Mössbauer effect study of a polycrystalline Fe$_{1+x}$Cr$_{2-x}$O$_4$ spinel grown by solid-state synthesis

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Abstract. Polycrystalline FeCr$_2$O$_4$ samples have been synthesized by the solid-state reaction method and studied with X-ray diffraction and Mössbauer spectroscopy. Rietveld refinement of X-ray diffraction pattern has been performed; obtained unit cell parameters are in a good agreement with ones in the literature. Mössbauer spectra were measured at room temperature and reveal by two components originating from the A and B sites of the spinel structure occupied by iron ions.

1. Introduction

A number of studies have been performed on the magnetic spinel compounds with a general formula AB$_2$O$_4$ (where A and B are the metal ions or a combination of them) due to their interesting magnetic, dielectric, and electrical properties [1-7]. Among them, a spinel-structure oxide FeCr$_2$O$_4$ (or ferrous chromite spinel) is a well-known compound with a cubic structure at room temperature (space group Fd$\bar{3}$m) and the lattice constant $a = 8.378$ Å. The A-site with the tetrahedral coordination is occupied by the Fe$^{2+}$ ions (3d$^6$ electronic configuration) and the octahedrally-coordinated B-site is occupied by the Cr$^{3+}$ ions (3d$^3$ electronic configuration). A different cation distribution takes place in the so-called inverse spinels: here, one-half of the cations B are in A positions and another one-half are share in a random way the B sites with the A ions. For the intermediate, or a mixed, case the general formula can be written as A$_x$B$_{1-x}$[A$_{1/2}$B$_{1/2}$]$_2$O$_4$, where the cations in the B site are shown in brackets, and $\delta = 1$ corresponds to the normal spinel and $\delta = 0$ to the inverse one. Recently, they have attracted an attention due to the peculiar magnetic and electronic properties [8,9].

It is well known that if the ferrous oxide is used as one of the starting materials for a solid state synthesis (even in an appropriate inert atmosphere or vacuum) the grown crystal has a modified spinel formula Fe$^{2+}$Fe$^{3+}$Cr$_{2-x}$O$_4$ due to the partial iron Fe$^{2+}$ ions oxidation to the Fe$^{3+}$ state. However, the XRD analysis cannot distinguish this cation distribution and there is lack of data in the literature where the Mössbauer spectroscopy is used for investigations of the samples grown by this method.

We present here the polycrystalline samples grown by a solid-state synthesis and Mössbauer spectroscopy studies of as grown and annealed crystals.

The article is organized as follows. Next section describes the growth procedure and XRD analysis studies. In section 3, the Mössbauer spectroscopy results are presented.
2. Sample preparation and powder X-ray diffraction
Polycrystalline FeCr$_2$O$_4$ samples were synthesized by the solid-state synthesis using Fe$_2$O$_3$ (Alfa Aesar, 99%), metallic Fe (99.97%) and Cr$_2$O$_3$ (Alfa Aesar, 99%) as starting reagents. The oxides were dried at a temperature 200°C for 16 hours. The stoichiometric mixture was thoroughly ground in an agate mortar for 3 hours in a glovebox with an inert atmosphere to avoid oxidation. The mixture in an alumina crucible was placed into the a vertical tube furnace. The chamber was evacuated down to 10$^{-2}$ mbar for several times using a vacuum pump and purged with a pure Ar (99.995%). The synthesis was carried out with a continuous evacuation of the chamber at a temperature of 1400°C for 12 hours. The resulting reaction product was checked for the formation of the desired phase and composition by the powder X-ray diffraction analysis (Bruker D8 ADVANCE, Cu Kα). Three synthesis attempts have been made. The reaction product of the first synthesis attempt (Sample 1) was visually homogeneous. The reaction products of two next syntheses (Sample 2 and 3) consisted of two components – it had the small black-colored inclusions in the total volume of a brown-colored sample. The powder X-ray diffraction pattern shows the spinel phase FeCr$_2$O$_4$ and a small amount of the residual Cr$_2$O$_3$. X-ray diffraction patterns of all the samples are very similar. The X-ray diffraction pattern of Sample 1 and of the brown-colored part of Sample 2 and their Rietveld refinement are shown in figure 1. The refined unit cell parameter values are 8.3754 and 8.3763 Å, respectively, and are in good agreement with the data obtained by Francombe [10]. Rietveld refinement was carried out in the FULLPROF software [11].

![Fig.1. X-ray diffraction patterns (black circles) of the synthesized polycrystalline FeCr$_2$O$_4$ Sample 1 (left panel) and brown-colored part of Sample 2 (right panel) at room temperature and their Rietveld refinement (red line).](image)

3. Mössbauer spectroscopy studies
$^{57}$Fe Mössbauer spectroscopy was conducted on synthesized samples in order to examine the valence and spin states of the iron ions in transmission geometry on a conventional spectrometer (WissEl Gmbh), operating in a constant acceleration mode. Measurements were carried out at room temperature. $^{57}$Co(Rh) (Ritverc Gmbh) with the activity of about 40 mCi was used as the source of a resonance radiation. The spectrometer velocity scale was calibrated using a thin metallic iron foil at room temperature (RT). The spectra were fitted using the SpectrRelax software [12]. Values of the isomer shifts are reported versus the center of gravity of α-Fe spectrum at RT. For the measurements, polycrystalline samples were carefully ground in an agate mortar to the fine powder state. The powder samples were used to prepare thin Mössbauer absorbers.

The Mössbauer spectrum of the Sample 1 recorded at room temperature is shown in Figure 2a. Two components are found in this spectrum, namely, a major doublet (spectral area is 76(1) %) and a minor
doublet (spectral area is 24(1) %). The major doublet had the following hyperfine parameters: isomer shift of 0.94(1) mm/sec, quadrupole splitting of 0.42(1) mm/sec, and the full-width at half-maximum (FWHM) of 0.31(1) mm/sec. The minor doublet had the following hyperfine parameters: isomer shift of 0.36(1) mm/sec, quadrupole splitting of 0.42(1) mm/sec, and FWHM of 0.30(1) mm/sec. The isomer shift value of the major doublet is characteristic for the high-spin ferrous (Fe$^{2+}$) ions in an oxygen tetrahedral coordination, and the isomer shift value of the minor doublet is characteristic for the high-spin ferric (Fe$^{3+}$) ions in an oxygen octahedral environment. We suppose that the major and the minor doublets are associated with iron ions in the A and B sites of the spinel structure, respectively, and therefore Fe$^{3+}$ ions substitute for the Cr$^{3+}$ ions. Quadrupole splitting is determined by quantization of quadrupole moment of nuclei in the electric field gradient (EFG). Consequently, the departure of observed ferrous doublet from expected ferrous singlet for ideal FeCr$_2$O$_4$ [13] should be assigned to the emergence of EFG due to aforementioned Fe$^{3+}$ substitution in the B sites.

Mössbauer spectra of brown-colored parts of Samples 2 and 3 are almost identical to each other. The Mössbauer spectrum of brown-colored part of Sample 2 at room temperature is shown in Figure 2b. Two components manifest itself in this spectrum, namely, a singlet (spectral area 87(1) %) and a doublet (spectral area 13(1) %). The isomer shift for the singlet is 0.92(1) mm/sec with FWHM of 0.51(1) mm/sec. Another component of the spectrum, the doublet, has the following hyperfine parameters: isomer shift 0.36(1) mm/sec, quadrupole splitting 0.41(1) mm/sec, and FWHM of 0.32(1) mm/sec. The isomer shift value of the singlet is characteristic for the high-spin ferrous ions in an oxygen tetrahedral environment and matches to the value reported earlier for the ferrous ions in A sites of the ideal FeCr$_2$O$_4$ [13]. Hyperfine parameters of the doublet agree with values for the ferric ion doublet observed in the spectrum of the Sample 1. However, spectral area of this component in the spectrum of the Sample 2 is almost two times less than in the spectrum of the Sample 1. The lesser content of Fe$^{3+}$ ions in the B sites determines low EFG and, consequently, leads to a small value or even to total vanishing of quadrupole splitting for component related to ferrous ions in the A sites. The appearance of the singlet in the spectrum is associated with this fact. The Mössbauer spectrum of black-colored inclusions in the Sample 2 (not presented here) is very complicated and contains a number of spectral components associated to a various valence and spin states of iron.

Fig. 2. Room temperature Mössbauer spectra of: a) Sample 1 and b) brown-colored part of Sample 2 (the synthesis product without black inclusions)

4. Conclusion
Polycrystalline FeCr$_2$O$_4$ samples were synthesized by the solid-state synthesis. To avoid ferrous ions oxidation the following precautions were taken: the reagents were grounded in a glovebox with an inert atmosphere of Ar, the furnace chamber was evacuated and purged with pure Ar several times, and a pump was used to continuously evacuate the chamber during sample synthesis procedure. Powder X-ray diffraction pattern shows two structural phases – FeCr$_2$O$_4$ and a small amount of unreacted Cr$_2$O$_3$. Crystal structure parameters were calculated using the Rietveld refinement technique. Information
about the iron ions environments and its electronic configurations was obtained by Mössbauer spectroscopy.

As the FeCr$_2$O$_4$ compound is susceptible to iron oxidation from the Fe$^{2+}$ to Fe$^{3+}$ state and chromium and iron ions have almost identical ionic radii and atomic scattering factors, X-ray diffraction alone is not enough to characterize the synthesized FeCr$_2$O$_4$ spinel. Analysis of the Mössbauer spectroscopy data is capable to provide an information on the iron ions environment and electronic configurations.

To avoid intermediate oxidation of iron ions during the solid state reaction we propose to use ferrous oxalate as an initial reagent since the whole number of iron ions in pre-synthesized mixture will be in the divalent state. FeCr$_2$O$_4$ synthesis results with the ferrous oxalate and chromium oxide used as starting materials will be published elsewhere.

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