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# Solubility of $Ce^{4+}$ and $Sr^{2+}$ in the pyrochlore lattice of $Gd_2Zr_2O_7$ for simulation of Pu and alkaline earth metal

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## Abstract

The solubility of $Ce^{4+}$ and $Sr^{2+}$ has been studied for the simulation of plutonium, and alkaline-earth metal elements, which are the common fission products in a nuclear fuel, in the zirconate pyrochlore lattice of $Gd_2Zr_2O_7$ by the A site substitution. A number of compositions with general stoichiometry $Gd_{2-x}Sr_xZr_2O_{7-x/2}$ and $Gd_{2-x}Sr_{x/2}Ce_{x/2}Zr_2O_7$ have been synthesized and characterized by powder XRD. From the XRD data, the solubility of $Sr^{2+}$ is estimated to be about 1.25 mol%. Further addition of $Sr^{2+}$ leads the separation of $SrZrO_3$ perovskite phase. The solubility of $Sr^{2+}$ increases to 2.5 mol% when substituted in combination with $Ce^{4+}$. The solubility of $Ce^{4+}$ is estimated to be about 12.5 mol% in the pyrochlore lattice of $Gd_2Zr_2O_7$. Further addition of $Ce^{4+}$ into the pyrochlore lattice leads to the formation of fluorite phase.

*Keywords:* Zirconate pyrochlore; Fluorite; Solubility; Powder XRD

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## 1. Introduction

With the development of advanced and newer generation reactors, the problem of safe disposal of the nuclear waste has become more acute and it has become utmost important to develop the newer techniques and the inert ceramic based matrices for the nuclear waste immobilization. In the interest of public acceptance and the safety, several groups all over the world are engaged in search for the inert matrix for the disposal of the plutonium [1–6]. A number of host lattices are considered attractive to act as an inert matrix for diluting plutonium, viz. multiphase ceramic–ceramic composites (MCC) based on zirconia, alumina or magnesia, $Al_5Y_3O_{12}$, MgO, $MgAl_2O_4$, ROX (rock like oxides) [7]. Several ceramic composites viz. yttria-stabilized-zirconia (YSZ)–$Al_2O_3$–$MgAl_2O_4$, YSZ–$MgAl_2O_4$ etc., have been proposed for this purpose. For the fixation of transuranic elements, the ceramic matrix seems to be a better choice as it has high thermodynamic stability for a longer time. The pyrochlore lattice ($A_2B_2O_7$) containing Zr as one of the cations with an ideal composition $M_2Zr_2O_7$ (M = tri and/or tetravalent cation) is considered to be the promising host matrix for fixation of high level nuclear wastes as it can retain the considerable amounts of actinides and lanthanides in its structure [8,9]. Lanthanum zirconate with pyrochlore structure is one of the important phases with wide solubility of simulated constituents of transuranic elements, and good chemical durability in water [10]. Yamazaki et al. [11] have studied the thermal expansion and solubility limits of Pu doped lanthanum zirconate by X-ray diffraction studies in air, vacuum and Ar–8% $H_2$ atmospheres and found the solubility to be 10, 35 and 100% of Pu, respectively, under different conditions. Lian et al. [12] have carried out the ion beam irradiation studies of pyrochlore $La_2Zr_2O_7$–$Ce_2Zr_2O_7$. They have studied the ion beam irradiation for Ce-doped $La_2Zr_2O_7$ with different average A site cation sizes and valence states using electron energy loss spectroscopy (EELS). It was found that $La_2Zr_2O_7$ is susceptible to ion irradiation induced amorphization. Their studies suggested that addition of $Ce^{4+}$ into $La_2Zr_2O_7$ structure increases the stability of $La_2Zr_2O_7$ waste form in a radiation environment due to the decrease in the average cationic radius at the A site. It has been also observed by them that the cation

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disordered fluorite structure is the final radiation damaged state for $Gd_2Zr_2O_7$ and other Zr rich pyrochlore regardless of the starting structure. In this manuscript, we report the solubility of $Ce^{4+}$ in combination with $Sr^{2+}$ to maintain the average cationic radius close to $Gd^{3+}$ and also the compensation of charge at A site in the pyrochlore $Gd_2Zr_2O_7$. It exists as a disordered fluorite phase at high temperature whereas it has an ordered pyrochlore crystal structure at lower temperatures in which the cations and the oxygen vacancies are ordered [13]. It shows order–disorder transition at comparatively high temperature of about 1550 °C [14] and also does not undergo ion beam induced amorphization [15]. It may be noted that Sr is a fission product with a long half life.

Owing to similarities in the physicochemical properties of ceria ($CeO_2$) and plutonia ($PuO_2$), ceria is widely used as surrogate material in place of plutonia [16]. Hence, plutonia fixation in the pyrochlore structure can be very well simulated using ceria. In order to find the solubility of $Ce^{4+}$ in $Gd_2Zr_2O_7$ pyrochlore lattice, we have studied the system $Gd_2O_3$–$CeO_2$–SrO–$ZrO_2$ with the stoichiometry $Gd_2Ce_{x/2}Sr_{x/2}Zr_2O_7$.

## 2. Experimental

$CeO_2$, $ZrO_2$ and $Gd_2O_3$ (purity 99.9%) powders used as starting materials, which were heated at 900 °C overnight before use. $SrCO_3$ was heated at 600 °C for 5 h before use. Nine compositions with the stoichiometry $Gd_{2-x}Sr_xZr_2O_{7-x/2}$ and 12 compositions in the stoichiometry $Gd_{2-x}Sr_{x/2}Ce_{x/2}Zr_2O_7$ were prepared. The stoichiometric amounts of the reactants for the respective mixtures were ground together thoroughly, pelletized and heated in three steps at 1200 °C for 36 h, ground, repelletized and heated at 1300 °C for 36 h and the final sintering was done at 1400 °C for 48 h. The heating and the cooling rates were 2 °C/min in all the three heating steps. The products obtained were characterized by powder X-ray diffraction (XRD). The XRD instrument used was Philips Model PW 1710 with monochromatized Cu Kα radiation. Silicon was used as an external standard.

## 3. Results and discussion

In our earlier work on substituted zirconate pyrochlore $Gd_2Zr_2O_7$ at B site [17], the solubility of $Ce^{4+}$ at B site was found to be 5 mol% in the pyrochlore lattice. Further addition of $Ce^{4+}$ resulted in the formation of defect fluorite phase and the extreme $Ce^{4+}$ rich compositions showed the C-type cubic phase. In this manuscript, we discuss the results of an attempt made to find the solubility of $Ce^{4+}$ in combination with $Sr^{2+}$ in the pyrochlore lattice of $Gd_2Zr_2O_7$ at A site. There are number of reports on the substituted pyrochlore. As early as in 1975, Chincholkar [18] reported the synthesis of $(A_3Ln)B_2O_7$ (A = Li, Na, K, B = Ti, Zr, Hf) with cubic pyrochlore structure. It was found that lattice parameter changes from 10.54 to 10.7 Å with various combinations of cations. McCauley and Hummel [19] tried several combinations in $(A^{2+}A'^{4+})B_2O_7$ (A = Ca, Si, Pb and A′ = Zr, Hf, Ce and Th, B = Ti and Sn). They obtained the cubic pyrochlore structure only for the compositions $(A^{2+}Ce)Ti_2O_7$ (A = Ca, Cd) and $(CdZr)Ti_2O_7$. Hayakawa and Kamizono [20] studied the simulation of high-level waste (HLW) elements like Ce, Nd and Sr in $La_2Zr_2O_7$ pyrochlore by changing the composition of pyrochlore phase within the three systems $La_2Zr_2O_7$–$Nd_2Zr_2O_7$, $La_2Zr_2O_7$–$2CeO_2{\cdot}2ZrO_2$ and $La_2Zr_2O_7$–$2(CeO_2{\cdot}SrO{\cdot}2ZrO_2)$. They found the solubility of $Ce^{4+}$ to be 27 mol% in $La_2Zr_2O_7$–$2CeO_2$–$2ZrO_2$ system. Because of the substitution of smaller cation $Ce^{4+}$ (ionic radius, 0.97 Å) for the larger cation $La^{3+}$ (ionic radius = 1.16 Å, eight-fold co-ordination) the lattice parameter of the pyrochlore phase decreased. The substitution of the pair of $Ce^{4+}$–$Sr^{2+}$, for two $La^{3+}$sites of $La_2Zr_2O_7$, the solubility of $Sr^{2+}$ was found to be 2.5 mol%. All the ionic radii are taken from the literature [21].

All the earlier reports describes the total substitution of A site cation by the combination of $Ce^{4+}$ and $Sr^{2+}$, or by the two $Ce^{4+}$ or partial substitution of A site cation by either $Nd^{3+}$ or $Ce^{4+}$ in $La_2Zr_2O_7$ pyrochlore [20,22]. In this manuscript, we report the partial substitution of A site cation by $Sr^{2+}$ and also with the combination of $Ce^{4+}$–$Sr^{2+}$.

For the system $Gd_{2-x}Sr_xZr_2O_{7-x/2}$, the solubility of $Sr^{2+}$ was found to be very low (about 1.2 mol%) in the pyrochlore

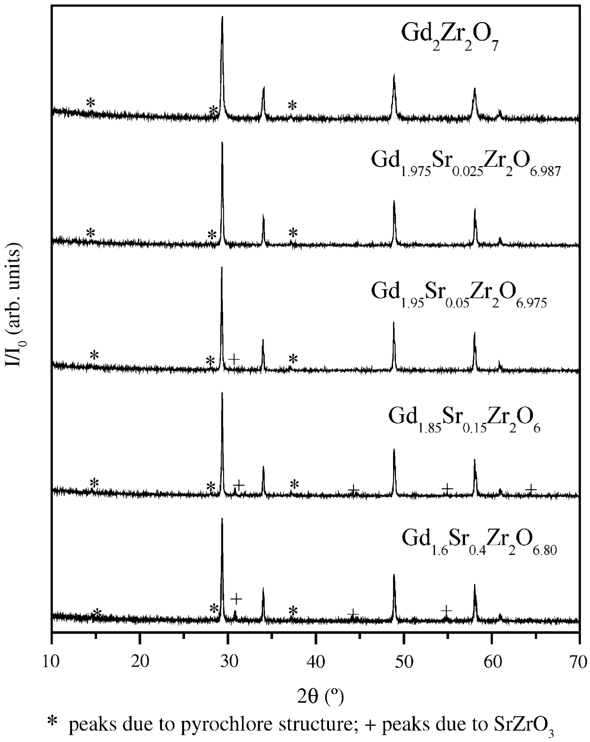

Fig. 1. Powder XRD patterns of some of the compositions in $Gd_{2-x}Sr_xZr_2O_{7-x/2}$.

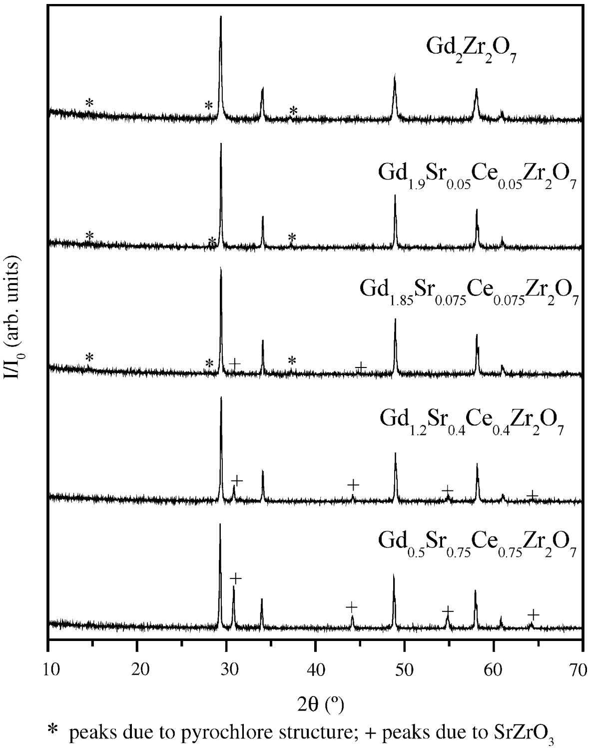

Fig. 2. Powder XRD patterns of some of the compositions in $Gd_{2-x}Sr_{x/2}Ce_{x/2}Zr_2O_7$.

lattice. Further addition of $Sr^{2+}$ resulted in the formation of $SrZrO_3$ phase. The amount of $SrZrO_3$ goes on increasing with increase in $Sr^{2+}$ content retaining the pyrochlore lattice parameters almost constant in this biphasic region. Fig. 1 shows the powder XRD patterns of some of the compositions in $Gd_{2-x}Sr_xZr_2O_{7-x/2}$ system. It can be seen from Fig. 1. that the intensity of the peaks due to $SrZrO_3$ phase increases with increase in Sr Content with concomitant reduction in the intensity of pyrochlore phase.

Like wise the $Gd_{2-x}Sr_{x/2}Ce_{x/2}Zr_2O_7$ system was also investigated. Fig. 2 shows powder XRD patterns of some of the compositions in this system and Table 1 shows the phase identification of the compositions synthesized for the stoichiometry $Gd_{2-x}Sr_{x/2}Ce_{x/2}O_7$ and the unit cell parameters determined for the various compositions. It can be seen that the unit cell parameters increase from $x = 0.0$ to 0.1 due to increase in the average ionic radii of the substituted cations (ionic radius for $Gd^{3+} = 1.053$ Å, $Ce^{4+} = 0.97$ Å and $Sr^{2+} = 1.26$ Å in eight coordination) but at the composition $Gd_{1.85}Sr_{0.075}Ce_{0.075}Zr_2O_7$, perovskite $SrZrO_3$ is formed. Thus it could be inferred that 2.5 mol% of $Sr^{2+}$ is soluble in the pyrochlore lattice when doped with in combination with smaller cation $Ce^{4+}$. Hence, the solubility of $Sr^{2+}$ is enhanced in pyrochlore lattice when it is substituted in conjunction with $Ce^{4+}$ at A site. As more $Sr^{2+}$ and $Ce^{4+}$ are added, the amount of $SrZrO_3$ formed also goes on increasing. It implies that whatever additional $Sr^{2+}$ is doped, it leaches out as $SrZrO_3$ whereas the $Ce^{4+}$ being smaller cation gets incorporated into the pyrochlore lattice. From Table 1, it can be seen that the unit cell parameter of $Gd_{1.85}Sr_{0.075}Ce_{0.075}Zr_2O_7$ is lower than the just previous composition. This is due to the reduction in the average ionic radius at the A site dopant cation (preferentially $Ce^{4+}$). It is presumed that the lattice parameter should increase by the introduction of $O^{2-}$ ion in the pyrochlore structure on account of an aliovalent substitution, i.e., $Gd^{3+}$ by $Ce^{4+}$ [23], which can be seen from Table 1, up to the composition $Gd_{1.80}Sr_{0.1}Ce_{0.1}Zr_2O_7$. On the other hand more and more substitution of $Ce^{4+}$, smaller cation for the $Gd^{3+}$, larger cation makes the lattice parameter decrease. These two effects compete in the same lattice and the net result is in decrease of the lattice parameter with the further addition of $Ce^{4+}$. It has been reported [22] that the Zr–O inter atomic distance increases with increasing $Ce^{4+}$ content suggesting the introduction of interstitial oxygen located adjacent to $Zr^{4+}$ by the addition of $Ce^{4+}$ at $La^{3+}$ site to maintain the condition of electro-neutrality in $Ce^{4+}$ substituted $La_2Zr_2O_7$. The same arguments should hold good in our system also. With increase in Zr–O distance, the oxygen coordination number around Zr also seem to increase suggesting that the additional oxygen required for charge balance, drives the system more close to the fluorite like structure. However, this needs to be confirmed. Thus, it can be seen from Table 1 that the lattice parameter goes on decreasing from composition $Gd_{1.80}Sr_{0.1}Ce_{0.1}Zr_2O_7$ to $Gd_{1.5}Sr_{0.25}Ce_{0.25}Zr_2O_7$. Further addition of $Ce^{4+}$, the pyrochlore phase changes to the fluorite phase. Hence the solubility of $Ce^{4+}$ is found to be 12.5 mol% in the pyrochlore lattice of $Gd_2Zr_2O_7$ in combination with $Sr^{2+}$, though it is a biphasic region.

Table 1
Compositions prepared in the stoichiometry $Gd_{2-x}Sr_{x/2}Ce_{x/2}Zr_2O_7$

| Composition | Phases present | Unit cell parameters of pyrochlore/ fluorite (Å) |
|---|---|---|
| $Gd_2Zr_2O_7$ | Pyrochlore | 10.5125(4) |
| $Gd_{1.95}Sr_{0.025}Ce_{0.025}Zr_2O_7$ | Pyrochlore | 10.5145(6) |
| $Gd_{1.925}Sr_{0.0375}Ce_{0.0375}Zr_2O_7$ | Pyrochlore | 10.5145(5) |
| $Gd_{1.90}Sr_{0.05}Ce_{0.05}Zr_2O_7$ | Pyrochlore | 10.5253(4) |
| $Gd_{1.85}Sr_{0.075}Ce_{.075}Zr_2O_7$ | Pyrochlore + $SrZrO_3$ | 10.5196(4) |
| $Gd_{1.80}Sr_{0.1}Ce_{0.1}Zr_2O_7$ | Pyrochlore + $SrZrO_3$ | 10.5359(2) |
| $Gd_{1.7}Sr_{0.15}Ce_{0.15}Zr_2O_7$ | Pyrochlore + $SrZrO_3$ | 10.5329(3) |
| $Gd_{1.6}Sr_{0.2}Ce_{0.2}Zr_2O_7$ | Pyrochlore + $SrZrO_3$ | 10.5300(3) |
| $Gd_{1.5}Sr_{0.25}Ce_{0.25}Zr_2O_7$ | Pyrochlore + $SrZrO_3$ | 10.5270(1) |
| $Gd_{1.2}Sr_{0.4}Ce_{0.4}Zr_2O_7$ | Fluorite + $SrZrO_3$ | 5.2580(1)[a] |
| $Gd_{1.0}Sr_{0.5}Ce_{0.5}Zr_2O_7$ | Fluorite + $SrZrO_3$ | 5.2560(1)[a] |
| $Gd_{0.5}Sr_{0.75}Ce_{0.75}Zr_2O_7$ | Fluorite + $SrZrO_3$ | 5.2637(3)[a] |

$SrZrO_3$ phase not refined.
[a] Fluorite.

## 4. Conclusions

$Sr^{2+}$ has a very low solubility in the pyrochlore lattice of $Gd_2Zr_2O_7$ at the A site, probably due to the large mismatch in the ionic sizes of $Sr^{2+}$ and $Gd^{3+}$. The solubility of $Sr^{2+}$ is enhanced to 2.5 mol% when substituted in combination with the smaller cation $Ce^{4+}$. The solubility of $Ce^{4+}$ is found to be 12.5 mol% in the pyrochlore lattice of $Gd_2Zr_2O_7$ in combination with $Sr^{2+}$. Further addition of $Ce^{4+}$ into the lattice resulted into the fluorite phase formation. These studies will be useful in designing new and better host lattices for immobilization of radioactive waste.

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