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COMMUNICATION

Mechanosynthesis of nanocrystalline fayalite, Fe₂SiO₄†

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Nanostructured fayalite (α-Fe₂SiO₄) with a large volume fraction of interfaces is synthesized for the first time *via* single-step mechanosynthesis, starting from a 2α-Fe₂O₃ + 2Fe + 3SiO₂ mixture. The nonequilibrium state of the as-prepared silicate is characterized by the presence of deformed polyhedra in the interface/surface regions of nanoparticles.

Complex oxides of the type M₂SiO₄ (M is a divalent metal cation) are important rock-forming silicates, as they belong to the most abundant phases of the Earth's crust and upper mantle. In particular, the Fe- and Mg-containing members, $(Fe_{1-x}Mg_x)_2SiO_4$, have been the subject of many studies.[1] In addition to their importance in geophysics, geology and materials science, these compounds are important due to their application as refractory materials, additives in cement concrete, acid-resistant containers, ceramic pigments, *etc*. Fe₂SiO₄ is known to exist in two structural modifications: orthorhombic α-Fe₂SiO₄ phase (the so-called *fayalite*) with the olivine structure and cubic γ-Fe₂SiO₄ phase with the spinel structure. Whereas fayalite is stable under ambient conditions, the spinel phase, first synthesized in 1958 by Ringwood,[2] is found to be stable in a wide range of high pressures and temperatures. γ-Fe₂SiO₄ can be obtained directly from its orthorhombic polymorph at about 4 GPa and 1000 °C.[3]

The present work is focused on the one-step synthesis of nano-fayalite *via* mechanochemical processing of the stoichiometric mixture of α-Fe₂O₃, Fe and SiO₂ precursors at ambient temperature. Although in the last few years a surge of investigations in the field of *mechanochemistry* has resulted in the preparation of a variety of nanostructured complex oxides by forcing a system to acquire metastable and nonequilibrium configurations,[4–6] to the best of our knowledge there is no report in the literature on the non-conventional mechanochemical route to synthesize Fe₂SiO₄. In this communication, the phase evolution during the mechanosynthesis of α-Fe₂SiO₄ is monitored by X-ray diffraction (XRD) and ^{57}Fe Mössbauer spectroscopy. Quantitative information on the short-range structure and hyperfine interactions in the far-from-equilibrium nanofayalite, provided by the nuclear spectroscopic technique, is complemented by an investigation of its magnetic behavior by means of SQUID magnetometry.

For the mechanochemical synthesis of α-Fe₂SiO₄, the α-Fe₂O₃, Fe and SiO₂ reactants (Merck) were mixed in a molar ratio of 2 : 2 : 3. The mixtures (10 g) were milled for various times t_m (up to 4 h) in a high-energy mill Fritsch Pulverisette 6 (Fritsch). A grinding chamber (250 cm³ in volume) and balls (10 mm in diameter) made of tungsten carbide were used. The ball-to-powder weight ratio was 40 : 1. Milling experiments were performed in an argon atmosphere at 550 rpm. The XRD patterns were measured using Cu Kα radiation. ^{57}Fe Mössbauer spectra were taken at 293 K in transmission geometry using a ^{57}Co/Rh γ-ray source. The derived isomer shifts are given relative to ^{57}Fe in Rh. The morphology of powders was studied using TEM (JEOL JEM-2100F). The temperature-dependent magnetic susceptibility was measured in a magnetic field of 0.1 T using a SQUID magnetometer.

As seen in Fig. 1, the XRD pattern of the non-milled mixture is characterized by diffraction peaks corresponding to the reactants α-Fe₂O₃, Fe and SiO₂. For milling times $t_m \geq 1$ h, clear evidence of new diffraction features that correspond to the α-Fe₂SiO₄ phase is observed. In the XRD pattern of the sample milled for 4 h (a product of the mechanochemical reaction), all diffraction peaks detected above the background are due to the fayalite phase (JCPDS PDF 34-0178).

Representative TEM micrographs of mechanosynthesized α-Fe₂SiO₄ at low and high magnifications are shown in Fig. 2. It is revealed that the material consists of nanoparticles with a size distribution ranging from about 5 to 25 nm; the average

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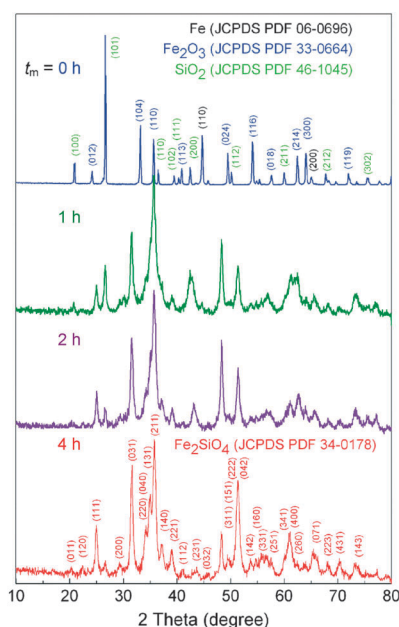‡ On leave from the Slovak Academy of Sciences, Košice, Slovakia.

Fig. 1 XRD patterns of the $2\alpha\text{-}Fe_2O_3 + 2Fe + 3SiO_2$ mixture milled for various times (t_m). Diffraction peaks of the reaction precursors and the product phase are denoted by Miller indices.
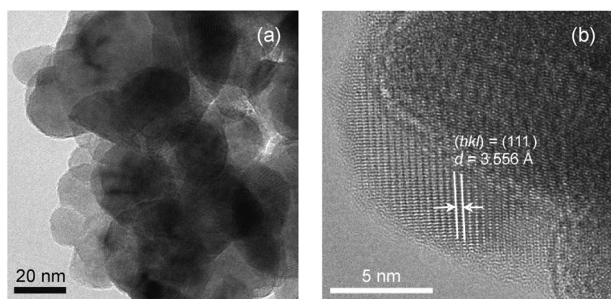

Fig. 2 (a) Bright-field and (b) high-resolution TEM micrographs of mechanosynthesized $\alpha\text{-}Fe_2SiO_4$ nanoparticles demonstrating their core–shell configuration with the thickness of the surface shell of about 1 nm.

crystallite size is estimated to be 13(2) nm. The nanoparticles are found to be roughly spherical, consisting of an ordered region (crystalline inner core) surrounded/separated by a structurally disordered surface shell/interface region. The HRTEM micrograph shows lattice fringes corresponding to the crystallographic plane (111) ($d = 3.556$ Å) of the $\alpha\text{-}Fe_2SiO_4$ phase. They cross the whole particle core demonstrating its single-crystalline character. The surface shell with a thickness of about 1 nm is also evident.

To determine the evolution of the product phase during milling in greater detail, the mechanochemical reaction was followed by ^{57}Fe Mössbauer spectroscopy (Fig. 3). As seen, with increasing t_m, sextets corresponding to $\alpha\text{-}Fe_2O_3$ and Fe collapse, and are gradually replaced by a central doublet characteristic of Fe^{2+} ions. It indicates that the milling generates a complex series of heterogeneous solid-state transformations, including redox reaction ($2Fe^{3+} + 2Fe^0 \rightarrow 3Fe^{2+}$) and formation reaction ($2\alpha\text{-}Fe_2O_3 + 2Fe + 3SiO_2 \rightarrow 3\alpha\text{-}Fe_2SiO_4$), which are completed after only 4 h. In this context, it should be noted that the preparation of Fe_2SiO_4 by a conventional solid-state route requires a number of stages, including homogenization of the powder precursors, their compaction, and finally prolonged treatment
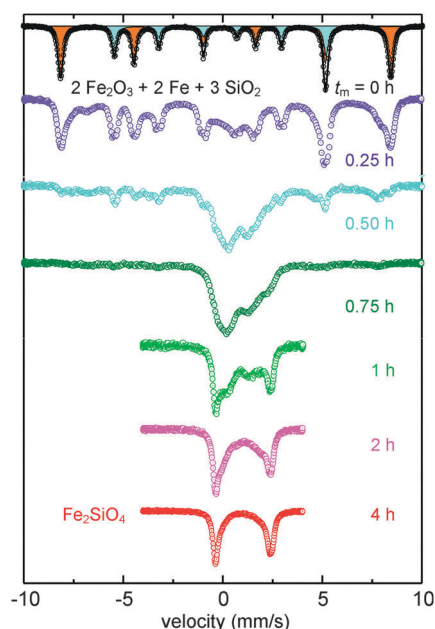

Fig. 3 ^{57}Fe Mössbauer spectra of the $2\alpha\text{-}Fe_2O_3 + 2Fe + 3SiO_2$ mixture milled for various times.

at considerably high temperatures under controlled oxygen fugacity.[1]

To separate the surface/interface effects from the core/bulk effects in the as-prepared nanoparticles and to determine their local ionic configuration, we analyzed in detail Mössbauer spectra of both mechanosynthesized nanofayalite and its bulk counterpart (synthesized by the standard ceramic route), see Fig. 4. The spectrum of the bulk silicate is well fitted by the superposition of two doublets with the hyperfine parameters listed in Table 1. These parameters are consistent with those of the olivine crystal structure of $\alpha\text{-}Fe_2SiO_4$, in which Fe^{2+} cations occupy two non-equivalent octahedral sites, [M1] and [M2], in equal proportions,
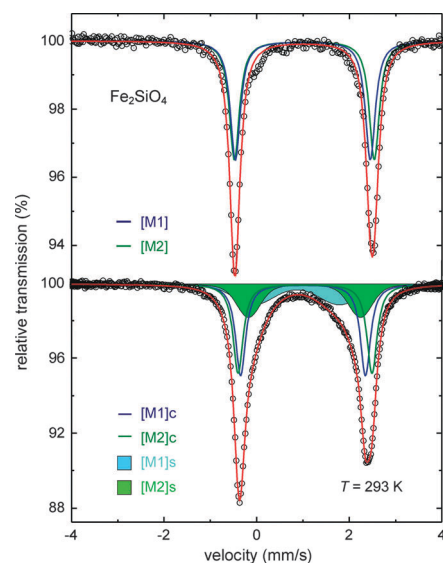

Fig. 4 ^{57}Fe Mössbauer spectra of (top) bulk $\alpha\text{-}Fe_2SiO_4$ and (bottom) nanosized mechanosynthesized $\alpha\text{-}Fe_2SiO_4$. [M1]c, [M2]c and [M1]s, [M2]s denote cation sites of octahedral coordination in the inner core and the surface shell of $\alpha\text{-}Fe_2SiO_4$ nanoparticles, respectively.

Table 1 Parameters obtained by fitting the Mössbauer spectra of bulk Fe_2SiO_4 and nanosized mechanosynthesized Fe_2SiO_4

| Material	Octahedral site of Fe^{2+}	IS (mm s^{-1})	QS (mm s^{-1})	σ (mm s^{-1})	I (%)
Bulk Fe_2SiO_4	[M1]	0.99(5)	2.91(4)	0.042(1)	50.1(3)
	[M2]	1.02(8)	3.02(1)	0.041(1)	49.9(4)
Nano Fe_2SiO_4	[M1]c	1.00(1)	2.69(6)	0.045(2)	30.0(4)
	[M2]c	1.04(5)	2.89(1)	0.046(2)	30.0(5)
	[M1]s	0.86(3)	1.86(5)	0.77(2)	20.0(7)
	[M2]s	1.03(3)	2.41(8)	0.40(1)	20.0(6)

IS: isomer shift; QS: quadrupole splitting; σ: Gaussian widths of the Voigt lines; I: relative intensity. A Lorentzian line width of 0.26 mm s^{-1} resulting from the fit of the spectrum of a bulk Fe_2SiO_4 was chosen for the fit of the spectrum of mechanosynthesized Fe_2SiO_4.

whereas Si^{4+} cations are coordinated by four O^{2-} ions to form SiO_4 tetrahedra (T). Thus, the crystal chemical formula emphasizing the site occupancy at the atomic level in the bulk α-Fe_2SiO_4 may be written as $[Fe]_{[M1]}[Fe]_{[M2]}Si_{(T)}O_4$.

The core–shell morphology of mechanosynthesized nanoparticles requires to fit their Mössbauer spectrum by a superposition of four subspectra (Fig. 4, bottom): two components account for Fe^{2+} nuclei in the well-crystallized core of Fe_2SiO_4 nanoparticles (denoted [M1]c and [M2]c) and two are associated with Fe^{2+} ions in the surface shell/interface regions of nanoparticles (denoted [M1]s and [M2]s). The Mössbauer lines corresponding to Fe atoms located at surfaces/interfaces are much broader than those belonging to the core of nanoparticles (compare $\sigma_{[M1]c}$, $\sigma_{[M2]c}$ and $\sigma_{[M1]s}$, $\sigma_{[M2]s}$ in Table 1). This provides clear evidence of a broad distribution of electric field gradients acting at the Fe^{2+} nuclei in the near-surface layers/interface regions of the nanomaterial. The distribution reflects the presence of strongly distorted octahedra around the ferrous ions in the surface/interface regions of the nanofayalite. Another striking feature is that the electric field gradients which act on Fe nuclei in the shell are found to be smaller than those experienced by Fe nuclei in the core of Fe_2SiO_4 nanoparticles. From Mössbauer measurements, it is concluded that the surface shell regions of mechanosynthesized nanoparticles are disordered due to broadly distorted albeit more symmetric octahedra ([M1]s and [M2]s octahedra with a reduced dispersion of Fe–O bond lengths). This finding is in agreement with recent NMR and Mössbauer investigations of mechanosynthesized Sn-containing nanooxides.[6]

From the intensity ratio $(I_{[M1]s} + I_{[M2]s})/(I_{[M1]c} + I_{[M2]c} + I_{[M1]s} + I_{[M2]s})$ the volume fraction (w) of the disordered surface/interface regions in the nanoolivine is estimated to be about 40%. Thus, the distribution of Fe ions in the mechanosynthesized Fe_2SiO_4 can be represented as $[Fe_{0.6}]_{[M1]c}[Fe_{0.6}]_{[M2]c}[Fe_{0.4}]_{[M1]s}[Fe_{0.4}]_{[M2]s}Si_{(T)}O_4$. Considering that nanoparticles are spherical with an average diameter $D = 13$ nm, the thickness of the disordered surface shell can be estimated to be $t = 1.02(1)$ nm ($w = 100[1 - (1 - 2t/D)^3]$). This value is in good agreement with the HRTEM results shown in Fig. 2 and is also comparable to that observed in other mechanochemically prepared nanooxides.[4–6]

One could expect that the presence of distorted octahedra in the nanofayalite would result in altered magnetic properties, as it has been observed for mechanosynthesized ferrites.[5] As seen in Fig. 5, the Néel temperature of the nanofayalite
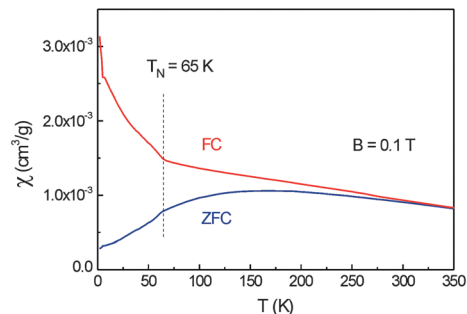
Fig. 5 Temperature-dependent magnetic susceptibility (ZFC and FC) for mechanosynthesized α-Fe_2SiO_4.

($T_N = 65.0(1)$ K) is not much different from that of the conventionally prepared bulk α-Fe_2SiO_4 (64.5 K).[7] However, the increase of the ZFC curve above T_N reflects a high aggregation level of the interacting fayalite nanoparticles. It indicates that there is no well-defined Néel temperature for the nanofayalite; rather, there is a distribution of Néel temperatures. We attribute this behavior to the presence of the canted surface spins due to broadly distorted octahedra as evidenced by Mössbauer spectroscopy. Note that similar findings have recently been reported for the mechanochemically prepared ilmenite ($FeTiO_3$).[8]

The present communication clearly demonstrates that nanostructured α-Fe_2SiO_4 can be synthesized at ambient temperature directly from its precursors, without the need for calcination at high temperatures under a controlled atmosphere, thus making the process very simple. The local structure of the as-prepared nanoparticles is characterized by deformed M1 and M2 octahedra in the surface/interface regions, whose volume fraction is about 40%. The Néel temperature of the nanofayalite is not significantly affected by the mechanochemical preparation route.

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