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Influence on the structural characteristic of defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$ under longer term annealing studied by ^{155}Gd Mössbauer spectroscopy

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Abstract

Three kinds of defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$, including the three single crystal samples with $x = 0.21$, 0.26 and 0.30, were investigated by ^{155}Gd Mössbauer spectroscopy at 12K. Difference in the structural characteristic under longer term annealing were confirmed by comparing the ^{155}Gd Mössbauer parameters of the polycrystalline samples sintered one time and twice at 1773K for 16h in air, respectively. The results indicated that the polycrystalline samples sintered twice have relatively equilibrated structure by comparing with the three single crystal samples. After being sintered twice, basically the local structure around the Gd^{3+} ions does not change, but the degree of the displacements of the six 48f oxygen ions from positions of cubic symmetry becomes slightly smaller, and distribution of the Gd^{3+} ions in the system becomes more homogeneous.

1. Introduction

Defect fluorite-based solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$ has been investigated widely as a good oxygen ion conductor and their ionic conductivities have a maximum value at about $x = 0.50$ [1]. Fig. 1 shows the local structure around the Gd^{3+} and Zr^{4+} ions in the ideal pyrochlore-type $Gd_2Zr_2O_7$ ($x = 0.50$) [2]. The Gd^{3+} and Zr^{4+} ions are coordinated by eight and six oxygen ions, respectively. In addition, the six oxygen ions in the 48f site are displaced from the position of the cubic symmetry. Recently, the $Gd_2Zr_2O_7$ ($x = 0.50$) compound was reported as a promoting candidate for immobilization of plutonium [3,4]. However, argument still exists about which is the more radiation-tolerant compound between the pyrochlore phase and the closely structurally related fluorite phase [5,6]. Structural and fundamental properties of the pyrochlore and fluorite phases in the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ need to be clarified deeply.

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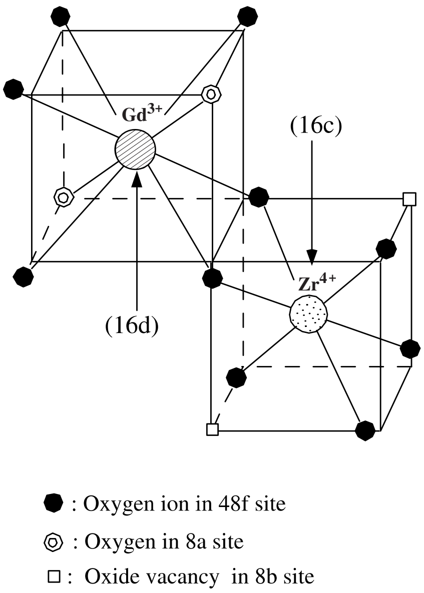

Fig. 1. Polyhedra of GdO_8 and ZrO_6 in the ideal pyrochlore-type $Gd_2Zr_2O_7$ ($x = 0.50$).

In this paper, ^{155}Gd Mössbauer Spectroscopy was applied for investigating the influence on the structural characteristic of defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$ under longer term annealing. Three kinds of defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$, including the three single crystal samples with $x = 0.21$, 0.26 and 0.30, were prepared and used in the present study. Difference was confirmed in the structural characteristic of the polycrystalline samples sintered one time and twice at 1773 K for 16 h in air. Comparing with the results of the single crystal samples, the polycrystalline samples sintered twice can be considerable to have relatively equilibrated structure as well as the single crystal samples.

2. Experimental

2.1. Synthesis of the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$

Three kinds of defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ samples were used in the present study. The first kind comprised three single crystal samples with $x = 0.21$, 0.26 and 0.30 purchased from Nippon Kenmazai Kogyo Corporation. The second kind were polycrystalline samples with $0.18 \leqslant x \leqslant 0.62$ synthesized by the wet chemical and ceramic method [7,8]. In the final step, all of the pellets were sintered at 1773 K for 16 h in air. The third kind were obtained by again sintering the second kind of samples at 1773 K for 16 h in order to investigate the differences of the structural properties sintered one time and twice, respectively.

2.2. Materials characterization

The crystal structures of all samples used in the present study were examined by powder X-ray diffraction (XRD). A conventional Rigaku RADIIC diffractometer with CuKα radiation ($\lambda = 1.54178$ Å) was used for measurement of their XRD patterns. The XRD data were collected with a step scan procedure (step interval: 0.02°; scan speed: 1° min^{-1}).

The ^{155}Gd Mössbauer measurements were performed with the developed ^{155}Eu/^{154}SmPd$_3$ (about 231 MBq) source. The preparation and evaluation of the developed ^{155}Eu/^{154}SmPd$_3$ (about 231 MBq) source are also published in the Journal of Nuclear Materials in detail (J. Wang et al. 2004). The ^{155}Gd Mössbauer spectra were measured on a Wissel Mössbauer measurement system as well as that reported previously [7–10]. The method applied for fitting the ^{155}Gd Mössbauer spectra is the same as that of the known standard absorbers, $GdPd_3$ and cubic Gd_2O_3. The $GdPd_3$ and cubic Gd_2O_3 compounds were selected as two standard absorbers for evaluating the performance of the developed ^{155}Eu/^{154}SmPd$_3$ (231 MBq) source.

3. Results and discussion

XRD analysis revealed that single-phases are formed for the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$. The fluorite phases exist for $0.18 \leqslant x < 0.45$ and $0.55 < x \leqslant 0.62$ and the pyrochlore phases for $0.45 \leqslant x \leqslant 0.55$. For the polycrystalline samples, the lattice parameters sintered one time are slightly longer than that sintered twice. The single-phase regions and the lattice parameters sintered twice are consistent with those reported previously [7,8,11]. The three single crystal samples with $x = 0.21$, 0.26 and 0.30 have fluorite-type structure and their lattice parameters are in fair agreement with those of the corresponding polycrystalline samples sintered twice. It is known that the true equilibrium structures of the fluorite and pyrochlore phases in the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ are very difficult to be determined since cation and anion diffusions exist in their crystal structures. However, the three single crystal samples can be considerable to have relatively equilibrated structure. Therefore, all of the polycrystalline samples sintered twice can be considered to have relatively equilibrated structure since the lattice parameters of the corresponding polycrystalline samples sintered twice are in fair agreement with those of the three single crystal samples. The results of ^{155}Gd Mössbauer spectroscopy support the consideration.

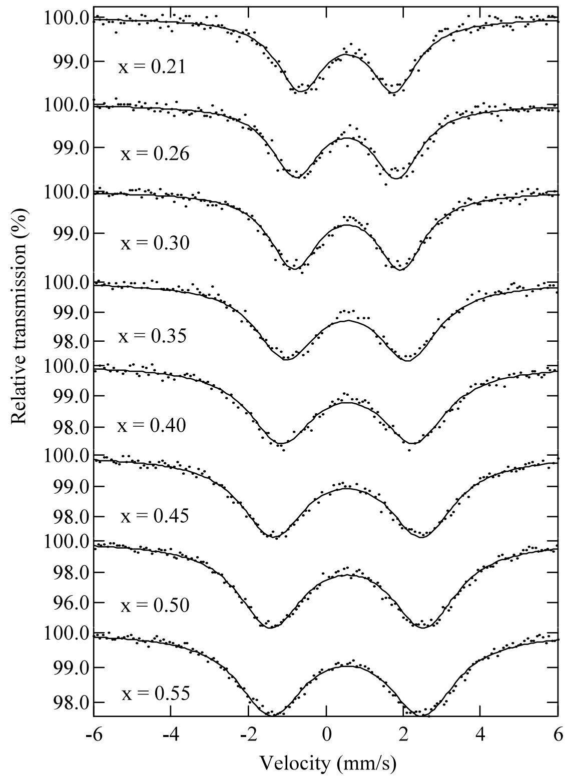

Fig. 2. ^{155}Gd Mössbauer spectra of the three single crystal samples with $x = 0.21$, 0.26, and 0.30 and of the polycrystalline samples with $x = 0.35$, 0.40, 0.45, 0.50, and 0.55 at 12 K sintered twice at 1773 K for 16 h in air.

Fig. 2 shows ^{155}Gd Mössbauer spectra of the three single crystal samples with $x = 0.21$, 0.26, and 0.30 and of the polycrystalline samples with $x = 0.35$, 0.40, 0.45, 0.50, and 0.55 at 12 K sintered twice. Their ^{155}Gd Mössbauer parameters are listed in Table 1. All of the spectra are typical electric quadrupole splitting pattern of ^{155}Gd [12]. They consist of single doublet, indicating basically the existence of one kind of Gd^{3+} site. The ^{155}Gd Mössbauer spectra of the three single crystal samples are very similar with that of the corresponding polycrystalline samples sintered twice. Some differences (line-width, degree of splitting, etc.) can be observed in the ^{155}Gd Mössbauer spectra of the polycrystalline samples sintered one time and twice, respectively.

Fig. 3 shows the plot of isomer shift (δ) against Gd content x for the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$. It is known that δ is a measure of the s-electron density at the Mössbauer nucleus and can be affected by local structure around the Mössbauer nucleus. In the case of ^{155}Gd, nuclear radius parameter, $\Delta R/R$, is negative, and the δ value increases with a decrease in s-electron density at the Gd nucleus [12]. The δ values for $0.18 \leqslant x \leqslant 0.50$ are nearly constant at about 0.55(1) mm s^{-1}. This seem to implies that local structure around the Gd^{3+} ions for $0.18 \leqslant x \leqslant 0.50$ is almost invariant from that of the ideal pyrochlore-type $Gd_2Zr_2O_7$ ($x = 0.50$) phase as that obtained from the EXAFS spectroscopy for the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.20 \leqslant x \leqslant 0.50$ [13]. However, the δ values increase slightly from 0.55 to 0.57 mm s^{-1} with increasing x for $0.50 < x \leqslant 0.62$. This indicated that slight variation of the local structure around the Gd^{3+} ions happens with increasing x in the region.

It is interesting that the three single crystal samples have the same δ values as the corresponding polycrystalline samples and no meaningful difference was observed in the δ values of the polycrystalline samples sintered one time and twice. From the same view point, it can

Table 1
^{155}Gd Mössbauer parameters of the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$ at 12 K

x (mol fraction of $GdO_{1.5}$)	δ (mm s^{-1})		e^2qQ (mm s^{-1})		2Γ (mm s^{-1})		Appendix
	One time	Twice	One time	Twice	One time	Twice	
0.18 (F)	0.55	0.55	5.10	5.03	1.55	1.45	
0.20 (F)	0.55	0.55	5.25	5.19	1.57	1.47	
0.21 (F)		0.55		5.26		1.43	Single crystal
0.25 (F)	0.55	0.55	5.67	5.59	1.62	1.50	
0.26 (F)		0.55		5.76		1.47	Single crystal
0.30 (F)	0.55	0.55	6.28	6.21	1.66	1.49	
0.30 (F)		0.55		6.25		1.45	Single crystal
0.35 (F)	0.55	0.55	6.80	6.74	1.95	1.81	
0.40 (F)	0.55	0.55	7.49	7.43	2.02	1.95	
0.45 (P)	0.55	0.55	8.26	8.22	2.05	1.99	
0.50 (P)	0.55	0.55	8.55	8.49	2.15	2.10	
0.55 (P)	0.56	0.56	8.36	8.32	2.11	2.05	
0.60 (F)	0.57	0.57	8.31	8.25	2.06	2.01	
0.62 (F)	0.57	0.57	8.15	8.10	1.98	1.85	

Experimental errors are ±0.01 mm s^{-1} for δ and ±0.05 mm s^{-1} for e^2qQ and 2Γ, respectively.

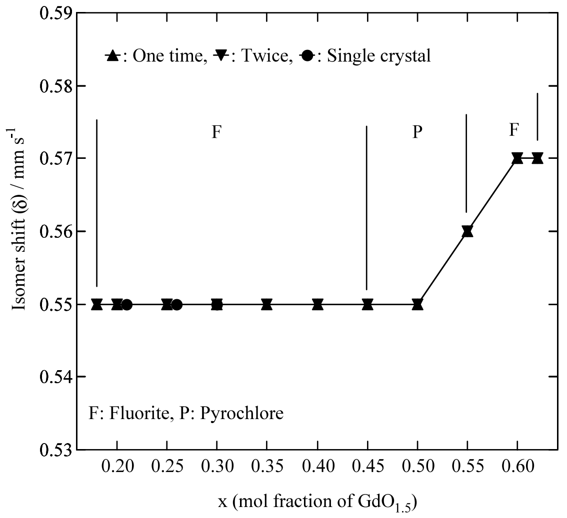

Fig. 3. Plot of isomer shift (δ) against Gd content x for the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$.

be considered that no clear difference exists in the local structure around the Gd^{3+} ions between the polycrystalline samples sintered one time and twice.

Fig. 4 shows the plot of quadrupole coupling constant (e^2qQ) against Gd content x for the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$. The e^2qQ values increase from 4.95 to 8.49 mm s^{-1} with increasing x for $0.18 \leqslant x \leqslant 0.50$ and decrease to 8.10(5) mm s^{-1} for $0.50 < x \leqslant 0.62$. There is a maximum value in the ideal pyrochlore-type $Gd_2Zr_2O_7$ ($x = 0.50$). A tendency was observed that the e^2qQ values of the polycrystalline samples sintered one time are slightly larger than that sintered twice. Moreover, the e^2qQ values of the three single crystal samples are in fair good agreement with those of the corresponding polycrystalline samples sintered twice.

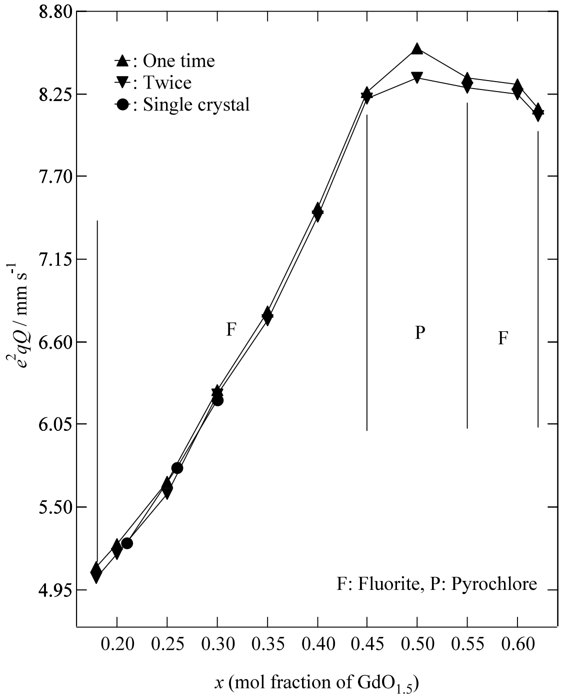

Fig. 4. Plot of quadrupole coupling constant (e^2qQ) against Gd content x for the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$.

It is known that the e^2qQ value reflects the magnitude of the electric field gradient at the Gd nucleus. In the case of ^{155}Gd, the lattice contribution of the electric field gradient is dominant since the Gd^{3+} ($4f^7$) ion has a highly symmetric valence electron distribution [12]. The lattice contribution of the electric field gradient originates from asymmetric location of the oxygen ions around the Gd^{3+} ions. Thus, from the e^2qQ value of the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$, we can know that displacements of the oxygen ions in the 48f site from positions of the cubic symmetry increase with increasing x for $0.18 \leqslant x < 0.50$ and decrease for $0.50 < x \leqslant 0.62$. The degree of the displacement is the largest one in the ideal pyrochlore-type $Gd_2Zr_2O_7$ ($x = 0.50$). Moreover, the degree of the displacements in the polycrystalline samples sintered twice are slightly smaller than that sintered one time. This is reasonable since a decrease in displacement of the oxygen ion around the Gd^{3+} ions is of benefit to form the more equilibrated structure.

Fig. 5 shows the plot of line-width (2Γ) against Gd content x for the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$. The trend of 2Γ with Gd content x is in some resemblance to that of e^2qQ as shown in Fig. 4. The 2Γ of the polycrystalline samples sintered twice are clearly smaller than that of the corresponding polycrystalline samples sintered one time. Furthermore, the 2Γ of the three single crystal samples are almost the same with that of the corresponding polycrystalline samples sintered twice.

It is clear that the 2Γ including those of the three single crystal samples are much broader than that of the ordinary Gd compounds, such as the selected standard absorber, $GdPd_3$ [$2\Gamma = 0.89(5)$ mm s^{-1}, 12 K]. The reason is mainly because the oxygen vacancies and disorders exist in the system. On the other hand, it should be noted that the 2Γ of the ideal pyrochlore-type $Gd_2Zr_2O_7$ ($x = 0.50$) is the broadest one among the system though its crystal structure should be ordered completely. The trend of the 2Γ indicated that the 2Γ become broader as the degree of ordering in the crystal structure of the system become larger. Other reason is also possible, such as fast paramagnetic relaxation effect and Goldansky–Karyagin effect caused by strongly anisotropic lattice vibration [14–18]. By the way, the broadest 2Γ does not originate from the magnetic ordering since the ideal

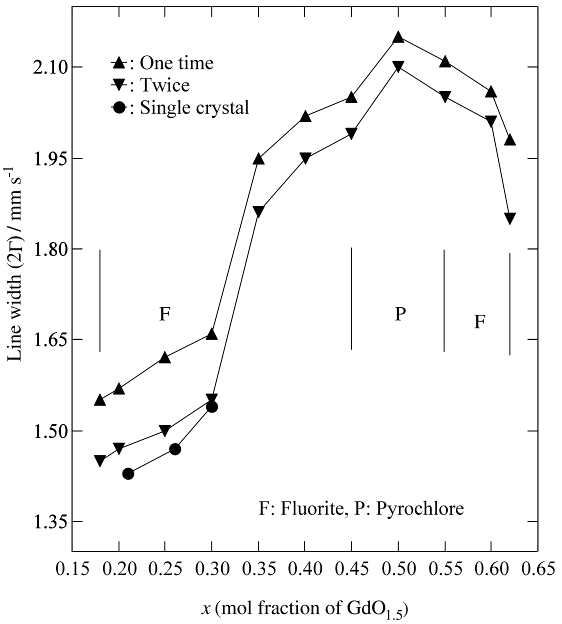

Fig. 5. Plot of line-width (2Γ) against Gd content x for the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$.

pyrochlore-type $Gd_2Zr_2O_7$ ($x = 0.50$) is paramagnetic from 4 K to room temperature as shown in Fig. 6.

In addition, distribution of the Gd^{3+} ions in the system become more homogeneous under longer term annealing since the 2Γ of the polycrystalline samples sintered twice are narrower than that of the corresponding samples sintered one time. Furthermore, there is a clear difference in the 2Γ between $x = 0.30$ and 0.35. The two samples were measured several times and almost the same results were obtained. It indicated that there is some structural change between $x = 0.30$ and 0.35, in accordance with the report that anti-phase domain structure of the pyrochlore-type phases appear from $x = 0.33$ [19].

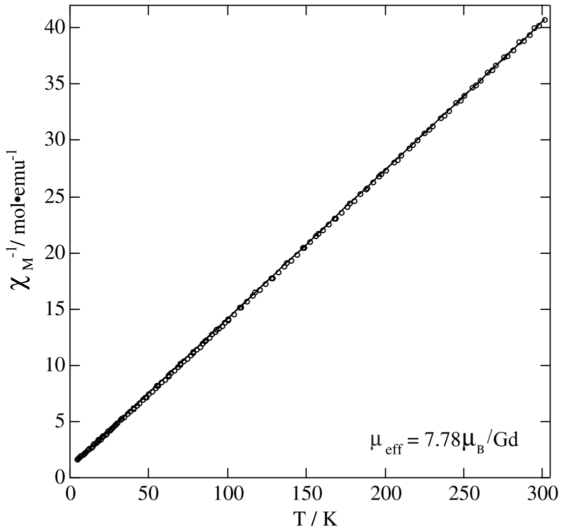

Fig. 6. Temperature dependence of magnetic susceptibility for the ideal pyrochlore-type $Gd_2Zr_2O_7$ ($x = 0.50$).

4. Conclusion

The fluorite- and pyrochlore-type compounds in the defect solid solution $Gd_xZr_{1-x}O_{2-x/2}$ with $0.18 \leqslant x \leqslant 0.62$ basically consist of one kind of Gd^{3+} site. The polycrystalline samples sintered twice have relatively equilibrated structure by comparing with the three single crystal samples with $x = 0.21$, 0.26 and 0.30. The differences of longer term annealing on the Mössbauer parameters have been observed. Local structure around the Gd^{3+} ions is almost invariant from that of the ideal pyrochlore-type structure at $x = 0.50$ (i.e., $Gd_2Zr_2O_7$) for $0.18 \leqslant x \leqslant 0.50$. However, the local structure changes slightly with increasing x for $0.50 < x \leqslant 0.62$. The oxygen ions around the Gd^{3+} ions are displaced from positions of cubic symmetry in the fluorite and pyrochlore phases and the degree of the displacement is the largest one in the ideal pyrochlore-type $Gd_2Zr_2O_7$ ($x = 0.50$). The broad line-widths mainly originate by the oxygen vacancies, disorder and heterogeneous distribution of the Gd^{3+} ions existing in the system, also affect by some other reasons. After the solid solution are sintered twice at 1773 K for 16 h in air, basically the local structure around the Gd^{3+} ions does not change, but degree of the displacements of the oxygen ions around the Gd^{3+} ions become slightly smaller, distribution of the Gd^{3+} ions in the system become more homogeneous.

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