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Direct determination of the cation disorder in nanoscale spinels by NMR, XPS, and Mössbauer spectroscopy

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Abstract

Quantitative microstructural information is obtained on the nonequilibrium cation arrangement in high-energy milled $MgAl_2O_4$, $ZnFe_2O_4$, and $NiFe_2O_4$ by means of ^{27}Al MAS-NMR, XPS, and ^{57}Fe Mössbauer spectroscopy, respectively. Independently of the ionic configuration in the nonactivated materials, the mechanically induced redistribution of cations was found to be directed towards the random arrangement. The cation inversion parameter of the nanosized milled spinels is compared with that of the bulk materials at high temperatures.

Keywords: Nanostructured materials; Mechanochemical processing; Order–disorder effects

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1. Introduction

Despite their deceptively simple structure, many spinels of the type $M(1)M(2)_2O_4$ exhibit complex disordering phenomena involving the redistribution of $M(1)^{2+}$ and $M(2)^{3+}$ cations over the sites of tetrahedral (A) and octahedral [B] coordination. To emphasize the site occupancy at the atomic level, the structural formula of 2–3 spinels may be formulated in greater detail as $(M(1)_{1-\lambda}M(2)_{\lambda})[M(1)_{\lambda}M(2)_{2-\lambda}]O_4$, where λ represents the so-called degree of inversion, which varies from $\lambda = 0$ for *normal spinel* to $\lambda = 1$ for fully *inverse spinel*. The value of $\lambda = 2/3$ corresponds to the random arrangement of cations. The cation order–disorder effects in spinels give rise to important consequences in their thermodynamics and 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 structural disorder in spinels in the past years (see, for example, [1] and references cited therein), this is the first report which quantitatively describes the change in the cation distribution when the particle size is reduced to nanometer level for spinels with different cation arrangement in the bulk state, i.e., for partly inverse spinel $MgAl_2O_4$ ($0 < \lambda < 1$), normal spinel $ZnFe_2O_4$ ($\lambda = 0$), and fully inverse spinel $NiFe_2O_4$ ($\lambda = 1$). The important impact of the present work from the methodology point of view is the first application of solid-state nuclear magnetic resonance spectroscopy (NMR) to the study of the mechanically induced structural disorder on a local atomic scale in spinels.

2. Experimental

The nanocrystalline $MgAl_2O_4$, $ZnFe_2O_4$, and $NiFe_2O_4$ samples were produced by high-energy milling of coarse high-purity spinel powders (further referred to as the nonactivated materials) in a SPEX 8000 shaker mill (Spex CertiPrep Inc., USA). A grinding chamber (50 cm^3 in volume) and a single ball (10 mm in diameter) made of zirconia ceramic were used. The ball-to-powder weight ratio was 10:1.

^{27}Al magic-angle spinning nuclear magnetic resonance (MAS-NMR) spectra were recorded at room temperature with a Bruker MSL 400 spectrometer at a spinning rate of 15 kHz. The applied magnetic field of 9.4 T corresponds to a ^{27}Al resonance frequency of 104.2 MHz. The ^{27}Al chemical shifts are referenced to an 1 M $Al(NO_3)_3$ aqueous solution. X-ray photoelectron spectroscopy (XPS) measurements were performed at room temperature with an ESCALAB 220iXL spectrometer (Fisons Instruments). Mössbauer measurements were carried out in transmission geometry at 6.4 K under 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 Rh. 'Recoil' software [2] was used for the quantitative evaluation of the Mössbauer spectra. The average canting angle, Ψ, was calculated from the ratio of the intensities of lines 2 and 1, $I_{2,1}$, according to $\Psi = 90^\circ - \arcsin[(3I_{2,1}/2)/(1 + 3I_{2,1}/4)]^{1/2}$.

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The degree of inversion of $MgAl_2O_4$, $ZnFe_2O_4$, and $NiFe_2O_4$ samples was calculated according to $I_{(A)}/I_{[B]} = \lambda/(2-\lambda)$ from the NMR, XPS, and Mössbauer sublattice intensities, respectively, corresponding to (A)- and [B]-site ions.

3. Results and discussion

High-resolution ^{27}Al MAS-NMR spectroscopy is used to characterize the mechanically induced disorder in $MgAl_2O_4$. Fig. 1 shows the ^{27}Al MAS-NMR spectrum of nonactivated $MgAl_2O_4$ and of material milled for 2 h. The spectra consist of two well-resolved peaks in the region characteristic of tetrahedrally coordinated Al^{3+} (chemical shift $\delta \approx 70$ ppm) and octahedrally coordinated Al^{3+} ($\delta \approx 8$ ppm) [3]. The degree of inversion of nonactivated $MgAl_2O_4$ is found to be $\lambda = 0.229(9)$, indicating a partly inverse spinel structure of the bulk aluminate. Fig. 1 clearly demonstrates that the milling of $MgAl_2O_4$ leads to a decrease of the concentration of Al^{3+} cations on [B] sites. The degree of inversion is found to be $\lambda = 0.307(1)$ for the material milled for 2 h. Thus, in $MgAl_2O_4$, the high-energy milling induces a homogeneous mechanochemical reaction, yielding a nonequilibrium cation distribution. Quantitatively, the reaction can be formulated as $(Mg_{0.77}Al_{0.23})[Mg_{0.23}Al_{1.77}]O_4 \rightarrow (Mg_{0.69}Al_{0.31})[Mg_{0.31}Al_{1.69}]O_4$.

The interesting observation is that the milling brings about both a noticeable broadening and a shift (towards negative chemical shifts) of the (A) and [B] spectral lines, implying a change in the local atomic environments of Al^{3+}(A) and Al^{3+}[B] ions. This variation may be explained by the effect of a mechanically induced deformation of both AlO_4 tetrahedra and AlO_6 octahedra [4].

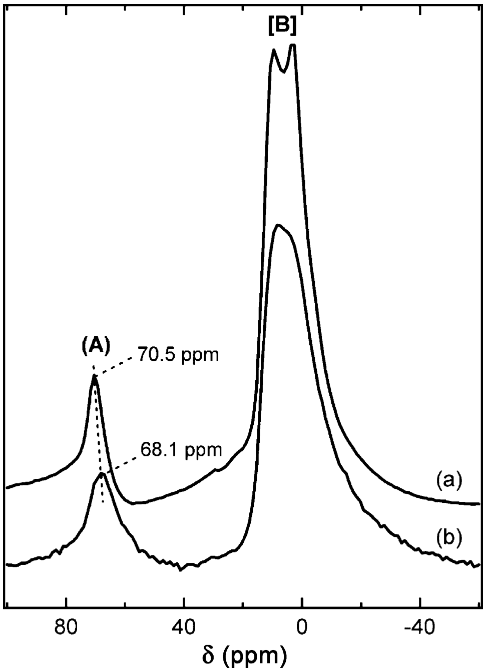

Fig. 1. ^{27}Al MAS-NMR spectrum of nonactivated $MgAl_2O_4$ (a) and of $MgAl_2O_4$ milled for 2 h (b).

The effect of high-energy milling on the cation distribution in $ZnFe_2O_4$ is investigated by XPS. The Zn $2p_{3/2}$ signal of the nonactivated $ZnFe_2O_4$ (Fig. 2(a)) consists of a single sharp peak located at 1021.8 eV, which corresponds to the tetrahedrally coordinated zinc ions [5]. This indicates that nonactivated $ZnFe_2O_4$ adopts the normal spinel structure ($\lambda = 0$). In contrast, the Zn $2p_{3/2}$ signal of the material milled for 18 min (Fig. 2(b)) consists of two peaks located at 1021.8 and 1023.2 eV, corresponding to Zn^{2+} ions on (A) and [B] sites, respectively [5]. A high population of Zn^{2+} in [B] sites ($\lambda = 0.412(3)$) is evidence that the milled $ZnFe_2O_4$ exhibits a partly inverse spinel structure. This observation is consistent with the results of the EXAFS investigations of nanoscale milled Zn-containing spinels [6,7]. Quantitatively, the mechanochemical reaction in $ZnFe_2O_4$ can be formulated as $(Zn)[Fe_2]O_4 \rightarrow (Zn_{0.59}Fe_{0.41})[Zn_{0.41}Fe_{1.59}]O_4$.

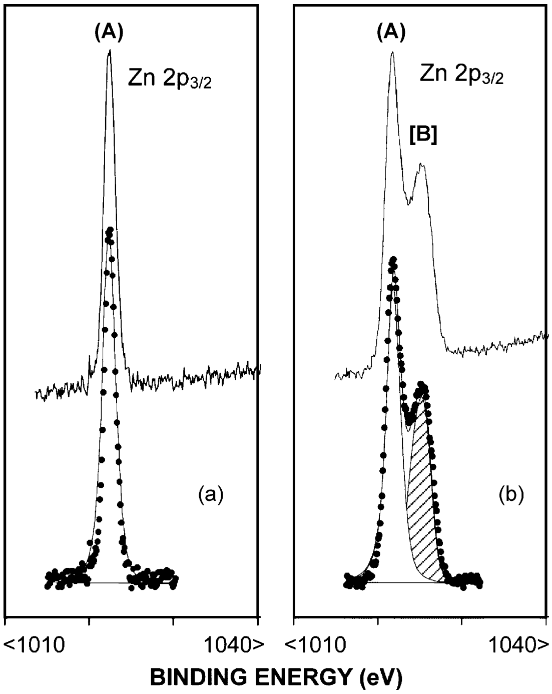

Fig. 2. XPS spectrum of nonactivated $ZnFe_2O_4$ (a) and of $ZnFe_2O_4$ milled for 18 min (b).

It should be noted that the mean free path of photoelectrons in zinc oxides for the Zn $2p_{3/2}$ signal is about 2 nm, leading to the value of the information depth of the XPS measurements of about 6 nm [5]. Thus, taking into account similar values of the information depth and the particle size of the milled $ZnFe_2O_4$ (≈8 nm) [1], it could be stated that the results of the XPS measurements reflects not only the surface structural disorder but also the interior structure of $ZnFe_2O_4$ nanoparticles.

In order to characterize the mechanically induced disorder in $NiFe_2O_4$, low-temperature Mössbauer measurements in conjunction with large external magnetic fields were found to be necessary. The high-field Mössbauer spectra of nonactivated $NiFe_2O_4$ and material milled for 2 h are compared in Fig. 3. The spectra consist of two sextets with isomer shifts of $IS_{(A)} = 0.25(4)$ mm/s and $IS_{[B]} = 0.36(3)$ mm/s characteristic of Fe^{3+} ions on (A) and [B] sites, respectively [8]. The degree of inversion of nonactivated $NiFe_2O_4$ (Fig. 3(a)) is found to be $\lambda = 0.998(3)$. The ratio of intensities of lines 2 and

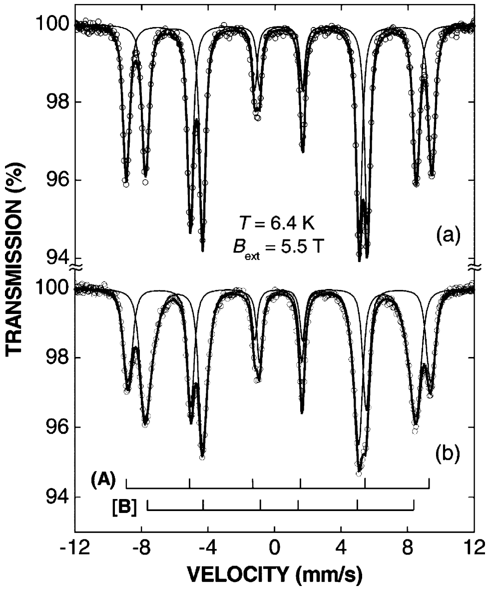

Fig. 3. ^{57}Fe Mössbauer spectrum of nonactivated $NiFe_2O_4$ (a) and of $NiFe_2O_4$ milled for 2 h (b).

1, $I_{2,1}$, is about 4/3, indicating that the spins are completely aligned in this material at 6.4 K ($\Psi_{(A)} = 0.1(1)°$, $\Psi_{[B]} = 0.2(1)°$) along the external magnetic field of 5.5 T. Thus, the bulk ferrite exhibits a fully inverse spinel structure with a Néel-type collinear spin arrangement of $(Fe\uparrow)[Ni\downarrow Fe\downarrow]O_4$. It is clearly demonstrated that the milling of $NiFe_2O_4$ leads to a decrease of the concentration of Fe^{3+} cations on (A) sites, see Fig. 3(b). The degree of inversion of the milled $NiFe_2O_4$ is found to be $\lambda = 0.721(3)$. The mechanically induced cation order–disorder reaction for $NiFe_2O_4$ can, therefore, be written as $(Fe)[NiFe]O_4 \rightarrow (Ni_{0.28}Fe_{0.72})[Ni_{0.72}Fe_{1.28}]O_4$. For the milled material, the average canting angles are found to be $\Psi_{(A)} = 24.4(8)°$ and $\Psi_{[B]} = 25.6(5)°$. Thus, the milled $NiFe_2O_4$ is structurally and magnetically disordered due to mechanically induced changes in the cation distribution and spin canting.

It is widely appreciated that the cation distribution in spinels is a complex function of processing parameters. For example, it was shown that above 1200 K, the degree of inversion of synthetic $MgAl_2O_4$ increases with increasing temperature from about 0.22–0.30 at 1662 K [9]. Similarly, O'Neill has shown that the degree of inversion of $ZnFe_2O_4$ increases from about 0.02 at 773 K to 0.2 at 1223 K [10]. According to these data, the degree of inversion reached in nanosized milled $MgAl_2O_4$ ($\lambda \approx 0.31$) and $ZnFe_2O_4$ ($\lambda \approx 0.41$) corresponds to that of the bulk samples at about 1700 K. Taking into account both impact-induced local heating and high local pressures (sometimes called "hot spots" or "thermal spikes") during the milling, the mechanically induced cation order–disorder process could be understood to occur at the moment of impact as a result of formation and freezing-in of high-energy localized states.

4. Conclusions

MAS-NMR, XPS, and Mössbauer spectroscopy provided valuable insight into the cation order–disorder mechanochemical process in $MgAl_2O_4$, $ZnFe_2O_4$, and $NiFe_2O_4$ spinels, respectively. It was revealed that high-energy milling of spinels, independently of their ionic configuration in the initial bulk state, induces a homogeneous mechanochemical reaction which tends to randomise cations among (A) and [B] lattice sites. Thus, for spinels with $\lambda = 0$ ($ZnFe_2O_4$), $\lambda = 1$ ($NiFe_2O_4$), and $0 < \lambda < 1$ ($MgAl_2O_4$), the mechanically induced cation redistribution is directed towards random arrangement ($\lambda = 2/3$). In $MgAl_2O_4$ and $NiFe_2O_4$ spinels, the mechanically induced cation order–disorder process is found to be accompanied by a deformation of polyhedron geometries and by the formation of noncollinear spin arrangements, respectively. Nanoscale milled spinels are in a far from equilibrium state with a structural disorder corresponding to that of bulk samples at high temperatures (≈1700 K).

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References

[1] V. Šepelák, I. Bergmann, S. Kipp, K.D. Becker, Z. Anorg, Allg. Chem. 631 (2005) 993–1003.
[2] K. Lagarec, D.G. Rancourt, Recoil—Mössbauer Spectral Analysis Software for Windows, Version 1.02, Department of Physics, University of Ottawa, Ottawa, 1998.
[3] R.L. Millard, R.C. Peterson, B.K. Hunter, Am. Mineral. 77 (1992) 44–52.
[4] N. Kashii, H. Maekawa, Y. Hinatsu, J. Am. Ceram. Soc. 82 (1999) 1844–1848.
[5] P. Druska, U. Steinike, V. Šepelák, J. Solid State Chem. 146 (1999) 13–21.
[6] N. Ponpandian, A. Narayanasamy, C.N. Chinnasamy, N. Sivakumar, J.-M. Greneche, K. Chattopadhyay, K. Shinoda, B. Jeyadevan, K. Tohji, Appl. Phys. Lett. 86 (2005) 192510-1–192510-3.
[7] S.A. Morrison, C.L. Cahill, E.E. Carpenter, S. Calvin, R. Swaminathan, M.E. McHenry, V.G. Harris, J. Appl. Phys. 95 (2004) 6392–6395.
[8] F. Menil, J. Phys. Chem. Solids 46 (1985) 763–789.
[9] S.A.T. Redfern, R.J. Harrison, H.St.C. O'Neill, D.R.R. Wood, Am. Mineral. 84 (1999) 299–310.
[10] H.St.C. O'Neill, Eur. J. Mineral. 4 (1992) 571–580.