

MECHANOSYNTHESIS OF NANOCRYSTALLINE IRON GERMANATE Fe_2GeO_4 WITH A NONEQUILIBRIUM CATION DISTRIBUTION

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Received: March 29, 2007

Abstract. A single-step synthesis of iron germanate (Fe_2GeO_4) nanoparticles with an average crystallite size of about 11 nm synthesized via mechanochemical processing of the $\alpha\text{-Fe}_2\text{O}_3/\text{Fe}/\text{GeO}_2$ mixture at room temperature is reported. Due to the ability of ^{57}Fe Mössbauer spectroscopy to discriminate between probe nuclei on inequivalent crystallographic sites provided by the spinel structure, valuable insight into the local cation disorder in mechanosynthesized Fe_2GeO_4 is obtained. In contrast to the bulk Fe_2GeO_4 with a normal spinel structure ($\lambda = 0$), the nanocrystalline mechanosynthesized Fe_2GeO_4 adopts a partly inverse spinel structure with a nonequilibrium cation distribution ($\lambda \approx 0.67$) and deformed polyhedron geometries. Quantitative microstructural information on the disordered cation arrangement provided by Mössbauer spectroscopy is complemented by XRD and TEM investigations revealing the nanoscale nature of the mechanosynthesized material.

1. INTRODUCTION

Iron germanate, Fe_2GeO_4 , as a *p*-type semiconducting material, is an important member of the spinel family of the type $M1_2M2O_4$, where *M1* and *M2* are divalent and tetravalent cations, respectively [1]. To emphasize the site occupancy at the atomic level, the structural formula of such 2-4 spinels may be written as $(M1_\lambda M2_{1-\lambda})[M1_{2-\lambda} M2_\lambda]O_4$, where parentheses and square brackets denote cation sites of tetrahedral (A) and octahedral [B] coordination, respectively. λ represents the so-called degree of inversion (defined as the fraction of the (A) sites occupied by $M1^{2+}$ cations). In the bulk state, Fe_2GeO_4 adopts the normal spinel structure ($\lambda = 0$), in which the cations Ge^{4+} and Fe^{2+} are fully ordered at (A) and [B] sites, respectively [2].

The preparation of Fe^{2+} -containing spinel oxides by the conventional solid-state (ceramic) route requires a number of stages, including homogenization of the powder precursors, compaction of the reactants, and finally prolonged heat treatment at considerably elevated temperatures under controlled oxygen fugacity [3]. One goal of modern materials research and development has been to identify simpler processing schemes that do not rely upon high-temperature treatments for inducing solid-state reactions [4]. In this article, we will report on the single-step synthesis of Fe_2GeO_4 via high-energy milling of the mixture of three precursors ($\alpha\text{-Fe}_2\text{O}_3$, Fe, GeO_2). To the best of our knowledge, the single-step mechanosynthesis of nanosized Fe_2GeO_4 particles has not been reported

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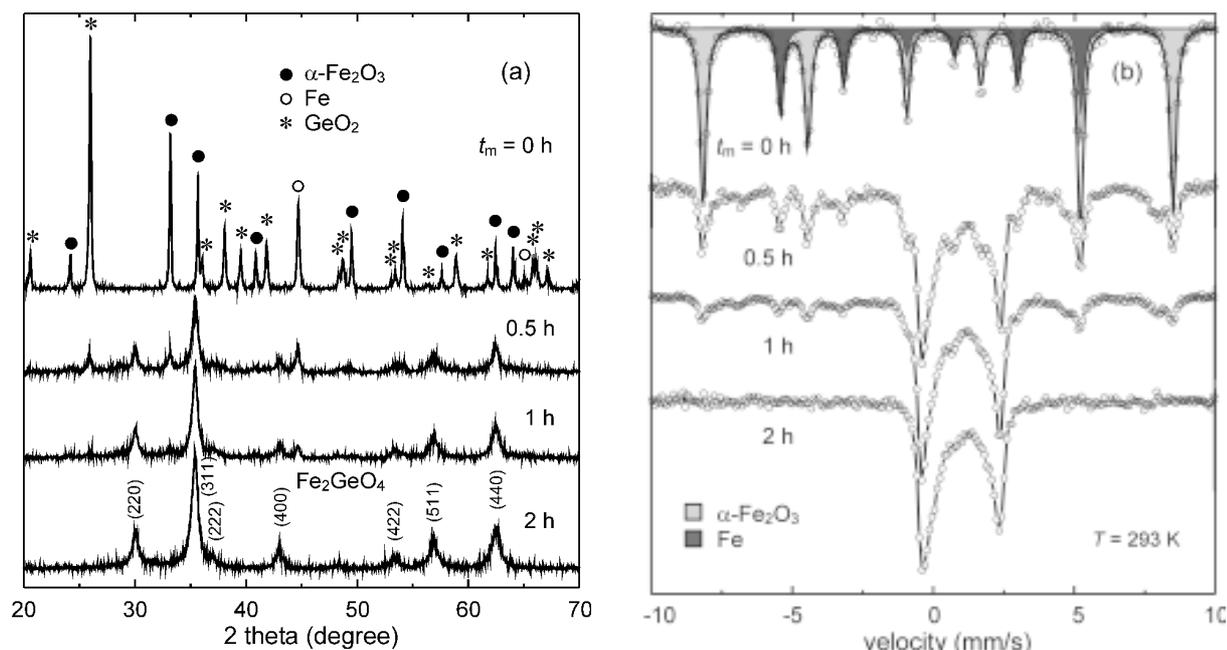


Fig. 1. XRD patterns (a) and room-temperature Mössbauer spectra (b) of the $\alpha\text{-Fe}_2\text{O}_3/\text{Fe}/\text{GeO}_2$ mixture milled for various times (t_m). Diffraction lines of the mechanosynthesized product (Fe_2GeO_4) are denoted by Miller indices.

before. Furthermore, for the first time, quantitative microstructural information is obtained on the nonequilibrium cation distribution in nanosized Fe_2GeO_4 .

2. EXPERIMENTAL

The mechanochemical route was used for the preparation of nanostructured Fe_2GeO_4 . A 10 g mixture of $\alpha\text{-Fe}_2\text{O}_3$, Fe, and GeO_2 reactants (Merck, Darmstadt, Germany) in the molar ratio of 2:2:3 was milled for various uninterrupted times (up to 2 h) in a Pulverisette 6 planetary ball mill (Fritsch, Idar-Oberstein, Germany) at room temperature under argon atmosphere at 600 rpm. 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 20:1.

Additionally, bulk Fe_2GeO_4 , which served as a reference sample in this study, was prepared from the mixture of $\alpha\text{-Fe}_2\text{O}_3$, Fe and GeO_2 precursors (in the molar ratio of 2:2:3) by the conventional solid-state route. The reaction samples were heated in the form of tablets (20 mm in diameter, 4 mm thick) in a previously evacuated silica tube at 1300K for 48 h. The single-phase nature of the bulk Fe_2GeO_4

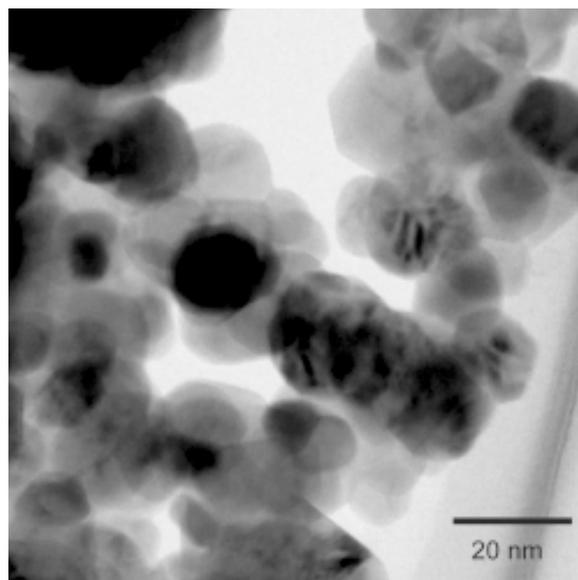


Fig. 2. TEM micrograph of nanoscale mechanosynthesized Fe_2GeO_4 .

sample was confirmed by X-ray diffraction and Mössbauer spectroscopy.

The X-ray powder diffraction (XRD) patterns were collected using a Philips X'Pert MPD diffractometer with $\text{Cu } K_\alpha$ radiation. XRD data were analyzed using the STOE software utilizing the

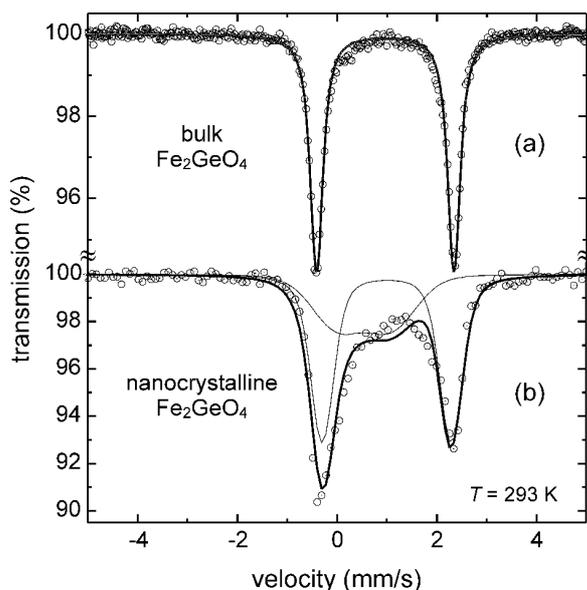


Fig. 3. Room-temperature Mössbauer spectra of bulk (a) and nanocrystalline mechanosynthesized Fe_2GeO_4 (b).

JCPDS PDF database. The morphology of powders and the sizes of individual crystallites were studied using a combined field-emission (scanning) transmission electron microscope (S)TEM (JEOL JEM-2100F). The room-temperature Mössbauer spectra were taken in transmission geometry using a $^{57}\text{Co}/\text{Rh}$ γ -ray source. The velocity scale was calibrated relative to ^{57}Fe in Rh. Recoil spectral analysis software [5] was used for the quantitative evaluation of the Mössbauer spectra. The degree of inversion, λ , characterizing the distribution of cations over the two inequivalent cation sublattices provided by the spinel structure, was calculated from the Mössbauer subspectral intensities ($I_{\text{A}}/I_{\text{B}} = (f_{\text{A}}/f_{\text{B}})(\lambda/(2-\lambda))$), assuming that the ratio of the recoilless fractions is $f_{\text{A}}/f_{\text{B}} = 1$.

3. RESULTS AND DISCUSSION

Fig. 1a shows XRD patterns of the $\alpha\text{-Fe}_2\text{O}_3/\text{Fe}/\text{GeO}_2$ mixture milled for various times. The XRD pattern of the starting powder (Fig. 1a, top) is characterized by sharp diffraction peaks corresponding to crystalline $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS PDF 33-664), Fe (JCPDS PDF 6-696) and GeO_2 (JCPDS PDF 36-1463). Already after 0.5 h of milling, qualitative changes are observed in the XRD patterns of the milled samples. Intensity of the Bragg peaks of the

individual educts decreases, and clear evidence is observed of diffraction features that correspond to the spinel (220) and (400) diffraction peaks. The increased intensity and shift to higher d -spacing of the most-intense peak (from $d = 0.2519$ nm to $d = 0.2534$ nm) also suggest the presence of the spinel (311) diffraction peak. After 2 h of milling, all XRD peaks detected above the background are due to the Fe_2GeO_4 phase (JCPDS PDF 25-359). The Rietveld analysis of the XRD data of the mixture milled for 2 h revealed both an average crystallite size of 11.5(2) nm and the presence of mean strains of $2.8(4) \cdot 10^{-3}$ in the produced complex oxide. Thus, nanocrystalline iron germanate is the product of the following mechanochemical reaction: $2\alpha\text{-Fe}_2\text{O}_3 + 2\text{Fe} + 3\text{GeO}_2 \rightarrow 3\text{Fe}_2\text{GeO}_4$.

To determine the phase evolution of the $\alpha\text{-Fe}_2\text{O}_3/\text{Fe}/\text{GeO}_2$ mixture during high-energy milling by an independently supporting method, the mechanochemical reaction was also followed by ^{57}Fe Mössbauer spectroscopy. As shown in Fig. 1b, with increasing milling time, sextets corresponding to $\alpha\text{-Fe}_2\text{O}_3$ ($B \approx 52$ T) and Fe ($B \approx 33$ T) become asymmetric towards the inside of each line, decrease in intensity, and are gradually replaced by a broad doublet with a central shift of about 0.9 mm/s characteristic of ferrous (Fe^{2+}) ions [6]. The Mössbauer spectrum of the mixture milled for 2 h does not reveal any magnetically-split line corresponding to $\alpha\text{-Fe}_2\text{O}_3$ or Fe (see Fig. 1b, bottom). This confirms that the mechanochemical synthesis method is feasible and complete. Compared to the traditional fabrication processes of Fe^{2+} -containing spinel oxides, the mechanochemical route used here represents a one-step, high-yielding and low-cost procedure for the synthesis of Fe_2GeO_4 nanoparticles.

TEM micrograph (Fig. 2) revealed that the mechanosynthesized Fe_2GeO_4 consists of crystallites mostly in the 8-15 nm size range, consistent with the average crystallite size determined by XRD. The shape of the majority of the crystallites appears to be spherical.

Fig. 3 compares the room-temperature Mössbauer spectra of both bulk (prepared by the conventional ceramic route) and nanoscale mechanosynthesized Fe_2GeO_4 . As clearly shown in Fig. 3a, the spectrum of the bulk Fe_2GeO_4 consists of a symmetric doublet with the parameters $IS = 0.96(4)$ mm/s and $QS = 2.75(4)$ mm/s characteristic of octahedrally coordinated Fe^{2+} ions [6]. This indicates that the bulk material adopts the normal spinel structure ($\lambda = 0$). Thus, crystal chemical formula emphasizing the site occupancy at the

atomic level in the bulk iron germanate can be written as $(\text{Ge})[\text{Fe}_2]\text{O}_4$. This is in contrast to the nanoscale mechanosynthesized Fe_2GeO_4 , whose Mössbauer spectrum is dominated by an asymmetric doublet (Fig. 3b). This doublet is well-fitted by a superposition of two subspectra; one accounting for Fe^{2+} nuclei at [B] sites (IS = 0.99(6) mm/s, QS = 2.7(2) mm/s) and one associated with Fe^{2+} ions at (A) sites (IS = 0.61(6) mm/s, QS = 1.2(3) mm/s) of the spinel structure [6]. The degree of inversion of nanocrystalline Fe_2GeO_4 , calculated from the relative intensities of subspectra, is found to be $\lambda = 0.67(5)$. It should be noted that this value of the degree of inversion corresponds nearly to the random distribution of cations ($\lambda = 2/3$) with maximum configurational entropy. Thus, the mechanosynthesized iron germanate exhibits a partly inverse spinel structure with a nonequilibrium cation distribution of $(\text{Fe}_{0.67}\text{Ge}_{0.33})[\text{Fe}_{1.33}\text{Ge}_{0.67}]\text{O}_4$. The present observation of the nonequilibrium cation distribution in Fe_2GeO_4 nanoparticles is consistent with previous studies of nanocrystalline complex oxides, where disordered ionic configuration was also observed; for details, see [7] and references therein. The broad shape of the Mössbauer spectral lines for mechanosynthesized Fe_2GeO_4 , in contrast to relatively narrow lines for the bulk material (compare lines a and b in Fig. 3), provides clear evidence of a wide distribution of electric field gradients acting at the Fe^{2+} nuclei in the nanomaterial. This variation may be explained by the effect of a mechanically induced deformation of both FeO_6 octahedra and FeO_4 tetrahedra. Similar findings have also been reported for other nanocrystalline complex oxides [8], where a nonequilibrium cation distribution was found to be accompanied by a deformation of polyhedron geometries.

4. CONCLUSIONS

Nanosized Fe_2GeO_4 with an average crystallite size of about 11 nm has been synthesized in a one-step mechanochemical route from the mixture of $\alpha\text{-Fe}_2\text{O}_3$, Fe, and GeO_2 precursors at room temperature. The nonconventional mechanochemical

route to Fe_2GeO_4 offers several advantages over traditional processing routes, including low-temperature solid-state reactions, fewer processing steps, and suitability for the low cost, large-scale production of nanopowders. It was revealed that the mechanosynthesized iron germanate exhibits a partly inverse spinel structure with a nonequilibrium cation distribution of $(\text{Fe}_{0.67}\text{Ge}_{0.33})[\text{Fe}_{1.33}\text{Ge}_{0.67}]\text{O}_4$. The mechanically induced formation of nanocrystalline Fe_2GeO_4 is found to be accompanied by a deformation of both FeO_6 octahedra and FeO_4 tetrahedra.

ACKNOWLEDGEMENTS

The work was supported by the Deutsche Forschungsgemeinschaft. Partial support by the APVV (Project 0728-07) VEGA (Grant 2/0065/08) and by the Alexander von Humboldt Foundation is gratefully acknowledged.

REFERENCES

- [1] P. Strobel, F.P. Koffyberg and A. Wold // *J. Solid State Chem.* **31** (1980) 209.
- [2] M.D. Welch, M.A. Cooper and F.C. Hawthorne // *Miner. Mag.* **65** (2001) 441.
- [3] R.J. Harrison, S.A.T. Redfern and H.St.C. O'Neill // *Am. Mineral.* **83** (1998) 1092.
- [4] V.V. Boldyrev // *Russ. Chem. Rev.* **75** (2006) 177.
- [5] K. Lagarec and D.G. Rancourt, *Recoil - Mössbauer Spectral Analysis Software for Windows, version 1.02* (Department of Physics, University of Ottawa, Ottawa, 1998).
- [6] F. Menil // *J. Phys. Chem. Solids* **46** (1985) 763.
- [7] V. Šepelák, A. Feldhoff, P. Heitjans, F. Krumeich, D. Menzel, F.J. Litterst, I. Bergmann and K.D. Becker // *Chem. Mater.* **18** (2006) 3057.
- [8] V. Šepelák, I. Bergmann, S. Kipp and K.D. Becker // *Z. Anorg. Allg. Chem.* **631** (2005) 993.