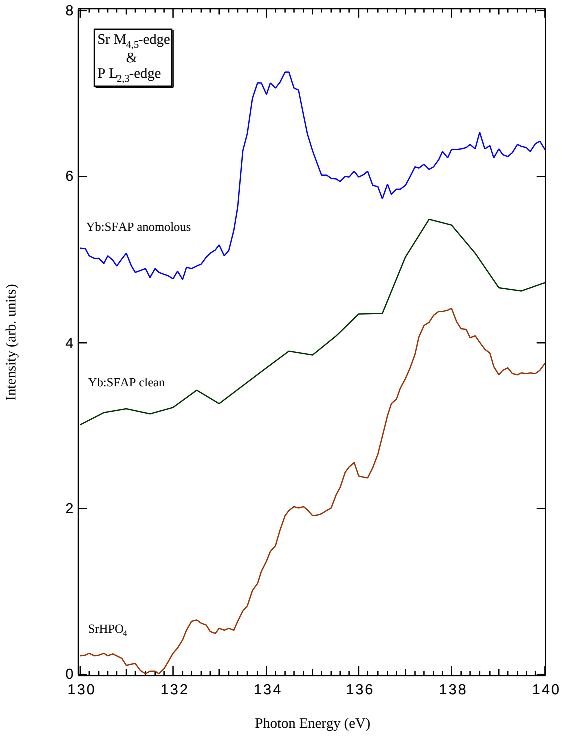

Figure 4. Sr $M_{4,5}$-edge and P $L_{2,3}$-edge photoabsorption spectra for the Yb:S-FAP crystals and Sr model compounds.

assigned to a transition from the O 1s core level to an unoccupied σ^* orbitals of the O-Sr and O–P bonds. A higher energy feature at ~543.6 eV is clearly visible in the spectra for clean Yb:S-FAP crsytal and Yb_2O_3 model compound, and is thus assigned to the presence of Yb^{3+}-O^{2-} complexes. This shoulder has a reduced intensity in the spectrum for the anomalous Yb:S-FAP crystal possibly indicating incomplete replacement of Sr^{2+}-F^- by Yb^{3+}-O^{2-} at site II.

4. Conclusions

X-ray photoemission (XPS) and x-ray photoabsorption (XAS) spectroscopy were used to examine the electronic structure of ytterbium doped strontium fluoroapatite (Yb:S-FAP) as a function of the crystallographic sites occupied by the Yb in the unit cell. Valence band photoemission results indicate that P and O p-states dominate the valence band electronic structure.

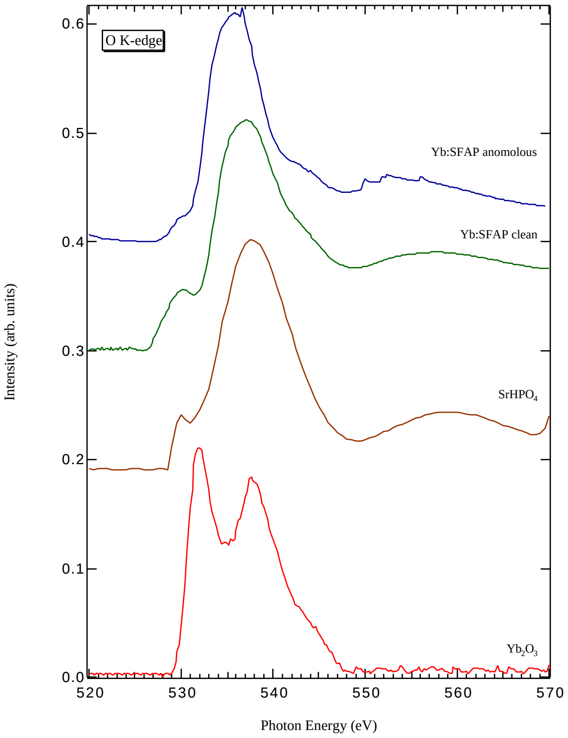

Figure 5. O K-edge photoabsorption spectra for the Yb:S-FAP crystals and the oxide model compounds.

The XAS results clearly show an obvious difference between the Yb in the clean crystal versus Yb in the anomalous crystal. XAS results also show that both dipole allowed Yb 4d → 4f transitions and weakly allowed 5p → 4f transition are enhanced with the formation of Yb^{3+}-O^{2-} complexes. Yb $N_{4,5}$-edge results also indicate that the anomalous absorption is due to Yb^{3+} at the high symmetry site I. O K-edge results also indicate the presence of Yb^{3+}-O^{2-} complexes in the clean Yb:S-FAP. Theoretical modeling will be required for a full understanding of the Yb chemistry in this material system.

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