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Radiation Tolerance of $A_2B_2O_7$ compounds at the Cubic-Monclinic Boundary

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Ceramic waste forms (CWF) provide attractive alternatives to the direct disposal of spent fuel or the immobilisation of high-level radioactive waste in borosilicate glass waste forms, due to their compliance with the principle nuclear safeguards agreements and relatively high aqueous durability respectively [1]. Over the design lifetime of CWFs, the actinide waste species they incorporate will undergo alpha decay releasing alpha particles and alpha recoil nuclei. These particles interact with host lattices. In some cases, this will lead to crystalline-amorphous transformations, volume expansion, cracking and reduced chemical durability due to increased surface area and decreased thermodynamic stability. Consequently there have been many studies of the radiation damage response of various potential waste form phases: including pyrochlores, defect fluorites, perovskites etc. [1, 2].

Some aspects of alpha decay damage can be simulated by irradiation with heavy ions. Consequently many *in situ* ion irradiation experiments have been conducted on various complex oxides. Two important parameters established in such studies are: the critical amorphisation dose, D_c, at a particular temperature and the critical temperature above which a material remains crystalline, T_c.

Recently Lumpkin et al. [3] compiled composition, structure and radiation damage data for 19 pyrochlore and defect fluorite $A_2B_2O_7$ compounds, applied multiple linear regression methods to their data and derived the following empirical equation for predicting T_c.

$$T_c = - 29738.6\ (x_{48f}) + 8457.7\ (a_0) - 1148.8\ (\text{ENDiff}) + 939.7\ (E_{dis}) \quad \ldots\ldots\ldots (1)$$

Where: x_{48f} is the x coordinate of oxygen atom on 48f position; a_0 is the unit cell dimension; ENDiff is the classical Pauling electronegativity difference and E_{dis} is the cation antisite and anion Frenkel disorder energy (goodness of fit: $R^2 = 0.991$; SD = 82.2 K). In essence, this parameterisation shows correlation of radiation tolerance of $A_2B_2O_7$ compounds with a change in the structure from pyrochlore to defect fluorite, a smaller unit cell dimension and lower cation-anion disorder energy.

$A_2Ti_2O_7$ compounds (where A is a lanthanide) form: defect fluorites when the ratio of the average ionic radii of the cations (r_A/r_B) is less than ~1.46; pyrochlores when r_A/r_B falls between 1.46 & 1.80 (eg. A = Lu to Eu for B = Ti) and layered perovskite-type phases when r_A/r_B greater than ~1.80. A subset of the data collated by Lumpkin et al. show that the T_c values of $A_2Ti_2O_7$ compounds increase with the ratio of the average ionic radii of metal cations to that of the anions (r_M/r_X) for A = Lu to Gd, then level off close to the cubic to monoclinic phase boundary for A = Eu & Sm. The purpose of this study was to probe the effect of structure &/or symmetry on T_c in $A_2Ti_2O_7$ compounds.

In this study, the radiation damage responses of one pyrochlore ($Gd_2Ti_2O_7$) and two layered perovskite phases ($La_2Ti_2O_7$, $Nd_2Ti_2O_7$) were monitored *in situ* during irradiation with 1 MeV Kr^{2+} ions using the Intermediate Voltage Electron Microscope-Tandem User Facility (IVEM-T) at Argonne National Laboratory. Figure 1 shows D_c versus T data for these compounds. Figure 2 shows T_c versus r_M/r_X data for the $A_XTi_2O_7$ compounds collected in this and previous studies. The measured T_c values

of $A_2B_2O_7$ compounds increase with r_M/r_X for A = Lu to Gd, then decrease for A = Eu to La. Given that our earlier work [3] shows there are a number of controls on the accumulation and recovery of radiation induced defects, it is reasonable to say that the change in slope of the curve of T_c versus r_M/r_X values of $A_2B_2O_7$ compounds occurs in the vicinity of the boundary between cubic and monoclinic symmetry.

Data from this and previous studies have elucidated the radiation damage response of $A_2Ti_2O_7$ phases at the boundary between cubic and monoclinic symmetry. Work is currently underway to develop empirical models capable of predicting the radiation damage response of different structural types.

References

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[4] The authors thank the IVEM-Tandem Facility staff at Argonne National Laboratory for assistance during ion irradiations. The Facility is supported as a User Facility by the U.S. DOE, Basic Energy Sciences, under contract W-31-10-ENG-38. Support for travel was provided by the Aust. Govt. funded Access to Major Research Facilities Program.

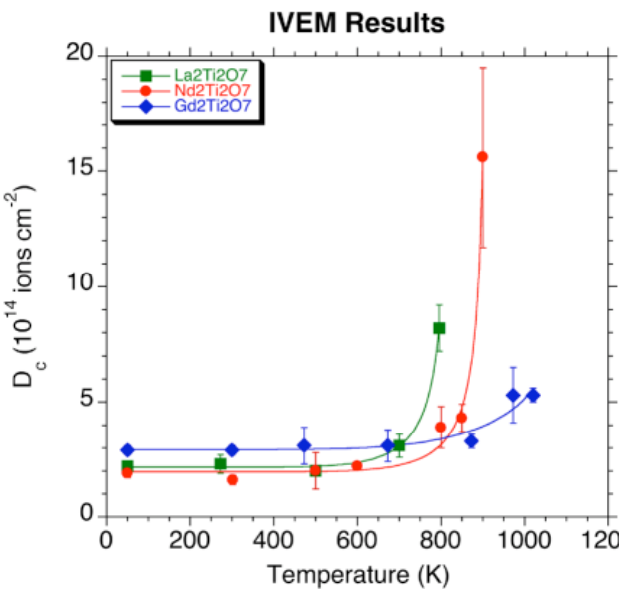

Figure 1. D_c (the critical dose for amorphisation) versus T data for $Gd_2Ti_2O_7$ (pyrochlore), $Nd_2Ti_2O_7$ and $La_2Ti_2O_7$ (layered perovskites).

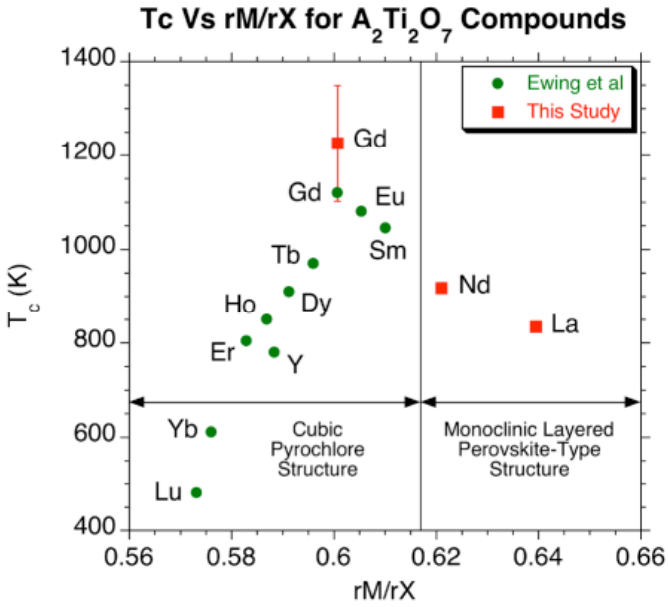

Figure 2. T_c (the critical temperature above which a material cannot be rendered amorphous) versus r_M/r_X (the ratio of the ionic radii of metal cations to that of the anions) for various $A_2Ti_2O_7$ compounds.

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