Fe₂O₃-Cr₂O₃ SYSTEM REVISED

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Hematite (a-Fe₂O₃) and eskolaite (Cr₂O₃) are typical examples of isostructural oxides with non-linear change of the lattice parameters in their solid solutions. This series was synthesized and characterized by X-ray and neutron powder diffraction, and Mössbauer and electronic spectroscopies. A region of the d-d electron transition of Fe(III) ions in near IR region (about 1000 nm) were found to be suitable for the solid solution characterization, because the transition does not suffer from strong overlaps of Fe(III) and Cr(III) transitions in electronic spectra in the Vis spectral range. Lattice parameters, verified by the comparison to data available in literature, showed that in several cases in the last decade solids of questionable quality were obtained and discussed in the hematite-eskolaite system. Neither X-ray nor neutron diffraction indicated cation ordering, hypothesized in two reports in 1990's. Magnetic structure of the solid solution at $0 < x < 0.6$, where $x = Cr/(Cr + Fe)$, is similar to that of hematite, but a different, yet unidentified magnetic ordering involving Fe(III) ions is established in solid solution $x = 0.8$ below its Néel temperature (about 150 K).

INTRODUCTION

Hematite (α-Fe₂O₃) and eskolaite (Cr₂O₃) are anttferromagnetic insulators with corundum structure. α-Fe₂O₃ and Cr₂O₃ form a continuous solid solution in the entire concentration range [1,2], that is exceptional in the group of corundum oxides. The lattice parameters of the solid solution decrease smoothly from α-Fe₂O₃ to Cr₂O₃ with a very strong deviation of the Vegard law: the lattice parameter a have positive and c negative deviations of the straight lines between the end members [2-4] (figure 1). Two possible hypotheses can explain the non-Vegardian behavior of the solid solution: cation ordering and specific interactions between cations. McCarty and Boehme [5] and later Busca et al. and Baraton et al. [6,7] observed a band in the Raman spectra of solid solution that was absent in the end members. Busca et al. considered that Raman band a consequence of the ilmenite-type ordering of Fe³⁺ and Cr³⁺ in FeCrO₃, although no superstructural reflections were apparent in X-ray diffraction patterns [5-7]. The other possible reason of the non-Vegardian behavior of α-Fe₂O₃-Cr₂O₃ series could be some specific interactions between cations, such as magnetic. Both the end members of the series are antiferromagnetically ordered at laboratory temperature (α-Fe₂O₃ below Néel temperature $T_N = 955$ K, α-Cr₂O₃ $T_N = 300$ K), but the spin

ordering in these oxides has different symmetry and is markedly weaker in Cr₂O₃. Magnetic structure of the solid solution has not yet been studied in more details.

The synthesis of solid solution of transition metal oxides requires a special care. Probably the sluggishness of solid-state diffusion caused biphasic nature of Fe₂O₃-Cr₂O₃ samples prepared by rather short, two-hour calcination [8]. Neither co-precipitated hydroxide precursors guaranteed obtaining single-phase solid solutions unless they were heated above 1000°C for several hours [9], likely because the parent "hydroxide" was in fact a mixture of FeOOH and Cr-enriched amorphous phase [6]. Heating sol-gel precursors [10] is probably the safest way to produce uniform samples. We hence synthesized the entire series α-(Cr,Fe)₂O₃ by a citrate-nitrate route with 30 hour crystallization at temperatures between 600 and 900°C. We checked the uniformity of samples by several methods. In the products we searched for indices of some kind of element segregation in the crystal lattice by evaluating crystal lattice parameters, neutron diffraction patterns and Mössbauer spectra.

The aim of this work was to re-evaluate some reports containing controversial results or hypotheses regarding miscibility, structure, and lattice parameters. Particular attention was hence paid to check of the quality of the solids synthesized.

EXPERIMENTAL

The samples were synthesized by the method reported earlier [11-13]. A solution of $Fe(NO_3)_3$ and $Cr(NO_3)_3$ with citric acid (citric acid to nitrate ions in ratio 2:3) in a minimal amount of water was evaporated on a hot plate and then calcined in an oven on air at 900°C (unless another calcination temperature is given). The heating up to 900°C lasted 30 min; the fast heating seems to be vital to avoid metal ion segregation due to faster kinetics of crystallization of the end members than their solid solution [14]. Ten-hour calcination steps were repeated three times with intermittent regrinding. Several samples were prepared by crystallization at lower temperatures (about 600°C) to evaluate possible immiscibility.

X-ray powder diffraction (XRD) was performed with Siemens D5005 (Bruker AXS, Germany) using CuK_α radiation (counting time 10 s, 0.02° step, 2Θ range 23-120°). Fullprof [15] and PowderCell [16] were used for XRD data processing. Neutron powder diffraction experiments were performed in Institute Laue-Langevin in Grenoble, France, using diffractometer D1B (λ = 2.52 Å, 2Θ range 30-110°, 400-cell detector, spectra accumulation 5 minutes for temperature dependence and 100 minutes for structural refinement).

The Néel temperatures T_N were measured to check the uniformity of elemental distribution within crystals similarly as in the previous study on Li-Fe-Mn-O spinels [13]. In principal, two magnetic parameters are used in routine measurements of Néel (Néel) temperatures: temperature dependence of magnetization, measured using, e.g., Néel balance [17], and temperature dependence of magnetic susceptibility, measured using, e.g., susceptibility bridge [18,19]. In this study, susceptibility bridge KLY-3S with furnace CS?3 (Agico Brno, Czech Republic) was used and the results were cross-checked by measurements on Néel balance in the Paleomagnetic laboratory of Utrecht University [17].

^{57}Fe Mössbauer spectra were taken in the transmission geometry and the velocity scale was calibrated using an a-iron foil. Low temperature spectra were taken in a closed-cycle cryostat. Program package CONFIT [20] was used for spectral processing to calculate atomic fractions I (intensities, subspectrum areas) of the spectrum components and their hyperfine induction B_{hf}.

Voltammetry was used to check uniformity of elemental distribution within crystals similarly as in our previous reports [1,11-13]. Voltammetric analysis of Fe-oxides is based on their reductive dissolution in acidic solution (0.5 M H_2SO_4). PC controlled potentiostat μAutolab (EcoChemie Utrecht, the Netherlands) was used with paraffin impregnated graphite as a working electrode, a saturated calomel reference, and a Pt plate as a counter-electrode. Samples were deposited on the working electrode by mechanical abrasion. Voltammetric curves were obtained at polarization rate 1 mV/s from open-circuit potential toward negative potentials.

Spectra of homogenized powdered samples were recorded using Perkin-Elmer Lambda 19 UV-Vis-NIR spectrometer equipped with integrating sphere coated by $BaSO_4$ for collecting the scattered light. Spectra (average from four scans) were recorded in the region 200 to 1200 nm with 1 nm increments in a double-beam mode using $BaSO_4$ as a reference and 2 mm thick quartz cells. Reflectance of a powdered sample is not proportional to the concentration of absorbing species. That is why the remission function $F(R_\infty)$ was used that is proportional to the concentration of absorption species. $F(R_\infty)$ is defined by the Schuster-Kubelka-Munk equation:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty}$$

where R_∞ is the diffuse reflectance from a semi-infinite layer. The noise was removed by application of a Fourier filter (cross 5 points).

RESULTS

According to TEM micrographs, the samples synthesized consisted of roughly rounded crystals with diameter decreasing from 1 μm (x = 0) to 0.2 μm (x = 1). The colour of samples calcined at 900°C changed continuously from grey-violet (x < 0.02) through black and brown to green (x > 0.98). All samples calcined at 900°C contained the single phase of the corundum structure. No splitting of diffraction lines (214) and (300) at larger angles (d ~ 1.4 Å) was observed as in the case of two-phase samples reported by Musić et al. [8,9]. Biphasic samples were obtained only for x = 0.5 and 0.6 at 600°C; above 650°C only single-phase samples were obtained.

In line with previous findings by other authors [5,6,7], no unindexed (superstructural) diffraction peaks were apparent in XRD patterns, and statistical evaluation of Rietveld structural refinement with corundum structure model was similar throughout the entire series independently on x (table 1). Also in the neutron powder diffractogram of sample x = 0.5 taken at T ≥ 700 K, ie. above its Néel temperature, all diffraction lines were indexed using simple corundum lattice (R_{Bragg} = 2.12, R_F = 1.66, R_{WP} = 3.98, spectrum taken at 710 K). Because of a different scattering power of Cr^{3+} and Fe^{3+} for neutrons, this observation proved unequivocally the lack of cationic superstructures R32, R3c, and R$\overline{3}$, that all should yield observable extra diffractions with respect to the simple corundum lattice.
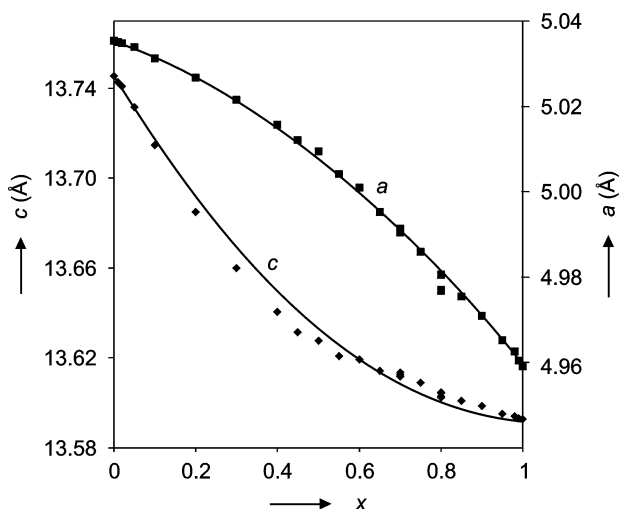
Figure 1. Left, the lattice parameters of the solid solution, experimental points are shown together with lines obtained from Steinwehr data [2].

Figure 2. Neutron powder diffraction patterns of samples $x =$ 0.4, 0.5, and 0.6 at room temperature. Magnetic diffractions are marked by ●. Patterns are diagonally offset for clarity.

Figure 3. Temperature dependence of the magnetization of the solid solution. Line and T_N denotes the Néel temperature of sample $x = 0.2$. The number at curves is compositional parameter x.

The lattice parameters plotted in figure 1 are in good agreement with the results published by Steinwehr [2] and Bhattacharya et al. [10]. The regression analysis yielded the following cubic fits of the lattice parameters of table 1:

$$a = 5.035 - 0.022*x - 0.072*x^2 + 0.019*x^3, R^2 = 0.998$$
$$c = 13.748 - 0.396*x + 0.392*x^2 - 0.151*x^3, R^2 = 0.999$$

The curve of c/a vs. x has a pronounced minimum at about $x \sim 0.4$ almost identical as in the Steinwehr report [2].

The homogeneity of the samples was also checked by voltammetry that is sensitive to the elemental heterogeneity of solid solutions [1,12,13]. The reductive dissolution of Cr-doped hematite under the given conditions yielded a voltammetric curve with a single current peak with potential linearly depending on x

$$E_P \text{ (V vs. SCE)} = -0.35 - 1.50*x, r^2 = 0.982,$$
$$\text{valid for } 0.02 < x < 0.24$$

The peak width in the half height of the reductive dissolution was only 90-130 mV and did not depend on the actual x value. No splitting or peak distortions were observed at $0.02 < x < 0.21$ that also indicated uniform elemental distribution between individual crystals. At $x > 0.24$ the reductive dissolution peak changed to a hardly discernible wave and at $x > 0.3$ it completely disappeared.

The values of the Néel temperature (antiferromagnetic/paramagnetic transition) were obtained by the measurement of the magnetic susceptibility and magnetization for $x < 0.4$ and $x < 0.5$, respectively (figure 3). At larger Cr content, the antiferromagnetic-paramagnetic transition was not observable using these respective methods. The Néel temperature T_N decreases linearly with x

$$T_N \text{ (K)} = 999 - 874*x, r^2 = 0.9983, \text{ valid for } x \leq 0.5$$

This simple linear dependence is similar to the reported behaviour of hematite substituted by 0-10 % Al, Ga, Cr, or In [21], and Li-Fe-Mn-O spinels [13]. The unique Néel temperature in each sample at $x < 0.5$ proved the elemental uniformity of the magnetic domains, because the presence of more populations of crystals or domains with different x would cause obtaining apparently more values of Néel temperature in one sample.

Powder neutron diffraction was used to check the magnetic structure of samples with $x = 0.4$, 0.5, and 0.6, of which magnetization and susceptibility so sharply decreased with respect to pure hematite. Surprisingly, the intensity of the magnetic diffraction lines (denoted by circles in figure 2) at room temperature remains practically the same in that range of x, although the overall magnetism of the samples decreased markedly. The magnetic diffractions are consistent with the spin ordering typical for hematite.
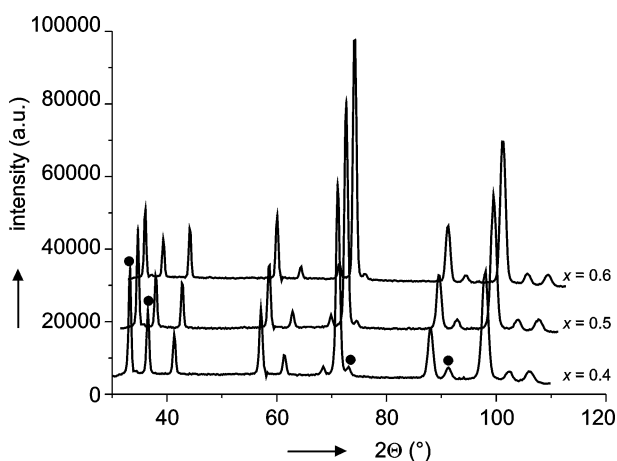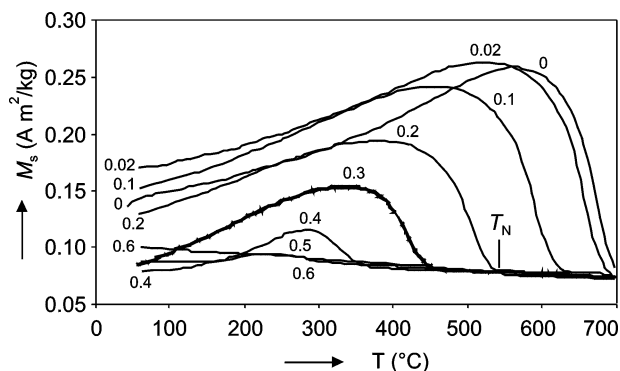
Table 1. The results of the Rietveld analysis of XRD patterns of selected samples obtained by calcination at 900°C.

$x = Cr/(Cr+Fe)$	z_{Me}	a (Ĺ)	c (Ĺ)	R_{Bragg}	R_p	R_{wp}
0.00	0.35505	5.0353	13.7456	6.70	5.69	21.50
0.01	0.355	5.0350	13.7427	5.56	4.72	20.70
0.02	0.35504	5.0348	13.7410	5.60	5.13	22.00
0.05	0.35474	5.0339	13.7318	7.19	5.71	26.60
0.10	0.35447	5.0313	13.7147	4.78	4.19	20.20
0.20	0.35376	5.0267	13.6850	4.59	4.33	19.90
0.30	0.35321	5.0216	13.6600	4.96	4.12	18.70
0.40	0.35255	5.0157	13.6405	4.71	4.22	19.20
0.45	0.3519	5.0121	13.6316	4.91	5.18	21.80
0.50	0.35168	5.0095	13.6278	5.00	4.77	19.30
0.55	0.35101	5.0042	13.6209	4.79	5.22	21.70
0.60	0.35069	5.0009	13.6194	5.18	4.97	20.10
0.65	0.34989	4.9953	13.6144	4.90	4.90	21.40
0.70	0.34996	4.9905	13.6130	5.32	5.09	20.40
0.75	0.34951	4.9860	13.6091	5.14	5.13	21.60
0.80	0.3491	4.9805	13.6046	4.62	4.39	19.00
0.85	0.34886	4.9755	13.6010	5.74	5.20	21.40
0.90	0.3484	4.9709	13.5986	4.41	4.41	18.70
0.95	0.34783	4.9653	13.5953	4.96	4.35	18.60
0.98	0.34753	4.9626	13.5943	4.92	4.37	19.20
0.99	0.34768	4.9605	13.5932	6.03	4.87	19.20
1.00	0.35142	4.9591	13.5929	6.09	5.19	19.30

The Mössbauer spectroscopy at laboratory temperature revealed magnetic interactions from $x = 0$ to at least $x = 0.6$ (table 2), although at $0.4 < x < 0.6$ the Mössbauer absorption slightly decreased. The spectra of the sample with $x = 0.6$ are shown in figure 4. Pure hematite ($x = 0$) was fitted with a single sextet (all Fe ions in hematite are in structurally and magnetically equivalent sites). At $x > 0$ the values of hyperfine field decreased, the sextets stepwise widened, and a set of sextets was necessary to fit the spectra. A set of sextets was already used to fit the Mössbauer spectra of eskolaite-hematite solid solutions [1] and 10-mol% Mg, Ti, or Sn containing hematites [22]. Berry et al. [22] used two sextets and interpreted the additional sextet as a signal of Fe ion with a substituent ion in the nearest neighbourhood. Probably because in the present series the extent of substitution was larger, the number of satellite sextets increased with growing x. The results of the Mössbauer data processing are collected in table 2. The dependence of the average values of the hyperfine field on the samples composition is shown in figure 5 together with some data taken from literature.

The room temperature Mössbauer spectrum of the sample $x = 0.8$ has only a doublet indicating magnetic disorder of Fe(III) ions. According to the extrapolation of T_N obtained by magnetic measurements we estimated that T_N is equal to room temperature actually at $x = 0.8$. This observation is in agreement with the change from sextet at $x = 0.5$ to doublet at $x = 0.67$ [3], and with collapsing sextet observed at $x = 0.665$ [10]. On the other hand, in samples reported by others [8, 9] with $x = 0.7$ traces of non-collapsed sextet [8] and even dominant sextet [9] probably indicated a non-uniform composition of solid solutions, probably the presence of particle populations with Fe content increased with respect to the mean composition.

Below ~150 K the spectrum of sample $x = 0.8$ changed to a sextet, a result rather surprising at so low concentration of Fe(III) in the oxide lattice. Accordingly, powder neutron diffraction patterns at $x = 0.8$ taken below 160-165 K exhibited a set of magnetic diffraction lines, that, however, differ from those in samples $x = 0.4$ to 0.6. The magnetic structure of sample $x = 0.8$ is to be solved in a subsequent work.

Table 2. Mössbauer spectroscopic parameters of the solid solutions. B_{HF} hyperfine field in Tesla.

x	B_{HF} (T) at 20 K	B_{HF} (T) at 298 K
0.0	54.11 ± 0.10	51.26 ± 0.06
0.1	53.14 ± 0.10	51.05 ± 0.03
0.2	52.87 ± 0.06	50.13 ± 0.03
0.3	52.59 ± 0.05	48.91 ± 0.06
0.4	52.16 ± 0.03	46.79 ± 0.12
0.45	51.86 ± 0.03	45.31 ± 0.16
0.5	51.55 ± 0.07	43.86 ± 0.18
0.55	51.25 ± 0.02	40.91 ± 0.26
0.6	51.00 ± 0.08	37.49 ± 0.43

The electronic spectra of the Fe^{3+} and Cr^{3+} oxides consist of four kinds of electron transitions assigned according to refs. [8,23-25] to the following phenomena: (i) *d-d* transitions (NIR and Vis region) of electrons from the ground state to the *d* orbitals with higher energies, which can be understood in the frame of ligand-field theory, (ii) ligand-to-metal charge transfer transitions (UV region), (iii) electron transitions from M(III) 3d to 4s and 4p orbitals (UV region), and (iv) electron pair transition (Vis to near UV region) arising from M(III)-M(III) pair interactions enabled by magnetic coupling between a pair of M(III) ions. The bands (iv) are more intense than the corresponding single electron transitions (i) in magnetically ordered Fe(III) oxides.
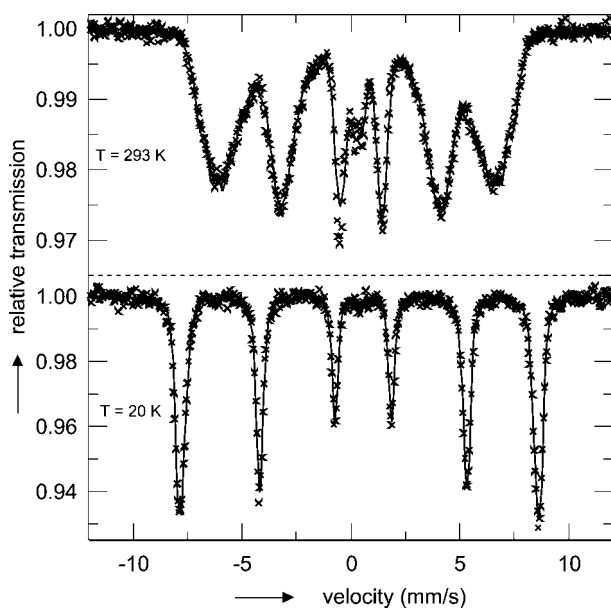
Analysis of the second derivative of the spectra showed that the introduction of about 5 % Cr_2O_3 to Fe_2O_3 leads to disappearance of the most intense Vis absorption band typical of hematite (electron pair transition $2(^6A_1) \rightarrow 2(^4T_1)$ at about 19 000 cm^{-1}, i.e. about 525 nm), which is considered to be a diagnostic band for hematite and Al-substituted hematite (see, e.g., ref. [25]). This is very important (and unpleasant) with respect to application of electronic spectroscopy for phase analysis according to the selected bands [25-27]. Similarly a doublet of Cr(III) *d-d* electron pair transitions at about 370 nm is vanishing at Fe/(Fe+Cr) > 0.15.

The difficulty of the electronic spectra processing due to the strong overlap of the individual absorption bands was already reported by Busca et al. [6], who concluded that the electronic spectra of the solid solutions are not suitable for their analysis. We succeeded in search for a suitable region in the spectra. An almost isolated band of Fe(III) $^6A_{1g} \rightarrow {}^4T_{1g}$ (^4G), $^4T_{2g}$ (^4G) transition is present in the NIR-Vis region (9 800-12 100 cm^{-1}, ie.

Figure 4. Mössbauer spectra of the sample *x* = 0.6 at room temperature and 20 K.
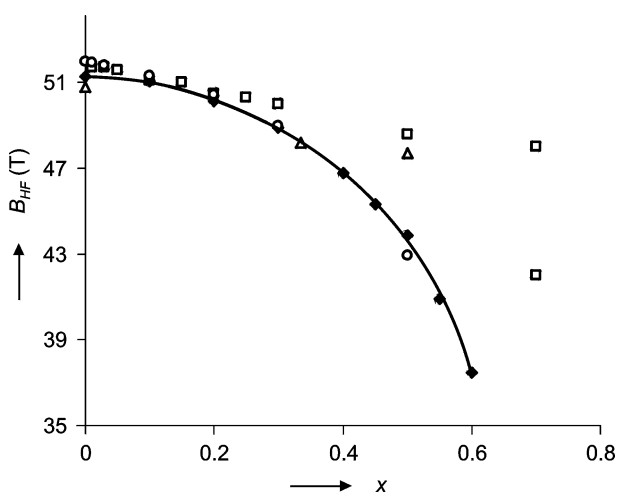

Figure 5. Hyperfine fields B_{HF} of solid solutions obtained in this work (full diamond), and B_{HF} published in refs. [8] (squares), [9] (circles), and [10] (triangles).
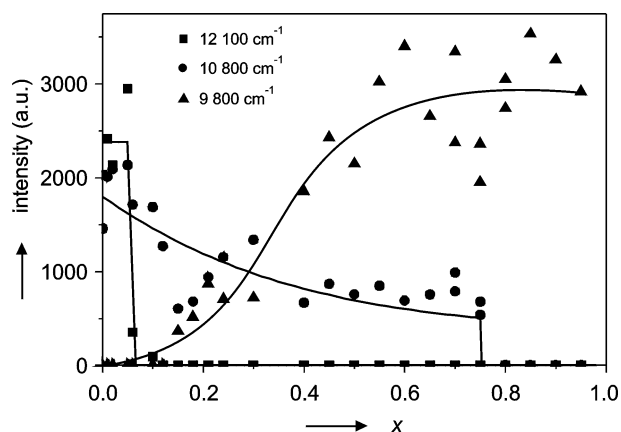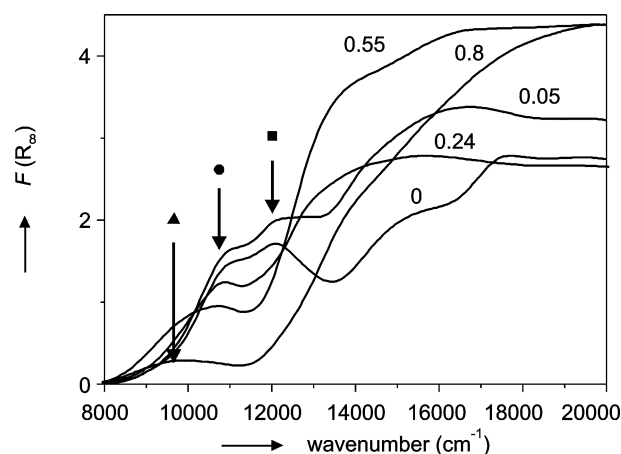

Figure 6. The detail of the near IR spectra of the solid solutions with a practically isolated *d-d* electron transition of Fe(III) ion (top) and the intensity of the band components (bottom). Band intensities are normalized to the molar fraction of Fe in the samples.

~1000 nm, figure 6). This transition is not overlapped by other Fe(III) and Cr(III) bands and can hence be utilized for the characterization of Fe(III) environment/coordination. To identify the bands position, analysis of the second derivative of the spectra and its decomposition to Gaussian bands were applied. Both approaches indicated three types of octahedral Fe(III) ions surroundings presented in $(Fe_{1-x}Cr_x)_2O_3$:

• Fe(III) ions surrounded exclusively by Fe(III) ions, yielding a doublet at 12 100 and 10 800 cm^{-1}, typical for pure hematite and present only in samples with very low x.

• Fe(III) ions in "perturbed" environment, probably with Cr(III) in the nearest neighbourhood, yielding a band at 10 800 cm^{-1}, prevailing in $0.1 < x < 0.8$.

• "Isolated" Fe(III) ions surrounded exclusively by Cr(III) ions, ie. Fe(III) ion in the eskolaite matrix, yielding a band at 9 800 cm^{-1} prevailing at $x > 0.8$.

Musić et al. [9] and Lenglet [24] assigned a band at ~700 nm as an 'intervalence charge transfer' Fe(III) - Cr(III) band in the solid solution. This assignment is rather surprising: the valence exchanges Fe(III) + Cr(III) $\leftrightarrow$ Fe(II) + Cr(IV) could hardly be expected at so small energy, as the charge transfer usually occurs in the UV region. On the other hand, there are two d-d electron transitions of Cr(III) at about 700 nm. The intensity of the 700 nm bands is significantly enhanced at $x < 1$ with respect to pure Cr_2O_3 ($x = 1$). Such increase of absorption could rather indicate the increase of the absorption coefficient of the Cr(III) d-d transitions due to the perturbation of Cr(III) coordination symmetry reflected in the change of transition selection rules (the electronic transitions corresponding to highly symmetric octahedral coordination are symmetrically forbidden). Generally, absorption of all symmetry forbidden single d-d electron transitions of Fe(III) and Cr(III) ions in the region 9 000 - 35 000 cm^{-1} is enhanced in the solid solution with respect to the end members. Moreover, the second derivative of the spectra indicates a shift and splitting of these absorption bands as compared to the end members of the solid solutions. This is an additional evidence of the perturbation of ions in octahedral coordination, followed by symmetry breaking, reflected in the removing of the degeneracy of electronic states.

DISCUSSION

Quality of samples prepared and questionable results in previous reports

The homogeneity of the samples rich in Fe was proved by the single voltammetric peaks of the reductive dissolution and by obtaining single values of the Néel temperature in the Fe-rich side of the series. A smooth continuous change in the structure of the near

IR absorption band of Fe(III) at $0.05 < x < 0.8$ indicate the oxide component mixing in the middle of the series. The phase purity/miscibility of the samples in the size range of the coherence length for X-ray powder diffraction (~5 nm) was proved by comparable statistical parameters in Rietveld refinement throughout the entire series. The samples obtained can hence be considered uniform in the size range of individual crystals that was not always valid in some previous reports on Fe_2O_3-Cr_2O_3 solid solutions.

The conclusion about solubility limit in the Fe_2O_3-Cr_2O_3 solid solutions at high temperatures (> 700°C) [8] is hence not correct. The "solubility limit" obtained at about 1000°C was only a result of an inappropriate synthesis method. The immiscibility due to kinetic reasons was reported at 600°C [14] and also observed in this work (600°C), but while the miscibility gap reported in [14] ranged from $x = 0.4$ to $x = 0.7$, in this report only samples $x = 0.5$ and 0.6 were biphasic. This indicates that the apparent immiscibility is mainly given by a sluggishness of the solid-solution crystallization.

Another unsubstantiated statement found in literature [8] is that the formation of solid solution depends on the synthesis conditions. In majority of previous reports [2,5,10,28], the lattice parameters are in very plausible agreement with the results obtained in this work, although the synthesis temperature varied from 400 to 900°C and divergent synthesis techniques were used (coprecipitated precursors, sol-gel intermediates, and solid-state synthesis). The deviation of the lattice parameters can hence only indicate non-equilibrium samples or doubtful elemental or phase composition of the solid solutions. E.g., according to the lattice parameters, the oxides reported in ref. [29] as solid solutions with x varying from 0 to 0.13 correspond to solid solutions with x two- to three times larger than reported. Similarly the sample with nominal values $x = 0.67$ reported in ref. [6] had lattice parameters corresponding to pure eskolaite $x = 1$. We hence found that from 11 reports [2,5-10,14,28-30] giving lattice parameters and evaluating phase purity of the solid solutions, in two reports [6,29] incorrect lattice parameters were found, in two [8,9] an incorrect statement about miscibility was given, and in two [6,7] an unsubstantiated hypothesis about cationic superstructure was stated, ie. in 5 of 11 reports unreliable facts and unjustified hypothesis were given although in all these cases the new findings could have been compared to correct ones in already published reports [2,5].

Mössbauer spectroscopy

The results of the room temperature Mössbauer spectroscopy obtained and found in literature are not always identical. The change of the sextets of the antiferromagnetically ordered solid solutions at low x to

doublets of paramagnetic solid solutions at large x occurs above $x = 0.6$ at room temperature, and hyperfine field smoothly decreases at growing x. Beside dilution of Fe(III) ions by Cr(III), the magnetic disorder phenomena could also be caused by the decrease of the particle size, leading to superparamagnetism (apparently paramagnetic behaviour below Néel temperature) at particle sizes in order of nanometers. However, this was not the case in this work as the particle size was always >100 nm. The curve of B_{HF} vs. x plotted in figure 5 hence mirrors only the influence of the Cr-for-Fe substitution. The points much above this curve and especially non-collapsed Mössbauer sextets at $x = 0.7$ [8] hence contradict to the results obtained by us and by other authors [2,9,10] and lead to a question about the samples quality.

Linear dependence of B_{HF} on x reported in ref. [30] is also a rather unusual result. The Néel temperature of the solid solutions is linearly dependent on x (as it was shown above), but the spontaneous magnetization of solids falls non-linearly with temperature: it start to decrease to zero very markedly on approaching to the Néel (or Curie) temperature. The curve connecting experimental points of B_{HF} vs. x in figure 5 is hence much closer to the theoretical expectation than a straight line.

Rejection of the superstructure hypothesis [6,7]

Three hypothetical superstructures can be derived from the parent corundum space group R$\bar{3}$c by lowering the space group symmetry at $x = 0.5$, namely R$\bar{3}$, R3c, and R32, with Fe and Cr ions in crystallographically non-equivalent sites. Simulation of the X-ray powder diffraction patterns shows that only R$\bar{3}$ and R32 space groups would yield additional superstructural peaks, but their intensity would be as low as ~ 0.2% with respect to the strongest diffraction of the parent corundum structure. The sensitivity of the neutron diffraction to such hypothetical superstructures is much better: the superstructural peaks would be obvious in all three superstructures. However, no such superstructural diffraction lines were observed in sample $x = 0.5$ using the neutron diffraction experiment above the sample Néel temperature; for that experiment, the sample synthesized at 650°C was chosen to minimize possible thermal disordering of the hypothetical superstructure. The result (absence of superstructural diffractions) excludes the ilmenite-type cation ordering proposed to interpret the Raman spectra of FeCrO$_3$ [6,7].

Few notes on magnetic structure of the solid solution

The solid solution preserves hematite-like spin ordering up to $x = 0.6$. In sample $x = 0.8$ another structure of magnetic interaction was observed by the neu-

tron diffraction experiment. Our attempts to index the magnetic diffraction lines in neutron powder diffractogram on the base of another substructural type derived from corundum were unsuccessful. The fact that Mössbauer spectra of the sample $x = 0.8$ below 150 K yields a sextet indicate that the Fe(III) ions are involved in the magnetic ordering. This can indicate that in sample $x = 0.8$ the Fe-O-Cr superexchange is probably established, because as large as 80 %-dilution of Fe(III) ions in the corundum lattice could hardly permit any magnetic ordering without participation of Cr(III).

CONCLUSION

Hematite α-Fe$_2$O$_3$ and eskolaite Cr$_2$O$_3$ forms a solid solution in the entire concentration range. Apparent immiscibility is only kinetically conditioned and observed after using inappropriate synthesis conditions. The lattice parameters can be easily used to check the composition of solid solutions. There is no evidence of a cationic superstructure of Fe(III) and Cr(III) ions in the solid solution.

The magnetic structure of the solid solution at $x = 0.8$ below its $T_N \sim 150$ K has not yet been described and is not a combination of the magnetic structure of the solid-solution end members. The magnetic ordering includes Fe(III) ions.

Cr-doping leads to obscuring electronic (diffuse reflectance Vis) spectra in the region of a diagnostic band for hematite (~19 000 cm^{-1}, i.e. ~525 nm). In spite of a strong overlap of the electronic absorption bands of Cr(III) and Fe(III), there is a region in the electronic spectra where an almost isolated transition of Fe(III) is observed (~10 000 cm^{-1}, i.e. ~1000 nm). The position of that band changes smoothly with the composition changing in the range $0.1 < x < 0.7$.

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PŘEHODNOCENÍ SYSTÉMU Fe₂O₃-Cr₂O₃

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Hematit (α-Fe₂O₃) a eskolait (Cr₂O₃) jsou typickými příklady izostrukturních oxidů s nelineární změnou mřížkových parametrů jejich tuhých roztoků. Jejich řada byla připravena a charakterizována RTG a neutronovou práškovou difrakcí a Mössbauerovou a elektronickou spektroskopií. Oblast *d-d* elektronových přechodů v Fe(III) iontech v blízké IČ oblasti (kolem 1000 nm) byla shledána vhodnou k charakterizaci tuhých roztoků, protože tento přechod takřka netrpí silným překryvem ostatních elektronových přechodů Fe(III) and Cr(III) ve viditelné oblasti. Mřížkové parametry, ověřené srovnáním s dostupnými publikovanými údaji, ukazují, že v několika případech diskutovaných v posledním desetiletí byly připraveny tuhé roztoky hematitu a eskolaitu nejisté kvality. Ani RTG a neutronová prášková difrakce neodhalila kationtovou superstrukturu, předpokládanou ve dvou publikacích z 90. let. Magnetická struktura tuhých roztoků při $0 < x < 0.6$, kde $x = Cr/(Cr+Fe)$, je podobná struktuře hematitu, ale odlišné a dosud neidentifikované magnetické uspořádání zahrnující ionty Fe(III) se tvoří v tuhém roztoku při $x = 0.8$ pod jeho Néelovou teplotou (kolem 150 K).