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Preliminary results of ^{57}Fe Mössbauer spectroscopy of metamict samarskite after one-hour high temperature annealing in argon

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Abstract. The preliminary results of ^{57}Fe Mössbauer spectroscopy and X-ray diffraction (XRD) of fully metamict samarskite dated at ~ 1500 Ma, which absorbed α -dose of 6.5×10^{17} α -decay mg^{-1} , are reported after one-hour annealing at 673, 873, 1173 and 1373 K in argon atmosphere. Metamict minerals contain radioactive elements that degrade their crystal structures over geological time. All the Mössbauer spectra obtained can be fitted to two quadrupole doublets assigned to Fe^{2+} and Fe^{3+} in octahedral positions. The relative contribution of Fe^{2+} (Fe^{2+}/Fe) reaches a minimum of 0.10 at 1173 K.

Keywords: samarskite • metamict minerals • Mössbauer spectroscopy • recrystallization

Introduction

Metamict minerals are a class of natural amorphous minerals that were initially crystalline. These minerals contain radioactive elements that degrade their crystal structure mainly by recoil nuclei from α -decays of ^{238}U , ^{232}Th , ^{235}U and their daughter products. Because of the natural occurrence of uranium and thorium, they can serve as analogs for radiation effects in high level nuclear waste [1]. Samarskite is a complex niobium tantalum titanium oxide with a general structural formula of ABO_4 ($\text{A}^{3+}\text{B}^{5+}\text{O}_4$), where $\text{A} = \text{Ca}, \text{Ti}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{REE}, \text{U}$ and Th , and $\text{B} = \text{Nb}$ and Ta [2]. A large massive fully metamict sample of samarskite was collected from pegmatites in Centennial Cone, Colorado (USA). The basic characteristic of sample is given in Table 1. The purpose of this work is to show changes in hyperfine parameters of investigated samarskite samples with the annealing temperature.

Materials and methods

The concentrations of ^{232}Th , ^{238}U and ^{235}U were obtained using the GX3020 HPGe detector (32% efficiency) and analysed using the Genie 2000 v.4 software. Untreated sample and samples after annealing at 673, 873, 1173 and 1373 K were powdered and prepared in the shape of a thin disc absorber. Mössbauer spectroscopy measurements were performed in transmission geometry at room temperature. A constant-acceleration spectrometer with a 50 mCi

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Table 1. Basic characteristic of samarskite sample from Centennial Cone (USA)

Age [Ma]	Fe [wt.%]	U [wt%]	Th [wt%]	Calculated dose [α -decay mg^{-1}] ^b
1400–1700 ^a	5.4	10.5	1.8	$6.5(7) \times 10^{17}$

^a [3]. ^b Dose has been calculated from the equation: $D = 8 \times N_{238}(e^{\lambda_{238}t} - 1) + 7 \times N_{235}(e^{\lambda_{235}t} - 1) + 6 \times N_{232}(e^{\lambda_{232}t} - 1)$, 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.

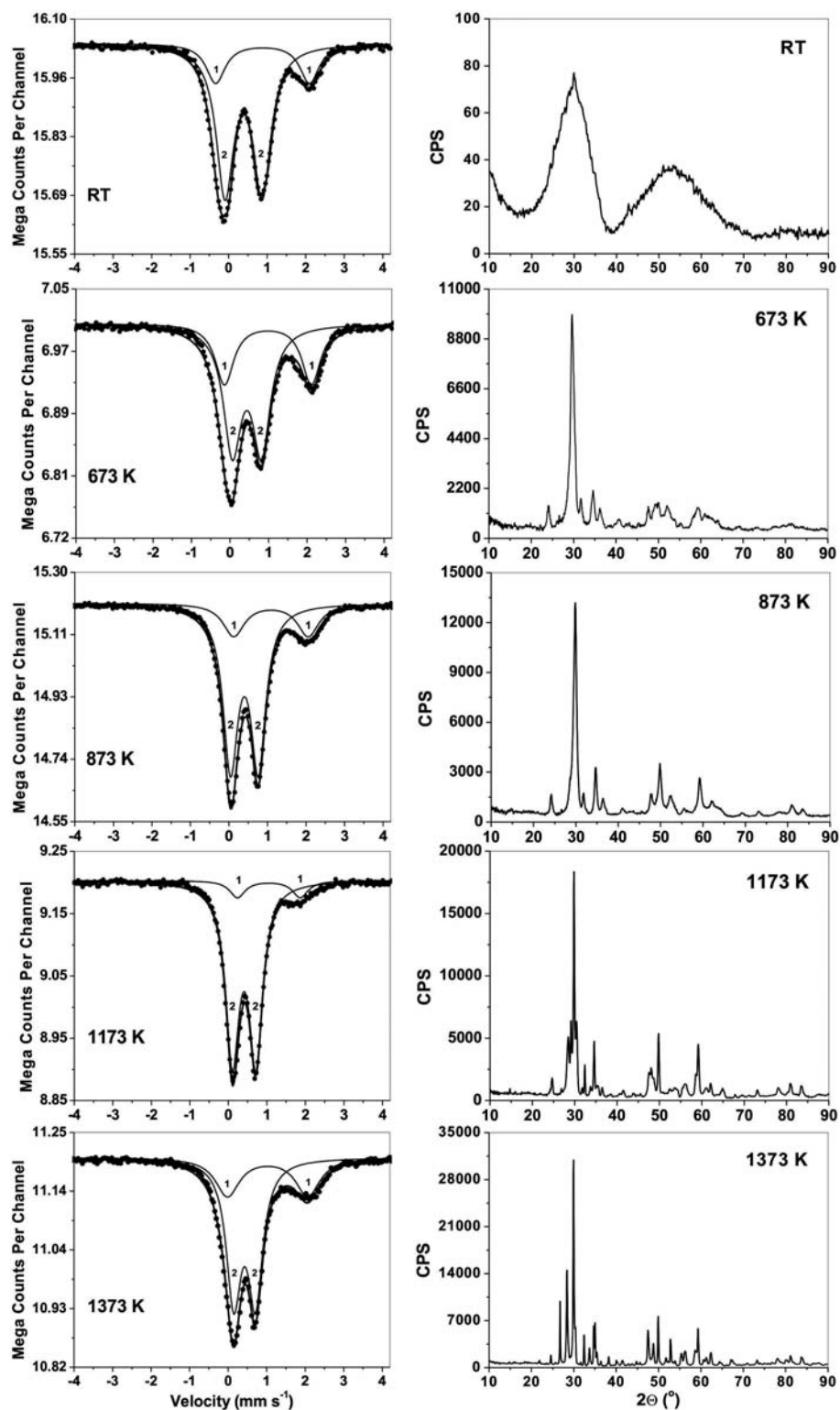


Fig. 1. ^{57}Fe Mössbauer spectra for samarskite samples annealed in argon for 1 hour at given temperature and corresponding XRD patterns ($\text{CuK}\alpha$ radiation). Solid dots – experimental data; thick solid line – fitted curve; thin solid line – fitted doublets.

$^{57}\text{Co}/\text{Rh}$ source was used. A proportional counter was employed to detect the transmitted Mössbauer γ radiation.

Results

The Mössbauer spectra of the untreated sample of samarskite and samples annealed at 673, 873, 1173 and 1373 K with corresponding XRD patterns are shown in Fig. 1. The hyperfine parameters derived from the fitting procedure are given in Table 2.

The lack of Bragg's peaks (Fig. 1, right) indicates complete metamictization of the untreated sample.

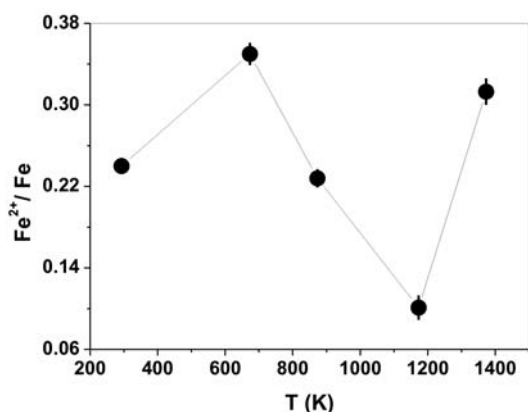


Fig. 2. The contribution of Fe^{2+} (Fe^{2+}/Fe) vs. annealing temperature.

Table 2. Hyperfine parameters from the ^{57}Fe Mössbauer spectra shown in Fig. 1 for annealed samarskite samples. Isomer shift values are given relative to the $\alpha\text{-Fe}$ standard at room temperature

T [K]	Doublet no.	χ^2	IS [mm·s ⁻¹]	QS [mm·s ⁻¹]	Γ^* [mm·s ⁻¹]	Assignment (CN)**	Intensity
Untreated sample	1	1.0	0.88(1)	2.46(1)	0.24(1)	Fe^{2+} (6)	0.24(1)
	2		0.39(1)	0.96(1)	0.27(1)	Fe^{3+} (6)	0.76(1)
673	1	1.0	0.98(1)	2.25(1)	0.29(1)	Fe^{2+} (6)	0.34(1)
	2		0.44(1)	0.75(1)	0.28(1)	Fe^{3+} (6)	0.66(1)
873	1	1.1	1.09(1)	1.93(2)	0.34(1)	Fe^{2+} (6)	0.23(1)
	2		0.40(1)	0.72(1)	0.23(1)	Fe^{3+} (6)	0.77(1)
1173	1	1.3	1.05(2)	1.63(3)	0.24(3)	Fe^{2+} (6)	0.10(1)
	2		0.41(1)	0.61(1)	0.21(1)	Fe^{3+} (6)	0.90(1)
1373	1	1.1	1.02(1)	2.08(2)	0.37(1)	Fe^{2+} (6)	0.31(1)
	2		0.43(1)	0.57(1)	0.23(1)	Fe^{3+} (6)	0.69(1)

* Half width at half maximum. ** Coordination number.

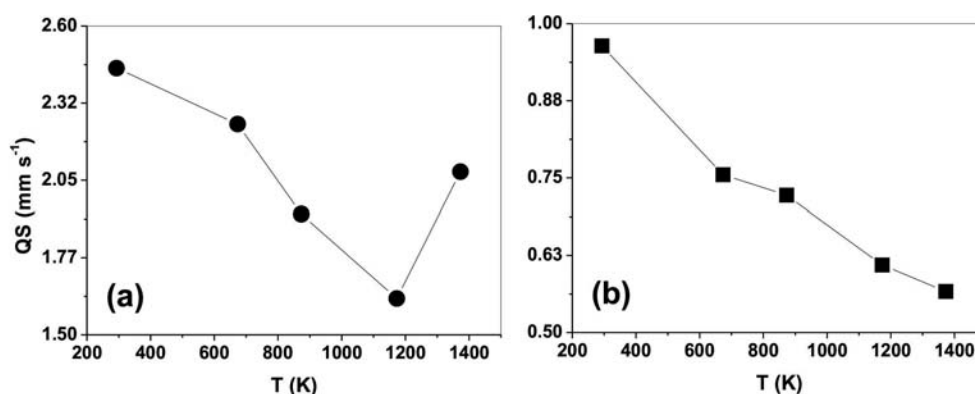


Fig. 3. Quadrupole splitting vs. annealing temperature for (a) Fe^{2+} component and (b) Fe^{3+} component.

A noticeable change is observed for sample annealed at 673 K and then with increasing temperature, the crystallinity of the annealed samples increased. Based on the quadrupole splitting distribution [4] in the first approximation, all the Mössbauer spectra can be fitted into one Fe^{2+} doublet (labelled no. 1) and one Fe^{3+} doublet (labelled no. 2, Fig. 1, Table 2). Isomer shift values (IS) indicate that both the Fe^{2+} and Fe^{3+} doublets represent iron ions in octahedral coordination [5, 6]. This observation agrees well with the site-occupancies derived from chemical composition of 19 different specimens of samarskite [2]. The relative contribution of Fe^{2+} (Fe^{2+}/Fe) was the highest after annealing at 673 K (0.34) and showed a minimum of 0.1 at 1173 K (Fig. 2). After annealing at 1373 K, the relative contribution of Fe^{2+} (0.31) was nearly the same as that obtained at 673 K.

Figures 3a and 3b show the values of the quadrupole splitting (QS) for Fe^{2+} and Fe^{3+} doublets vs. annealing temperature. As can be seen in Fig. 3, the quadrupole splitting values of the Fe^{2+} and Fe^{3+} components decreased with increasing temperature, except for the sample annealed at 1373 K where the QS value was higher than that observed at 1173 K for Fe^{2+} doublet. Similar to the Fe^{2+} contribution (Fig. 2), the sample annealed at 1173 K is characterized by the lowest QS value of the Fe^{2+} doublet (Fig. 3a). Figures 4a and 4b show the variation of isomer shift values for Fe^{2+} and Fe^{3+} doublets vs. annealing temperature. As can be seen in Fig. 4, the

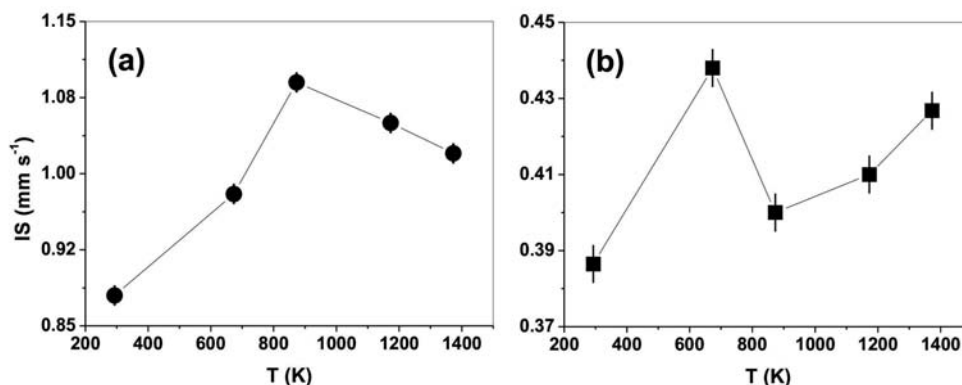


Fig. 4. Isomer shifts vs. annealing temperature for (a) Fe^{2+} component and (b) Fe^{3+} component.

lowest IS values are observed for untreated sample for both the Fe^{2+} and Fe^{3+} components. It can also be observed that the IS values increased for the samples annealed at 673 and 873 K, and at 673 K for the Fe^{2+} and Fe^{3+} doublets, respectively. Unlike the quadrupole splitting, the isomer shift variations of the Fe^{2+} and Fe^{3+} components vs. temperature are uncorrelated.

The high-temperature phase of samarskite is most probably accompanied with doubling of the 'a' cell dimension and consequently may have the structural formula of $\text{AA}'\text{B}_2\text{O}_8$ with a mixed coordination structure [2]. If so, Fe^{2+} and Fe^{3+} may occupy different cation sites. This suggestion seems to be supported by the observed variations of the hyperfine parameters.

Conclusions

The changes in Mössbauer hyperfine parameters and XRD patterns indicate that after one-hour annealing in argon, the transition from metamict to a crystalline structure of samarskite from Centennial Cone begins at 673 K. For the sample annealed at 1173 K, the lowest contribution of Fe^{2+} was observed. The changes in both Fe^{2+} and Fe^{3+} components combined with variations in quadrupole splitting and isomer shift values suggest a significant structural rearrangement of the samarskite polymorph at this temperature and above.

More experiments in which samarskite samples are annealed at a wide range of temperatures and time will be done in order to trace the structural

changes around Fe positions that are associated with the recrystallization process.

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