Variable-Temperature Mössbauer Spectroscopy of Nano-Sized Maghemite and Al-Substituted Maghemites

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Abstract: Synthetic aluminum-substituted maghemite samples, γ-$(Fe_{1-x}Al_x)_2O_3$, have been prepared by thermal decomposition of Al-lepidocrocite (γ-$Fe_{1-x}Al_xOOH$), with x = 0, 0.04, 0.06, 0.14 and 0.18. The particles are needle-shaped and the mean crystallite diameter along the [311] crystallographic direction was found to be between 2.0 and 5.0 nm. Mössbauer spectra were collected at 6 K and from 80 K up to 475 K at steps of 25 K. In a wide range of temperatures the spectra of the non-substituted sample consist of a superposition of a broad sextet and a superparamagnetic doublet, whereas for the Al-maghemites this range is much smaller. From the temperature variation of the fractional doublet area two different parameters were defined: the temperature corresponding to a 50/50 doublet-sextet spectrum ($T_{1/2}$), and the temperature below which the doublet ceases to exist (T_0). These two parameters ($T_{1/2}$ and T_0) decrease from 390 K and 92 K (Al-free sample), to 118 K and 64 K (4 mole % Al) and to 100 K and 48 K (18 mole % Al), respectively. The average hyperfine fields at 6 K undergo a steep drop in going from the Al-free sample (H_{hf} = 506 kOe) to the sample with 4 mole % Al (H_{hr} = 498 kOe), but for higher substitutions the effect is much smaller. The A- and B-site quadrupole splittings, obtained from the data between 220 K and 475 K, were found as: $\tau E_{Q.A}$ = 0.86 ± 0.04 mm/s and $\tau E_{Q.B}$ = 0.65 ± 0.04 mm/s for the 4 mole % Al sample. The *characteristic Mössbauer temperature*, determined from the temperature dependence of the average isomer shift, was found to be in the range of 500 – 600 K.

Key Words: Al substitution • Maghemite • Mössbauer effect

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