XANES Study of the Valance States in the Rutile Structure $FeTiTaO_6$ and $Fe(Ti_{0.8}M_{0.2})TaO_6$ (M= Zr, V)

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At present, there is a great interest to develop new piezoelectric/ferroelectric/relaxor ferroelectric and multiferroic materials that do not contain environmentally unfriendly lead. BiMnO, $BiFeO_3$ and the recently synthesized Bi_2FeCrO_6 are among the lead-free multiferroics that attract current attention. Moreover, there is an interest to bring d^0 and d^n ($0<n<10$) transition metal atoms together in complex oxides to realize multiferroic properties. Considering that rutile TiO_2 sits on the verge of an instability that tends to drive the material towards ferroelectric behavior, we believed that complex rutile oxides containing Ti^{4+}: $3d^0$ together with another d^0 atom such as Ta^{5+}/Nb^{5+} and an appropriate d^n atom would exhibit novel ferroic/multiferroic properties. Recently, Mani and co-workers has been report that rutile $FeTiTaO_6$ have relaxor ferroelectric behavior, with transition temperature around 550 K.

On the other hand, the X-ray absorption spectroscopy (XAS) using synchrotron radiation is a powerful tool to investigate the structural and electronic properties of element of interest present in a sample. In this study, we focus on the oxidation state by measuring X-ray absorption near-edge structure (XANES) spectra. The authors dope Zr (Group IV-b) and V (Group V-b) to Ti (Group IV-b) site in $FeTiTaO_6$, and making sample chemical formula of $Fe(Ti_{0.8}M_{0.2})TaO_6$ (M = Zr, V). By doping different group element to Ti Site, we believes it will change electronic configuration of d-orbital state, and may affect the electric and magnetic properties. The Fe, Ti, Zr, V *K*-edges and the Ta L_3-edge XANES spectra were recorded in fluorescence mode for synthesized powders mounted on a Scotch tape at a beam line BL01C and BL17C, respectively.

The Ti *K*-edge XANES spectra of $FeTiTaO_6$, $Fe(Ti_{0.8}Zr_{0.2})TaO_6$ and $Fe(Ti_{0.8}V_{0.2})TaO_6$ along with two standard, rutile TiO_2 (Ti^{4+}) and Ti_2O_3 (Ti^{3+}) are shown in Fig. 1(a). It is well known that the chemical shift of the main absorption edge to lower energy with decreasing valence of transition metals is a powerful tool for probing unknown valence of a transition metal. In Fig. 1(a), a dashed line at the absorption coefficient value of 0.5 is included to elucidate the chemical shift. The $FeTiTaO_6$, $Fe(Ti_{0.8}Zr_{0.2})TaO$ and $Fe(Ti_{0.8}V_{0.2})TaO_6$ spectrum is close to Rutile TiO_2 (Ti^{4+}). This evidence indicates that electron configuration of Ti in $FeTiTaO_6$, $Fe(Ti_{0.8}Zr_{0.2})TaO_6$ and $Fe(Ti_{0.8}V_{0.2})TaO_6$ sample is d^0 (Ti^{4+}). Figure 1(b) shows the Zr *K*-edge XANES spectra of $Fe(Ti_{0.8}Zr_{0.2})TaO_6$ compare with two standards Zr foil (Zr^{0+}) and ZrO_2 (Zr^{4+}), and in Fig. 1(c) display the V *K*-edge XANES spectra of $Fe(Ti_{0.8}V_{0.2})TaO_6$ compare with standards VO_2 (V^{4+}) and V_2O_5 (V^{5+}). In view of the absorption coefficient value of ~0.5, the Zr *K*-edge spectrum of samples is close to ZrO_2 (Zr^{4+}) and the electron configuration is d^0. Moreover, the V *K*-edge spectrum of samples is close to VO_2 (V^{4+}), thus the electron configuration is d^1. In addition, the Fe *K*-edge XANES spectra and Ta L_3-edge XANES spectra of samples also show that the oxidation state of Fe is Fe^{3+} (d^5), and the the Ta is Ta^{5+} (d^0). Base on the above XANES results, only Fe^{3+} (d^5) and V^{4+} (d^1) may have unpaired electrons. Moreover, according to our magnetic measurements, the magnetic moment of $FeTiTaO_6$ and $Fe(Ti_{0.8}Zr_{0.2})TaO_6$ samples is about ~1μ_B, but the magnetic moment of $Fe(Ti_{0.8}V_{0.2})TaO_6$ is about ~3μ_B. The results indicates that Fe^{3+} (d^5) in these samples is in low spin state (string field). The results is in good agreement with our XANES analysis.

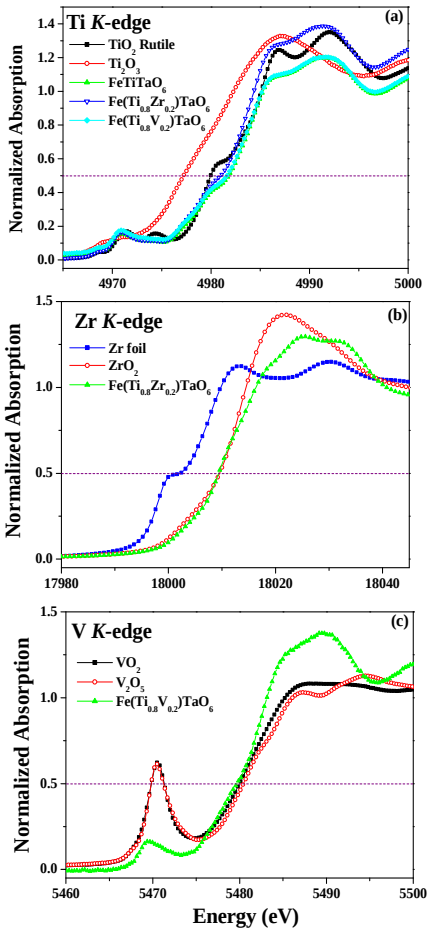

Fig. 1: (a) Ti *K*-edge XANES spectra of $FeTiTaO_6$, $Fe(Ti_{0.8}Zr_{0.2})TaO_6$, $Fe(Ti_{0.8}V_{0.2})TaO_6$ along with two standards of Rutile TiO_2 (Ti^{4+}) and Ti_2O_3 (Ti^{3+}). (b) Zr *K*-egde XANES spectra of $Fe(Ti_{0.8}Zr_{0.2})TaO_6$ with two standards of Zr foil (Zr^0) and ZrO_2 (Zr^{4+}). (c) V *K*-edge XANES spectra of $Fe(Ti_{0.8}V_{0.2})TaO_6$ with two standard of VO_2 (V^{4+}) and V_2O_5 (V^{5+}).