



Investigation of the electronic structure and structural stability of $Gd_2Ti_{2-x}Sn_xO_7$ pyrochlore-type oxides by XANES

Aluri Esther Rani and Andrew P. Grosvenor

Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5C9

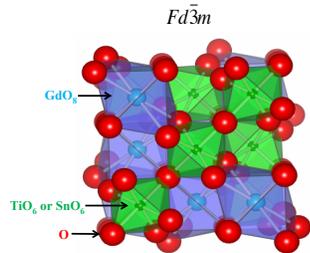


Abstract

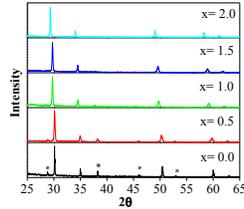
There has been a great interest in recent years to use titanate and stannate pyrochlores as host materials for the immobilization of radioactive elements (actinides), especially plutonium. To develop these materials, the effect of composition on the structural stability and electronic properties of these materials needs to be examined [1]. $Gd_2Ti_{2-x}Sn_xO_7$ ($0 \leq x \leq 2$) was synthesized by the ceramic method and investigated by X-ray absorption near edge spectroscopy (XANES), which allows for the study of the effect of elemental substitution on bonding and the electronic structure of materials [2,3]. Examination of metal K- and L₃-edge XANES spectra from the $Gd_2Ti_{2-x}Sn_xO_7$ system allowed for the elucidation of how the metal-oxygen bond covalency affects the electronic structure of these materials with increasing Sn content. As x increases, the Ti-O bonds become more ionic while the Sn-O bonds become more covalent, leading to changes in energy and intensity of the collected spectra.

Glancing angle XANES (GA-XANES) was performed to study the damaged surface layer of $Gd_2Ti_{2-x}Sn_xO_7$ pellets after being irradiated by a beam of high-energy Au^{1+} ions. GA-XANES allows for the investigation of the metal oxidation state, bonding environment, and coordination number (CN) of the damaged surface layer [4]. The investigation of these materials by GA-XANES after irradiation suggests that a significant distortion occurs at the Ti- and Sn-site with a change in CN and bonding environment being observed.

Crystal structure of $Gd_2Ti_{2-x}Sn_xO_7$ [5]



Powder XRD



- Increase in unit cell with greater Sn content
- $Sn^{4+}=0.690\text{\AA}$, $Ti^{4+}=0.605\text{\AA}$ [6]
- Decrease in super structural peak intensities with greater Sn content due to the increased average scattering power of Sn [7]

Experimental

Synthesis: $Gd_2O_3 + (2-x) TiO_2 + (x) SnO_2 \xrightarrow[9 \text{ days}]{1400^\circ\text{C, air}} Gd_2Ti_{2-x}Sn_xO_7$

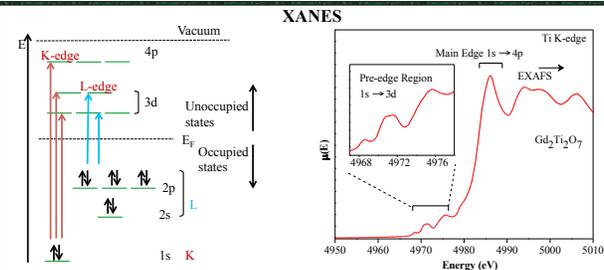
$Y_2O_3 + (2-x) TiO_2 + (x) SnO_2 \xrightarrow[9 \text{ days}]{1400^\circ\text{C, air}} Y_2Ti_{2-x}Sn_xO_7$

Powder XRD: Phase purity and lattice constants were analyzed using a PANalytical Empyrian powder XRD

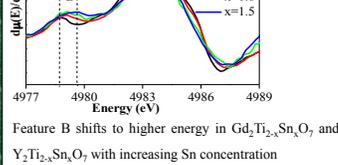
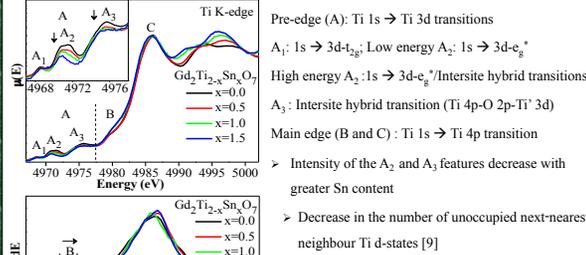
Implantation: Sintered pellets were irradiated with 2 MeV Au^{1+} ions to a fluence of 5×10^{15} ions/cm² using the Tandatron accelerator at Interface Science Western (ISW), University of Western Ontario

XANES: **Beamline:** PNC/XSD-CAT 20-BM beamline at the APS
Data Collection (XANES): 13 element Ge detector, or a single element Vortex detector
Calibration: Ti K-edge: Ti metal (4966 eV), Sn L₃-edge: SnO₂ powder (3929 eV)

DOS calculations: Partial DOS calculated using LMTO - atomic spheres approximation, 512 k-points [8]

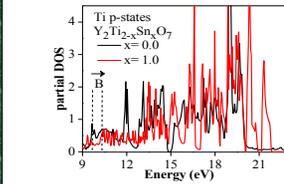


Ti K-edge XANES

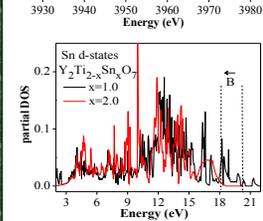
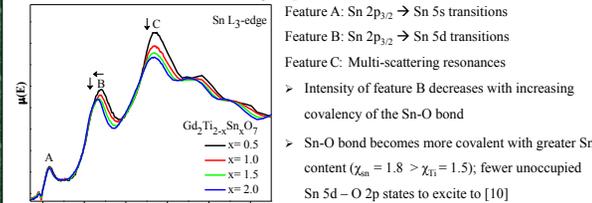


Feature B shifts to higher energy in $Gd_2Ti_{2-x}Sn_xO_7$ and $Y_2Ti_{2-x}Sn_xO_7$ with increasing Sn concentration

- Ionic character of Ti-O bond increases and Ti develops a more positive charge ($\chi_{Ga} = 1.8 > \chi_{Ti} = 1.5$) [10]
- Shift of Feature B confirmed by examination of Ti 4p partial DOS calculations from $Y_2Ti_{2-x}Sn_xO_7$



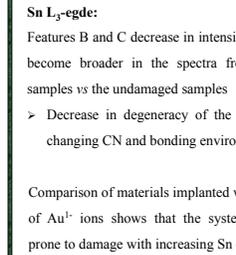
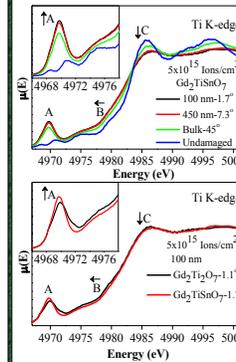
Sn L₃-edge XANES



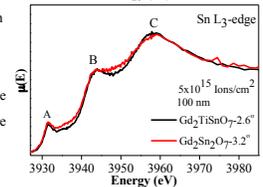
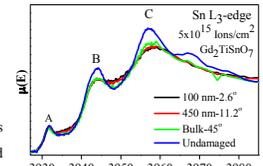
Feature B shifts to lower energy with greater Sn content in $Gd_2Ti_{2-x}Sn_xO_7$ and $Y_2Ti_{2-x}Sn_xO_7$

- Increase in Sn-O bond covalency with greater Sn content; greater screening of Sn nuclear charge
- Confirmed by examination of Sn 5d partial DOS from $Y_2Ti_{2-x}Sn_xO_7$

GA-XANES of damaged materials



Comparison of materials implanted with the same dose of Au^{1+} ions shows that the system becomes more prone to damage with increasing Sn concentration



Conclusions

- Examination of Ti K- and Sn L₃-edge XANES spectra shows that the Ti-O bonds become more ionic while the Sn-O bonds become more covalent in $Gd_2Ti_{2-x}Sn_xO_7$ (and $Y_2Ti_{2-x}Sn_xO_7$) with greater Sn content
- A greater understanding of the effect of covalency on the metal-oxygen bonds has been achieved
- GA-XANES spectra of damaged $Gd_2Ti_{2-x}Sn_xO_7$ samples shows that significant distortions of the Ti and Sn-sites occurs with increasing Sn content
- XANES studies of materials before and after being damaged can assist in developing crystalline oxides for the sequestration of nuclear waste elements

References

- [1] G. R. Lumpkin, K. L. Smith, M. G. Blackford, K. R. Whittle, *Chem. Mater.*, **2009**, 21, 2746-2754. [2] M. Lytle, et al., *Plant.*, **1998**, 206, 293-299. [3] F. de Groot, *Chemical Reviews.*, **2001**, 101, 1779-1808. [4] D.P. Reid, N.C. Hyatt, *Nucl. Instrum. Met. Phys. Res. B.* **2010**, **268**, 1847-1852. [5] B. C. Chakoumakos, *Pyrochlore, McGraw-Hill Yearbook of Science & Technology 1987*, Boston, 1986,393. [6] R. D. Shannon, *Acta Cryst.*, **1976**, A32, 751-767. [7] K. W. Eberman, Ph.D. Thesis, M.I.T, Cambridge, 1998. [8] O. K. Andersen, O. Jepsen, *Phys. Rev. Lett.*, **1984**, 53, 257. [9] J. A. Sigrist, M. W. Gaultois, A. P. Grosvenor, *J. Phys. Chem. A.* **2011**, 115, 1908-12. [10] A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **1958**, 5, 264. [11] Westre, T. E.; Kennepohl, P.; DeWitt, J. G.; Hedman, B.; Hodgson, K. O.; Solomon, E. I., *J. Amer. Chem. Soc.*, **1997**, 119 (27), 6297-6314

Acknowledgements

Dr. Robert Gordon (PNC/XSD-CAT; APS), Mr. Jack Hendrix (ISW)

