

Recrystallization in fully metamict gadolinite from Ytterby (Sweden), annealed in air and studied by ^{57}Fe Mössbauer spectroscopy

DARIUSZ MALCZEWSKI*

Faculty of Earth Sciences, University of Silesia, Bedzinska 60, 41-200 Sosnowiec, Poland

ABSTRACT

^{57}Fe Mössbauer annealing studies of fully metamict gadolinite from Ytterby (Sweden) have been carried out in air from 373 to 1473 K. The Mössbauer spectrum of the untreated sample, dated at 1795 Ma and absorbed α -dose 1.07×10^{16} α -decay/mg, is characterized by two broad peaks solely from Fe^{2+} components in octahedral coordinations. The corresponding quadrupole splitting distribution (QSD) shows two distinct maxima at 1.59 and 2.16 mm/s, which reflect the post-metamictization distributions of Fe^{2+} positions up to heating at 773 K. Changes in the Mössbauer hyperfine parameters are observed only after heating to 873 K, at which point the first Fe^{3+} component from the oxidation of Fe^{2+} appears. The relative contribution of $\text{Fe}^{3+}/\Sigma\text{Fe}$ reaches a maximum of 0.54 at 1073 K and then decreases with increasing temperature. A new Fe^{3+} doublet is observed in the samples heated from 1173 to 1473 K. This doublet is characterized by extremely high quadrupole splitting ranging from 2.51 to 2.66 mm/s, implying extreme distortion of the coordination octahedra in partially and fully crystalline gadolinite. The transition from metamict to crystalline structure begins at 1133 K where the Mössbauer spectrum is represented by one Fe^{2+} doublet and one Fe^{3+} doublet. Both doublets suggest a uniform transitional octahedral site over the whole structure. With increasing annealing temperature, the line widths of the Fe^{2+} doublet decrease, and, at high temperatures, an asymmetry of the absorption peaks is observed. The sample becomes completely recrystallized after annealing at 1373 K, and at this point the Mössbauer spectra are nearly exact superpositions of the pure Fe^{2+} and Fe^{3+} (present in minor proportion) in synthetic gadolinites.

Keywords: Gadolinite, metamict minerals, Mössbauer spectroscopy, annealing, amorphous materials

INTRODUCTION

Metamict minerals contain radioactive elements that degrade their crystal structures. The degradation occurs primarily through progressive overlapping recoil nuclei collision cascades from α -decays of ^{238}U , ^{232}Th , ^{235}U , and their daughter products. Because of the natural occurrence of U and Th in these minerals, they serve as natural analogues for radiation effects in high-level nuclear waste (Ewing et al. 2000). Ternary solid solutions of gadolinite ($\text{REEFe}^{2+}\text{Be}_2\text{Si}_2\text{O}_{10}$), calciogadolinite ($\text{CaREE}_2\text{Fe}^{3+}\text{Be}_2\text{Si}_2\text{O}_{10}$), and hingganite ($\text{REE}_2\text{H}_2\text{Be}_2\text{Si}_2\text{O}_{10}$), where REE means rare earth elements and yttrium, are collectively named gadolinites (Ito and Hafner 1974). The basic structure of gadolinites consists of sheets of SiO_4 and BeO_4 tetrahedra interconnected by layers of distorted iron octahedra and eight-coordinated Y, REE, U, and Th (Miyawaki et al. 1984).

Figure 1 shows the distorted Fe octahedron in crystalline gadolinite based on the work of Miyawaki et al. (1984). As seen in Figure 1, the bond lengths Fe-O5 and Fe-O5' of 2.035 Å are considerably shorter than the other bond lengths Fe-O4 and

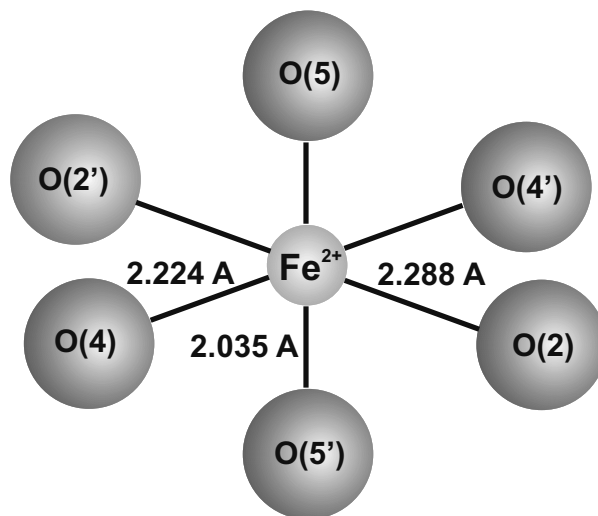


FIGURE 1. FeO_6 distorted octahedron in a crystalline gadolinite (after Miyawaki et al. 1984). The prime symbol (') denotes coordination of oxygen atoms from the next tetrahedral sheet. The oxygen anions O5, O5', O4, and O2 are shared with the REE polyhedron.

* E-mail: dariusz.malczewski@us.edu.pl