Effect of Order-Disorder Transition on Thermal Conductivity of Gd$_2$Zr$_2$O$_7$ Ceramics

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Abstract. Rare earth zirconates have been considered as promising candidates for thermal barrier coatings, with extremely low thermal conductivity which is usually attributed to their unique pyrochlore/fluorite structure. In order to investigate the different influence of pyrochlore and fluorite structure on thermal conductivity, Gd$_2$Zr$_2$O$_7$ ceramics with pyrochlore and fluorite structure were prepared separately by controlling the sintering temperature, and the thermal conductivities of the samples sintered at different temperatures were measured and investigated. The results show that the structure of Gd$_2$Zr$_2$O$_7$ changes gradually from pyrochlore to fluorite as the sintering temperature increases from 1450°C to 1600°C, accompanying with a thermal conductivity decreasing first and then increasing. The minimum value of thermal conductivity appears on the sample with pyrochlore structure nearby the phase transition temperature range, rather than that with fluorite structure. Other than the transition of structure, structural distortion in the lattice approaching phase transition may lead to a distinct decrease of thermal conductivity.

1. Introduction
With the development of heat engines, the conventional thermal barrier coating material yttria stabilized zirconia (YSZ) can not meet the growing demand. In recent decades, rare earth zirconates have been of keen concern as promising candidates for thermal barrier coatings. Previous studies have shown that the thermal conductivity of rare earth zirconates is nearly 30% lower than YSZ [1, 2]. It is generally believed that this extremely low thermal conductivity is due to its unique pyrochlore/fluorite structure [3, 4].

The rare earth zirconates (A$_2$Zr$_2$O$_7$, A is the rare earth element) crystallize in two different structures according to the ratio of cation radius. When r(A$^{3+}$)/r(Zr$^{4+}$) ≤ 1.46, the zirconates (A = La ~ Gd) keep pyrochlore structure (P); When 1.46 ≤ r(A$^{3+}$)/r(Zr$^{4+}$) ≤ 1.78, the zirconates (A = Gd ~ Yb) crystallize into fluorite structure (F) [5]. The difference between the two structures is whether the oxygen vacancies in the lattice are ordered. The cations of A$^{3+}$ and Zr$^{4+}$ in pyrochlore structure occupy 16d and 16c sites respectively, while the oxygen vacancy is fixed at the center of four Zr$^{4+}$ tetrahedrons. The cations and oxygen vacancies in the fluorite structure are randomly distributed. It is indicated that the ordered-disordered transition of oxygen vacancies in these two structures may lead to a distinct variation of the thermal conductivity.

Until now, the thermal conductivities of the oxides with pyrochlore and fluorite structure have been extensively investigated. For example, Ren XR et al prepared La$_{2-x}$Yb$_x$Zr$_2$O$_7$ (x = 0 ~ 1) with pyrochlore and fluorite structures by changing the doping content of Yb ions, and investigated the variation of the thermal conductivity [6]. Fabrichnaya O et al observed that doping of Y$_2$O$_3$ into Sm$_2$Zr$_2$O$_7$ lattice induces a transformation from pyrochlore to fluorite, accompanying with a significant increase of thermal
conductivity \[7\]. However, all these investigations involve the doping which will change the compositions and then affect the thermal conductivity. So, it is difficult to separate out the effect of the crystal structure itself.

Some rare earth zirconates have been revealed to undergo a pyrochlore-fluorite transition under certain temperatures \[8\]. Therefore, these isomers are expected to exclude the effect of composition variation, and their thermal conductivities can be compared to investigate the effect of the crystal structure separately. An appropriate transition temperature is very important for the preparation of the samples. Zhou L et al reported that the temperature range of the phase transition of Gd\(_2\)Zr\(_2\)O\(_7\) is between 1500 °C and 1550 °C \[9-10\], which is a suitable temperature to densify the samples. In this paper, the isomers of Gd\(_2\)Zr\(_2\)O\(_7\) with pyrochlore and fluorite structure were prepared by controlling the sintering temperatures, and the thermal conductivities of samples with different sintering temperatures were measured and investigated to determine the effect of the pyrochlore-fluorite transition.

2. Experiment

Gd\(_2\)Zr\(_2\)O\(_7\) powder was prepared by chemical precipitation method. Gd\(_2\)O\(_3\) (purity ≥ 99.9\%) and ZrOCl\(_2\)·8H\(_2\)O (purity ≥ 99.9\%) were used as starting materials with ammonia as precipitant. Gd\(_2\)O\(_3\) powder was precalcined at 1000 °C for 10 h to eliminate hydroxide and/or carbonate, and dissolved in the diluted nitric acid. ZrOCl\(_2\)·8H\(_2\)O powder was dissolved in deionized water. These two solutions were mixed uniformly in the stoichiometric ratio and then added dropwise into an excess solution of aqueous ammonia with vigorous stirring to obtain gel-like precipitates. The precipitates were filtered and washed with deionized water for three times and ethanol for two times. The washed precipitates were then dried and calcined at 800 °C for 5 h for crystallization.

The prepared powder was pressed into pellets by uniaxial cold pressing followed by isostatic cold pressing (200 MPa). In order to obtain Gd\(_2\)Zr\(_2\)O\(_7\) ceramics with pyrochlore and fluorite structure respectively, the compacts were sintered pressurelessly at different temperatures of 1450 °C, 1500 °C, 1550 °C and 1600 °C for 10h.

Phase analysis was performed by X-ray diffractometer (Bruker D8 Advance) with CuK\(\alpha\) radiation. Continuous scans were conducted within a scanning range of 20 ° ~ 80 ° and with a scanning speed of 8 °/min.

The Raman spectra of samples at room temperature was recorded on a microscopic confocal Raman spectrometer (HORIBA Jobin Yvon, LabRAW HR Evolution, France). An argon ion laser beam with a wavelength of 633 nm was focused on a freshly polished surface of sample with a spot diameter of 1.25 μm. The full power of the incident beam is 7500 μW/cm\(^2\). The signal was collected for 20 s and accumulated for 2 times.

The thermal conductivities of the samples were determined using formula (1) by measuring their thermal diffusivity.

\[
\kappa_{\text{exp}} = C_p \cdot \rho \cdot \lambda
\]

Where \(C_p\) is the heat capacity of constant pressure, \(\rho\) is the density of the sample, and \(\lambda\) is the thermal diffusivity of the sample at a certain temperature.

Heat capacity \((C_p)\) was calculated and fitted by the Neumann-Kopp law, and the molar heat capacity data was obtained from the Thermodynamics Handbook \[11\]. It has been verified that the calculated values were within around 3% ~ 5% of the experimental values \[15\]. Bulk density \((\rho)\) was measured using the Archimedes technique with an immersion medium of deionized water. In this paper, the relative densities of the samples are between 96 % and 99 %. Thermal diffusivity \((\lambda)\) was measured by laser flash method (Netzsch LFA 427) in pure Ar atmosphere. The samples were machined to be coplanar with a thickness of approximately 1 mm and a diameter of 10 mm. Prior to the measurements, both sides of each sample were coated with colloidal graphite to ensure maximum absorption and emissivity. The measurement was carried out from room temperature to 700 °C at intervals of 100 °C. Each value was measured for 3 times and took the average.
Moreover, since porosity has a significant effect on the thermal conductivity, the thermal conductivity values should be used to extrapolate those of fully dense samples for the sake of comparison by the Maxwell relation [3].

\[ \kappa_0 = \frac{k_{\text{exp}}}{1 - 1.5\phi} \]  

Where \( \kappa_0 \) is the thermal conductivity of the fully dense sample, and \( \phi \) is the porosity.

3. Results and discussion

3.1. Structure characterization

Figure 1 shows the XRD patterns of Gd2Zr2O7 samples sintered at different temperatures. Compared with the standard XRD patterns of Gd2Zr2O7, it reveals that only the sample sintered at 1600 °C are defective fluorite structure, whereas all the other samples sintered below 1550 °C keep pyrochlore structure. The occurrence of (311), (331) and (511) peaks, as marked in Figure 1, suggests the presence of the super-lattice of pyrochlore structure. It can be seen from the figure that these super-lattice peaks are getting weaker with the increase of the sintering temperature until 1600 °C when they disappear. It indicates that the isomers of Gd2Zr2O7 with pyrochlore and fluorite structure have been prepared successfully by controlling the sintering temperatures.

Raman spectra were also performed to confirm the difference of the two structures, as shown in Figure 2. It can be seen from the figure that there is no significant difference for the Raman spectra of all the samples, even the fluorite sample. As we know, the typical Raman spectrum of fluorite structure has only one Raman active vibration mode related to the oxygen ion at the site of \( 8c \) [13]. However, the sample sintered at 1600 °C shows multiple Raman peaks, which is inconsistent with previous XRD results.

Factor group analysis shows that the Raman vibration of the A2B2O7 pyrochlore structure have the following six vibration modes [14]:

\[ \Gamma(R) = A_{1g} + E_{g} + 4T_{2g} \]  

In order to further investigate the structure variation of the samples, the Raman spectra of all the samples were fitted using Lorentzian function. A representative fitting result of Raman spectrum of the sample sintered at 1450 °C is shown in Figure 2. Compared with the previous Raman spectra analysis of the pyrochlore structure [15-16], five Raman vibration modes were determined as marked in Figure 2, that is, the \( T_{2g} \) mode at 597.4 cm\(^{-1}\), the \( A_{1g} \) mode at 537.7 cm\(^{-1}\), the \( E_{g} \) mode at 401.3 cm\(^{-1}\), the \( T_{2g} \) mode at 340.2 cm\(^{-1}\), and the \( T_{2g} \) mode at 304.9 cm\(^{-1}\). In addition, there may be a \( T_{2g} \) mode at \( \sim 470 \) cm\(^{-1}\) according to the previous report [16], which cannot be observed due to the weak peak intensity.

Figure 1 XRD patterns of Gd2Zr2O7 samples  
Figure 2 Raman spectra of Gd2Zr2O7 samples at different sintering temperatures
It can be seen from the fitting results of Raman spectra that all the samples have 5 ~ 6 Raman active vibration modes. The wave number and relative intensity of Raman peaks show no distinct variation just with slight broadening. Compared with XRD, Raman scattering is expected to be more sensitive to the short-range structure in the lattice. So the inconsistent results between XRD and Raman indicate that the transition of Gd₂Zr₂O₇ from pyrochlore to fluorite structure may be a displacive phase transition during which the bonds and chemical environment vary little and result in similar Raman spectra.

![Figure 3](image)

Figure 3 Detailed information of Raman spectra of Gd₂Zr₂O₇ samples at different sintering temperatures: (a) Raman shift; (b) Full widths at half-maximum

Raman shift and full widths at half-maximum (FWHM) of the Raman spectra are shown in Figure 3. It can be seen from Figure 3(a) that the Raman shifts of various vibration modes of Gd₂Zr₂O₇ ceramics remain almost unchanged with the increasing sintering temperature. As shown in Figure 3(b), the FWHM varies greatly with the increasing sintering temperature. The FWHM of T₂g (1) and A₁g increases first and then decreases with the increase of the sintering temperature with a maximum at 1550 °C. As we know, the Raman line broadening usually originates from structural disorder or lattice strain. So the variation of the FWHM may indicate that the disorder in the lattice of pyrochlore Gd₂Zr₂O₇ ceramics increases with the increasing sintering temperature until the order-disorder transition occurs. The sample sintered at 1550 °C which is in the phase transition zone retains the most disordered state, whereas the counterpart sample sintered at 1600 °C may be in a state with disordered oxygen vacancies in long range as indicated by XRD pattern and with a more relaxed lattice in short range due to the phase transition as indicated by Raman spectrum. Moreover, the variation of the FWHM of E₉ and T₂g (2) is quite different from the above vibration modes. There is a significant decrease at 1550 °C rather than 1600 °C. However, it does not mean that the degree of order increases. The decrease of the number of corresponding vibration modes may be responsible for the decrease of FWHM. It is generally believed that the A₁g, E₉ and three T₂g vibration modes are related to the oxygen ion at the site of 48f, and only one T₂g vibration mode is related to the oxygen ion at the site of 8b. Therefore, the significant decrease of the FWHM of E₉ and T₂g (2) at 1550 °C may be attributed to the decrease of 48f oxygen ions due to the increasing anti-site defects in pyrochlore lattice.

3.2. Thermal conductivity of the samples

Figure 4 shows the thermal conductivity of all the samples as a function of the measuring temperature. The thermal conductivity was calculated by formula (1) and corrected by formula (2). It can be seen from the figure that the thermal conductivity gradually decreases as temperature increases with a slight increase above 500 °C. Generally speaking, the variation of thermal conductivity is usually related to the variation of the heat capacity and phonon mean free path of materials. At low temperature, the defects in the lattice will lead to the phonon scattering, resulting in the decrease of the mean free path and consequently the thermal conductivity. However, when the temperature is above certain value, the mean free path of phonon will reach its limit, and the heat capacity is close to 3R. The thermal conductivity
would not decrease any more. The slight increase in the figure can be attributed to the increase of the thermal radiation as photons at high temperature[7].

![Figure 4](image1.png)  ![Figure 5](image2.png)

**Figure 4** Thermal conductivity variation with temperature of the samples at different sintering temperatures  
**Figure 5** Variation of thermal conductivity at 500 °C of the samples as a function of the sintering temperature

In order to investigate the effect of order-disorder transition on thermal conductivity, the thermal conductivity data of all the sample at 500 °C were compared, as shown in Figure 5. It can be seen from the figure that the thermal conductivity decreases remarkably with the increasing sintering temperature from 1450 °C to 1550 °C, and surprisingly increases at 1600 °C. The sample sintered at 1550 °C shows a lowest thermal conductivity among all the samples, rather than the one sintered at 1600 °C.

In common sense, the cations and oxygen vacancies in the defective fluorite structure are completely disordered, whereas those in pyrochlore structure are ordered. The samples with defective fluorite structure are expected to show a lower thermal conductivity than those with pyrochlore structure. If we just compare the thermal conductivity of the sample sintered at 1600 °C with those sintered at 1450 °C or 1500 °C which show a more ideal pyrochlore structure as indicated by XRD, the fluorite Gd$_2$Zr$_2$O$_7$ seems to show a lower thermal conductivity. However, it can not reach this conclusion from the rest of our results. The thermal conductivity of the sample sintered at 1550 °C which is still pyrochlore structure is lower than that of the sample sintered at 1600 °C which is considered to be fluorite structure as indicated by XRD. It demonstrates that the transition of structure is not the only factor to affect the variation of the thermal conductivity.

According to the XRD and Raman results, the pyrochlore structure is getting more disorder with the increasing sintering temperature from 1450 °C to 1550 °C, which is consistent with the variation of thermal conductivity. It reveals that the ordering of oxygen vacancies in the perfect pyrochlore structure results in higher thermal conductivity, and structural distortion leads to the decrease of thermal conductivity. For the sample sintered at 1550 °C, the pyrochlore structure is heavily distorted approaching the imminent breakdown, though still with statistical order of the cations and oxygen vacancies in long range. The most serious structural distortion leads to the lowest thermal conductivity.

Raman spectra reveal that the defective fluorite Gd$_2$Zr$_2$O$_7$ is not completely disordered, but is in a similar bonds and chemical environment with the pyrochlore. The transition from pyrochlore to defective fluorite does not lead to a distinct disorder in oxygen vacancies as well as a distinct decrease of thermal conductivity. On the contrary, the transition may relax the serious structural distortion in the lattice, which results in an increase of thermal conductivity.

**4. Conclusion**

Gd$_2$Zr$_2$O$_7$ ceramics with pyrochlore and fluorite structure were prepared separately by controlling the sintering temperature. XRD patterns show that Gd2Zr2O7 gradually from pyrochlore to fluorite as the sintering temperature increases from 1450 oC to 1600 oC. However, Raman spectra reveal that the
defective fluorite Gd2Zr2O7 is not completely disordered, but is in a similar bonds and chemical environment with the pyrochlore.

With the increasing sintering temperature, thermal conductivities of Gd2Zr2O7 ceramics decreases for the samples with pyrochlore structure, and then increases for the sample with fluorite structure. The sample sintered at 1550 oC with a pyrochlore structure nearby the phase transition zone shows a lowest thermal conductivity, rather than that with fluorite structure. It reveals that the transition of structure is not the only factor to affect the variation of the thermal conductivity. Structural distortion in the lattice approaching phase transition may lead to a distinct decrease of thermal conductivity.

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