

One-step mechanosynthesis of nanocrystalline oxides

Vladimir Šepelák^{1,2}, Paul Heitjans³ and Klaus Dieter Becker⁴

Fe²⁺-, Fe³⁺-, and Sn⁴⁺-based complex oxides, namely, Fe₂GeO₄, CaFe₂O₄ and Ca₂SnO₄ nanopowders were prepared via single -step mechanosynthesis performed at room temperature. The mechanically induced formation of a nanooxide product phase was followed by XRD, ⁵⁷Fe Mössbauer spectroscopy, and NMR. It is demonstrated that the mechanosynthesis of the complex oxide can proceed very rapidly (up to 4 h). This is in a strong contrast to the conventional solid-state synthesis of the complex oxides, which requires prolonged exposure at considerably elevated temperatures. It was revealed that the main structural features of the mechanosynthesized oxides are nonequilibrium cation distribution and distorted oxygen polyhedra.

Key words: Mechanochemistry; Mechanosynthesis; Nanooxide; XRD; Mössbauer spectroscopy; NMR

Introduction

The preparation of complex oxides by a conventional 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 (Schmalzried, 1981). 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 (Avvakumov et al., 2001; Boldyrev, 2006; Šepelák et al., 2010). In our recent work, a great effort has been directed towards the single-step mechanosynthesis of Fe- and Sn-based complex oxides. To the best of our knowledge, there are only a few reports available in the literature on the single-step synthesis of these compounds (see, e.g. Berchmans et al., 2010; Šepelák et al., 2006; Šepelák et al., 2007; Šepelák et al., 2008; Šepelák et al., 2009 and references therein).

In the present work, selected examples are presented of the mechanochemical reactions leading to the formation of nanocrystalline Fe- and Sn-based complex oxides. The nonequilibrium structural state of the nanooxides is characterized by Mössbauer spectroscopy and NMR.

Experimental

The mechanochemical synthesis of the complex oxides was performed in a Pulverisette 6 planetary ball mill (Fritsch, Idar-Oberstein, Germany) at room temperature. 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 air at 600 rpm.

The XRD patterns were collected using a PW1820 Philips powder diffractometer (Philips, Eindhoven, Netherlands) with Cu K α radiation. The JCPDS PDF database was utilized for the phase identification of the compounds.

Room-temperature ⁵⁷Fe Mössbauer spectra were taken in transmission geometry using a ⁵⁷Co/Rh γ -ray source. The velocity scale was calibrated relative to ⁵⁷Fe in Rh.

¹¹⁹Sn MAS NMR measurements were performed on an Infinity Plus 500 spectrometer (Varian Chemagnetics, U.S.A.). During the measurements, the samples were rotated in 3.2 mm rotors at a spinning speed of 24 kHz. The magnetic field of 11.8 T corresponded to a Larmor frequency of 186.3 MHz. The spectra were referenced to SnO₂ with a shift of -604.3 ppm.

¹ RNDr. Vladimír Šepelák, DrSc., Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

² Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, 04353 Košice, Slovakia, vlsep@saske.sk

³ Prof. Dr. Paul Heitjans, Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Callinstr. 3a, 30167 Hannover, Germany

⁴ Prof. Dr. Klaus Dieter Becker, Institute of Physical and Theoretical Chemistry, Braunschweig University of Technology, Hans-Sommer-Str. 10, 38106 Braunschweig, Germany

Results and discussion

The $2\text{Fe}_2\text{O}_3/2\text{Fe}/3\text{GeO}_2$ mixture was used to mechanosynthesize the Fe^{2+} -containing complex oxide, namely, iron germanate (Fe_2GeO_4). XRD patterns (Fig. 1) clearly illustrate that with increasing milling time, the diffraction peaks corresponding to crystalline educts decrease in intensity, and after 2 h of milling, all XRD peaks detected above the background are due to the Fe_2GeO_4 phase (JCPDS PDF 25-359). Thus, nanocrystalline iron germanate (average particle size of about 11 nm) is the product of the following mechanochemical reaction: $2\text{Fe}_2\text{O}_3 + 2\text{Fe} + 3\text{GeO}_2 \rightarrow 3\text{Fe}_2\text{GeO}_4$. The analysis of Mössbauer data revealed that the mechanosynthesized Fe_2GeO_4 exhibits a partly inverse spinel structure with a nonequilibrium cation distribution of $(\text{Fe}_{0.67}\text{Ge}_{0.33})[\text{Fe}_{1.33}\text{Ge}_{0.67}]\text{O}_4$ (Šepelák et al., 2008). This is in contrast to the bulk (conventionally prepared) material that adopts the normal spinel structure of $(\text{Ge})[\text{Fe}_2]\text{O}_4$, in which Ge^{4+} and Fe^{2+} are fully ordered at tetrahedral (A) and octahedral [B] sites, respectively (Šepelák et al., 2008).

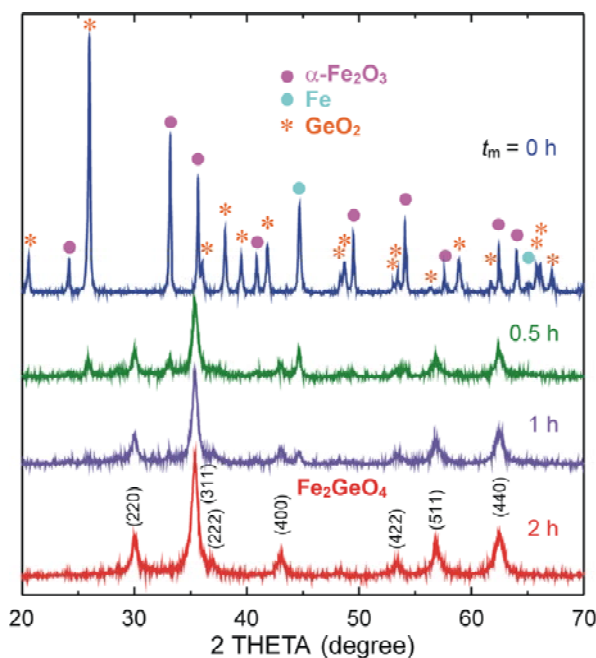


Fig. 1. XRD patterns illustrating the mechanosynthesis of Fe_2GeO_4 from the $\text{Fe}_2\text{O}_3/\text{Fe}/\text{GeO}_2$ mixture. Milling times (t_m) are indicated in the figure. Diffraction lines of the mechanosynthesized Fe_2GeO_4 spinel are denoted by Miller indices.

In the case of the mechanosynthesis of calcium ferrite (CaFe_2O_4), the mechanically induced evolution of the $\text{Ca}/\alpha\text{-Fe}_2\text{O}_3$ mixture, submitted to high-energy milling, was followed by ^{57}Fe Mössbauer spectroscopy (Fig. 2). The spectrum of the starting mixture shows a sextet with a magnetic hyperfine field of 51.6(4) T corresponding to $\alpha\text{-Fe}_2\text{O}_3$. With increasing milling time, the sextet becomes asymmetric toward the inside of each line, slowly collapses, and is gradually replaced by a central doublet. This spectral component can be assigned to the CaFe_2O_4 product with orthorhombic structure (Berchmans et al., 2010). In the present case, it is clear that oxygen present in the vial atmosphere is involved in the rapid one-step mechanosynthesis of CaFe_2O_4 ($\text{Ca} + \text{Fe}_2\text{O}_3 + \frac{1}{2}\text{O}_2 \rightarrow \text{CaFe}_2\text{O}_4$).

The slightly asymmetrical central doublet in the spectrum of mechanosynthesized ferrite (Fig. 2) indicates the presence of at least two crystallographically nonequivalent iron positions in the structure. This spectrum is hence fitted by using two quadrupole doublets corresponding to the ferrite. The estimated isomer shifts values ($\text{IS}_1 = 0.216(7)$ mm/s, $\text{IS}_2 = 0.210(1)$ mm/s) of the doublet components are both typical for ferric (Fe^{3+}) ions in sites octahedrally coordinated by oxygen (Menil, 1985). The quadrupole splittings of the spectral components ($\text{QS}_1 = 0.613(7)$ mm/s, $\text{QS}_2 = 0.924(2)$ mm/s) reflect different values of the electric field gradients acting on Fe^{3+} nuclei in the two nonequivalent octahedral positions of the mechanosynthesized material. These values are larger than those reported for the conventionally synthesized (bulk) CaFe_2O_4 ($\text{QS}_1 = 0.30$ mm/s, $\text{QS}_2 = 0.75$ mm/s) (Hudson and Whitfield, 1967; Tsipis et al., 2007). Note that larger electric field gradients are produced by an asymmetric electronic charge distribution around the iron ions due to the distortion of polyhedra. For both octahedrally coordinated sites, the relative intensities of the spectral components are found to be almost equal, reflecting the same occupation factor of iron cations within these structural units. Thus, the crystal chemical formula of the mechanosynthesized material can be written as $\text{Ca}[\text{Fe}]_{\text{oct1}}[\text{Fe}]_{\text{oct2}}\text{O}_4$, where brackets enclose Fe^{3+} cations in nonequivalent distorted oxygen octahedra.

The mechanochemical synthesis of nanocrystalline Sn^{4+} -containing complex oxide is illustrated in Fig. 3. This figure shows ^{119}Sn MAS NMR spectra of the $2\text{CaO}/\text{SnO}_2$ mixture milled for various t_m . The spectrum of the initial mixture shows a sharp resonance at -604.5 ppm corresponding to the Sn atoms located in SnO_6 octahedra in the crystal structure of SnO_2 . After $t_m = 0.5$ h, a shoulder appears on its right side and a new peak appears at -547.5 ppm, which is assigned to Ca_2SnO_4 (Šepelák et al., 2009). After $t_m = 4$ h, the spectrum is dominated by the line of Ca_2SnO_4 and the peak of the SnO_2 educt has disappeared completely. The broadened shape of NMR spectral lines indicates the presence of a broad distribution of local structures around the Sn nuclei (deformed SnO_6 octahedrons) in the mechanochemical synthesized stannate.

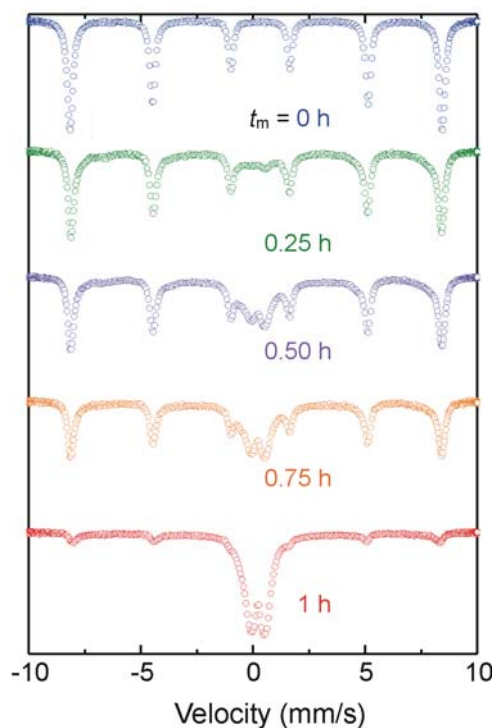


Fig. 2. Room-temperature ^{57}Fe Mössbauer spectra of the $\text{Ca}/\alpha\text{-Fe}_2\text{O}_3$ powders milled for various times.

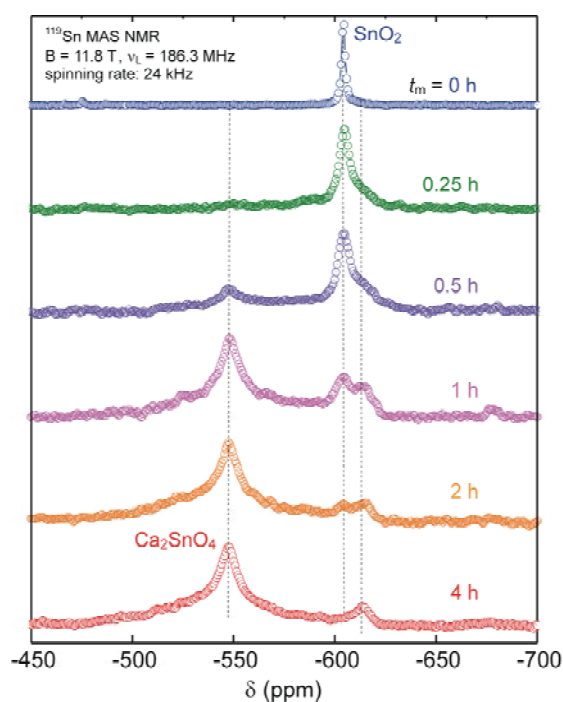


Fig. 3. The mechanochemical reaction $2\text{CaO} + \text{SnO}_2 \rightarrow \text{Ca}_2\text{SnO}_4$ followed by ^{119}Sn MAS NMR.

Conclusions

It is demonstrated that nanocrystalline complex oxides can be synthesized in a relatively short reaction time at room temperature in a one-step mechanochemical route. This nonconventional approach 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. In this respect, the work, concerning the mechanochemistry of oxides, contributes to the search for novel sustainable production routes of functionally tailored nanomaterials. The nonequilibrium structural state of mechanochemical oxides is characterized by the nonequilibrium cation distribution and the deformed polyhedron geometry.

Acknowledgements

The work is supported by the DFG in the framework of the Priority Program "Crystalline Nonequilibrium Phases" (SPP 1415) and by the VEGA (2/0097/14).

References

- Avvakumov, E., Senna, M., Kosova, N. *Soft Mechanochemical Synthesis: A Basis for New Chemical Technologies*, Kluwer Academic Publishers, Boston, 2001.
- Berchmans, L.J., Myndyk, M., Da Silva, K.L., Feldhoff, A., Šubrt, J., Heitjans, P., Becker, K.D., Šepelák, V.; J. Alloy. Compd. 500 (2010) 68.
- Boldyrev, V.V.: Russ. Chem. Rev. 75 (2006) 177.
- Hudson, A., Whitfield, H.J.: J. Chem. Soc. A (1967) 376.
- Menil, F.: J. Phys. Chem. Solids 46 (1985) 763.
- Schmalzried, H.: *Solid State Reactions*, Verlag Chemie, Weinheim, 1981.
- Šepelák, V., Becker, K.D., Bergmann, I., Suzuki, S., Indris, S., Feldhoff, A., Heitjans, P., Grey, C.P.: Chem. Mater. 21 (2009) 2518.
- Šepelák, V., Bergmann, I., Diekmann, A., Heitjans, P., Becker, K.D.: Rev. Adv. Mater. Sci. 18 (2008) 349.
- Šepelák, V., Bergmann, I., Feldhoff, A., Heitjans, P., Krumeich, F., Menzel, D., Litterst, F.J., Campbell, S.J., Becker, K.D.: J. Phys. Chem. C 111 (2007) 5026.
- Šepelák, V., Bergmann, I., Indris, S., Feldhoff, A., Heitjans, P., Becker, K.D. In: *Experimental and Theoretical Studies in Modern Mechanochemistry*, F. Delogu, G. Mulas (eds.), *Transworld Research Network, Kerala, 2010*, pp. 191-206.
- Šepelák, V., Feldhoff, A., Heitjans, P., Krumeich, F., Menzel, D., Litterst, F.J., Bergmann, I., Becker, K.D.: Chem. Mater. 18 (2006) 3057.
- Tsipis, E.V., Pivak, Y.V., Waerenborgh, J.C., Kolotygin, V.A., Viskup, A.P., Kharton, V.V.: Solid State Ionics 178 (2007) 1428.