# EXAFS Study of the Local Structure $FeTiTaO_6$ and $Fe(Ti_{0.8}M_{0.2})TaO_6$ (M= Zr, V) Systems Based on the Rutile Structure

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It is well known that transition metal oxides with $d^0$ electronic configuration undergo a second-order Jahn–Teller distortion of the $MO_6$ (M = metal) octahedra arising from a mixing of empty $d^0$ states of the transition metal with the O 2*p* states. The distortion seems to be at the heart of several of the interesting dielectric/ ferroelectric properties of $d^0$ transition metal containing perovskite oxides such as $PbTiO_3$, $BaTiO_3$, $PbZr_{1-x}Ti_xO_3$, and $Pb_3MgNb_2O_9$. Recently, Mani and co-workers has been report that $FeTiTaO_6$ rutile structure have relaxor ferroelectric behavior with transition temperature around 550 K. Thus, in this study, 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 local structure of these samples. $Fe(Ti_{0.8}M_{0.2})TaO_6$ (M = Zr, V) samples were synthesized by solid-state reaction using $Fe_2O_3$, $TiO_2$, $ZrO_2$, $V_2O_5$ and $Ta_2O_5$ as raw materials. Stoichiometric homogeneous mixtures of highly pure raw materials were obtained by thorough grinding. The mixture was calcined in air at 1300°C for 24 hours. The Ti *K*-edge extended X-ray absorption fine structure spectra (EXAFS) were recorded in fluorescence mode for synthesized powders mounted on a Scotch tape at a beam line BL17C.

Fig. 1 (a), (b) and (c) show the Fourier transforms of the $k^3$-weighted Ti *K*-edge EXAFS spectra of $FeTiTaO_6$, $Fe(Ti_{0.8}Zr_{0.2})TaO_6$ and $Fe(Ti_{0.8}V_{0.2})TaO_6$, respectively. The data range taken for transformation is from 3.81 to 10.67 $Å^{-1}$. Structure parameters were obtained from fitting in *R*-space in the interval of 0.839~2.086 Å. The solid lines and empty cicles represent the experimental and fitting data. The first prominent peak in the FT spectra is assigned to the Ti-O contribution. The bond length between atoms, coordination number, Debye-Waller factor and EXAFS fitting parameter are listed in Table 1. As see from Table 1, all of the Ti-O bond length of $Fe(Ti_{0.8}Zr_{0.2})TaO_6$ sample is bigger than that of $FeTiTaO_6$. Moreover, the Ti-O bond length of $Fe(Ti_{0.8}V_{0.2})TaO_6$ sample is smaller than that of $FeTiTaO_6$. According to our XANES analysis, we found that the valance states is $Ti^{4+}$, $Zr^{4+}$ and $V^{4+}$ in $FeTiTaO_6$, $Fe(Ti_{0.8}Zr_{0.2})TaO_6$ and $Fe(Ti_{0.8}V_{0.2})TaO_6$ samples. Thus, the above EXAFS results can be explained by substitution of bigger size $Zr^{4+}$ [0.72 Å for CN (coordination number) = 6] and smaller $V^{4+}$ ions (0.58Å for CN = 6) in the $Ti^{4+}$ site (0.605 Å for CN = 6), respectively. Moreover, it is noted that Debye-Wall factor for $Fe(Ti_{0.8}V_{0.2})TaO_6$ sample is bigger than other samples. The results indicate that $TiO_6$ octahedral in $Fe(Ti_{0.8}V_{0.2})TaO_6$ sample is more disorder.

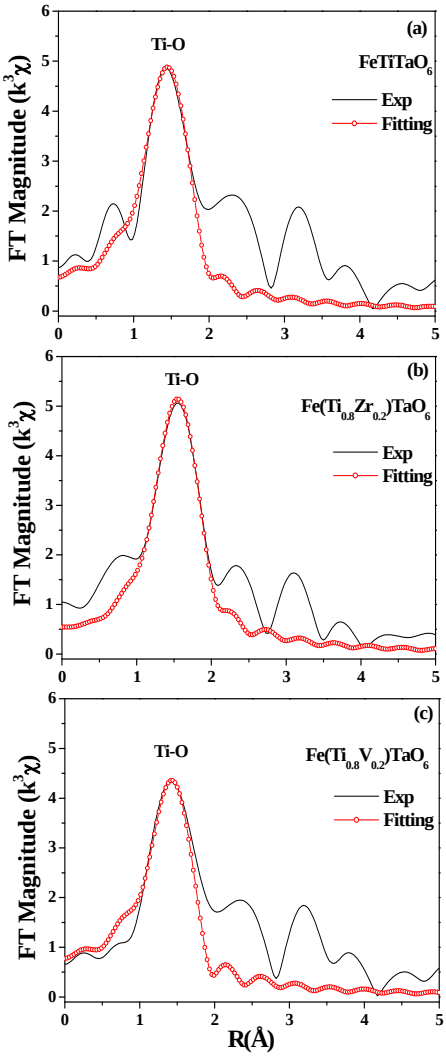


**Fig. 1:** (a), (b) and (c) shows the Fourier transforms of the $k^3$-weighted Ti *K*-edge EXAFS sapectra of $FeTiTaO_6$, $Fe(Ti_{0.8}Zr_{0.2})TaO_6$ and $Fe(Ti_{0.8}V_{0.2})TaO_6$, respectively.

**Table. 1:** The EXAFS fitting parameters of $FeTiTaO_6$, $Fe(Ti_{0.8}Zr_{0.2})TaO_6$ and $Fe(Ti_{0.8}V_{0.2})TaO_6$ samples.

| Sample | k space range ($Å^{-1}$) [3.81,10.67] | | Bound length (Å) | Coordination number (N) | Debye-Waller factor ($σ^2$) |
|---|---|---|---|---|---|
| $FeTiTaO_6$ | R space range (Å) [0.957,1.994] | Ti-O | 1.876(0) | 3.22(8) | 0.009(2) |
| | | Ti-O | 2.029(7) | 1.61(4) | 0.009(7) |
| V=57.126 | r-factor fitting 0.011(9) | | | | |
| $Fe(Ti_{0.8}Zr_{0.2})TaO_6$ | R space range (Å) [0.977,2.086] | Ti-O | 1.924(8) | 3.27(2) | 0.009(2) |
| | | Ti-O | 2.086(1) | 1.63(6) | 0.009(7) |
| V=61.775 | r-factor fitting 0.006(6) | | | | |
| $Fe(Ti_{0.8}V_{0.2})TaO_6$ | R space range (Å) [0.839,2.038] | Ti-O | 1.912(5) | 3.08(0) | 0.010(7) |
| | | Ti-O | 1.920(4) | 1.54(0) | 0.011(2) |
| V=56.152 | r-factor fitting 0.043(3) | | | | |