

Radiation Tolerance of $A_2Ti_2O_7$ Materials - A Question of Bonding?

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ABSTRACT

The resistance of $Ln_2Ti_2O_7$ (Ln = lanthanide) compounds to radiation damage is an important topic in the understanding and development of new materials by which radioactive nuclear waste can safely be immobilised. A model has been developed, from previously published density functional theory and molecular orbital theory simulations of the band structure for $Ln_2Ti_2O_7$ materials. This model provides a chemical interpretation of radiation stability.

INTRODUCTION

Ceramic waste forms provide attractive properties, in comparison with borosilicate glasses, for the direct disposal of actinides, due to their enhanced leach resistance and long term durability. $A_2B_2O_7$ compounds (which include materials with pyrochlore and monoclinic slab perovskite structures), are constituent phases in the SYNROC system of waste storage, and have been proposed by the DOE as the basis for storing U and Pu high-level waste. Over geological time waste forms incorporating radioactive species will experience alpha decay. This can lead to swelling and cracking that might affect durability. The response of pyrochlores to radiation damage is complex and controlled by several factors. For example, $La_2Zr_2O_7$ and $La_2Hf_2O_7$ behave differently under identical conditions [1], $La_2Zr_2O_7$ being more resistant to radiation damage than $La_2Hf_2O_7$. However, the mechanism for the increased stability is not fully understood, and a proposed theory based on molecular orbitals is proposed in this paper for the $Ln_2Ti_2O_7$ series of compositions.

$Ln_2Ti_2O_7$ – STRUCTURE TYPES

The $Ln_2Ti_2O_7$ compounds can exist in two different structural forms at room temperature: pyrochlore and a monoclinic layered perovskite, primarily dependent on the radius ratio of the A and B cations, e.g., La and Ti. As outlined below the predominant stability range for pyrochlore is R_a/R_b of 1.46-1.78, in these samples pyrochlore is found for Sm-Lu, while a monoclinic relative of perovskite is found for La, Pr and Nd.

In the systems $La_2Ti_2O_7$, $Pr_2Ti_2O_7$ and $Nd_2Ti_2O_7$, structurally similar to $Ca_2Nb_2O_7$, the arrangement of the cations is different from pyrochlore and similar to perovskite[2,3]. The Ln-cations are located in four different irregular polyhedra with coordination number ranging from 7 to 9, while the Ti-cations remain octahedrally co-ordinated by oxygen.

The pyrochlore structure type[4,5], $A_2B_2X_6Y$ is a superstructure of the fluorite (MX_2) structure, and is based upon a $2 \times 2 \times 2$ supercell containing M_4O_8 , with ordered vacancies in the

oxide anionic lattice. An alternative description for pyrochlore is that of two interpenetrating 3D networks composed of a B_2X_6 framework in which the (111) layers have the hexagonal tungsten bronze (HTB) topology[5] and an A_2Y anti-cristobalite type network. The A cations are located within the centre of ‘puckered’ hexagonal rings, the chair form, containing six oxygens, located on the 48f site. Normal to the mean plane are two additional 8a oxygens in a linear configuration and the complete set of 8 oxygens gives rise the distorted cubic co-ordination of the A cation. The distance between the A cation and the 8a anion is shorter than the length between the A cation and the 48f oxygen. If this later interaction is disregarded, then the structure can be idealised as two interpenetrating networks. While this is conceptually useful there will always be bonding interaction between the A cations and all the anions which surround them.

RADIATION RESISTANCE OF PYROCHLORES

Previous ion irradiation studies[6-11] of $Ln_2Ti_2O_7$ compounds, show that T_c does not vary linearly across the period. From La to Gd the T_c increases (stability decreases) and from Tb to Lu, the T_c decreases (stability increases). Both of these trends are effectively linear, when plotted as a function of the average cation radius, this is shown in Figure 1.

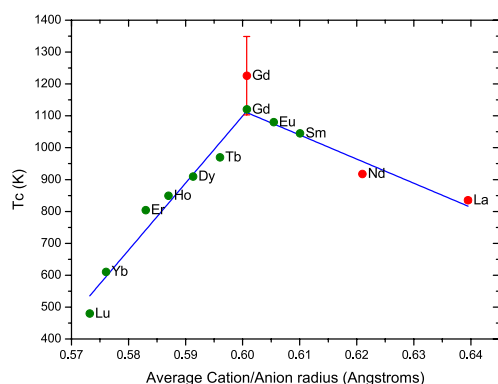


Figure 1. Plot of T_c against average cation/anion radius. Plots for Gd-Lu are from Ewing et al. [7], while La, Nd and Gd are from Smith et al. [10]. The two linear lines are indicators for the semi-linear relationship. The error bars are plotted for La, Nd and Gd from Smith et al.[10].

Previously we have reported a method [12], based on a statistical survey of published irradiation data, for predicting the T_c for pyrochlores based on the electronegativity of the cations, the 48f-x position, unit cell size, and the ionic radius-ratio. This method predicts the T_c to within ~ 80 K.

THE ELECTRONIC BAND STRUCTURE OF $Ln_2Ti_2O_7$ COMPOUNDS

There have been two reports on the electronic band structure of both monoclinic and pyrochlore structure types for $Ln_2Ti_2O_7$. The band structure of $La_2Ti_2O_7$ has been published by Hwang et al., [13] using DFT calculations, and a summary of the results are shown below:

- i) The valence bands are primarily composed of O-2p, which are partially hybridized with Ti-3d. The contribution from La-orbitals is very small as spatially they are not close enough to allow orbital overlap.
- ii) The conduction band is primarily Ti-3d in character, but these are split into two bands with the O-2p, probably due to crystal-field splitting. The La-4f and La-5d orbitals, unoccupied and partially localized, do contribute to the conduction band.

When crystalline samples, $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{PrLaTi}_2\text{O}_7$, $\text{Pr}_2\text{Ti}_2\text{O}_7$, $\text{Nd}_2\text{Ti}_2\text{O}_7$, and $\text{NdLaTi}_2\text{O}_7$ were prepared and examined by diffuse reflectance spectroscopy it was determined that increasing the 4f electrons would lower the Ln-4f level. This lower Ln-4f level would then start to interact with the valence and conduction bands. This is schematically shown in Figure 2 for $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{Pr}_2\text{Ti}_2\text{O}_7$ and $\text{Nd}_2\text{Ti}_2\text{O}_7$. The relationship between the photocatalytic activity and band structure was outlined by Hwang et al[13], and directly related to the band structure of the system.

The pyrochlore titanates Sm-Er, Yb and Lu have had their electronic structure determined by Nemoshkalenko et al., using DFT simulations, and X-ray photoelectron spectroscopy (XPS)[14] and as with the monoclinic systems the two main regions in the structure, the valence and conduction bands, are outlined below:

- i) The valence bands are predominantly formed from the oxygen-2s and lanthanide-5p orbitals, which overlap with the Ti-3p and Ln-5s making recorded XPS difficult to interpret.
- ii) When the peak positions for the three peaks (A, B, C), recorded in the XPS spectra above 20eV, are plotted a trend is seen. This trend is indicated in Figure 2, and shows that the peaks A and B change substantially, while peak C remains fairly constant. Nemoshkalenko et al., assigned the peaks to the following orbital states:
 - i. Peak A, and B – the $\text{Ln-5p}_{1/2}$ and $\text{Ln-5p}_{3/2}$ respectively
 - ii. Peak C – the O-2s derived states, and is assigned to TiO_6 octahedra (48f-oxygen).
- iii) In the range 15-0 eV it is shown that the O-2p is hybridized with the Ti-3d and Ln-5d orbitals, with two features at 3.8eV and 6.4eV. These energy levels are often found in perovskite-like lattices containing TiO_6 octahedra and are indicative of strong hybridisation between the Ti-3d and O-2p orbitals. It is this bonding that is responsible for the ability of the TiO_6 to distort in the $\text{Ln}_2\text{Ti}_2\text{O}_7$ pyrochlores.

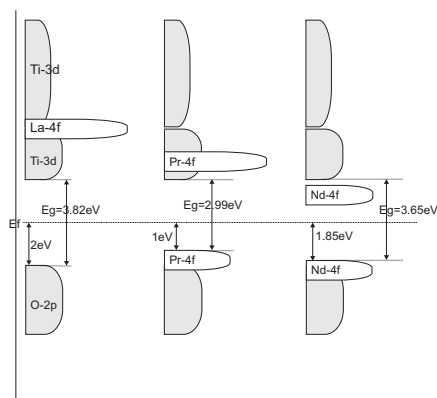


Figure 2. Diagrammatic representation of the orbital structure for $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{Pr}_2\text{Ti}_2\text{O}_7$ and $\text{Nd}_2\text{Ti}_2\text{O}_7$. Image based on that previously published by Hwang et al.[13].

The conduction band is split into two parts; the states above the gap are formed primarily by Ti-3d and O-2p orbitals. These are separated from the Ln-5d orbitals which in turn hybridise with the 8a O-2p orbitals. It should be noted that there is stronger hybridisation within the two networks rather than between the networks. There is some interaction between the Ti-3d and Ln-5d orbitals via O-2p orbitals. It is also noted that this second gap reduces in size due to the downshift of Ln-5d, 8a O-2p, and 48f O-2p interactions and the increase of Ti-3d and O-2p interactions as the Ln is increased from Sm to Gd, and then decreases Dy-Lu.

i.e., decreasing the strength/interaction between the two networks. This is shown schematically in Figure 4.

The above results are outlines from the previous work by Hwang et al.[13], and Nemoshkalenko et al.[14], there is further information present in both papers that for brevity has not been included in this paper. In addition to these papers the reader is recommended to view other works by Panero et al.[15], and Lian et al.[6,11], where similar results are presented. If these results are compared with the equations derived by Lumpkin et al.[12] for pyrochlore based materials, then it can be seen that there is a correlation.

COMPARISON OF BAND STRUCTURES AND PYROCHLORE RADIATION RESISTANCE

If the two previous works are compared with experimental results the following trends are observed:

- i) As the number of singly filled f-orbitals in the structure increases, the f-orbitals begin to decrease in energy, the higher energy unoccupied orbitals decrease in their respective energies, and start to lie within the band gap. However, once the orbitals begin to doubly fill then the orbitals begin to rise in energy.

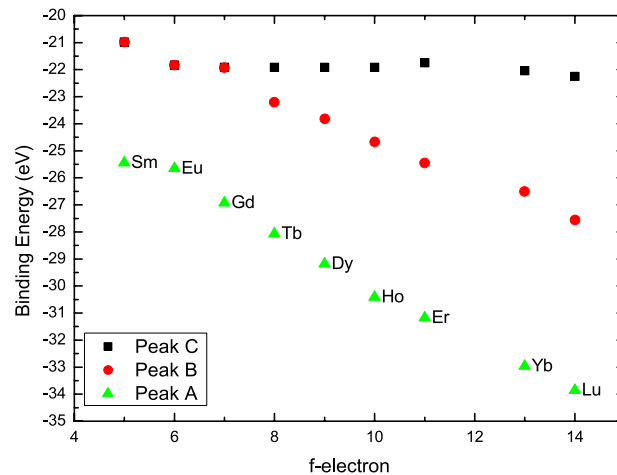


Figure 3. Peak positions for the peaks A,B and C previously published by Nemoshkalenko et al[14]. This figure has been simplified to show the measured peak positions, a more complex version can be found in original reference.

- ii) Increasing the electron number of the lanthanide elements also changes the position of the 48f-x oxygen, i.e. the relaxation into the vacancy within the anion array, and changes the location in energy of the 5d and 5p-orbitals. The changes in these orbital energies also change the nature of the bonding within the AO_8 and TiO_6 frameworks. The movement away from 0.375 decreases the stability of the AO_8 unit, thus in $\text{Gd}_2\text{Ti}_2\text{O}_7$ (which has a 48f-x of 0.428); this unit is the most asymmetric AO_8 unit of the $\text{Ln}_2\text{Ti}_2\text{O}_7$ pyrochlores.
- iii) The change in the energy levels of the Ln 5d and 5p-orbitals, coupled with the effect of shifting the 48f-x oxygen, and its effect on the Ti-3d and O-2p orbital overlap give rise to changes in the bonding between the two networks in the structure i.e. AO_8 and TiO_6 . The reduction in orbital overlap reduces the degree of interaction between the two networks, i.e., decreasing the strength/interaction between the two networks. This is shown schematically in Figure 4.

The trends in the radiation resistance of $\text{Ln}_2\text{Ti}_2\text{O}_7$ compounds, along with the observations by Nemoshkalenko et al., and Hwang et al., suggest the following. As the lanthanide changes from La-Nd the optical band gap shrinks, but within this gap there are vacant 4f-orbitals that can provide a mechanism for new, possibly temporary, bonds to develop. At Sm the structure changes to pyrochlore. At this point a new factor is introduced, the predominantly favoured bonding within the interpenetrating networks. This accompanies the band gap decreasing in energy, with the vacant 4f-orbitals providing a stepping stone to the higher energy orbitals. The decrease in the band gap and the change in bonding within and between chains effectively inverts once you reach Gd, $4f^7$, the last of the singly filled f-orbitals. From Tb-Lu the process begins to reverse, i.e., the band gap increases and the vacant 4f-orbitals begin to move out of the gap, while the bonding within the polyhedral chains begins to favour bonding between the networks.

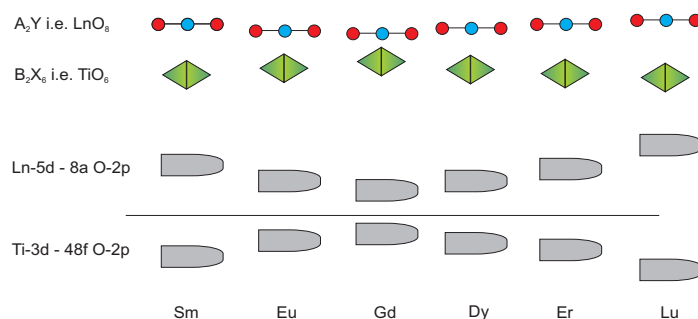


Figure 4. Schematic illustration showing (bottom) the gap closing between the Ln-5d/8a O-2p and Ti-3d/48f O-2p orbitals. The top part for the figure indicates the separation and level of interaction between the two networks in the pyrochlore structure, the closer the A_2Y and B_2X_6 are the greater the interaction.

If the process of ion-irradiation is taken sequentially, the incoming charged atoms, e.g. Kr, impact the system. This Kr cation kinetically imparts energy into the solid during impact, electronically and thermally, both exciting the system, and some form of atomic displacement – the cascade of damage. This energetically unfavoured system then relaxes to form a structure which can be crystalline/amorphous – stable/metastable the exact form dependent on temperature/pressure. Once relaxation begins the orbitals available for bonding become important for two reasons. Firstly if the orbital is not present then it cannot be used for bonding, secondly the additional energy levels available allow for electron promotion and subsequent relaxation further away in the lattice. Hwang et al[13] reported in their study that the unoccupied 4f-level in $\text{Nd}_2\text{Ti}_2\text{O}_7$ had the effect of reducing its photocatalytic activity in water splitting. This reduction was ascribed to the 4f-levels acting as electron-trapping sites. A similar process can be envisaged during this stage of the relaxation process.

As the system begins to relax orbital overlap begins to affect the process. As outlined above the greater the overlap between the titanium 3d and the lanthanide 5d and 5p-orbitals with the oxygen 2p-orbitals the stronger the intrachain bonds for the AO_8 and TiO_6 become. Since this is linked with filling of the Ln 4f-orbitals, the further away from Gd, the weaker these bonds become, and the stronger the interchain bonds become. Therefore it would be expected that at

Gd the GdO_8 and TiO_6 polyhedra are 'comfortable' being semi-isolated, giving rise to the high critical temperature. This is shown schematically in Figure 4. However, moving away from Gd, drives the atoms to arrange in a manner that increases the AO_8 and TiO_6 linkage, and as such a pyrochlore-structure is favoured, thus reducing the critical temperature.

CONCLUSION

A model has been developed that provides a basis for understanding the response of $\text{Ln}_2\text{Ti}_2\text{O}_7$ to radiation damage, based on the application of molecular orbital theory. It is hoped that this theory can be applied in a more general manner to help predict the stability of other potential waste forms.

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