PARTICLE SIZE DEPENDENT CATION DISTRIBUTION IN LITHIUM FERRITE SPINEL LiFe$_5$O$_8$

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Abstract. The particle size dependent cation distribution in lithium ferrite (LiFe$_5$O$_8$) is investigated by means of in-field Mössbauer spectroscopy at 5K. The mechanically induced reduction of the average particle size of LiFe$_5$O$_8$ to the nanometer scale is accompanied by a decrease of the concentration of Fe^{3+} cations on tetrahedral sites and an increase on the octahedral sites. Quantitative information on the degree of inversion of LiFe$_5$O$_8$ is complemented by TEM investigations of the nanoscale material.

1. INTRODUCTION

Lithium ferrite, LiFe$_5$O$_8$, is a technologically important spinel of the type $(M1_{1-\lambda}M2_\lambda)[M1_{\lambda-0.5}M2_{2.5-\lambda}]O_4$, where $M1$ and $M2$ are monovalent and trivalent cations, respectively. Here, parentheses enclose cations in tetrahedral (A) coordination and square brackets denote octahedral [B] cation sites. λ represents the so-called degree of inversion, defined as the fraction of (A) sites occupied by $M2^{3+}$ cations. It varies from 0.5 to 1. The value of $\lambda = 5/6$ corresponds to the random arrangement of cations. To emphasize the site occupancy on the atomic level, the structure formula of bulk LiFe$_5$O$_8$ may be written as $(Fe)[Li_{0.5}Fe_{1.5}]O_4$. Thus, bulk LiFe$_5O_8$ adopts the inverse spinel structure ($\lambda = 1$) in which all Li$^+$ ions and 3/5 of the Fe^{3+} ions occupy the [B] sites, whereas the remaining Fe^{3+} cations occupy the (A) sites.

It is widely appreciated that the cation order-disorder effects in spinels give rise to important consequences in their properties. Therefore, the study of the local structure of these compounds is of primary importance. Although numerous papers have been published on the mechanically induced cation disorder in 2-3 spinels in the past years (see, for example, [1] and references therein), to the best of our knowledge, this is the first report which quantitatively describes the change in the cation distribution in a 1-3 spinel (LiFe$_5$O$_8$) when the particle size is reduced to the nanometer level.

2. EXPERIMENTAL

Bulk LiFe$_5$O$_8$ was prepared from a mixture of Li$_2$CO$_3$ and α-Fe$_2$O$_3$ (in the molar ratio of 1:5) by the conventional solid-state (ceramic) method. The single-phase nature of the bulk LiFe$_5$O$_8$ sample was confirmed by X-ray diffraction and Mössbauer spectroscopy.

Nanocrystalline LiFe$_5$O$_8$ was produced by high-energy milling of the bulk material in a Spex 8000

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shaker mill (Spex CertiPrep Inc., USA). A grinding chamber (50 cm³ in volume) and a single ball (10 mm in diameter) made of zirconia ceramics were used. The ball-to-powder weight ratio was 10:1 (see [12] for the production of further nanocrystalline oxide ceramics with Spex 8000 shaker mill).

The ^{57}Fe Mössbauer spectroscopic measurements were carried out in transmission mode at 5K in an external magnetic field of 5.5 T applied perpendicular to the γ-ray direction. A $^{57}Co/Rh$ γ-ray source was used. The velocity scale was calibrated relative to ^{57}Fe in a Rh matrix. Recoil spectral analysis software [2] was used for the quantitative evaluation of the Mössbauer spectra. The degree of inversion, λ, was calculated from the Mössbauer subspectral intensities ($I_{(A)}/I_{[B]} = (f_{(A)}/f_{[B]})(λ/(2.5-λ))$), assuming that the ratio of the recoilless fractions is $f_{(A)}/f_{[B]} = 1$.

The morphology of powders and the sizes of individual particles were studied using a combined field-emission (scanning) transmission electron microscope (S)TEM (JEOL JEM-2100F).

3. RESULTS AND DISCUSSION

High-energy milling of as prepared bulk $LiFe_5O_8$ with an average grain size exceeding 100 nm leads to the reduction of its particle size to the nanometer scale. Fig. 1 shows an HR-TEM micrograph of the nanocrystalline $LiFe_5O_8$ powder consisting of particles mostly in the 6-10 nm size range. The shape of the majority of them appears to be spherical and they tend to form bigger agglomerates.

To determine the ionic configuration in both bulk and nanocrystalline $LiFe_5O_8$, we found it necessary to perform low-temperature Mössbauer measurements in conjunction with large external magnetic fields (B_{ext}). Without application of an external magnetic field, the local hyperfine magnetic fields $B_{(A)}$ and $B_{[B]}$ acting on the Fe^{3+} nuclei in the spinel sublattices of bulk $LiFe_5O_8$ are very similar, as demonstrated in Fig. 2a and in [3]. Thus, the corresponding Mössbauer subspectra are overlapping and it is difficult to resolve them. In the case of a nanoscale ferrite, the hyperfine interactions at (A) and [B] sites additionally possess a more or less distributive character [1]. Under these conditions, the separation of the (A) and [B] subspectra is an even more difficult problem. In the presence of an external magnetic field, B_{ext} adds to $B_{(A)}$ and subtracts from $B_{[B]}$ as a consequence of the antiparallel alignment of the spins of Fe^{3+} cations at (A) and [B] spinel sites. Thus, the use of the large external magnetic field creates an effective separation of
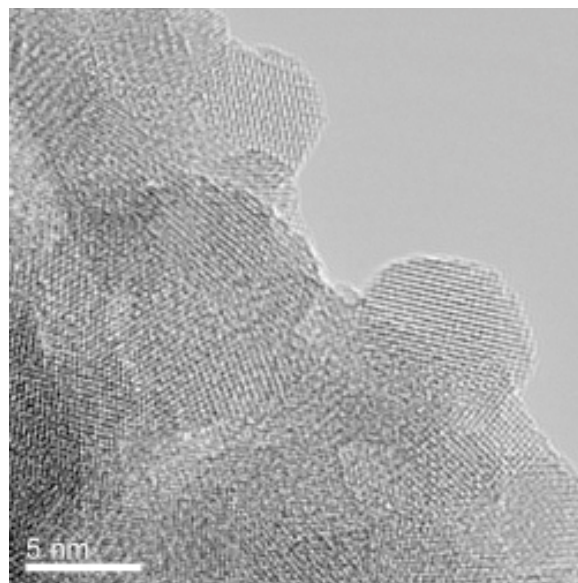

Fig. 1. HR-TEM micrograph of nanoscale $LiFe_5O_8$.

the overlapping subpatterns, thereby allowing an accurate determination of the cation distribution [1,4]. Simultaneous use of low temperatures further simplifies the evaluation of the Mössbauer spectra, because it suppresses magnetic relaxation effects (collective magnetic excitations, superparamagnetism) associated with the presence of small particles [5].

Figs. 2b and 2c compare the in-field Mössbauer spectra with the completely resolved (A) and [B] subspectra for both bulk and nanosized $LiFe_5O_8$ taken at 5K. The spectra consist of two sextets with the isomer shift being of $IS_{(A)} = 0.25(1)$ mm/s and $IS_{[B]} = 0.36(1)$ mm/s being characteristic of Fe^{3+} ions on (A) and [B] sites, respectively [6]. It is found that the average sublattice magnetic fields experienced by Fe^{3+} ions in the nanomaterial ($B_{(A)} = 49.3(1)$ T, $B_{[B]} = 53.1(1)$ T) are reduced in comparison with those acting on iron nuclei in the bulk $LiFe_5O_8$ ($B_{(A)} = 51.0(1)$ T, $B_{[B]} = 53.3(1)$ T). The degree of inversion of the bulk $LiFe_5O_8$ is found to be λ = 1.00(1). Thus, the bulk ferrite adopts the fully inverse spinel structure of $(Fe)[Li_{0.5}Fe_{1.5}]O_4$. Fig. 2c demonstrates that the reduction of the particle size of $LiFe_5O_8$ leads to a decrease of the concentration of Fe^{3+} cations on (A) sites. The degree of inversion of nanosized $LiFe_5O_8$ is found to be λ = 0.90(2). This value indicates that with decreasing particle size, the cation distribution is directed to-
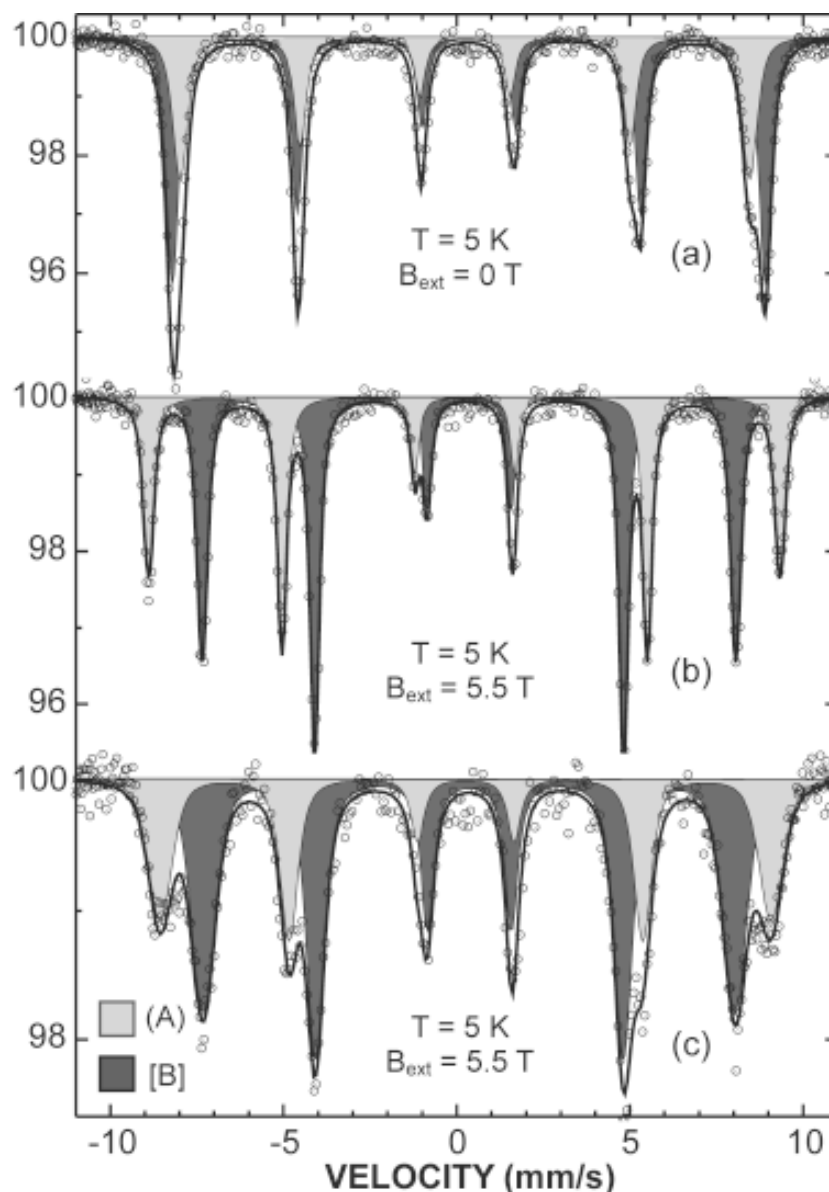
Fig. 2. (a) Low-temperature (5K) Mössbauer spectrum of bulk LiFe$_5$O$_8$ taken at zero applied magnetic field. Low-temperature Mössbauer spectra of (b) bulk and (c) nanocrystalline LiFe$_5$O$_8$ taken in an external magnetic field of 5.5 T applied perpendicular to the γ-ray direction.

wards random arrangement. Thus, the crystal chemical formula emphasizing the site occupancy at the atomic level for the nanocrystalline ferrite can be written as (Li$_{0.1}$Fe$_{0.9}$)[Li$_{0.4}$Fe$_{1.6}$]O$_4$. The present observation of a nonequilibrium cation distribution in LiFe$_5$O$_8$ nanoparticles is consistent with previous studies of nanocrystalline complex oxides, where disordered ionic configuration was also observed; for details see [7] and references therein. Although nanoscale LiFe$_5$O$_8$ was the subject of

Mössbauer investigations in numerous papers [8-10], to the best of our knowledge, the nonequilibrium cation distribution has never been reported before. It should also be emphasized that in these papers, the Mössbauer measurements of the LiFe$_5$O$_8$ nanoparticles were done without application of an external magnetic field. According to our experience, the cation distributions merely determined from zero-field Mössbauer spectra have to be considered with reserve, especially when

conclusions are drawn from spectra with low resolution or poor statistics.

The broad shape of the Mössbauer spectral lines for nanoscale $LiFe_5O_8$ (half width at half maximum of the Lorentzian line $\Gamma = 0.21$ mm/s), in contrast to relatively narrow lines for the bulk material ($\Gamma = 0.14$ mm/s), provides evidence for a wide distribution of magnetic fields acting on the Fe^{3+} nuclei in the nanomaterial. This variation may be explained by the effect of a mechanically induced deformation of FeO_6 and FeO_4 polyhedra. Similar findings have also been reported for other nanocrystalline complex oxides [11], where nonequilibrium cation distributions were found to be accompanied by a deformation of polyhedron geometries.

4. CONCLUSIONS

Nanosized $LiFe_5O_8$ with an average particle size of about 8 nm has been prepared by the mechanochemical method. The comparative in-field Mössbauer study of bulk and nanosized $LiFe_5O_8$ revealed that with decreasing particle size, the cation distribution tends to randomize. In contrast to bulk $LiFe_5O_8$ with a fully inverse structure, nanocrystalline $LiFe_5O_8$ exhibits a partly inverse structure with a nonequilibrium cation distribution ($\lambda \approx 0.9$) and deformed polyhedron geometries.

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