^{57}Fe Mössbauer spectroscopy of annealed metamict davidite

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Abstract. This paper reports preliminary results of ^{57}Fe Mössbauer spectroscopy and X-ray diffraction (XRD) studies of metamict davidite samples $(La,Ce,Ca,Th)(Y,U,Fe)(Ti,Fe,Mn)_{20}(O,OH)_{38}$ after high temperature annealing in an argon atmosphere. The Mössbauer spectra show a gradual decrease of quadrupole splitting and line width values of an Fe^{3+} doublet with increasing annealing temperature. Rather unexpected feature of these spectra for an Fe^{2+} doublet is a considerable increase of the line width with progressive crystallinity and a simultaneous decrease of both quadrupole splitting and isomer shift values. Changes of the hyperfine parameters as a function of the annealing temperature appeared as sensitive indicators of the thermal recrystallization process of metamict davidite similar to metamict silicates.

Key words: davidite • metamict minerals • recrystallization • Mössbauer spectroscopy

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Introduction

Davidite (multiple oxides) – $(La,Ce,Ca,Th)(Y,U,Fe)(Ti,Fe,Mn)_{20}(O,OH)_{38}$ belongs to the group of metamict minerals [3, 7]. Metamict minerals are a class of natural amorphous materials which were initially crystalline but self-radiation damage mainly from alpha decays of ^{238}U, ^{232}Th, ^{235}U series inside the structure can produce partially or fully amorphization (metamictization) of these minerals [1, 2]. Investigations of these materials are important because minerals containing large concentrations of uranium and thorium can serve as natural analogues for radiation effects in high-level nuclear waste form (HLW) [6, 8]. Davidite is isostructural with the crichtonite – a group of minerals having a structure based on a close-packed anion framework with the mixed stacking sequence ABCBCACABA with rare earth elements REE M(0), occupying a site in the anion framework and five cation sites M(1)-M(5) [3]. According to this refinement, U^{4+} ions do not substitute for REE in M(0), but occupies an octahedral site M(1) along with Y and small REE (Er, Yb). The remaining small metal ions, mainly Ti^{4+} and Fe^{3+} occupy a tetrahedral site M(2) and three other octahedral sites M(3), M(4) and M(5) [3]. Investigated davidite samples, massive grayish black with vitreous-metallic lustre, were found in granite pegmatite from

Table 1. Basic characteristics of the davidite sample from Bektau-Ata, Kazakhstan

Age (Ma)	Fe (wt.%)	U (wt.%)	Th (wt.%)	Calculated dose[b] (α-decay/mg)
270(20)[a]	19.0	1.47	0.31	$1.47(17) \times 10^{16}$

[a] Permian granitoid massif.

[b] Dose has been calculated from the equation: $D = 8 \times N_{238}(e^{t\lambda 238} - 1) + 7 \times N_{235}(e^{t\lambda 235} - 1) + 6 \times N_{232}(e^{t\lambda 232} - 1)$, where N_{238}, N_{235} and N_{232} are the present number of atoms of ^{238}U, ^{235}U and ^{232}Th per milligram, λ_{238}, λ_{235} and λ_{232} are the decay constants of ^{238}U, ^{235}U and ^{232}Th, t is the geologic age.

Permian granitoid massif Bektau-Ata, Kazakhstan. Basic characteristics of the davidite sample are given in Table 1.

Experimental

The concentrations of ^{232}Th, ^{238}U and ^{235}U were calculated based on gamma-ray activities of ^{228}Ac, (^{232}Th), ^{226}Ra, ^{214}Pb, ^{214}Bi (^{238}U) and ^{235}U. Gamma-ray spectrum was collected using a characterized HPGe detector (30% efficiency) and analyzed using the Genie 2000 v.3 software package.

Untreated sample and samples after annealing in argon at 673, 873, 1073 and 1273 K were powdered and prepared in the shape of a thin disc absorber. The Mössbauer transmission spectra were recorded at room temperature using a constant acceleration spectrometer, a multichannel analyzer with 1024 channels and a linear arrangement of ^{57}Co/Rh source (= 50 mCi), absorber and detector. The spectrometer velocity was calibrated with a high purity α-Fe foil. X-ray powder diffraction (XRD) patterns were obtained using a SIEMENS D5000 diffractometer in the Θ-Θ system and CuK_α radiation in the scan mode with step size 0.02° and step time 5 s at each point.

Results and discussion

The Mössbauer spectra of the davidite samples after one-hour annealing in argon at 673, 873, 1073, 1273 K, and untreated sample with the corresponding X-ray powder diffraction patterns are shown in Fig. 1. The hyperfine parameters derived from fitting procedure are given in Table 2.

The Mössbauer spectrum of davidite (Fig. 1, Table 2) can be fitted to two quadrupole doublets assigned to Fe^{2+} (doublet no. 1) and Fe^{3+} (doublet no. 2) in octahedral positions. From the crystalline structure of davidite, results that these doublets correspond to Fe^{2+} and Fe^{3+} in octahedral M(3) site. As can be seen in Fig. 1, the corresponding XRD pattern shows a high degree of amorphization (metamictization) of this mineral according to high-absorbed α-dose in the structure (Table 1).

For the Fe^{2+} component, Mössbauer spectra of the annealed davidite samples at 673, 873 and 1073 K show decreasing quadrupole splitting (QS) of this doublet together with increasing half-width (Γ) and increasingly poor determination of the doublet's contribution (Fig. 2, Table 2). This ferrous component completely vanishes after heating at 1273 K. The results are the some kind of unexpected because with progressive recrystallization the spectral lines should become narrow as a metamict structure is reconstituted [5]. This, however, was not the case (Fig. 2). On the other hand, similar behavior of an Fe^{2+} component was presented in an extensive study devoted to alpha-decay damage in titanite [4]. This seems similar to metamict titanite because for metamict davidite the damage process is accompanied by the reduction of Fe^{3+} to Fe^{2+}, which resides in the aperiodic domains. These damage regions can incorporate much more hydrogen (as OH) than is contained in crystalline state, presumably as a result of post damage diffusion of H into the structure. Conversely, recrystallization process is accompanied by intense dehydroxylation (as H_2O) with simultaneous oxidation Fe^{2+} to Fe^{3+}.

Table 2. List of ^{57}Fe hyperfine fit parameters of all spectra (Fig. 1). Isomer shift values IS are given relative to the α-Fe standard at room temperature. The uncertainties are given from fitting procedure using the MOS MOD and MEP software

T (K)	Doublet no.	χ^2	IS (mm/s)	QS (mm/s)	Γ (mm/s)	Assignment (CN)[*]	A^{**} (%)
Untreated sample		1.0					
	1		0.94(2)	2.23(1)	0.22(2)	Fe^{2+} (6)	13.1(18)
	2		0.366(3)	0.766(6)	0.279(4)	Fe^{3+} (6)	86.9(16)
673		1.0					
	1		1.01(4)	1.78(6)	0.36(5)	Fe^{2+} (6)	18.5(42)
	2		0.346(5)	0.712(9)	0.270(6)	Fe^{3+} (6)	81.5(29)
873		1.1					
	1		0.84(6)	1.30(8)	0.49(9)	Fe^{2+} ($\geq$6)	18.9(73)
	2		0.365(4)	0.691(9)	0.239(6)	Fe^{3+} (6)	81.1(46)
1073		1.3					
	1		0.81(7)	1.02(8)	0.46(9)	Fe^{2+} ($\geq$6)	18.8(81)
	2		0.375(7)	0.688(4)	0.223(5)	Fe^{3+} (6)	81.2(57)
1273		1.1					
	2		0.374(2)	0.644(6)	0.232(4)	Fe^{3+} (6)	100

[*] Coordination number.　[**] Relative area.
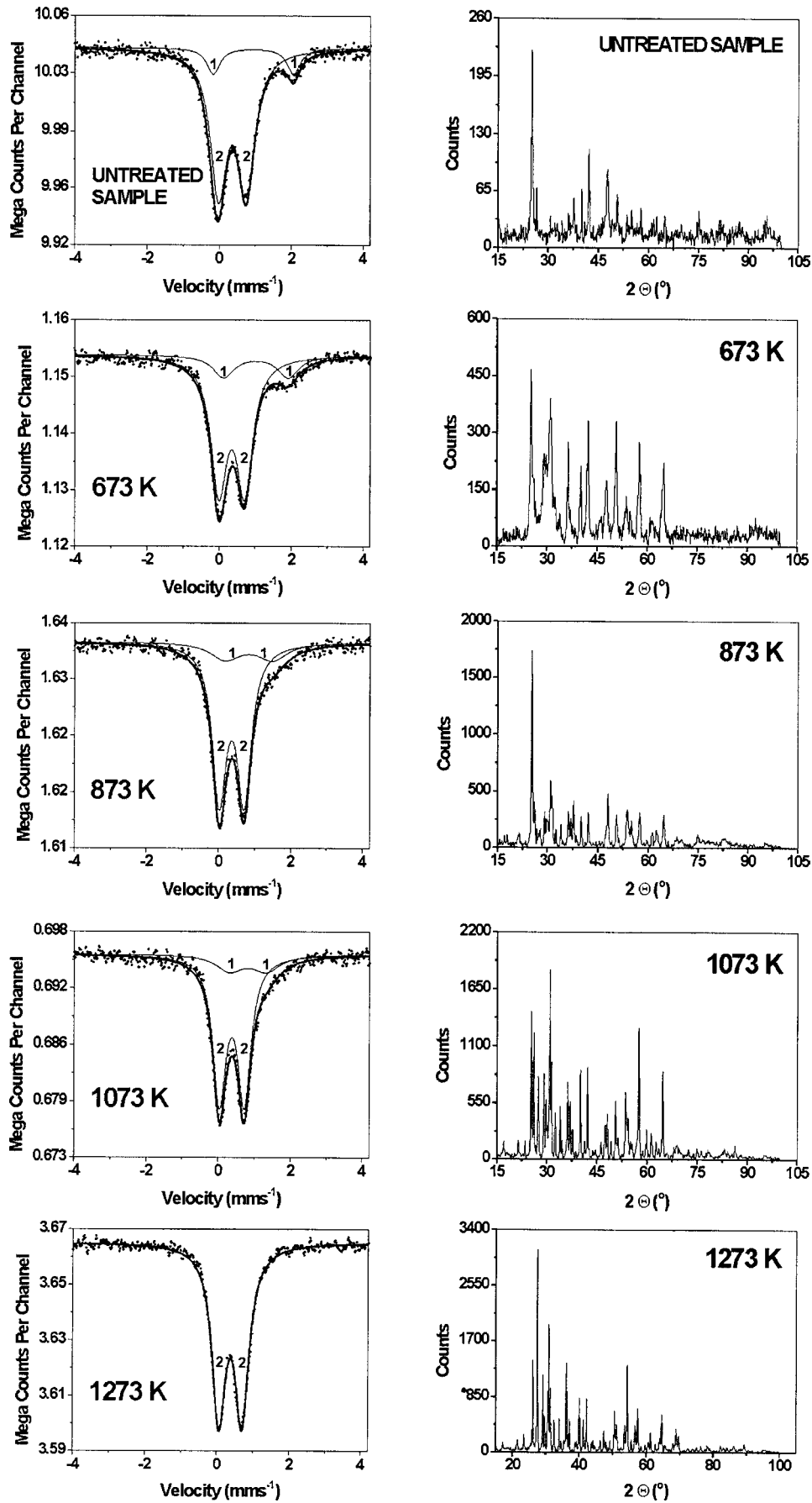
Fig. 1. Room-temperature Mössbauer spectra and corresponding X-ray diffraction patterns of davidite samples after annealing at given temperatures.
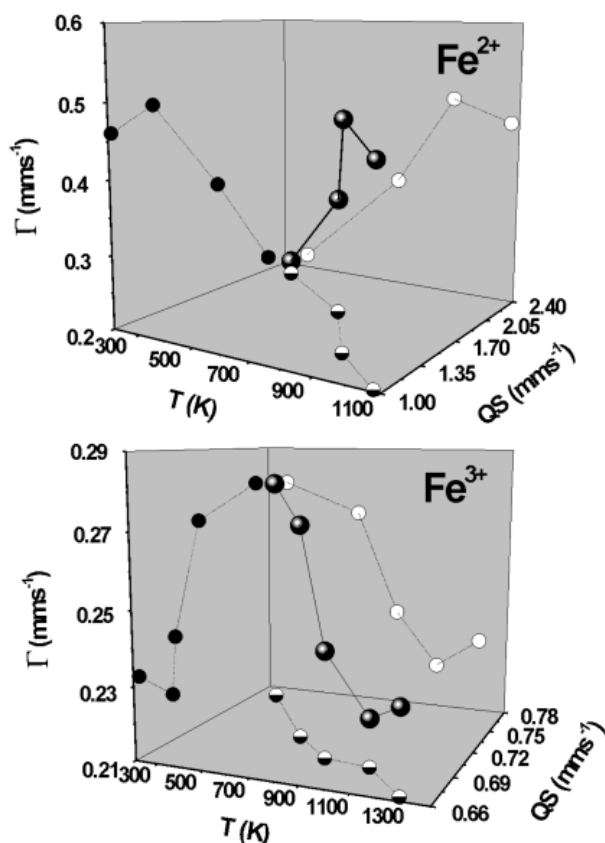
Fig. 2. Variations of the half-widths and quadrupole splittings as a function of the annealing temperature (black spheres) for Fe^{2+} doublet (top) and Fe^{3+} doublet (bottom). White circles – projection on the T-Γ plane; black and white circles – projection on the T-QS plane; black circles – projection on the QS-Γ plane. The uncertainties are within the black sphere sizes.

The quadrupole splitting (Fig. 2, Fe^{2+}) and isomer shift values (Table 2, doublet no. 2) were observed to decrease with progressive annealing most probably indicating decreasing coordination number of these Fe^{2+} positions.

As may be expected, the changes of Γ and QS values of the predominant Fe^{3+} doublet demonstrate a falling tendency. As can be seen in Figs. 1 and 2, with progressive annealing the half-width of this doublet narrowed together with decreasing quadrupole splitting. In opposite to the Fe^{2+} component isomer shift of the Fe^{3+} doublet varies in relatively narrow range from 0.35 mm·s^{-1} (673 K) to 0.37 mm·s^{-1} (1273 K). These results indicate that Fe^{3+} octahedron become more regular as the crystalline structure of davidite is reconstituted. Fitting

the spectra with one Fe^{2+} and one Fe^{3+} doublet indicated a relatively constant Fe^{2+} to Fe^{3+} ratio, i.e., 0.15(2), 0.22(5), 0.23(9) and 0.23(9) from the untreated a sample to sample heated at 1073 K, respectively.

Conclusions

The annealing behavior of metamict davidite is similar to that observed in metamict titanite. Crystalline davidite usually has iron in the trivalent state. However, the Mössbauer spectrum for untreated davidite shows that Fe is present in both Fe^{2+} and Fe^{3+} states with relative contribution of 0.13 and 0.87, respectively. The Fe^{2+} doublet vanishes completely after annealing at 1273 K in argon. It seems reasonable to conclude that the formation of significant amounts of Fe^{2+} in metamict davidite is associated with self-radiation damage from alpha decays of ^{238}U, ^{232}Th, ^{235}U series inside the structure. Changes of the hyperfine parameters vs. annealing temperature of the Fe^{3+} component can serve as sensitive indicators of the metamictization stage of davidite specimens.

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