Mössbauer Spectroscopy of Annealed Metamict Gadolinite $REE_2Fe^{2+}Be_2Si_2O_{10}$ from 473 to 873 K in Air

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The effect of medium-temperature annealing on fully metamict gadolinite was studied using Mössbauer spectroscopy. Metamict minerals contain radioactive elements that degrade their crystal structure. Mössbauer spectra for samples annealed at 473, 573, 673, and 773 K can be fitted to two Fe^{2+} quadrupole doublets and do not show the presence of a Fe^{3+} component. After heating at 773 K, an increase in the quadrupole splitting of the first Fe^{2+} component and the line width of both Fe^{2+} components is observed. The Fe^{3+} component appears after annealing at 873 K.

topics: Mössbauer spectroscopy, metamict minerals, gadolinite, radiation damage

1. Introduction

Gadolinite $REE_2Fe^{2+}Be_2Si_2O_{10}$, where REE denotes rare earth elements, yttrium, uranium, and thorium, belongs to metamict minerals [1–3]. Radioactive elements in metamict minerals damage the crystal structure primarily due to recoil nuclei from α-decays of ^{238}U, ^{232}Th, ^{235}U, and their daughter products [4]. These minerals are widely used in geochronology and can serve as natural analogs of radiation effects in high-level nuclear waste [5–7]. Their crystalline structure can be restored by heating in an inert atmosphere. A pitch-black sample of fully metamict gadolinite used in this study was collected in pegmatites from Ytterby (Sweden). The sample is dated at 1.8 Ga with a calculated total absorbed α-dose of 1.07×10^{16} α-decay mg^{-1} [8, 9].

Mössbauer spectra of gadolinite from Ytterby annealed from 373 to 773 K in air (spectra without fitting) were presented in a previously published paper [9]. The research aimed to record changes in the hyperfine parameters of Fe^{2+} components and their possible oxidation to Fe^{3+} associated with the annealing process from 473 to 773 K.

2. Materials and methods

After breaking the sample, smaller fragments were placed in ceramic evaporators and annealed for 1 h in a muffle furnace with temperature stabilization of ± 2 K. For Mössbauer spectroscopy, the fragments were ground into a powder and prepared in a thin disc. The Mössbauer transmission spectra were recorded at room temperature using a constant acceleration spectrometer, a multichannel analyzer with 512 channels, and a linear $^{57}Co/Rh$ source (= 50 mCi) absorber and detector arrangement. The Mössbauer spectra were numerically analyzed using the fitting Recoil code, and all doublets were fitted with Lorentzian lines. The velocity scale was calibrated using α-Fe' foil.

3. Results and discussion

The ^{57}Fe Mössbauer spectra of the annealed gadolinite samples from 473 to 773 K are shown in Fig. 1. The hyperfine parameters derived from the fitting procedure are summarized in Table I.

The Mössbauer spectrum of the untreated sample is a superposition of two dominant Fe^{2+} distributions with maxima at 1.59 and 2.16 mm/s and with relative contributions of 0.47 and 0.53, respectively [9]. Based on this distribution, the Mössbauer spectra of the samples annealed from 473 to 773 K were fitted to two quadrupole doublets, labeled as '1' and '2' (Table I, Fig. 1). Doublet no. 1 represents Fe^{2+} octahedra that have undergone contraction, while the doublet no. 2 represents Fe^{2+} octahedra that have undergone expansion during metamictization [10].

TABLE I

Parameters for ^{57}Fe Mössbauer spectra of gadolinite samples annealed in air (Fig. 1). Here, χ^2 denotes the accuracy of the fit.

Annealing temperature [K]	No.	χ^2	δ [mm/s]	Δ [mm/s]	Γ [mm/s]	Assignment [CN]	Rel. area
473	1	1.1	0.94(2)	1.55(4)	0.56(3)	$Fe^{2+}(6)$	0.45(6)
	2		1.08(1)	2.14(3)	0.54(2)	$Fe^{2+}(6)$	0.55(6)
573	1	1.4	0.95(2)	1.55(4)	0.56(3)	$Fe^{2+}(6)$	0.43(6)
	2		1.07(1)	2.15(3)	0.54(2)	$Fe^{2+}(6)$	0.57(7)
673	1	1.3	0.96(1)	1.59(3)	0.60(2)	$Fe^{2+}(6)$	0.49(4)
	2		1.08(1)	2.17(3)	0.54(2)	$Fe^{2+}(6)$	0.51(5)
773	1	1.6	0.93(4)	1.63(3)	0.64(3)	$Fe^{2+}(6)$	0.51(3)
	2		1.07(2)	2.17(2)	0.58(2)	$Fe^{2+}(6)$	0.49(3)

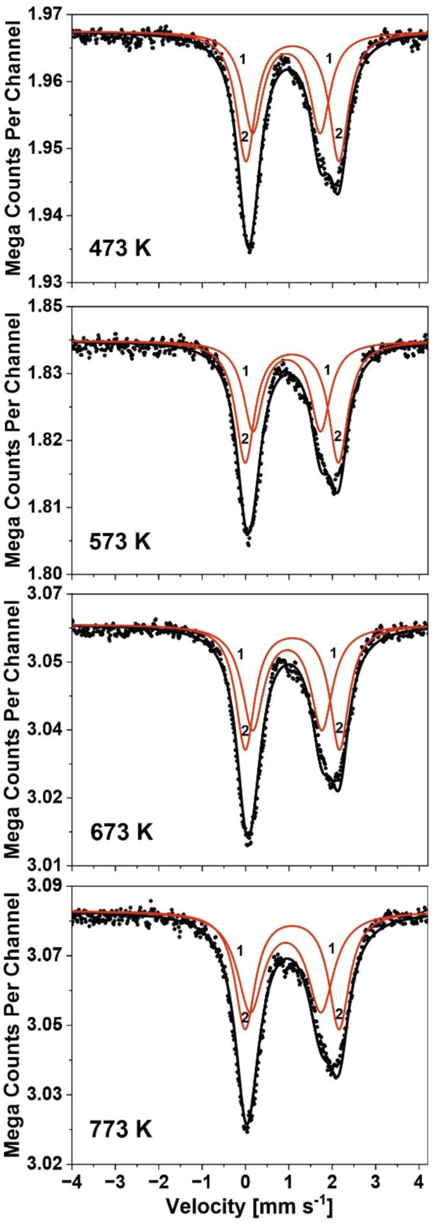

Fig. 1. Mössbauer spectra for gadolinite samples annealed in air for 1 h at the given temperatures.

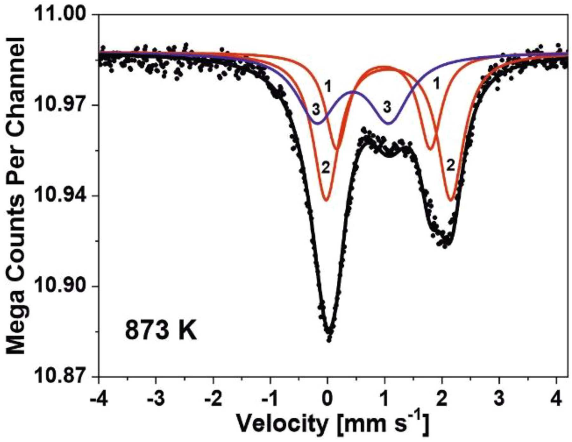

Fig. 2. Mössbauer spectrum for gadolinite sample annealed in air for 1 h at 873 K [9].

The isomer shift of doublet no. 1 having an average value of $\delta = 0.95$ mm/s, within the measurement uncertainty, remains constant in the annealing range of 473–773 K, while the quadrupole splitting increases from $\Delta = 1.55$ mm/s in the spectra of samples annealed at 473 K and 673 K to $\Delta = 1.63$ mm/s for the sample annealed at 773 K.

Similarly, for doublet no. 2, the value of the isomer shift $\delta \sim 1.08$ mm/s does not change, while the value of the quadrupole splitting increases slightly from $\Delta = 2.14$ mm/s in the spectrum of the sample annealed at 473 K to $\Delta = 2.17$ mm/s in the spectrum after annealing at 773 K (Table I, Fig. 1). In the annealing range from 473 to 673 K, a larger relative contribution — on average 0.53 — was from component no. 2. After annealing at 773 K, doublet no. 1 is characterized by a higher relative contribution of 0.51.

An apparent change in the Mössbauer spectrum is observed for the sample heated at 873 K [9]. As shown in Fig. 2, after annealing at 873 K, the Fe^{3+} component appears — labeled as no. 3 — with a relative contribution of 0.31 (Table II).

TABLE II

Parameters for ^{57}Fe Mössbauer spectrum of gadolinite sample annealed at 873 K (Fig. 2).

Annealing temperature [K]	No.	χ^2	δ [mm/s]	Δ [mm/s]	Γ [mm/s]	Assignment [CN]	Rel. area
873	1	0.98	0.97(1)	1.64(2)	0.48(2)	Fe^{2+}(6)	0.25(7)
	2		1.06(2)	2.18(2)	0.54(2)	Fe^{2+}(6)	0.44(7)
	3		0.44(2)	1.26(1)	0.84(2)	Fe^{3+}(6)	0.31(4)

As seen in Table II, the Fe^{3+} component is characterized by a very large line width $\Gamma = 0.84$ mm/s, which results from the oxidation of Fe^{2+} represented by doublet no. 1. Component no. 1 represents those Fe^{2+} octahedra that have contracted during the metamictization process. Hence, preferential oxidation of Fe^{2+} from these structural positions is observed. In contrast, the relative contribution of component no. 2, representing the octahedra that expanded during metamictization, does not change noticeably.

4. Conclusions

Annealing of metamict gadolinite from 473 to 773 K in air for 1 h does not result in oxidation of Fe^{2+} to Fe^{3+}. The Mössbauer spectra of gadolinite fragments annealed in this temperature range consist of two Fe^{2+} quadrupole doublets. The indicator of slow structural changes in the annealing range of 473–773 K is the observed increase in the quadrupole splitting of the first Fe^{2+} component and the line width of both Fe^{2+} components. The Fe^{3+} component with a relative contribution of 0.31 is formed only after heating at 873 K. The presented results indicate that the gadolinite phase, $REE_2Fe^{2+}Be_2Si_2O_{10}$, is resistant to oxidation.

Acknowledgments

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