Pyrochlore-defect Fluorite Phase Transitions and Stability in the $Y_2Sn_{2-x}Zr_xO_7$ System

Massey de los Reyes[1*], Karl R Whittle[1], Robert G Elliman[2], Nestor J Zaluzec[3], Sharon E Ashbrook[4], Martin R Mitchell[4], Gregory R Lumpkin[1]

[1]Institute of Materials Engineering, Australian Nuclear Science and Technology Organisation, Sydney, NSW 2234, Australia

[2]Department of Electronic Materials Engineering, Research School of Physics and Engineering, Australian National University, Canberra ACT 0200, Australia

[3]Materials Science Division, Argonne National Laboratory, Chicago, IL 60439, United States

[4]School of Chemistry, University of St. Andrews, St. Andres, Fife KY16 9AR, United Kingdom

*Corresponding author: Email mry@ansto.gov.au

Abstract: The $Y_2Sn_{2-x}Zr_xO_7$ pyrochlore series undergoes a phase transformation from a cubic pyrochlore structure type (Fd3m) to defect fluorite (Fm3m) actuated by an increase in Zr content, coupled with thermal annealing above 1500 °C. X-ray diffraction analysis reveals the onset of a pyrochlore to defect fluorite transition at $Y_2Sn_{0.8}Zr_{1.2}O_7$ with the loss of long range ordering. This is confirmed further by selected area electron diffraction (SAED) illustrating shorter range ordering in the defect fluorite phase incommensurate with unit cell size. This transformation however, occurs at a much higher Zr content than that predicted by classical radius ratio models. The diffuse scattering features observed in electron diffraction patterns of defect fluorite phases indicate some form of shorter range ordering involving compositional-displacive structural modulation. The behaviour of these materials during irradiation will be discussed and linked with the observed structural parameters (diffuse scattering, unit cell size).

Introduction: The development of radiation resistant materials has been an area of increasing interest over the years, particularly with the competitive position of nuclear fusion reactors as potential contributors to sustainable future energy [1]. A great deal of effort has centred upon the mechanisms that govern radiation tolerance in materials, especially complex oxides, with research focused primarily on understanding the cumulative decay processes of encapsulated radionuclides over time as well as the simulation of both α-decay and neutron damage effects using ion beam irradiation[7-9]. In amongst promising materials, fluorite and fluorite related structures such as pyrochlore and zirconolite have been found exceptionally popular due to their compositional diversity and structural compatibility with radionuclide species [2,3]. Previous studies have shown compositions such as $Y_2Zr_2O_7$ and $Y_2Hf_2O_7$ exceptionally stable to heavy ion irradiation, maintaining its structure at 25 K using 1.5 MeV Xe^+ [4,5]. Additionally, $Y_2Sn_2O_7$ is one of the most radiation resistant of the pyrochlores, retaining its crystallinity at fluences of up to 6×10^{15} ions/cm^2 with 1 MeV Kr^{2+} irradiation at room temperature [6].

Figure 1 shows a set of four representative SAED patterns in this series, providing direct evidence of the materials microstructure. Typically, the sharp diffraction maxima observed in Fig. 1a associates well to a highly ordered pyrochlore unit cell showing weak superlattice diffraction spots in amongst brighter reflections indexed according to a fluorite-type unit cell. When the amount of Zr is increased, diffraction turns from pyrochlore (doubling of the fluorite structure type) to defect fluorite as observed from the decrease in prominent diffraction spots along the [110] zone axis (Fig. 1b-d). At the same time, this change also brings about the onset of a few remnant spots around fundamental Bragg reflections, which correlate to diffuse scattering or satellite reflections that are characteristic of modulated structures. These patterns indicate a type of intermediate ordering between pyrochlore and fluorite type structures.

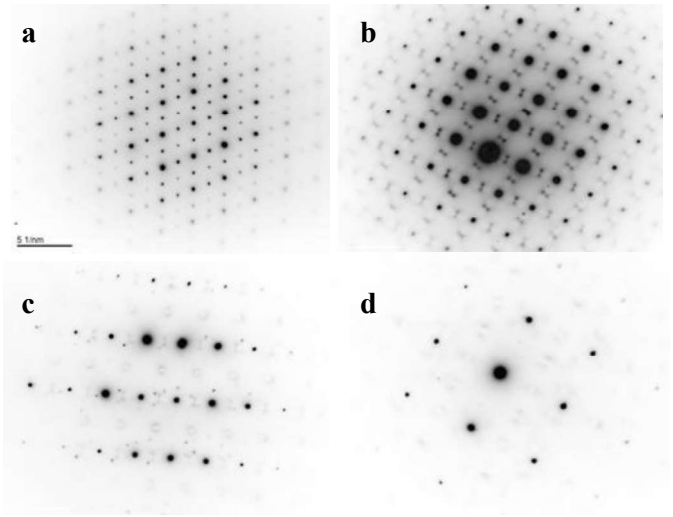

Fig 1. Selected area diffraction patterns of **a**. $Y_2Sn_2O_7$, **b**.$Y_2Sn^{0.8}Zr_{1.2}O_7$ **c**. $Y_2Sn0.{}_6Zr_{1.4}O_7$and **d**. $Y_2Zr_2O_7$

Upon irradiation, it can be seen that compositions with the fluorite structure type appear radiation resistant with no such evidence for a crystalline-to-amorphous phase transition. In Fig. 2, all Bragg spots belonging to fluorite are still prominent in SAED patterns for $Y_2Sn_{0.4}$ $Zr_{1.6}O_7$ when subjected to 1 MeV Kr^{2+} irradiation at room temperature.

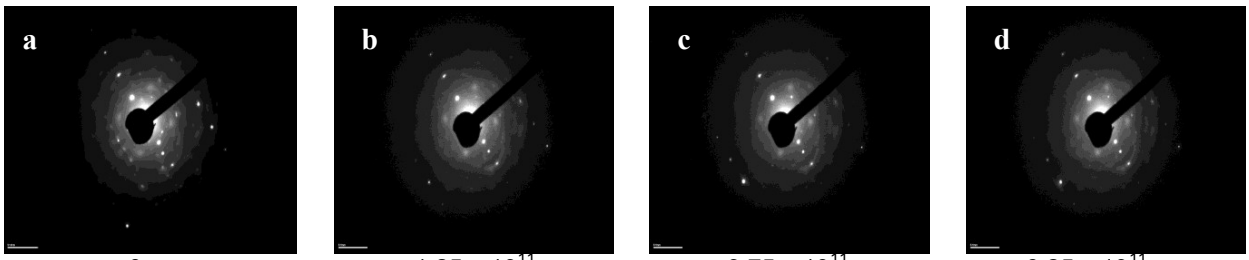

Fig 2. Sequence of SAED patterns along the [110] zone axis for $Y_2Sn_{0.4}Zr_{1.6}O_7$ exposed to 1 MeV Kr^{2+} irradiation. The corresponding dose has been listed below the diffraction patterns in ions/cm^2.

Acknowledgements

The authors thank the IVEM-Tandem Facility staff, especially P. Baldo and E. Ryan at Argonne National Laboratory for their assistance during irradiation work. We acknowledge financial support from the Access to Major Research Facilities Programme (a component of the International Science Linkages Programme established under the Australia Government's innovation statement, Backing Australia's Ability).

References

[1] K. L. Murty, I. Charit, "Structural materials for Gen-IV nuclear reactors: Challenges and opportunities", J. Nucl. Mater, vol. 383, pp. 189-195, 2008.

[2] K.E Sickafus, "Radiation tolerance of complex oxides", Science, vol. 289, pp. 748-751, 2000

[3] R. C. Ewing, J. Lian, L.M. Wang, "Ion beam-induced amorphisation of the pyrochlore structure-type: A review", MRS Proceedings, vol. 792, pp. 37-48, 2003.

[4] G. R. Lumpkin, K. R. Whittle, S. Rios, K. L. Smith, N. J. Zaluzec, "Temperature dependence of ion irradiation damage in the pyrochlores $La_2Zr_2O_7$ and $La_2Hf_2O_7$", J. Phys: Condens. Matter, vol. 16, pp. 8557-8570, 2004.

[5] K. E. Sickafus, R. W. Grimes, J. A. Valdez, A. Cleave, M. Tang, M. Ishimaru, S. M. Corish, C. R, Stanek, B. P. Uberuaga, "Radiation-induced amorphisation resistance and radiation tolerance in structurally related oxides, Nat. Mater, vol. 6, pp. 217-233, 2007.

[6] R. Devanathan, "Radiation damage evolution in ceramics", Nucl. Instr. Meth. Phys. Res. B, vol. 267, pp. 3017–3021, 2009.