Pyrochlores: Potential multifunctional materials

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Abstract

Pyrochlores are important class of materials from the point of view of diverse technological applications like in luminescence, ionic conductivity, nuclear waste immobilization etc. It has been found that Gd₂Zr₂O₇ is the most suitable pyrochlore for nuclear waste immobilization because it is extremely stable under radiation environment. An optimum size difference between Gd⁴⁺ and Zr⁴⁺ facilitates antisite formation in Gd₂Zr₂O₇, which renders exceptionally high radiation stability to it. Immobilization of Nd⁴⁺ and Ce⁴⁺, which are surrogate materials of Am⁵⁺ and Pu⁵⁺, respectively, in Gd₂Zr₂O₇ lattice has been discussed in the article. Advanced Heavy Water Reactor (AHWR) will generate Al, Th, F in addition to other nuclear wastes. Immobilization of Th and Al in Gd₂Zr₂O₇ is also described in this article.

Introduction

Among the ternary metallic oxides, compounds of the general formula, A₂B₂O₇ (A and B are metals), represent a family of phases isostructural to the mineral pyrochlore, (NaCa)(NbTa)O₆F/(OH)[1]. The space group of the ideal pyrochlore structure is Fd³m and there are eight molecules per unit cell (Z=8). In A₂B₂O₇ pyrochlores, A is usually a trivalent rare earth ion, but can also be a mono, divalent cation and B may be 3d, 4d or 5d transition element having an appropriate oxidation state required for charge balance to give rise to the composition A₂B₂O₇ [2]. The pyrochlore crystal structure also tolerates vacancies at the A and O sites to a certain extent with the result that cation and anion migration within the solid is feasible. Recently, it has been shown by our group that anion rich pyrochlores like Ce₂Zr₂O₇ are also possible [3]. The pyrochlore structure is closely related to the fluorite structure AX₂, except that there are two cation sites and one-eighth of the anions are absent as shown in the Fig. 1[4]. For the ordered pyrochlore, A₂B₂O₇, the phase stability of the superstructure is basically determined by the A and B site cation radius ratio. It is worth noting here that compounds with similar cationic radii are more likely to form as disordered fluorites than ordered pyrochlores, for instance, Er₂Zr₂O₇ having r_A/r_B~1.39 crystallizes as a disordered fluorite structure whereas Er₂Ti₂O₇ with r_A/r_B~1.66 crystallizes as a ordered pyrochlore structure.

Since more number of (3+, 4+) ions are possible, therefore, large number of pyrochlores having (3+, 4+) cations are reported in literature compared to pyrochlores having (2+, 5+) cations. Recently, (1+, 6+) pyrochlores like KO₃Zr₂O₈ are reported in the literature [5]. In general, pyrochlores exhibit a wide variety of interesting physical properties because a diverse range of constituent ions can be chosen to obtain the desired properties. The electrical properties of the pyrochlores vary from highly insulating through semiconducting...
to metallic behaviour. It has been reported that few rare-earth molybdate and ruthenate pyrochlores show semiconductor to metal transition. Pyrochlores like Cd$_2$Re$_2$O$_7$ exhibit superconductivity at lower temperature [6]. The system where the A and B ions are in the maximum possible oxidation states, exhibits excellent dielectric properties. The electrical properties of the pyrochlores having Bi ion, like Bi$_2$Ru$_2$O$_7$, are interesting, because the lone pair of electron on Bi contributes to the electrical property of the compound. Many of the pyrochlores like La$_2$Zr$_2$O$_7$ act as thermal barrier coating whereas some other systems like Y$_2$Sn$_2$O$_7$, act as excellent host matrices for photoluminescence. Oxide ion conduction is also possible in pyrochlores if the compositions are tuned properly [7, 8]. High pressure response of pyrochlore is also worth mentioning. Mostly researchers have found that pyrochlores transform to fluorite phase or some other phases at higher pressure. Recently, it has been found that they can transform to starting reactants too [9]. In addition, pyrochlores are excellent host matrices for nuclear waste immobilization because it can dissolve various lanthanides, actinides and other elements which are generated from nuclear reactors. It has been found that stability of the pyrochlores under radiation environment increases with decrease in radius ratio.

This can be explained on the basis of antisite defect formation. The energy deposited due to irradiation can be dissipated by swapping the A and B cations and the structure transforms to defect fluorite form. However, in case of pyrochlores having large difference in ionic radii of A and B cations cannot exchange their sites. Therefore, these pyrochlores amorphize under high irradiation dose to dissipate the extra energy [10]. Hence, Gd$_2$Zr$_2$O$_7$ was chosen as a suitable host material for fixation of some of the nuclear waste products.

Sample Preparation

Few samples were prepared by standard solid state route. The constituent oxides were preheated at 900°C overnight to remove moisture and other volatile impurities. Stoichiometric amounts of the reactants were weighed to get the various compositions. The homogenized mixtures were then subjected to a three-step heating protocol with intermittent grindings. The XRD patterns of samples were recorded on a Philips X’pert Pro XRD unit in static air condition with monochromatized Cu-Ka radiation. The XRD patterns of samples were recorded on a Philips X’pert Pro XRD unit in static air condition with monochromatized Cu-Ka radiation. Since the starting materials are high melting point solids, therefore to complete the reaction high temperature is required. Raman spectra were recorded using a 632.8nm line from a He–Ne laser.
laser and the scattered light was analyzed using a single-stage spectrograph. It can be mentioned here that few samples were prepared by gel combustion method also. In this method the nitrates of the constituent elements and glycine were mixed in desired ratio and then heated till 100°C, which ultimately gives rise to transparent gel. The gel undergoes combustion at higher temperature. The formed powder is then calcined to remove carbon and unreacted organic materials.

Result and Discussion

1. Solubility of Nd\textsuperscript{3+} in Gd\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} and Y\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} pyrochlores

A series of compositions having nominal compositions Nd\textsubscript{2-y}Gd\textsubscript{y}Zr\textsubscript{2}O\textsubscript{7} (0.0 ≤ y ≤ 2.0) was prepared by standard solid state route and analyzed by XRD and Raman spectroscopy. It has been found that with increase in Gd\textsuperscript{3+} content in the series the lattice parameter decreases, which is attributed to the relative ionic size of Nd\textsuperscript{3+} and Gd\textsuperscript{3+}. This also establishes the monophasic nature of all the products in this series. Structural analysis has been done by using Rietveld refinement programme Fullprof-2005. The most important observation of the present investigation is that, with increase in Gd content in the series, the system undergoes change from ordered pyrochlore to disordered pyrochlore. Originally, in pyrochlore structure all the oxygens are not equivalent. The oxygen at 48f position is surrounded by two A and two B cations and 8a position has four B neighboring atoms, and 8b position is surrounded by four A cations. The coordinate of 48f oxygen is (x, 0.125, 0.125). The x-parameter of 48f oxygen is indicator of the degree of disorder in the system. The x parameters of 48f oxygen in perfect pyrochlore and highly disordered pyrochlore are 0.3125 and 0.375, respectively. Initially the value of the x parameter increases linearly on incorporation of Gd in Nd\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, which indicates an increase in disorder in the system. However, there is a distinct change in the slope at Nd\textsubscript{0.2}Gd\textsubscript{1.8}Zr\textsubscript{2}O\textsubscript{7}, composition, which suggests that the degree of disorder increases abruptly from that composition onward.

XRD studies are more sensitive to disorder in the cationic sublattice compared to anionic sublattice, whereas, Raman spectroscopy is primarily sensitive to oxygen-cation vibrations and is an excellent probe for local disorder. The Raman spectroscopic investigation has been found to provide unequivocal information to distinguish between a pyrochlore, disordered pyrochlore and a defect fluorite material, because these phases differ essentially with respect to local disorder around the A or B cations. Therefore, all the compounds were further investigated by Raman spectroscopy over the frequency range 200–800 cm\textsuperscript{-1} to investigate the exact composition at and beyond which a distinct pyrochlore lattice undergoes a transformation to disordered pyrochlore.

The six Raman active modes of pyrochlore are distributed as A\textsubscript{1g} + E\textsubscript{g} + 4F\textsubscript{2g}. The observed Raman spectrum of the pyrochlore structure of Nd\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} and the different mode frequencies, agree quite well with the values reported in literature. The width of different modes also increases with increasing Gd concentration (not shown). As mentioned earlier, a gradual increase in the 48f oxygen x-parameter was observed till y ≈ 1.8 beyond which there is sudden change in the slope even though the radius ratio r\textsubscript{A}/r\textsubscript{B} changes linearly. The change in slope observed in the frequency vs Gd content curve and the sudden increase in width in the Raman modes for y ≥ 1.8 can be related to this discontinuous change in the 48f oxygen x-parameter. As the size difference between “average” A cation and B cation decreases with increase of Gd content, the system has a tendency to transform from perfect pyrochlore to defect pyrochlore [11, 12].

In another attempt, Nd was incorporated in Y\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, which was expected to be a stable material under radiation environment. The samples were prepared...
following the same protocol. Structural analysis on Nd$_{2-y}$Y$_y$Zr$_2$O$_7$ (0.0 ≤ y ≤ 2.0) series has also been done by using Rietveld refinement programme Fullprof-2008. It has been found that with increase in Y$^{3+}$ content in the solid solution, the structure transforms from ideal pyrochlore to defect fluorite through a biphasic region. The decrease in lattice parameter with increase in Y$^{3+}$ content in the series, is due to lower ionic radius of Y$^{3+}$ (0.93Å) than that of Nd$^{3+}$ (1.02Å) in eight fold co-ordination. It is noticeable that the lattice parameters remain unchanged for the two compositions in the region from Nd$_{0.8}$Y$_{1.2}$Zr$_2$O$_7$ to Nd$_{0.4}$Y$_{1.6}$Zr$_2$O$_7$, which indicates that these two compositions are a biphasic mixture of pyrochlore and defect fluorite. During refinement it has been assumed that in Nd$_2$Zr$_2$O$_7$, the 8a site remains totally vacant. With increase in Y$^{3+}$ content in the series, the 8a site also gets populated with concomitant depopulation at 48f site. The occupancy at 8b site remains almost constant. The involvement of 8a oxygen and 48f oxygen in disordering also has been verified by Raman spectroscopy. Another end member i.e. Y$_2$Zr$_2$O$_7$ crystallizes as defect fluorite structure.

In order to further substantiate the present work, Raman spectroscopic investigation has been performed on all the samples. All the six modes of pyrochlores have been found in the Raman spectra. The qualitative nature of the Raman bands remain similar till Nd$_{1.2}$Y$_{0.8}$Zr$_2$O$_7$ (y = 0.8) which suggest that these compositions are pyrochlore only. Beyond this, the Raman spectra show huge broadening for the biphasic samples y = 1.2 and 1.6. The Raman spectra of another end member i.e. Y$_2$Zr$_2$O$_7$, which has been found as disordered fluorite by XRD, is also too broad [13].

2. Solubility of Ce in Gd$_2$Zr$_2$O$_7$, pyrochlore

It is well known that cerium and plutonium share many common properties specially thermophysical ones. So in order to investigate the solubility of plutonium in Gd$_2$Zr$_2$O$_7$ matrix, cerium has been chosen as surrogate material. Reduction of Ce$^{4+}$ to Ce$^{3+}$ has been done, by heating the powder samples in the presence of Zr sponge and low oxygen partial pressure.

In order to investigate the structural aspects of the compositions in the series Gd$_{2-x}$Ce$_x$Zr$_2$O$_7$ (0.0 ≤ x ≤ 2.0), XRD data has been recorded and analyzed. All the products were found to have pyrochlore type lattice, which is characterized by the presence of typical super-lattice peaks at for 14° (111), 27° (311), 37° (331), (using Cu-Kα as radiation source) etc. A shift of the diffraction peaks towards lower angle on Ce incorporation clearly indicates, that the cell parameters of the doped pyrochlores increase as the content of Ce increases. The cell parameters for each composition, along with both the end members were calculated using POWDERX programme. The lattice parameter of these solid solutions increases on incorporation of cerium. The ionic radii of Gd$^{3+}$ and Ce$^{3+}$, in 8-fold coordination, are 0.98Å and 1.04Å, respectively. Therefore, based on the relative ionic size considerations, one can explain the increasing trend in the lattice parameter of pyrochlore, upon incorporation of cerium ion at the Gd sites.

The pyrochlore phase exists throughout the homogeneity range and could be attributed to $r_A/r_B$ ($r_A$ and $r_B$ are the ionic radii of the A and B cations, respectively) ratio which varies from 1.46 (in Gd$_2$Zr$_2$O$_7$) to 1.58 (in Ce$_2$Zr$_2$O$_7$), which is within the limiting radius ratio, required for the stabilization of pyrochlore structure. Another interesting observation was that, the intensity of characteristic super-structure peaks for pyrochlore systematically increases on going from Gd$_2$Zr$_2$O$_7$ to Ce$_2$Zr$_2$O$_7$ in the series. This observation can also be explained based on the radius ratio. As the radius ratio increases, the structure becomes more and more ordered and subsequently, the intensities of the super-structure peaks increase.

In order to investigate the thermal behaviour of these...
pyrochlores, XRD data has been recorded at higher temperature. In case of Gd$_2$Zr$_2$O$_7$, the lattice parameter increases almost linearly with increase in temperature. The samples having the compositions $x=0.3$ to $x=1.2$ also show increasing trend in lattice parameter with temperature. The lattice parameters, calculated after cooling to room temperature from 1273K show that it is smaller than the initial lattice parameter room temperature calculated at room temperature. In case of these samples, the increase in lattice parameter due to thermal effect predominates over the decrease in lattice parameter due to aerial oxidation. It is interesting to observe the change in lattice parameters of heavily cerium substituted samples ($x=1.5$, 1.8, 2.0). Initially, the lattice parameters show a decreasing trend till the temperature reaches 673K, and then it starts to increase as the temperature increases. The reason is that, all the substituted samples undergo aerial oxidation of Ce$^{3+}$ to Ce$^{4+}$ at elevated temperature, which leads to decrease in lattice parameter. Interestingly, after formation of Ce$^{4+}$, it remains in the solid solution only. The ionic radius of Ce$^{4+}$ is smaller than that of Ce$^{3+}$, hence the lattice parameter decreases upon heating. The samples having $x=1.5$ to 2.0, show an increasing trend in lattice parameter after 673K, because the solid solution starts to expand with increase in temperature. Another interesting aspect is that, though Ce$^{4+}$ has formed in the solid solution, but it does form any secondary phase. The phase, Ce$_2$Zr$_2$O$_6$, can be considered as anion rich pyrochlore. In the present study, it has been found that Gd$_2$Zr$_2$O$_7$, and Ce$_2$Zr$_2$O$_7$ form a solid solution over the entire homogeneity range. The oxidation state of cerium could not alter the degree of solubility of cerium in Gd$_2$Zr$_2$O$_7$. During oxidation of Ce$^{3+}$ to Ce$^{4+}$, extra oxygen is introduced into the lattice but still the pyrochlore lattice remains undisturbed.

3. Solubility of Th and Al in Gd$_2$Zr$_2$O$_7$ pyrochlore

It has been stated earlier that Al and Th are expected to be generated from Advanced Heavy Water Reactors (AHWR). An attempt has been made to show the dissolution of Th and Al in Gd$_2$Zr$_2$O$_7$ by substituting Gd by Th and Zr by Al of Gd$_2$Zr$_2$O$_7$. The substitution of Al$^{3+}$ at Zr$^{4+}$ site can compensate for the extra oxygen formed due to the incorporation of Th$^{4+}$ at Gd$^{3+}$ site, which is expected to increase the solubility of Th$^{4+}$ in Gd$_2$Zr$_2$O$_7$ [14].

The samples having nominal composition Gd$_{2-x}$Th$_x$Zr$_{2-x}$Al$_x$O$_7$ ($0.0 \leq x \leq 2.0$) were prepared by gel-combustion method. The XRD patterns of all the products in Gd$_{2-x}$Th$_x$Zr$_{2-x}$Al$_x$O$_7$ ($0.0 \leq x \leq 2.0$) series were recorded and analyzed. A few representative XRD patterns are shown in Fig 2. Pure Gd$_2$Zr$_2$O$_7$ crystallizes as pyrochlore, which is evident by the presence of super-lattice peaks at $2\theta = 14^{\circ}(111)$, $27^{\circ}(311)$, $37^{\circ}(331)$, $45^{\circ}(511)$ (using Cu K$\alpha$ as radiation source). It is observed from that, the compositions corresponding to $x=0.0$ to $x=0.4$, adopt pyrochlore structure. A systematic shift of the diffraction peaks towards lower angle on Th and Al incorporation clearly indicates, that the cell parameters of the substituted pyrochlores increase as the content of Th and Al increase.

The cell parameters of all the compositions were calculated using POWDERX programme which
that with an increase in fluence, there is only a broadening of the diffraction lines. No signature of amorphization was observed even at the highest fluence. Fig. 3 shows the Grazing Incidence X-Ray Diffraction (GIXRD) plots for virgin Nd$_2$Zr$_2$O$_7$ and the irradiated Nd$_2$Zr$_2$O$_7$ at different fluences. The broadening is attributed to the disorder caused by irradiation. The peak positions of the pyrochlore do not change, which means that there is no change in the size of the lattice. One more interesting observation is that, the superstructure peaks get diminished. This suggests that the extra energy due to irradiation, gets dissipated due to swapping (i.e. anti-site formation) of the ions since the radius ratio ($r_A/r_B$) of the ions was close to that of defect fluorite. Even the sample with the highest fluence shows no signature of amorphization.

The Raman spectra of the samples appear quite similar which suggest that no major change in structure of Nd$_2$Zr$_2$O$_7$ has taken place due to irradiation, except minor broadening (not shown). The probable reason could be that part of Al$^{3+}$ resides at some interstitial sites of the host pyrochlore.

4. Radiation stability of Gd$_2$Zr$_2$O$_7$ and Nd$_2$Zr$_2$O$_7$, under low energy ion beam

It has been mentioned earlier that these pyrochlore materials could be used for waste immobilization. In order to investigate their stability in radiation environment, Gd$_2$Zr$_2$O$_7$ and Nd$_2$Zr$_2$O$_7$ pellets were irradiated with 300 KeV Ar$^+$ ions at fluences ranging from $1 \times 10^{16}$ to $5 \times 10^{17}$ ion/cm$^2$. It was observed,show an increasing trend as a function of Th and Al content upto x=0.4. An interesting result has been observed in the trend of cell parameters of the samples. The ionic radii of Gd$^{3+}$ and Th$^{4+}$, in 8-fold coordination, are 0.98Å and 1.05 Å and the ionic radii of Zr$^{4+}$ and Al$^{3+}$ are 0.72Å and 0.54Å in six fold coordination. Thus the average increase of cationic radii at A site will be smaller than the average decrease in cationic radii at B site. Therefore, a simultaneous incorporation of Th$^{4+}$ and Al$^{3+}$ at Gd$^{3+}$ and Zr$^{4+}$ site, respectively, should result in a decrease in cell parameters. However, the cell parameter increases in Gd$_{2-x}$Th$_x$Zr$_{2-x}$Al$_x$O$_7$ series on increasing x. The probable reason could be that part of Al$^{3+}$ resides at some interstitial sites of the host pyrochlore.
In case of Gd\(_2\)Zr\(_2\)O\(_7\), also, the peaks are broadened and the superstructure peaks also disappear, which means the structure turns to defect fluorite (Fig. 4). The broadening is due to disorder as a result of irradiation. Since the size of the cations does not differ much it favours antsite defect formation.

The huge broadening in Raman spectra is due to inherent disorder in Gd\(_2\)Zr\(_2\)O\(_7\) system, even in the absence of irradiation (not shown). Upon irradiation, the disorder increases but the systems remain crystalline only.

Conclusions

It can be concluded that Nd, the surrogate of Am, can be completely dissolved in Gd\(_2\)Zr\(_2\)O\(_7\) and partially in Y\(_2\)Zr\(_2\)O\(_7\). It has again been shown, that an element like Ce which is a simulant of Pu can be completely dissolved in Gd\(_2\)Zr\(_2\)O\(_7\). The other two elements Th and Al also show 20mol% solubility in Gd\(_2\)Zr\(_2\)O\(_7\) matrix. The ion beam irradiation study reveals, that Gd\(_2\)Zr\(_2\)O\(_7\) and Nd\(_2\)Zr\(_2\)O\(_7\) are extremely stable under radiation environment.

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References


**Forthcoming Symposium**

**Third Asia-Pacific Symposium on Radiation Chemistry APSRC 2010**

&

**Trombay Symposium on Radiation and Photochemistry TSRP 2010**

The third Asia-Pacific Symposium on Radiation Chemistry (APSRC-2010) incorporating tenth Trombay Symposium on Radiation & Photochemistry (TSRP- 2010), organized by BARC in association with the Indian Society for Radiation and Photochemical Sciences (ISRAPS), will be held from September 14 (Tuesday) to September 17 (Friday) at Treasure Island Resorts, Lonavala, INDIA. The scientific program of the symposium will consist of keynote addresses and about 50 invited lectures of 20 to 30 minutes duration in the field of Radiation and Photochemistry, and about 150 contributory poster papers. The main topics include:

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Submission of manuscript for contributory papers | 15 Jun 2010
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