diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application
www.diffusion-fundamentals.org, ISSN 1862-4138; © 2005-2010

Mössbauer Spectroscopy for Studying Chemical Reactions

Vladimír Šepelák,[*,1,2] Paul Heitjans,[3] Klaus-Dieter Becker[4]*

[1] Karlsruhe Institute of Technology, Institute of Nanotechnology,
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[2] On leave from the Slovak Academy of Sciences, 04353 Košice, Slovakia
[3] Leibniz University Hannover, Institute of Physical Chemistry and Electrochemistry,
Callinstr. 3a, 30167 Hannover, Germany
[4] Braunschweig University of Technology, Institute of Physical and Theoretical Chemistry,
Hans-Sommer-Str. 10, 38106 Braunschweig, Germany

E-Mail: vladimir.sepelak@int.fzk.de

Presented at the Bunsen Colloquium: Spectroscopic Methods in Solid State Diffusion and Reactions
September 24th – 25th, 2009, Leibniz University Hannover, Germany

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 [1]. 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 [2]. In our recent work, a great effort has been directed towards the single-step mechanosynthesis of *Fe^{2+}-containig oxides* (*e.g.*, Fe_2GeO_4, Fe_2SiO_4) [3], *Fe^{3+}-containing spinels* ($Li_{0.5}Fe_{2.5}O_4$, $NiFe_2O_4$, $MgFe_2O_4$) [4-9], *Al^{3+}-containing spinels* ($MgAl_2O_4$, $ZnAl_2O_4$, $NiAl_2O_4$) [10,11], and *Sn^{4+}-containing complex oxides* of the type M_2SnO_4 (M = Ca, Zn) [12]. 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.*, Refs. [3-12] and references therein). In the present work, examples are presented of the mechanochemical reactions leading to the formation of nanocrystalline complex oxides. Mössbauer spectroscopy is employed to follow the mechanosynthesis route and to characterize the structural state of the resulting nanophases at the atomic level.

Fig. 1 shows the mechanically induced phase evolution of a $2Fe_2O_3 : 2Fe : 3GeO_2$ mixture [3]. XRD patterns clearly illustrate that with increasing milling time (t_m), 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). ^{57}Fe Mössbauer measurements show that with increasing t_m, sextets corresponding to α-Fe_2O_3 and Fe are gradually replaced by a broad asymmetric doublet with a central shift of about 0.9 mm/s characteristic of Fe^{2+} ions. Thus, nanocrystalline iron germanate (average particle size D = 11 nm) is the product of the following mechanochemical reaction: $2\,Fe_2O_3 + 2\,Fe + 3\,GeO_2 \rightarrow 3\,Fe_2GeO_4$. The analysis of Mössbauer data revealed that the mechanosynthesized Fe_2GeO_4 exhibits a partly inverse spinel structure with a nonequilibrium cation distribution of $(Fe_{0.67}Ge_{0.33})[Fe_{1.33}Ge_{0.67}]O_4$ [3]. This is in contrast to the bulk (conventionally prepared) material that adopts the normal spinel structure of $(Ge)[Fe_2]O_4$, in which Ge^{4+} and Fe^{2+} are fully ordered at tetrahedral (A) and octahedral [B] sites, respectively [3].

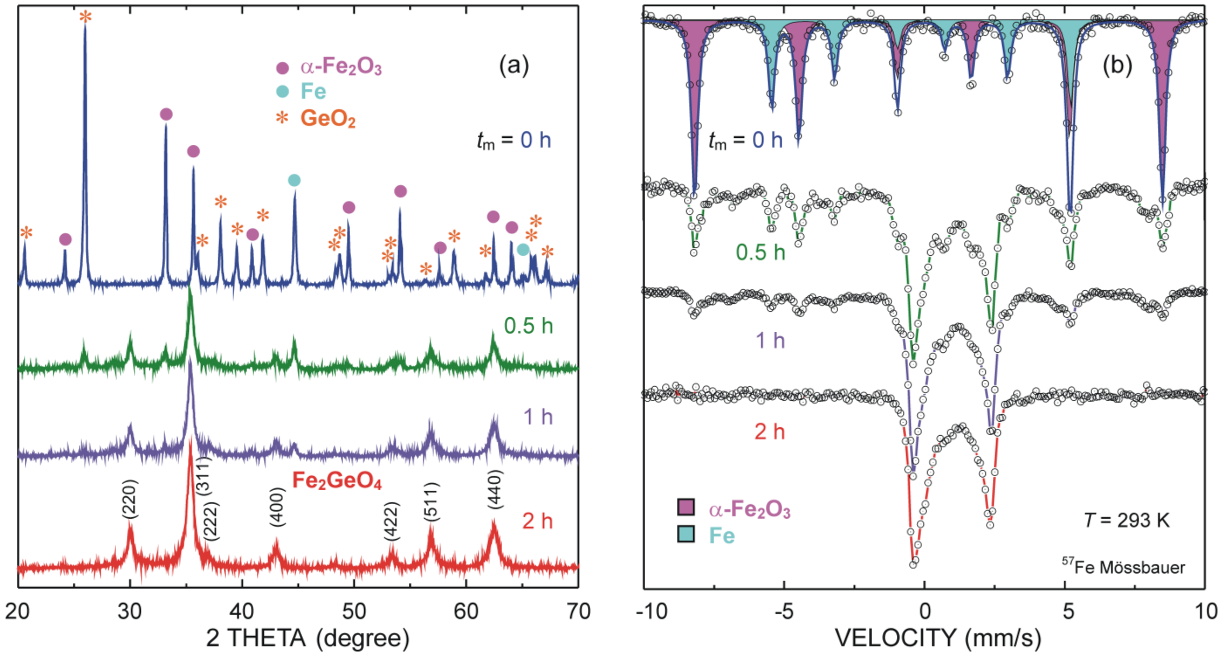

Fig. 1 (a) XRD patterns and (b) room-temperature ^{57}Fe Mössbauer spectra illustrating the mechanosynthesis of Fe_2GeO_4 from the Fe_2O_3 : Fe : GeO_2 mixture. Milling times (t_m) are indicated in the figure. Diffraction peaks of the mechanosynthesized Fe_2GeO_4 spinel are denoted by Miller indices.

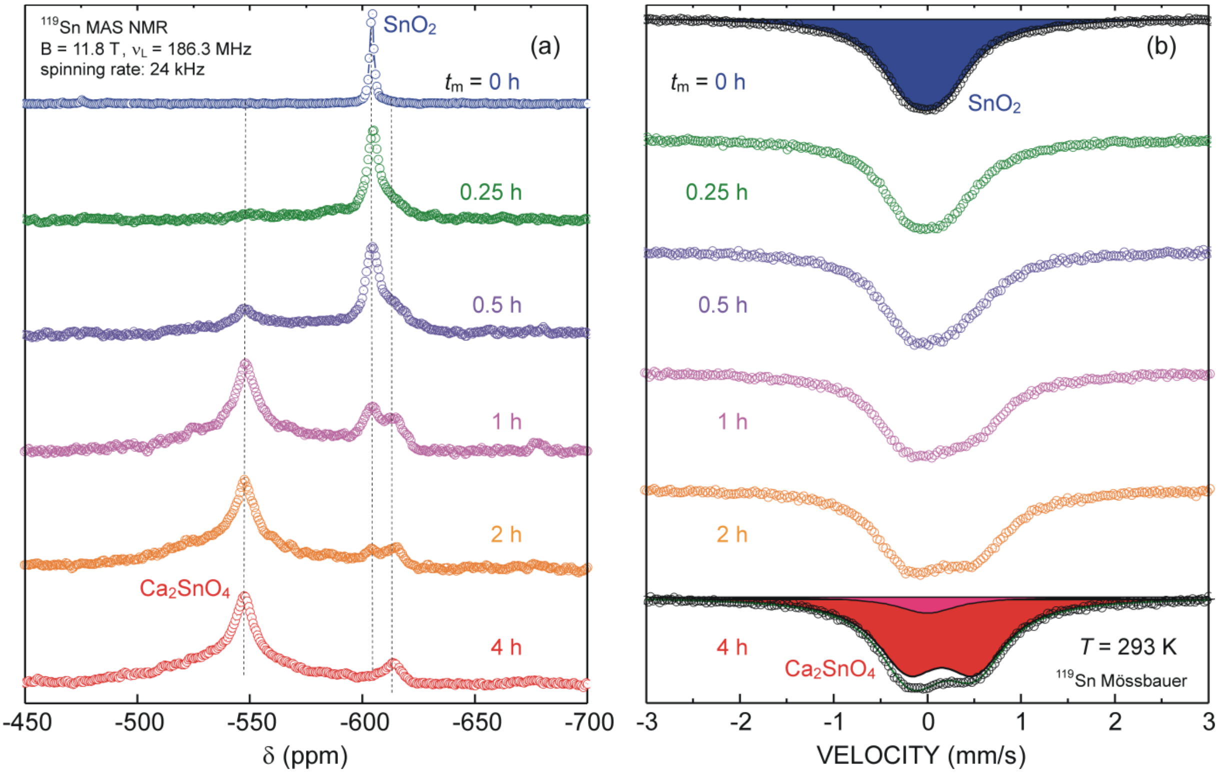

Fig. 2 The mechanochemical reaction 2 CaO + $SnO_2 \rightarrow Ca_2SnO_4$ followed by (a) ^{119}Sn MAS NMR and (b) ^{119}Sn Mössbauer spectroscopy.

The mechanosynthesis of a nanocrystalline Sn^{4+}-containing complex oxide is illustrated in Fig. 2. The mechanochemical reaction $2\,MO + SnO_2 \rightarrow M_2SnO_4$ (M = Ca, Zn) represents a very convenient model reaction for studies of changes in the local structure during mechanosynthesis since the tin nucleus can serve as a local probe in both NMR as well as Mössbauer measurements. In our work [12], ^{119}Sn MAS NMR and ^{119}Sn Mössbauer spectroscopy were employed to follow the mechanosynthesis of Ca_2SnO_4. Fig. 2a shows ^{119}Sn MAS NMR spectra of the 2CaO : 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 [12]. After t_m = 4 h, the spectrum is dominated by the peak of Ca_2SnO_4 and the peak of the SnO_2 educt has disappeared completely. Note that a small peak at 614 ppm can be assigned to $CaSnO_3$. Similarly, ^{119}Sn Mössbauer spectroscopy revealed that with increasing t_m, the singlet corresponding to SnO_2 gradually evolves to a broad doublet that is well fitted by a superposition of two subspectra (Fig. 2b); a major one (93%) accounting for octahedrally coordinated Sn^{4+} in Ca_2SnO_4 and a minor one associated with the $CaSnO_3$ phase [12]. The broadened shape of Mössbauer and NMR spectral lines indicates the presence of a broad distribution of local structures around the Sn nuclei (deformed SnO_6 octahedrons) in the mechanosynthesized stannate.

Results obtained clearly demonstrate that a variety of nanocrystalline complex oxides can be synthesized in a relatively short reaction time at room temperature in a one-step mechanochemical route [3-12]. 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, also contributes to the search for novel sustainable production routes of functionally tailored nanomaterials.

Acknowledgement. The work is supported by the DFG in the framework of the Priority Program *"Crystalline Nonequilibrium Phases"* (SPP 1415). Partial support by the AvH Foundation, the APVV (Project 0728-07) and by the VEGA (2/0065/08) is gratefully acknowledged.

References

[1] H. Schmalzried, Solid State Reactions, Verlag Chemie, Weinheim, 1981.
[2] (a) V. V. Boldyrev, Russ. Chem. Rev. 75 (2006) 177-189. (b) E. Avvakumov, M. Senna, N. Kosova, Soft Mechanochemical Synthesis: A Basis for New Chemical Technologies, Kluwer Academic Publishers, Boston, 2001.
[3] V. Šepelák, I. Bergmann, A. Diekmann, P. Heitjans, K. D. Becker, Rev. Adv. Mater. Sci. 18 (2008) 349.
[4] I. Bergmann, V. Šepelák, A. Feldhoff, P. Heitjans, K. D. Becker, Rev. Adv. Mater. Sci. 18 (2008) 375.
[5] V. Šepelák, I. Bergmann, A. Feldhoff, P. Heitjans, F. Krumeich, D. Menzel, F. J. Litterst, S. J. Campbell, K. D. Becker, J. Phys. Chem. C 111 (2007) 5026.
[6] V. Šepelák, P. Heitjans, K. D. Becker, J. Therm. Anal. Calorim. 90 (2007) 93.
[7] V. Šepelák, A. Feldhoff, P. Heitjans, F. Krumeich, D. Menzel, F. J. Litterst, I. Bergmann, K. D. Becker, Chem. Mater. 18 (2006) 3057.
[8] V. Šepelák, I. Bergmann, D. Menzel, A. Feldhoff, P. Heitjans, F. J. Litterst, K. D. Becker, J. Magn. Magn. Mater. 316 (2007) e764.
[9] I. Bergmann, V. Šepelák, K. D. Becker, Solid State Ionics 177 (2006) 1865.
[10] V. Šepelák, S. Indris, P. Heitjans, K. D. Becker, J. Alloy. Compd. 434 (2007) 776.
[11] V. Šepelák, S. Indris, I. Bergmann, A. Feldhoff, K. D. Becker, P. Heitjans, Solid State Ionics 177 (2006) 2487.
[12] V. Šepelák, K. D. Becker, I. Bergmann, S. Suzuki, S. Indris, A. Feldhoff, P. Heitjans, C. P. Grey, Chem. Mater. 21 (2009) 2518.