Development and evaluation of a new ^{155}Eu/^{154}SmPd$_3$ source for use with ^{155}Gd Mössbauer spectroscopy

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Abstract

A ^{155}Eu/^{154}SmPd$_3$ (about 231 MBq) source for use with ^{155}Gd Mössbauer spectroscopy was developed by a novel method. In the novel method, the isotopically enriched ^{154}SmPd$_3$ compound was prepared by the conventional solid state reaction of ^{154}Sm(HCOO)$_3$ and PdH$_x$ in a hydrogen atmosphere at 1273 K for 18 h, which is simpler than the previously reported method. In order to increase the reaction areas, palladium fine particles used to synthesize the PdH$_x$ hydride were prepared by a chemical solution process. Performance of the newly developed source was evaluated by observing the ^{155}Gd Mössbauer spectra of known compounds, GdPd$_3$ and cubic Gd$_2$O$_3$ at 12 K. The obtained results indicated that the developed source is fine enough to investigate the structural characteristic of various materials containing gadolinium.
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1. Introduction

It is well known that Mössbauer spectroscopy has become a standard technique in solid state research, which, in many cases, provides microscopic information that cannot be obtained in other ways. On the Mössbauer resonance of ^{155}Gd, three Mössbauer transitions of ^{155}Gd have been known (60, 86.5, 105.3 keV) [1]. Considering the Mössbauer fraction and the line-width, together with the other nuclear factors, which affect the

hyperfine splitting, the 86.5 keV transition is the most convenient one for applying for the investigation of materials containing gadolinium. A ^{155}Gd Mössbauer quadrupole split spectrum normally has the appearance of doublet because of small quadrupole moment of the 86.5 keV excited state. Up to now, many researches (most by Cashion's group) have been reported on the Mössbauer resonance of ^{155}Gd using the 86.5 keV transition [1]. Most of them were mainly concentrated on the physical properties of materials containing gadolinium.

There is wide interest in investigating the structural properties of various materials containing gadolinium by ^{155}Gd Mössbauer spectroscopy, especially Gd(III) complexes and defect solid solution systems. We developed a new ^{155}Eu/^{154}SmPd$_3$ (about 231 MBq) source for use with ^{155}Gd Mössbauer spectroscopy by a novel method which is simplified in preparation of the

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isotopically enriched $^{154}SmPd_3$ compound compared with that reported by Prowse et al. [2]. In the novel method, the $^{154}SmPd_3$ compound was prepared by the conventional solid state reaction in a hydrogen atmosphere. Furthermore, palladium fine particles used to synthesize starting material PdH_x hydride were prepared by a chemical solution process in order to increase the reaction areas. Gd(III) cyano assembled complexes and Gd(III)-β-diketonato complexes have been investigated using the newly developed $^{155}Eu/^{154}SmPd_3$ (about 231 MBq) source and correlation between crystal structure and electric field gradient at the Gd^{3+} ions was confirmed [3,4].

In this paper, the development and evaluation of the newly developed $^{155}Eu/^{154}SmPd_3$ (about 231 MBq) source for use with ^{155}Gd Mössbauer spectroscopy was reported in detail. High performance of the newly developed source was proved by observing the ^{155}Gd Mössbauer spectra of known compounds, $GdPd_3$ and cubic Gd_2O_3. The $GdPd_3$ compound is iso-structural with the source compound, $^{154}SmPd_3$ and its ^{155}Gd Mössbauer spectra was known to show single line pattern [5]. The cubic Gd_2O_3 compound have two crystallographically inequivalent Gd^{3+} sites and the population is 3:1, which can be identified clearly by ^{155}Gd Mössbauer spectroscopy [6]. The obtained results in the present study indicated that the newly developed source is single line and fine enough to investigate the structural characteristic of materials containing gadolinium.

2. Experimental

2.1. Preparation of the $^{155}Eu/^{154}SmPd_3$ source

The isotopically enriched $^{154}SmPd_3$ compound was prepared by using the conventional solid state reaction of $^{154}Sm(HCOO)_3$ with PdH_x in a hydrogen atmosphere. $^{154}Sm(HCOO)_3$ was synthesized by starting materials $^{154}Sm_2O_3$ (Wako, 96.5%) and HCOOH (Wako, 50%). PdH_x was synthesized by reacting palladium fine particles and dried hydrogen gas with a pressure of 600 Torr in an evacuated system at room temperature. In order to increase the reaction areas, the palladium fine particles were used instead of commercial palladium plate (Rare Metallic, 99.9%). This point is also different from that reported previously [2].

The palladium fine particles were synthesized according to the following chemical solution process. The palladium plate was dissolved into aqua regia and the obtained solution was evaporated. The residue was dissolved into distilled water again. The aqueous solution was stirred continuously and HCOOH (Wako, 88%) was slowly added. Black precipitation was produced and the color of the solution changed from black to colorless after NaOH (Wako, 99.9%) was added. The precipitate was cooked for about 2 h at 373 K and then was filtered, washed by distilled water and dried in a vacuum desiccator for several days. Schemes of the main reactions are shown as the follows:

$$2Pd + 2HCl + 2HNO_3 \rightarrow PdCl_2 + Pd(NO_3)_2 + 2H_2\uparrow \tag{1}$$

$$PdCl_2 + Pd(NO_3)_2 + NaOH \rightarrow 2Pd(OH)_2\downarrow + 2NaCl + 2NaNO_3 \tag{2}$$

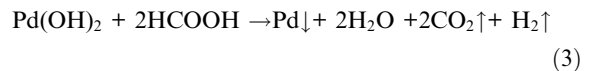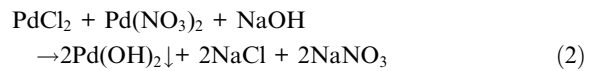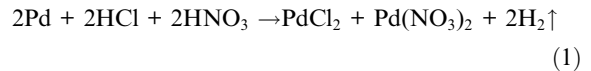$$Pd(OH)_2 + 2HCOOH \rightarrow Pd\downarrow + 2H_2O + 2CO_2\uparrow + H_2\uparrow \tag{3}$$

Fig. 1 shows the apparatus for preparing the isotopically enriched $^{154}SmPd_3$ compound. $^{154}Sm(HCOO)_3$ and PdH_x were mixed and ground intimately with a molar ratio of $^{154}Sm:Pd = 1:3$. The mixture was pelletized to a disc (ϕ 10 mm), which was wrapped with tantalum sheet as an oxygen getter and titanium sheet to prevent it reacting with the quartz tube. The dried hydrogen gas was passed through the quartz tube and outgased to air with an average pressure of 200 Torr. In the final step, the sample was calcined at 1273 K for 18 h in the hydrogen atmosphere.

Prepared $^{154}SmPd_3$ (312.4 mg) pellet was wrapped with aluminum sheet with 99.99% purity and irradiated by JRR-3M-HR-1 reactor (the flux of neutrons: $6.0 \times 10^{13} cm^{-2} s^{-1}$) for 67 h in Japan atomic energy research institute (JAERI). After irradiation, the sample was left in JAERI for one month in order to wait for the palladium activity to die. Scheme of the nuclear reaction was shown as the follow:

$$^{154}Sm(n, \gamma)^{155}Sm(\beta^-, 22 \min)^{155}Eu(\beta^-, 4.96y)^{155}Gd$$
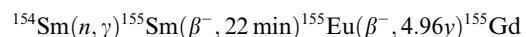
Finally, the newly developed $^{155}Eu/^{154}SmPd_3$ source was obtained. It was mounted to an aluminum holder and again wrapped by aluminum sheet with 99.99% purity. Araldite adhesive was used in order to mount the source on the holder tightly.
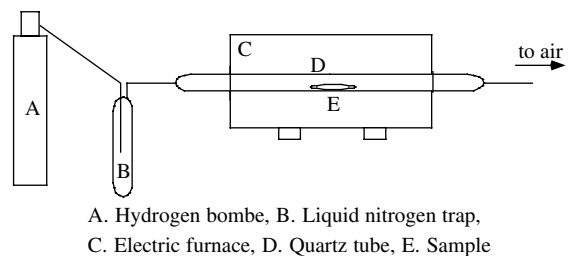

A. Hydrogen bombe, B. Liquid nitrogen trap,
C. Electric furnace, D. Quartz tube, E. Sample

Fig. 1. Apparatus for preparing the enriched isotopes $^{154}SmPd_3$ compound.

2.2. Synthesis of the standard absorber GdPd₃

The GdPd$_3$ and cubic Gd$_2$O$_3$ compounds were selected as standard absorbers for evaluating the newly developed source. As mentioned above, [155]Gd Mössbauer spectroscopic studies on the GdPd$_3$ and cubic Gd$_2$O$_3$ compounds have been reported by the Cashion's group. In the present study, the GdPd$_3$ compound was synthesized by arc-melting gadolinium and palladium metals with high purity in a molar ratio 1:3. After arc-melting, the weight loss is less than 0.1%, indicating that the evaporations of the gadolinium and palladium metals are very little. The GdPd$_3$ compound was annealed in vacuum at 1273 K for 20 h before the measurements of its powder X-ray diffraction (XRD) patterns and [155]Gd Mössbauer spectrum. The cubic Gd$_2$O$_3$ compound was purchased from Wako Pure Chemical Industries, Ltd. and used as received.

2.3. Materials characterization

The crystal structures of all compounds used in the present study were examined by XRD. A conventional Rigaku RADIIC diffractometer with Cu Kα 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}). In addition, the samarium content in [154]Sm(HCOO)$_3$ was analyzed by chelatometry.

According to the method reported by Prowse et al., the product was mixed hydrides after the mixture of [154]Sm(HCOO)$_3$ and PdH$_x$ was calcined at high temperature in a hydrogen atmosphere [1]. However, the product obtained in the present study was confirmed as [154]SmPd$_3$, not as [154]SmPd$_3$H$_x$ or [154]SmH$_x$ and PdH$_x$, by the channeling method using nuclear reaction ^{1}H(^{11}B,α)αα [7]. In the channeling method, hydrogen is detected by measuring the α particles produced by sending an ^{11}B beam in the channeling direction. As a reference, hydrogen amount in ErH$_2$ was firstly detected. ErH$_2$ was synthesized by reacting erbium metal with hydrogen gas at 1123 K for 4 h and confirmed to have a cubic structure. It is known that lanthanide di-hydrides, LnH$_x$, have a cubic structure for $1.94 < x < 2.08$ [8]. After the validity of the channeling method using nuclear reaction ^{1}H(^{11}B,α)αα was proved by detecting hydrogen amount in ErH$_2$, hydrogen amount in SmPd$_3$ was also tested. SmPd$_3$ was synthesized from natural Sm$_2$O$_3$ (Wako, 99.9%) and PdH$_x$ according the method using for preparing [154]SmPd$_3$ in the present study.

2.4. [155]Gd Mössbauer measurement

The [155]Gd Mössbauer measurements were performed with the newly developed [155]Eu/[154]SmPd$_3$ (about 231 MBq) source. The [155]Gd Mössbauer spectra were measured on a Wissel Mössbauer measurement system (MDU-1200, MVC-450, etc.). Both the source and sample containing 115 mg Gd cm^{-2} were kept at 12 K in a cryostat equipped with a closed-cycle refrigerator [9]. The diameter of the sample holder was 15 mm. The 86.5 keV γ-rays were counted with a pure Ge detector. The Doppler velocity was also calibrated by measuring a ^{57}Fe Mössbauer spectrum of α-iron foil. The [155]Gd Mössbauer spectrum of the standard absorbers, GdPd$_3$ and cubic Gd$_2$O$_3$ were fitted in terms of one or two single, quadrupole-split pentet ($I_g = 3/2$, $I_e = 5/2$, $\eta = 0$) of the Lorentzian lines [10]. The quadrupole moments used for the ground and excited states of the 86.5 keV transition are $Q_g = 1.50$ b and $Q_e = 0.18$ b, respectively [6]. The magnetic interaction was not included in the curve fitting. The isomer shift (δ) was referred to the source.

3. Results and discussion

In the process for preparing PdH$_x$ at room temperature, the sample became very hot and the hydrogen pressure decreased from 600 to 590 Torr. This indicated that the palladium fine particles reacted with hydrogen gas at room temperature in a pressure of 600 Torr. Fig. 2 shows the XRD patterns of PdH$_x$, [154]SmPd$_3$ and SmPd$_3$. For a
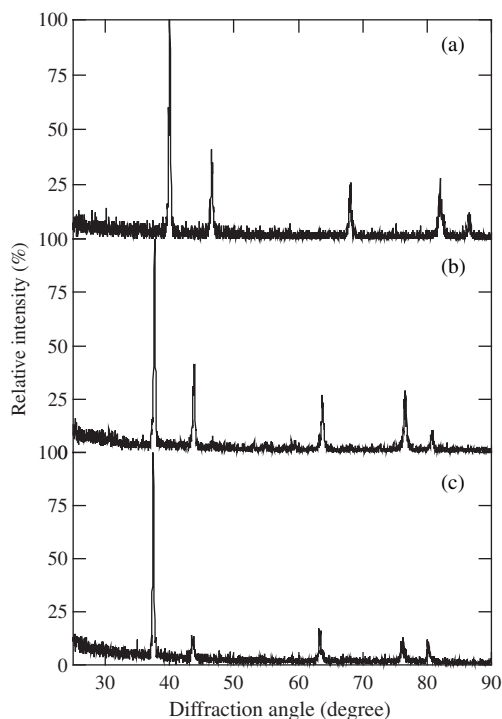

Fig. 2. Powder X-ray diffraction (XRD) patterns of PdH$_x$ (a), [154]SmPd$_3$ (b) and SmPd$_3$ (c). SmPd$_3$ was synthesized by arc-melting method.

comparison, $SmPd_3$ was synthesized by arc-melting samarium and palladium metals with high purity in a molar ratio 1:3. PdH_x has similar XRD patterns with those of $^{154}SmPd_3$ and $SmPd_3$. However, the diffraction peaks of $^{154}SmPd_3$ and $SmPd_3$ were shifted to lower angles than those of PdH_x. This indicated that lattice parameter of PdH_x is smaller than that of $^{154}SmPd_3$ and $SmPd_3$ though all of them have a cubic structure. The lattice parameters are 388.5(2) pm for PdH_x, 409.3(2) pm for $^{154}SmPd_3$ and 409.5(2) pm for $SmPd_3$. The lattice parameter of $^{154}SmPd_3$ is the same as that of $SmPd_3$ within the experimental error. In other words, XRD indicated that $^{154}SmPd_3$ is the same compound as $SmPd_3$.

In addition, the results of the channeling detection of hydrogen using the nuclear reaction $^1H(^{11}B, \alpha)\alpha\alpha$ indicated that the hydrogen amount in $SmPd_3$ is very small compared with that of ErH_2. And even considering difference of the host lattices of hydrogen in ErH_2 and $SmPd_3$, the hydrogen amount in $SmPd_3H_x$ has an upper limit of $x = 0.03$. This is consistent with that obtained from XRD.

Therefore, we can conclude that the product obtained in the present study is $^{154}SmPd_3$, not samarium and palladium hydrides. Prowse et al. reported that the mixed hydrides should be further dissociated in a vacuum induction furnace and then melted in argon-arc furnace in order to obtain $^{154}SmPd_3$ [1]. However, $^{154}SmPd_3$ is successfully prepared by only using the conventional solid state reaction of $^{154}Sm(HCOO)_3$ with PdH_x in a hydrogen atmosphere at 1273 K for 18 h. The method is clearly simpler than that reported by Prowse et al.

Fig. 3 shows ^{155}Gd Mössbauer spectra of the known compounds, $GdPd_3$ and cubic Gd_2O_3 at 12 K obtained in the present study. ^{155}Gd Mössbauer spectrum of $GdPd_3$ is a single line peak and can be fitted well without including the electric quadrupole interaction and magnetic ordering. This is consistent with that reported by Cashion's group. The observed linewidth [$2\Gamma = 0.89(5)$ mm s^{-1}] is comparable to the natural linewidth ($2\Gamma_{nat} = 0.50$ mm s^{-1}) [1]. The linewidth of 0.89(5) mm s^{-1} is slightly larger than that obtained by Prowse et al. ($2\Gamma = 0.80$ mm s^{-1}) [2,5], but a direct comparison cannot be made because Prowse et al. have not given the absorber thickness. Since $GdPd_3$ is iso-structural with the source compound $^{154}SmPd_3$, the observed isomer shift of +0.03(1) mm s^{-1} is close to zero. ^{155}Gd Mössbauer spectrum of cubic Gd_2O_3 shows two doublet peaks with an area ratio 3:1. The two doublet peaks imply that two kinds of Gd^{3+} sites exist in cubic Gd_2O_3 and molar ratio of them is 3:1. The obtained Mössbauer parameters of cubic Gd_2O_3 are consistent with that reported by Cashion et al. [6]. Therefore, the prepared source is fine enough to apply for investigating the solid state properties of materials containing gadolinium.
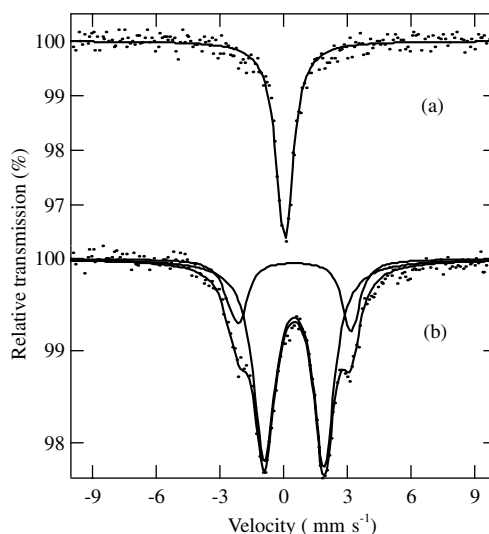

Fig. 3. ^{155}Gd Mössbauer spectra of the known compounds, $GdPd_3$ (a) and cubic Gd_2O_3 (b) at 12 K obtained in the present study.

4. Conclusion

The fine $^{155}Eu/^{154}SmPd_3$ (about 231 MBq) source use for ^{155}Gd Mössbauer spectroscopy was successfully developed by the novel method described above. The novel method is simpler than that reported by Prowse et al. in preparing the isotopically enriched $^{154}SmPd_3$ compound. In addition, the palladium fine particles as starting material for synthesizing PdH_x can be prepared by the chemical solution process. High performance of the newly developed source was proved by the selected standard absorbers, $GdPd_3$ and cubic Gd_2O_3. The ^{155}Gd Mössbauer spectrum of $GdPd_3$ is a considerably narrow single line and the observed linewidth [$2\Gamma = 0.89(5)$ mm s^{-1}] is comparable to the natural linewidth ($2\Gamma_{nat} = 0.50$ mm s^{-1}). The obtained Mössbauer result of cubic Gd_2O_3 is completely consistent with that obtained by the Cashion's group.

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