RADIATION TOLERANCE OF $A_2Ti_2O_7$ COMPOUNDS AT THE CUBIC-MONOCLINIC BOUNDARY

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1. Introduction

Ceramic waste forms provide attractive alternatives to the direct disposal of spent fuel or the immobilisation of high-level radioactive waste in borosilicate glass. They are particularly suited for the disposal of actinide wastes (e.g., from partitioning strategies, or for excess Pu from defence purposes) and furthermore they exhibit very low dissolution rates in aqueous fluids, making them attractive candidates for certain repository scenarios (e.g., deep disposal). For general background information on these materials, including studies of the crystal chemistry, aqueous durability, and the behaviour of natural analogues in geological systems, readers are referred to references [1-4]. Over the design lifetime of ceramic waste forms, the actinide elements will undergo alpha decay, resulting in damage to the crystalline structure primarily due to alpha-recoil collision cascades. In certain materials, this will lead to a crystalline-amorphous transformation accompanied by volume expansion and reduced chemical durability. The performance in aqueous fluids may be compromised by cracking, increased surface area, and decreased thermodynamic stability of the amorphous phase. Consequently, the radiation damage effects have been of particular interest in ceramic waste forms. Detailed reviews of radiation damage effects can be found in references [5-7].

Some aspects of the alpha decay process have been simulated by irradiation with heavy ions under controlled experimental conditions. In this study, we conducted *in situ* ion irradiation experiments using the IVEM-Tandem Facility at Argonne National Laboratory to determine the radiation response of $Gd_2Ti_2O_7$ pyrochlore and two monoclinic, layered perovskite-type phases, $Nd_2Ti_2O_7$ and $La_2Ti_2O_7$. For each compound, the critical amorphization dose $\boldsymbol{D_c}$ was determined as a function of temperature and used to establish $\boldsymbol{T_c}$, the critical temperature, above which the compound remains crystalline. Together with previous data for the $A_2Ti_2O_7$ compounds, our results show a clear reversal in the trend of $\boldsymbol{T_c}$ versus the cation-anion radius ratio $\boldsymbol{r_M/r_X}$.

Our experimental results are discussed in the general context of the potential factors that control the susceptibility of a given compound to amorphisation, which include aspects of the structure, bonding, and disorder energy. For the $A_2Ti_2O_7$ compounds we also show that the critical temperature correlates with the electronic structure (e.g., $4f$ occupancy) of lanthanide cations. This appears to be a unique result in the world of ion irradiation studies, but the story is complicated by the phase transition from pyrochlore to the layered perovskite structure in this system. Our ultimate goal here is to illustrate the need for a detailed understanding of the physical processes of radiation damage and the potential for predictive modelling of waste form performance.

2. Ion Irradiation Experiments

The data discussed in this paper have been obtained by a number of investigators using *in situ* ion irradiation of thin TEM samples at the IVEM-Tandem Facility using 1.0 or 1.5 MeV Kr ions. The IVEM, or Intermediate Voltage Electron Microscope, is equipped with sample holders capable of cooling and heating the specimen during ion irradiation. Thus, the irradiations can be performed over a range of temperature, with the typical output being a plot of the critical amorphisation dose versus temperature. A detailed description of the experimental procedures and practical issues relating to the use of thin TEM samples can be found elsewhere [8] and is not repeated here. Our experiments with $Gd_2Ti_2O_7$, $Nd_2Ti_2O_7$, and $La_2Ti_2O_7$ were performed using 1.0 MeV Kr ions. Results of these experiments are shown in Figure 1 where we find that the two monoclinic, layered perovskite-type compounds with A = Nd and La have an intercept dose close to 2 x 10^{14} ions cm^{-2} compared with 3 x 10^{14} ions cm^{-2} for the pyrochlore with A = Gd. These values are typical of titanate compounds that amorphise easily. Note, however, that the curves for the two monoclinic compounds increase rapidly above about 700 K and cross the curve for $Gd_2Ti_2O_7$. This indicates that the critical temperatures of the monoclinic compounds are lower than that of the cubic pyrochlore.

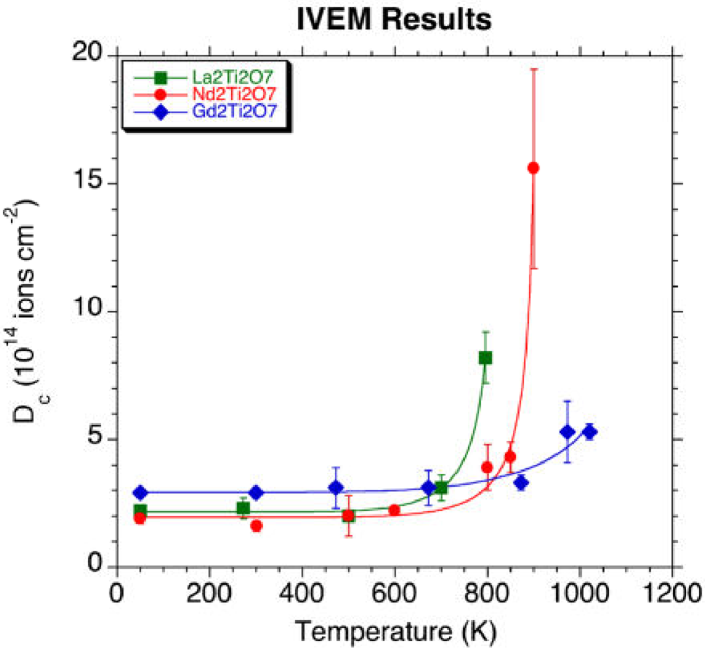

Figure 1 Plot of the critical amorphisation dose versus temperature for $Gd_2Ti_2O_7$ pyrochlore and two layered perovskites, $Nd_2Ti_2O_7$ and $La_2Ti_2O_7$.

For each compound, the dose-temperature curves can be analysed using non-linear least squares methods to extract the critical temperature for amorphisation (**T_c**), the intercept dose at zero Kelvin (**D_{c0}**), and the activation energy for damage recovery (**E_a**), based on Equation (1) given below:

$$D_c = D_{c0}/(1 - e[(E_a/k)(1/T_c - 1/T)]) \qquad (1)$$

Although the activation energies calculated using this equation are often unrealistically low (e.g., < 0.1 eV), it is useful for the determination of both the intercept dose and critical temperature. The latter parameter is most commonly used for studies of radiation tolerance and our data reveal **T_c** values of 1226 ± 123 K for $Gd_2Ti_2O_7$, 918 ± 3 K for $Nd_2Ti_2O_7$, and 835 ± 7 K for $La_2Ti_2O_7$. The value determined in this study for $Gd_2Ti_2O_7$ is somewhat higher than that given in previous work (1120 K) summarised by Ewing et al. [7], but this does not affect the trend of the data or the basic conclusion of this work.

Including data from the literature, the critical temperatures of the $A_2Ti_2O_7$ pyrochlore compounds are shown in Figure 2 as a function of the cation-anion radius ratio (**r_M/r_X**), a classical Pauling crystal structure parameter. Figure 2 shows that all of the lanthanide titanate pyrochlores can be amorphised and that they have critical temperatures above about 430 K. However, we can now see that the critical temperature rises dramatically with increasing cation-anion radius ratio from Lu to Gd, then decreases again from Eu to La. Interestingly, this two part trend appears to be related to the 4*f* electron occupancy of the lanthanide cation which decreases from 14 for Lu^{3+} (full 4*f* occupancy) to 7 for Gd^{3+} (4*f* exactly half filled) to 0 for La^{3+}. Another aspect of our current work, shown in Figure 2, is the phase transformation from pyrochlore to the layered perovskite structure, which at room temperature occurs between the compounds with A = Sm and Nd. The presence of this phase transition suggests that there may be structural controls on the damage recovery process.

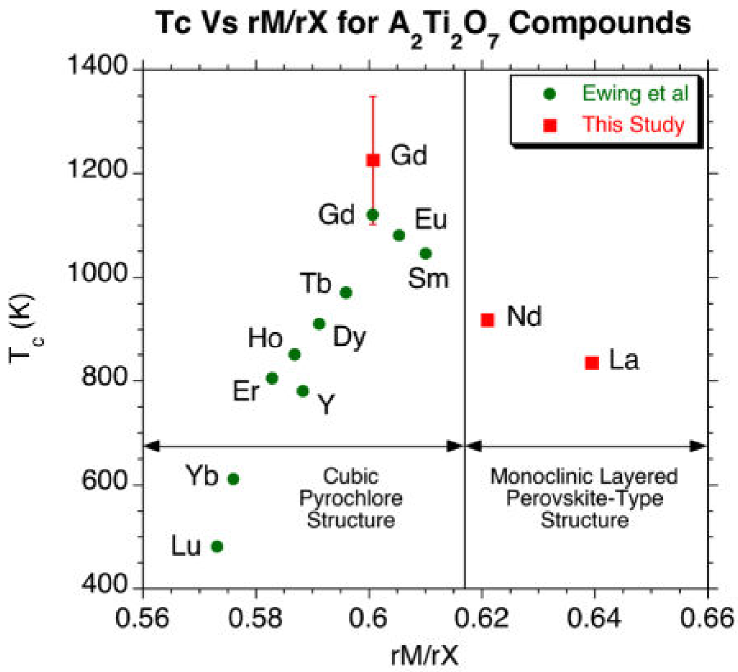

Figure 2 Plot of the critical amorphisation temperature versus the metal cation to anion radius ratio for 12 compounds. Note the peak in T_c *at Gd and the position of the room temperature phase transition from pyrochlore to the layered perovskite phase between Sm and Nd*

3. Empirical models and predictions

In a more general analysis of a larger data set for pyrochlore and defect fluorite compounds, we previously performed a statistical analysis for synthetic samples with A = a trivalent lanthanide element and B = tetravalent Ti, Zr, Sn, or Hf. The analysis was conducted using multiple linear regression methods, with T_c as the dependent variable. The following independent variables were considered: the X anion coordinate (x_{48f}), unit cell edge (a_0), cation radius ratio (r_A/r_B), cation-anion radius ratio (r_M/r_X), the classical anion-cation Pauling electronegativity difference between the average metal cation and oxygen (ΔX_p), and the anion Frenkel-cation antisite disorder energy (E_{dis}) as determined by computational methods [9]. The best statistical model derived from these data relates the critical temperature to the following structural, bonding, and energy parameters:

$$T_c = -29738.6(x_{48f}) + 8457.7(a_0) - 1148.9(\Delta X_p) + 939.7(E_{dis}) \qquad (2)$$

The model presented above is highly significant with $R^2 = 0.991$ and a standard deviation of 82 K for the predicted value of T_c. We have also demonstrated that Equation (2) is capable of predicting the critical temperatures of compounds that were not used in the model (see Table 1). In recent work performed at the IVEM-Tandem Facility, we used Equation (2) as a guide for planning our experiments on pyrochlore and defect fluorite compounds in the $La_{2-x}Y_xHf_2O_7$, $Nd_2Ti_{2-x}Zr_xO_7$, and $Y_2Ti_{2-x}Sn_xO_7$ series with a fair degree of success, although the preliminary results suggest that the predictions for the Sn pyrochlores are systematically higher than the observed critical temperatures. Furthermore, we have predicted the critical temperatures for two natural pyrochlore compounds $NaCaNb_2O_6F$ and $NaCaTa_2O_6F$. Even though they are not III-IV pyrochlores, the critical temperatures of the two natural samples are also predicted reasonably well by the empirical model, suggesting that this model or a development thereof, might be applicable to pyrochlore compounds in general, although this remains to be tested in detail.

Compound	Observed T_c	Predicted T_c
$La_{1.6}Y_{0.4}Hf_2O_7$	500 K	470 K
$Nd_2Zr_{1.2}Ti_{0.8}O_7$	~ 780 K	580 K
$Y_2Ti_{1.6}Sn_{0.4}O_7$	670 K	710 K
$Y_2Ti_{1.2}Sn_{0.8}O_7$	330 K	550 K
$Y_2Ti_{0.4}Sn_{1.6}O_7$	< 150 K	200 K
$NaCaNb_2O_6F$	730 K	790 K
$NaCaTa_2O_6F$	880 K	730 K

Table 1 Observed and predicted critical temperatures for pyrochlore compounds

The empirical model presented above indicates that the critical temperature is negatively correlated with the x_{48f} anion coordinate, e.g., T_c decreases as the structure becomes more fluorite-like. The unit cell parameter a_0, much like r_M/r_X, exhibits a positive correlation with T_c, indicating that radiation tolerance is correlated with a smaller unit cell dimension and hence a smaller unit cell volume. The volume, of course, would be a useful variable when comparing the behaviour of different structure types. The model also demonstrates that the electronegativity difference is negatively correlated with the critical temperature, indicating that radiation tolerance is promoted by increased ionic bonding between all atoms of the structure. The positive correlation between T_c and E_{dis} indicates that radiation tolerance is favoured by lower cation antisite – anion Frenkel disorder energies in the III-IV pyrochlore composition space.

Using the above empirical model, we determined the T_c response surface for III-IV pyrochlores as a function of the ionic radii of the A-site and B-site cations. The results are presented in Figure 3 in the form of a two dimensional contour map of the predicted critical temperature. The T_c contours are nearly horizontal in the vicinity of the smaller B-site cations such as Ti, Ru, and Mo (r_B = 0.060-0.065 nm), but curve upwards toward the right side of the figure in the vicinity of the larger B-site cations Sn, Hf, and Zr (r_B = 0.069-0.072 nm). The form of the contour lines in Figure 3 also reflect, to a certain extent, the data plotted in Figure 2 by rising steeply from zero Kelvin and then showing a decline in the rate of temperature change at the higher temperatures. This result is consistent with the rollover of T_c observed for $A_2Ti_2O_7$ compounds.

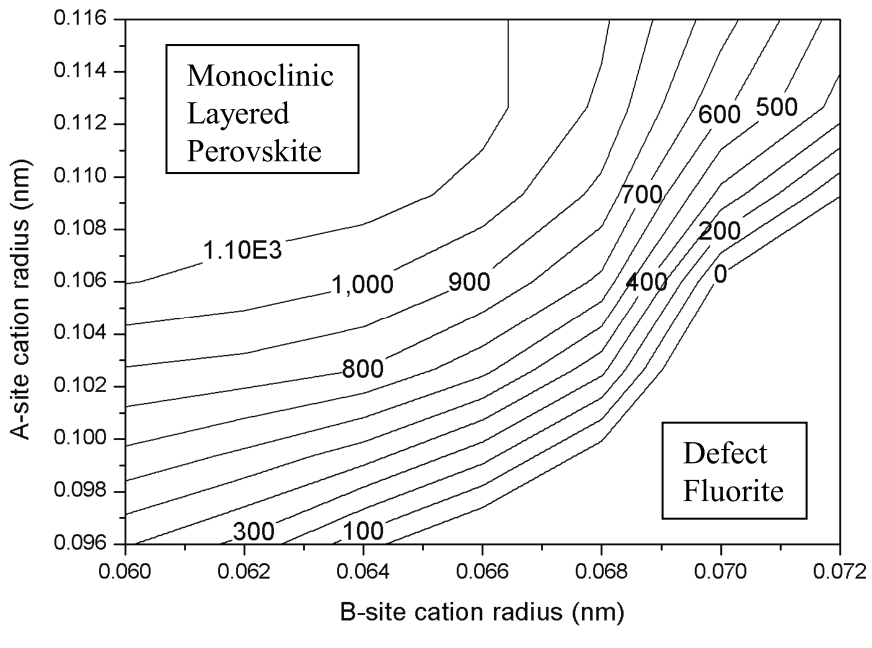

Figure 3 Predicted critical temperatures for III-IV $A_2B_2O_7$ compounds. Pyrochlore structures exist between the stability fields of layered perovskite and defect fluorite (schematic only)

4. Discussion

A recent review of radiation damage effects in oxide pyrochlores by Ewing and coworkers [7] illustrated the importance of electronic structure and bonding through comparison of compositions with otherwise similar properties such as the A-B cation radius ratio. In this paper, we demonstrate an apparent relationship between the 4*f* electron occupancy of the lanthanide cation with $\boldsymbol{T_c}$ in $A_2Ti_2O_7$ compounds, although this effect is complicated by the pyrochlore – layered perovskite phase transition. One possible interpretation of this work is that there are fundamental differences in the radiation damage response of the pyrochlore and layered perovskite structures. This possibility would have to be tested by conducting (if possible) ion irradiation experiments on different polymorphs of the same compound.

Based on the results of *ab initio* calculations of structure and bonding of simple oxides, Trachenko and coworkers [10, 11] suggested that short-range covalent and long-range ionic contributions to the total force field between any given pair of atoms interact to produce a “landscape” of potential energy. The full three-dimensional expression of this landscape, with its various energy minima (and activation barriers) in a crystal determines the ability to recover the disorder produced by an atomic collision cascade. In this scenario, short-range covalent contributions lead to highly directional bonds and a number of distinct potential energy minima that act as barriers to recovery of periodicity in the vicinity of the collision cascade. Long-range ionic contributions simplify the energy landscape, thereby minimizing the barriers to recovery of atomic periodicity. Although the use of simple parameters such as the Pauling electronegativity difference has limited value, the empirical model discussed in the present work does support the role of ionicity in promoting radiation tolerance in pyrochlore compounds. However, the model also indicates that structural and energetic parameters are also important, and recent studies have also revealed correlations between $\boldsymbol{T_c}$ and thermodynamic properties (e.g., enthalpy of formation from the oxides) [12, 13].

Finally, we note some caveats to this work and briefly mention future research directions. The predictive model described above is strictly applicable only to pyrochlore – defect fluorite thin films irradiated with 1.0 MeV Kr ions as $\boldsymbol{T_c}$ is known to vary with ion mass and energy. Therefore, there is a clear need to address the mass-energy effects as well as the behaviour of thin films versus bulk samples. This issue is related in part to the possible effects of surface area on the properties of thin film specimens, for example, the surface itself may serve as a sink for defects thereby changing the properties of the thin film with respect to the bulk material. The linear regression method employed hitherto has limitations, thus some effort is being directed toward the application of non-linear methods. We are currently investigating the potential application of other measures of bonding in these materials. Provided that a useful set of parameters sensitive to radiation response exist, then similar analyses could be performed for other compounds, thus providing valuable information on the role of structure type, bonding, and other properties on radiation tolerance.

5. Conclusion

We have shown that an apparent relationship exists between the 4*f* electron occupancy of the lanthanide cation with the critical temperature for amorphisation in $A_2Ti_2O_7$ compounds with A = Y or lanthanides from La to Lu. This observation is complicated by the presence of a structural phase transition from pyrochlore to a layered perovskite-type phase in this system. In more general terms, this study shows that radiation damage data can be statistically quantified as a function of structural, bonding, and disorder energy parameters. Furthermore, we suggest that the statistical approach may be generally applicable to pyrochlore systems with a range of A-site and B-site cation valence combinations. Together with predictive models based on radiation damage kinetics [7], the empirical approach offers an attractive means to predict waste form performance. However, it is clear that a major effort is still required in order to understand the details of radiation tolerance in these complex systems.

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7. References

[1] Fielding P.E. and White, T.J., “Crystal chemical incorporation of high level waste species in aluminotitanate-based ceramics: valence, location, radiatio damage, and hydrothermal durability”, *Journal of Materials Research*, Vol. **2**, 1987, pp. 387-414

[2] Stefanovsky S.V., Yudintsev S.V., Gieré R., and Lumpkin G.R., “Nuclear waste forms”, In Gieré R. and Stille P. (eds.), Energy, Waste, and the Environment: a Geochemical Perspective, Geological Society, London, Special Publications, Vol. **236**, 2004, pp. 36-63

[3] Lumpkin G.R., “Alpha-decay damage and aqueous durability of actinide host phases in natural systems”, *Journal of Nuclear Materials*, Vol. **289**, pp. 136-166

[4] Lumpkin G.R., Smith K.L., Gieré R., and Williams C.T., “Geochemical behaviour of host phases for actinides and fission products in crystalline ceramic nuclear waste forms”, In Gieré R. and Stille P. (eds.), Energy, Waste, and the Environment: a Geochemical Perspective, Geological Society, London, Special Publications, Vol. **236**, 2004, pp. 89-111

[5] Ewing R.C., Weber W.J., and Clinard F.W. Jr., “Radiation effects in nuclear waste forms for high-level radioactive waste”, *Progress in Nuclear Energy*, Vol. **29**, 1995, pp. 63-127

[6] Weber W.J., Ewing R.C., Catlow C.R.A., Diaz de la Rubia T., Hobbs L.W., Kinoshita C., Matzke Hj., Motta A.T., Nastasi M., Salje E.K.H., Vance E.R., and Zinkle S.J., “Radiation effects in crystalline ceramics for the immmobilization of high-level nuclear waste and plutonium”, *Journal of Materials Research*, Vol. **13**, 1998, pp. 1434-1484

[7] Ewing R.C., Weber W.J, and Lian J., “Nuclear waste disposal – pyrochlore ($A_2B_2O_7$): nuclear waste form for the immobilization of plutonium and “minor” actinides”, *Journal of Applied Physics*, Vol. **95**, 2004, pp. 5949-5971

[8] Lumpkin G.R., Whittle K.R., Rios S., Smith K.L., and Zaluzec N.J., “Temperature dependence of ion irradiation damage in the pyrochlores $La_2Zr_2O_7$ and $La_2Hf_2O_7$”, *Journal of Physics: Condensed Matter*, Vol. **16**, 2004, pp. 8557-8570

[9] Minervini L., Grimes R.W., and Sickafus K.E., “Disorder in pyrochlore oxides”, *Journal of the American Ceramic Society*, Vol. **83**, 2000, pp. 1873-1878

[10] Trachenko K., “Understanding resistance to amorphization by radiation damage”, *Journal of Physics: Condensed Matter*, Vol. **16**, 2004, pp. R1491-R1515

[11] Trachenko K., Pruneda J.M., Artacho E., and Dove M.T., “How the nature of the chemical bond governs resistance to amorphization by radiation damage”, *Physical Review B*, Vol. **71**, 2005, paper 184104, pp. 1-5

[12] Helean K.B., Ushakov S.V., Brown C.E., Navrotsky A., Lian J., Ewing R.C., Farmer J.M., and Boatner L.A., “Formation enthalpies of rare earth titanate pyrochlores”, *Journal of Solid State Chemistry*, Vol. **177**, 2004, pp. 1858-1866

[13] Lian J., Helean K.B., Kennedy B.J., Wang L.M., Navrotsky A., and Ewing R.C., "Effect of structure and thermodynamic stability on the response of lanthanide stannate pyrochlores to ion beam irradiation", *Journal of Physical Chemistry B*, Vol. **110**, 2006, 2343-2350