A One-Step Mechanochemical Route to Core−Shell Ca_2SnO_4 Nanoparticles Followed by ^{119}Sn MAS NMR and ^{119}Sn Mössbauer Spectroscopy

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Calcium stannate (Ca_2SnO_4) nanoparticles with an average size of about 15 nm were synthesized via single-step mechanochemical processing of binary oxide precursors at room temperature. High-resolution TEM studies revealed a nonuniform structure of mechanosynthesized Ca_2SnO_4 nanoparticles consisting of an ordered core surrounded by a disordered surface shell region. The inner core of a Ca_2SnO_4 nanoparticle possesses a fully ordered orthorhombic structure, and the surface shell exhibits the thickness of about 1.5 nm. The volume fraction of surface shell regions in the nanostructured mechanosynthesized stannate is estimated to be about 50%. Because of the ability of both solid-state ^{119}Sn MAS NMR and ^{119}Sn Mössbauer spectroscopies to probe the local environment of Sn nuclei, valuable complementary insight into the local structural disorder in mechanosynthesized Ca_2SnO_4 was obtained. It was concluded that the near-surface layers of stannate nanoparticles are disordered because of broadly distorted geometry of SnO_6 octahedra. The octahedra are deformed in such a way that they become more regular.

Introduction

Interest in ternary tin-based oxides (stannates) of the type M_2SnO_4 (M is a divalent metal cation) has greatly increased in the past few years because their potential applications such as photoelectrical devices, chemical sensors, functional coatings, and transparent conducting electrodes.[1] The application of stannates as anode materials in Li-ion batteries, as photocatalysts for degradation of organic pollutants in aqueous solutions, and as working electrodes in dye sensitized solar cells has also been demonstrated.[2−5] Ca_2SnO_4 is an important member of the stannate family. This complex oxide was studied as a crystallite growth inhibitor in SnO_2 for gas sensor applications.[6] The anodic behavior of this compound was also investigated for Li-ion batteries.[7] In a further application, Ca_2SnO_4 is used as a host material of phosphors, where Eu, Ce, and Y are employed as activators.[8−10]

The crystal structure of Ca_2SnO_4 is analogous to that of Sr_2PbO_4 and belongs to the space group *Pbam*.[11] The

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(1) Zeng, J.; Xin, M.; Li, K.; Wang, H.; Yan, H.; Zhang, W. *J. Phys. Chem. C* **2008**, *112*, 4159.

(2) Rong, A.; Gao, X. P.; Li, G. R.; Yan, T. Y.; Zhu, H. Y.; Qu, J. Q.; Song, D. Y. *J. Phys. Chem. B* **2006**, *110*, 14754.

(3) Wang, W. W.; Zhu, Y. J.; Yang, L. X. *Adv. Funct. Mater.* **2007**, *17*, 59.

(4) Tan, B.; Toman, E.; Li, Y.; Wu, Y. *J. Am. Chem. Soc.* **2007**, *129*, 4162.

(5) Krishnakumar, V.; Ramamurthi, K.; Kumaravel, R.; Santhakumar, K. *Curr. Appl. Phys.* **2009**, *9*, 467.

(6) Min, B. K.; Choi, S. D. *Sens. Actuators, B* **2004**, *99*, 288.

(7) Sharma, N.; Shaju, K. M.; Rao, G. V. S.; Chowdari, B. V. R. *J. Power Sources* **2005**, *139*, 250.

(8) Yamane, H.; Kaminaga, Y.; Abe, S.; Yamada, T. *J. Solid State Chem.* **2008**, *181*, 2559.

(9) Yamashita, T.; Ueda, K. *J. Solid State Chem.* **2007**, *180*, 1410.

(10) Fu, S.-L.; Yin, T.; Chai, F. *Chin. Phys.* **2007**, *16*, 3129.

(11) (a) Trömel, M. *Z. Anorg. Allg. Chem.* **1969**, *371*, 237. (b) Trömel, M. *Naturwissenschaften* **1976**, *54*, 17.

10.1021/cm900590d CCC: $40.75

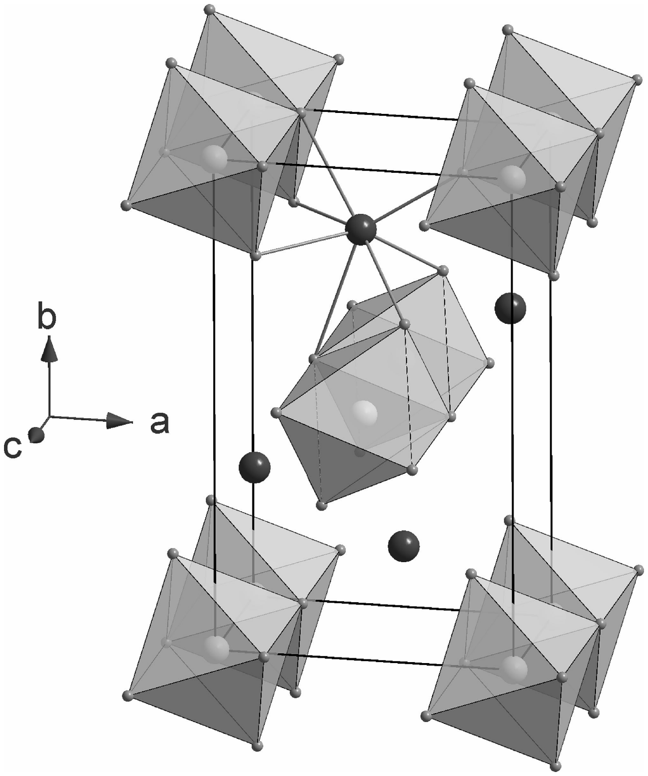

Figure 1. Crystal structure of Ca_2SnO_4 (space group *Pbam*) consisting of chains of edge-sharing SnO_6 octahedra and Ca^{2+} ions (dark spheres) coordinated to seven oxygen ions.

orthorhombic unit cell comprises chains of edge-sharing SnO_6 octahedra. These chains are connected by Ca^{2+} ions that are coordinated to seven oxygen atoms (Figure 1). The preparation of Ca_2SnO_4 by the classical solid-state reaction requires a number of stages, including homogenization of the powder precursors, compaction of the reactants, and finally prolonged heat treatment at considerably elevated temperatures.[11] 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.[12] Among the many types of preparation techniques, the nonconventional mechanochemical synthesis (mechanosynthesis)[13] has been recognized as a powerful route to novel, high-performance, and low-cost materials including oxides.[14] Although a surge of investigations in the field of mechanochemistry has resulted in the preparation of various complex oxides, studies on the mechanosynthesis of stannates are very scarce in the literature.[15,16] From available data, the mechanosynthesis of Zn_2SnO_4[15] and $CaSnO_3$[16] may be mentioned.

In this article, we will report on the single-step synthesis of nanocrystalline Ca_2SnO_4 via high-energy milling of binary oxide precursors (CaO and SnO_2) at room-temperature. The important impact of the present work, from the methodology point of view, is the application of ^{119}Sn magic angle spinning (MAS) nuclear magnetic resonance (NMR) and of ^{119}Sn Mössbauer spectroscopy to the study of the mechanically induced formation reaction ($2\,CaO + SnO_2 \rightarrow Ca_2SnO_4$). The two spectroscopies are remarkably complementary in the present case insofar as NMR spectroscopy is concerned with the nuclear ground state of ^{119}Sn nuclei which possess spin $I = 1/2$ and thus exclusively reflects magnetic and chemical shift interactions experienced by the nuclei. On the other hand, Mössbauer spectroscopy involves transitions between the ground and first excited nuclear state where the latter possesses spin $I = 3/2$, and thus, the spectroscopy is sensitive to nuclear quadrupole interactions. In the absence of local magnetic fields, as in the present case, this is the only interaction influencing the Mössbauer spectrum. To conclude, NMR spectroscopy reveals magnetic and chemical interactions while Mössbauer spectroscopy provides information of the quadrupolar interactions experienced by the nuclei of ^{119}Sn. The combination of both spectroscopies therefore provides the full information to be gained on interactions acting on ^{119}Sn. In this context, the Ca_2SnO_4 formation reaction represents an excellent model system for studies of changes in the local structure during mechanosynthesis because the tin nucleus ^{119}Sn can serve as local probe in both NMR as well as Mössbauer measurements. Thus, for the first time, microstructural information is obtained on the local (short-range) disorder in nanostructured Ca_2SnO_4 synthesized in a one-step mechanochemical process. In addition, the phase evolution during the mechanosynthesis as well as the phase composition, particle size, and morphology of the reaction product were monitored with comprehensive techniques including X-ray diffraction (XRD) and electron microscopy.

Experimental Section

For the mechanochemical synthesis of Ca_2SnO_4, mixtures of CaO and SnO_2 reactants (Merck, Darmstadt, Germany) were mixed in a molar ratio of 2:1 and used as starting materials. The $2\,CaO + SnO_2$ mixtures (10 g) were milled for various times (up to 4 h) in a Pulverisette 6 planetary ball mill (Fritsch, Idar-Oberstein, Germany) at room temperature. A grinding chamber (250 cm^3 in volume) and balls (10 mm in diameter) made of tungsten carbide were used. The ball-to-powder weight ratio was 20:1. Milling experiments were performed in air at 600 rpm.

Additionally, bulk Ca_2SnO_4 and $CaSnO_3$ (polycrystalline stannates with an average crystallite size exceeding 100 nm), which served as reference samples in this study, were prepared from stoichiometric amounts of reagent-grade precursors ($CaCO_3$ and SnO_2) by the conventional solid-state (ceramic) route. Powdered reactants were at first homogenized and then pressed into tablets in order to obtain a high degree of compaction. The reaction tablets were finally sintered at 1273 K for 24 h.

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(12) Bruckmann, A.; Krebs, A.; Bolm, C. *Green Chem.* **2008**, *10*, 1131.

(13) (a) Avvakumov, E.; Senna, M.; Kosova, N. *Soft Mechanochemical Synthesis: A Basis for New Chemical Technologies*; Kluwer Academic Publishers: Boston, 2001. (b) Boldyrev, V. V. *Russ. Chem. Rev.* **2006**, *75*, 177.

(14) (a) 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* **2007**, *111*, 5026. (b) Šepelák, V.; Feldhoff, A.; Heitjans, P.; Krumeich, F.; Menzel, D.; Litterst, F. J.; Bergmann, I.; Becker, K. D. *Chem. Mater.* **2006**, *18*, 3057. (c) Zyryanov, V. V. *Russ. Chem. Rev.* **2008**, *77*, 105.

(15) (a) Belliard, F.; Connor, P. A.; Irvine, J. T. S. *Solid States Ionics* **2000**, *135*, 163. (b) Nikolić, N.; Srećković, T.; Ristić, M. M. *J. Eur. Ceram. Soc.* **2001**, *21*, 2071. (c) Ivetić, T.; Vuković, Z.; Nikolić, M. V.; Pavlović, V. B.; Nikolić, J. R.; Minić, D.; Ristić, M. M. *Ceram. Int.* **2008**, *34*, 639.

(16) Berry, F. J.; Wynn, P.; Jiang, J.; Mørup, S. *J. Mater. Sci.* **2001**, *36*, 3637.

The XRD patterns were collected using a PW 1820 powder diffractometer (Philips, Netherlands) with Cu Kα radiation. The microstructural characteristics (crystallite size and strains) were obtained from the Rietveld analysis of the XRD data using the PowderCell program.[17] The JCPDS PDF database[18] was utilized for phase identification using the STOE software.

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) with an ultra-high-resolution pole piece that provides a point resolution better than 0.19 nm at 200 kV. An energy-dispersive X-ray (EDX) spectrometer (Oxford Instruments INCA 200 TEM) with an ultrathin window allowed for chemical analysis within grains of the mechanosynthesized material. Prior to TEM investigations, powders were crushed in a mortar, dispersed in ethanol, and fixed on a copper-supported carbon grid.

^{119}Sn MAS NMR measurements were performed on an Infinity Plus 500 spectrometer (Varian Chemagnetics, U.S.A.). A rotor-synchronized spin−echo pulse sequence was used to avoid dead-time effects during data acquisition. Typically, 200 scans were acquired with a repetition delay of 200 s. The magnetic field of 11.8 T corresponded to a Larmor frequency of $\nu_L = 186.3$ MHz. The samples were rotated in 3.2 mm rotors at a spinning speed of 24 kHz. The spectra were referenced to SnO_2 with a shift of −604.3 ppm.[19]

^{119}Sn Mössbauer spectroscopic measurements were carried out in transmission mode at room temperature. ^{119}Sn in $CaSnO_3$ was used as the γ-ray source. The velocity scale was calibrated relative to ^{119}Sn in $CaSnO_3$. Recoil spectral analysis software[20] was used for the quantitative evaluation of the Mössbauer spectra. A Lorentzian line width of 0.39 mm/s resulting from the fit of the spectrum of a standard bulk Ca_2SnO_4 was chosen for the fit of the spectrum of mechanosynthesized Ca_2SnO_4.

Results and Discussion

The mechanically induced evolution of the 2 CaO + SnO_2 mixture submitted to high-energy milling was followed by XRD. Figure 2 shows XRD patterns of the 2 CaO + SnO_2 mixture milled for various times. For comparison, the XRD patterns of the Ca_2SnO_4 and $CaSnO_3$ standard samples (bulk materials prepared by the conventional ceramic route) are also presented at the bottom of Figure 2.

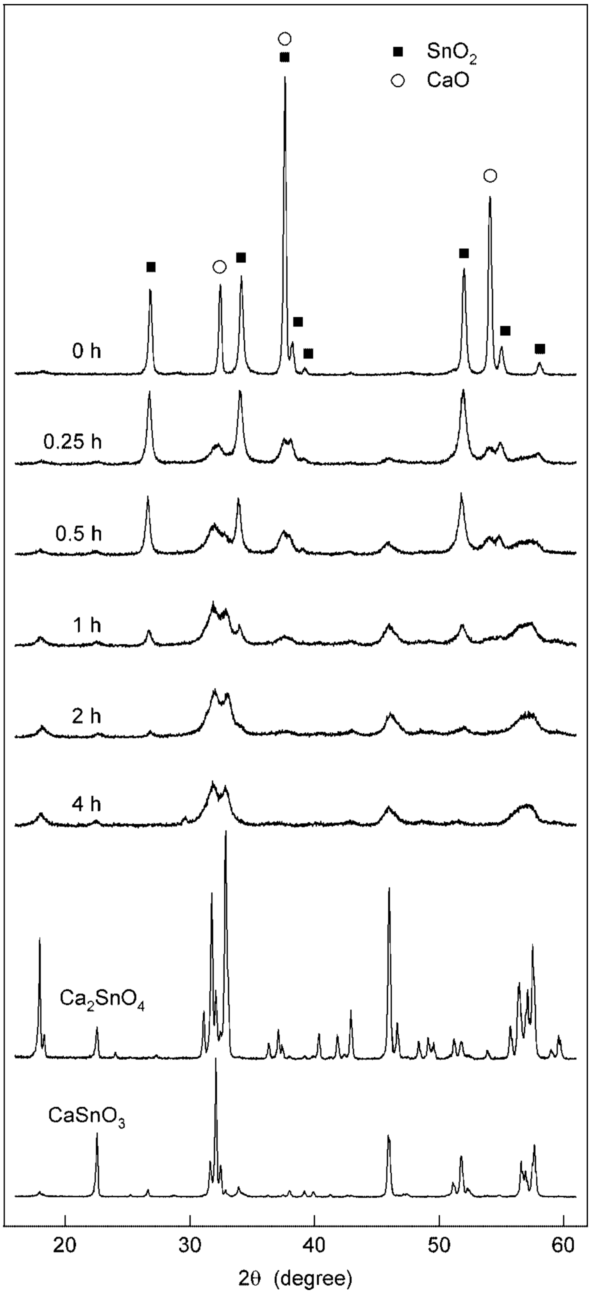

Figure 2. XRD patterns of the 2 CaO + SnO_2 mixture milled for various times (up to 4 h) in comparison with those of the bulk Ca_2SnO_4 and $CaSnO_3$ standards prepared by the conventional ceramic route. The intensity scale of the XRD patterns is normalized to that of the XRD pattern of the starting powder.

The XRD pattern of the starting powder is characterized by sharp diffraction peaks corresponding to crystalline CaO (JCPDS PDF 37−1497) and SnO_2 (JCPDS PDF 41−1445).[18] With increasing milling time, XRD reveals a gradual broadening of the Bragg peaks of the individual oxides because of the reduction of their crystallite size and the accumulation of strains in their structure. Simultaneously, the intensity of the diffraction peaks corresponding to the simple oxides gradually decreases; the peaks of the educt phases disappear completely after 4 h of mechanical treatment. For milling times $t_m \geq 1$ h, qualitative changes are observed in the XRD patterns of the milled samples; clear evidence is observed of new diffraction features that correspond to the orthorhombic Ca_2SnO_4 phase (see Figure 2). In the XRD pattern of the sample milled for 4 h (a product of the mechanochemical reaction), all diffraction peaks detected above the background are due to the Ca_2SnO_4 phase (JCPDS PDF 46−0112).[18] This confirms that the mechanochemical synthesis of Ca_2SnO_4 is feasible and complete. Compared to the traditional synthesis route to Ca_2SnO_4,[11] the mechanochemical process used here represents a one-step, high-yield, low-temperature, and low-cost procedure for the synthesis of Ca_2SnO_4.

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(17) Kraus, W.; Nolze, G. *PowderCell for Windows, version 2.4*; Federal Institute for Materials Research and Testing: Berlin, Germany, 2000.

(18) *Joint Committee on Powder Diffraction Standards (JCPDS) Powder Diffraction File (PDF)*; International Centre for Diffraction Data: Newton Square, PA, 2004.

(19) Clayden, N. J.; Dobson, C. M.; Fern, A. *J. Chem. Soc., Dalton Trans.* **1989**, 843.

(20) Lagarec, K.; Rancourt, D. G. *Recoil−Mössbauer Spectral Analysis Software for Windows, version 1.02*; Department of Physics, University of Ottawa: Ottawa, ON, 1998.

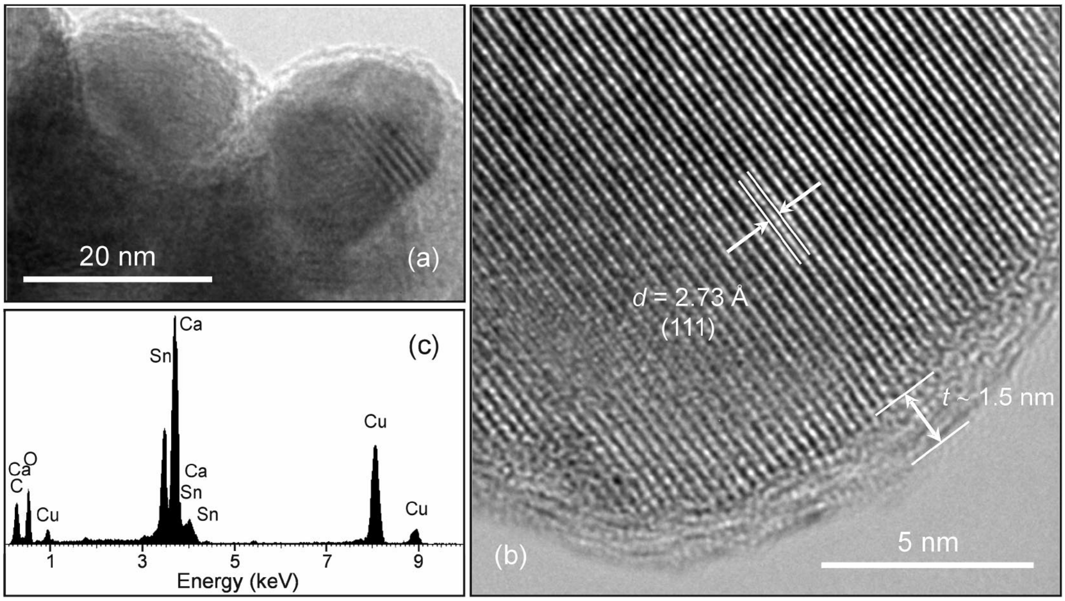

Figure 3. (a) Bright-field and (b) high-resolution TEM images of nanocrystalline mechanosynthesized Ca_2SnO_4. The core−shell configuration of mechanosynthesized nanoparticles with the thickness of the surface shell of about 1.5 nm is evident. The lattice fringes correspond to the crystallographic plane (111) (d = 2.73 Å) of the Ca_2SnO_4 phase (JCPDS PDF 46−0112). (c) EDX spectrum of nanocrystalline mechanosynthesized Ca_2SnO_4.

The presence of the peak at 32.07° in the XRD pattern of the conventionally prepared Ca_2SnO_4 (see Figure 2, bottom) indicates that this sample contains a small amount of the perovskite phase $CaSnO_3$ (JCPDS PDF 31−0312).[18] Note that this phase as a byproduct often accompanies the conventional synthesis of Ca_2SnO_4; even the Ca_2SnO_4 phase listed in the JCPDS PDF database contains the trace impurity of $CaSnO_3$.[18] The broad shape of XRD lines for mechanosynthesized stannate, in contrast to relatively narrow lines for the bulk Ca_2SnO_4 (see Figure 2), provides clear evidence of a nanoscale nature of the mechanosynthesized material. Because of this, from the present XRD measurements, it is not clear whether the perovskite phase is also present in the mechanosynthesized sample. This can only be seen from ^{119}Sn MAS NMR and ^{119}Sn Mössbauer spectroscopic measurements, see below. The Rietveld analysis of the XRD data revealed both an average crystallite size of 15(2) nm and the presence of mean strains of $4.8(4) \times 10^{-3}$ in the mechanosynthesized stannate.

Representative TEM micrographs of nanocrystalline mechanosynthesized Ca_2SnO_4 at low and high magnifications are shown in Figure 3. They reveal that the mechanosynthesized stannate consists of crystallites mostly in the 13−17 nm size range, consistent with the average crystallite size determined by XRD. Nanoscale crystallites are found to be roughly spherical (see bright-field TEM image in Figure 3a). An interesting observation is that the mechanosynthesized Ca_2SnO_4 nanoparticles possess the so-called core−shell structure consisting of an ordered inner core surrounded by a disordered surface shell region. The high-resolution TEM image (Figure 3b) shows lattice fringes corresponding to the crystallographic plane (111) (d = 2.73 Å) of the Ca_2SnO_4 phase (JCPDS PDF 46−0112).[18] The lattice fringes cross the whole particle core demonstrating the single-crystalline character of the nanoparticles. The thickness of the disordered surface shell estimated from high-resolution TEM was found to be about 1.5 nm (Figure 3b).

Assuming a spherical shape of nanoparticles and taking both their average diameter (D = 15 nm) and the thickness of their surface shell (t = 1.5 nm) as determined experimentally by XRD and TEM, one can easily deduce quantitative information on the volume fraction of surface shell regions to volume of whole particles ($w = V_{\mathrm{shell}}/(V_{\mathrm{core}} + V_{\mathrm{shell}})$) in the nanomaterial; $w = [1 - (1 - 2t/D)^3]$. The estimated value of $w = 0.488$ indicates that about 50% of atoms in the mechanosynthesized stannate are in a structurally disordered state located in the surface shell of nanoparticles. The structurally nonuniform core−shell structure of nanoparticles with the relatively large volume fraction of surface shell regions (~50%) has recently been reported for mechanosynthesized $NiFe_2O_4$,[14a] $MgFe_2O_4$,[14b] and ball-milled nanocrystalline $LiNbO_3$.[21] The shell thickness in mechanosynthesized Ca_2SnO_4 is comparable to that observed in other nanosized mechanochemically prepared complex oxides.[14,21,22]

To exclude the presence of chemical elements originating from the abrasion of the milling tools (vial and balls made of WC), we carried out further local EDX spectroscopic analyses in several regions of the mechanosynthesized product. As can be seen in the representative EDX spectrum (Figure 3c), Ca, Sn, and O were the main elemental components and no impurity was detected in the sample. Note that the spectral lines corresponding to Cu and C in the EDX spectrum originate from the copper-supported carbon grid.

To determine the phase evolution of the 2 CaO + SnO_2 mixture during high-energy milling in greater detail and to provide insight into the local structural disorder in stannate

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(21) Heitjans, P.; Masoud, M.; Feldhoff, A.; Wilkening, M. *Faraday Discuss.* **2007**, *134*, 67.

(22) (a) Muroi, M.; Street, R.; McCormick, P. G.; Amighian, J. *Phys. Rev. B* **2001**, *63*, 184414. (b) Heitjans, P.; Indris, S. *J. Phys.: Condens. Matter* **2003**, *15*, R1257. (c) Heitjans, P.; Indris, S. *J. Mater. Sci.* **2004**, *39*, 5091. (d) Zhang, Y. D.; Ge, S. H.; Zhang, H.; Hui, S.; Budnick, J. I.; Hines, W. A.; Yacaman, M. J.; Miki, M. *J. Appl. Phys.* **2004**, *95*, 7130.

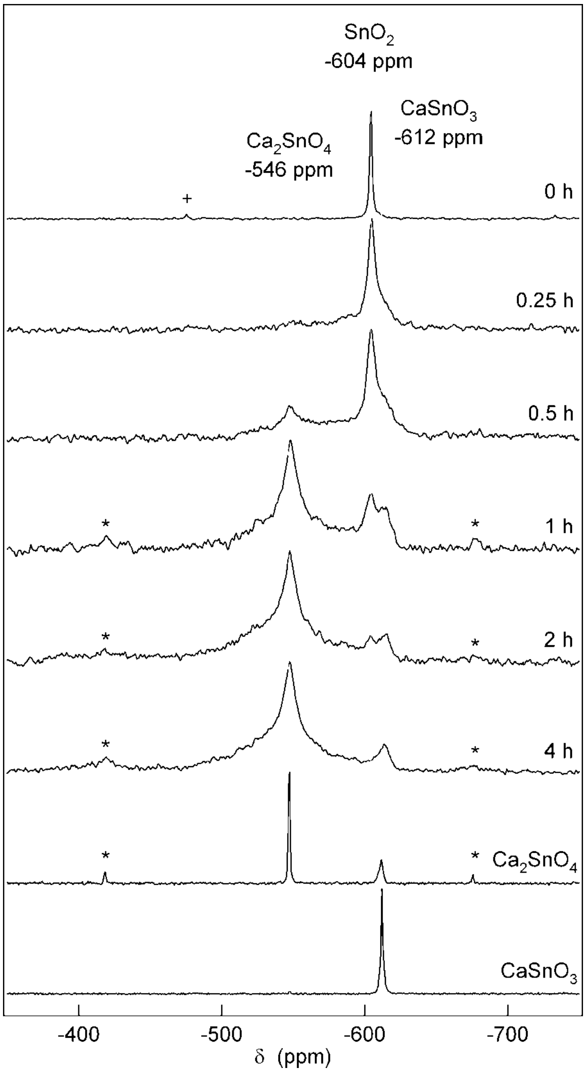

Figure 4. ^{119}Sn MAS NMR spectra of the 2 CaO + SnO_2 mixtures milled for various times. The two spectra at the bottom belong to Ca_2SnO_4 and $CaSnO_3$ prepared by the conventional ceramic route. Spinning sidebands associated with the resonances at −546 and −604 ppm are marked with * and +, respectively.

nanoparticles, the mechanochemical reaction was also followed by ^{119}Sn MAS NMR. This nuclear spectroscopic method has been proven to be exceptionally sensitive to changes in the local structure around the tin ions (i.e., to distortions of the oxygen polyhedra) as well as to their charge state.[23] Figure 4 compares ^{119}Sn MAS NMR spectra of the 2 CaO + SnO_2 mixtures milled for various times with those of the bulk Ca_2SnO_4 and $CaSnO_3$ standards. The spectrum of the initial mixture shows a sharp resonance at −604 ppm corresponding to the Sn atoms located in SnO_6 octahedra in the crystal structure of SnO_2.[24] With increasing milling time, the resonance line corresponding to SnO_2 broadens significantly, slowly collapses, and is gradually replaced by a new broadened resonance line at −546 ppm. This spectral component arises from octahedrally coordinated Sn^{4+} cations in Ca_2SnO_4.[19] It should be mentioned in this context that the line assigned to the Ca_2SnO_4 phase is clearly visible after only 30 min of milling (see Figure 4). Further milling leads to a gradual increase of its relative intensity. Note that a small peak appearing in the spectra at −612 ppm belongs to $CaSnO_3$.[25] After 4 h of milling, the NMR spectrum of the milled mixture is dominated by the line of Ca_2SnO_4 and the resonance peak of the educt SnO_2 has disappeared completely.

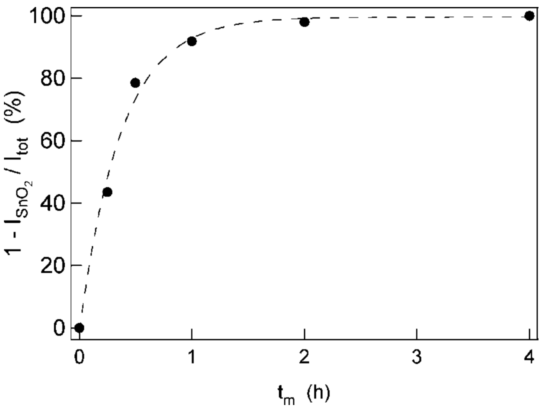

Figure 5. Time-dependent progress of reaction demonstrating the complete conversion of the educt phases during the mechanochemical synthesis.

The well-resolved ^{119}Sn MAS NMR subspectra corresponding to SnO_2, Ca_2SnO_4 and $CaSnO_3$ allow an accurate determination of the degree of conversion in the course of the present mechanochemical reaction. Figure 5 illustrates the change in the integral intensity of the NMR spectral line corresponding to SnO_2, I_{SnO_2}, relative to the total spectral intensity, I_{tot}, reflecting a gradual conversion of the binary oxides to the stannate phases during milling. It is clearly seen that the mechanochemical reaction is completed in a relatively short time (4 h). Integration of the peak intensities, including the spinning sidebands, in the spectrum of the sample milled for 4 h shows that about 93% of the Sn atoms are located in the mechanosynthesized Ca_2SnO_4 phase. Taking into account that the presence of the perovskite $CaSnO_3$ phase in the mechanosynthesized product is not registered by XRD (see Figure 2), the appearance of the resonance line corresponding to $CaSnO_3$ in the NMR spectrum of this sample (~7% of the total spectral intensity) gives evidence of the fact that the NMR active ^{119}Sn nuclei provide a very sensitive probe for both the estimation of the yield of a mechanochemical reaction and the concurrent identification of nanostructured Ca_2SnO_4 and $CaSnO_3$.

Another striking feature observed is the broad shape of the NMR lines of the mechanosynthesized product, in contrast to the relatively narrow lines of the bulk stannates (Figure 4), implying a change in the local atomic environment of the octahedrally coordinated Sn^{4+} cations. This variation may be explained by the presence of a broad distribution of local environments around the Sn nuclei due to the mechanically induced deformation of SnO_6 octahedra. Similar findings have also been reported for spinel-type

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(23) MacKenzie, K. J. D., Ed. *Multinuclear Solid-State NMR of Inorganic Materials*; Pergamon Materials Series: Amsterdam, 2002; Vol. 6.

(24) Cossement, C.; Darville, J.; Gilles, J.-M.; Nagy, J. B.; Fernandez, C.; Amoureux, J.-P. *Magn. Reson. Chem.* **1992**, *30*, 263.

(25) Vega, A.; Vallet-Regi, M.; Gonzales-Calbet, J. M.; Alario-Franco, M. A. *Acta Crystallogr., Sect. B* **1986**, *42*, 167.

oxides such as aluminates and ferrites,[26] where the particle size reduction to the nanometer range was found to be accompanied by a deformation of polyhedron geometries. Taking into account the core−shell configuration of mechanosynthesized stannate nanoparticles evidenced by HR-TEM (see Figure 3b), it can be assumed that the deformed SnO_6 octahedra are located in the surface shell regions of the nanomaterial. This is also consistent with recent work on spinel ($MgAl_2O_4$),[27] where, apart from the tetrahedral and octahedral cation coordinations, the presence of additional 5- and 3-fold coordinated cation sites in the near-surface layers of nanoparticles due to local structural distortion has been observed. Moreover, in some cases, the surface shell regions of nanooxides were found to be even amorphous[21,22b,c] or structurally disordered because of the nearly random distribution of cations and the canted spin arrangement.[14a,b,28] Note that no more detailed information on the symmetry of the local structure, e.g., distortions of the SnO_6 octahedra, can be provided for mechanosynthesized stannate because a nuclear quadrupole moment of the nucleus ^{119}Sn is absent (due to its spin $I = 1/2$), and consequently, its interaction with electric field gradients being present at the site of the nuclei does not occur.

Information on the short-range structural disorder in the mechanosynthesized stannate provided by NMR is complemented by ^{119}Sn Mössbauer spectroscopic measurements. In contrast to ^{119}Sn MAS NMR, ^{119}Sn Mössbauer spectroscopy makes use of the excited state of Sn nuclei ($I = 3/2$) and therefore is very sensitive to the interaction of the nuclear quadrupole moment with electric field gradients. Figure 6 shows Mössbauer spectra of the 2 CaO + SnO_2 mixture milled for various times in comparison with the spectrum of Ca_2SnO_4 prepared by the ceramic route. The spectrum of the starting powder is characterized by a doublet with an average isomer shift IS = −0.016(2) mm/s and a quadrupole splitting QS = 0.354(1) mm/s corresponding to octahedrally coordinated Sn^{4+} cations in SnO_2. Note that because of a relatively large Lorentzian line width of 0.398(6) mm/s, typical of ^{119}Sn Mössbauer spectroscopy, the doublet appears as a singlet in the spectrum. During the early stages of milling (for $t_m \leq 0.25$ h), Mössbauer spectroscopy merely reveals a broadening of the doublet. However, for times $t_m \geq 0.5$ h, the splitting of the doublet gradually increases, resulting in the formation of an asymmetric doublet structure. The spectrum of the sample milled for 4 h is well-fitted by a superposition of two subspectra; one dominating doublet with hyperfine parameters $IS_1 = 0.153(3)$ mm/s and $QS_1 = 0.722(4)$ mm/s accounting for octahedrally coordinated Sn cations in Ca_2SnO_4 and one minor singlet ($IS_2 = 0$ mm/s, $QS_2 = 0$ mm/s) associated with Sn cations in $CaSnO_3$. Thus, Mössbauer spectroscopy also reveals the presence of a small amount of the perovskite phase in the mechanosynthesized material.

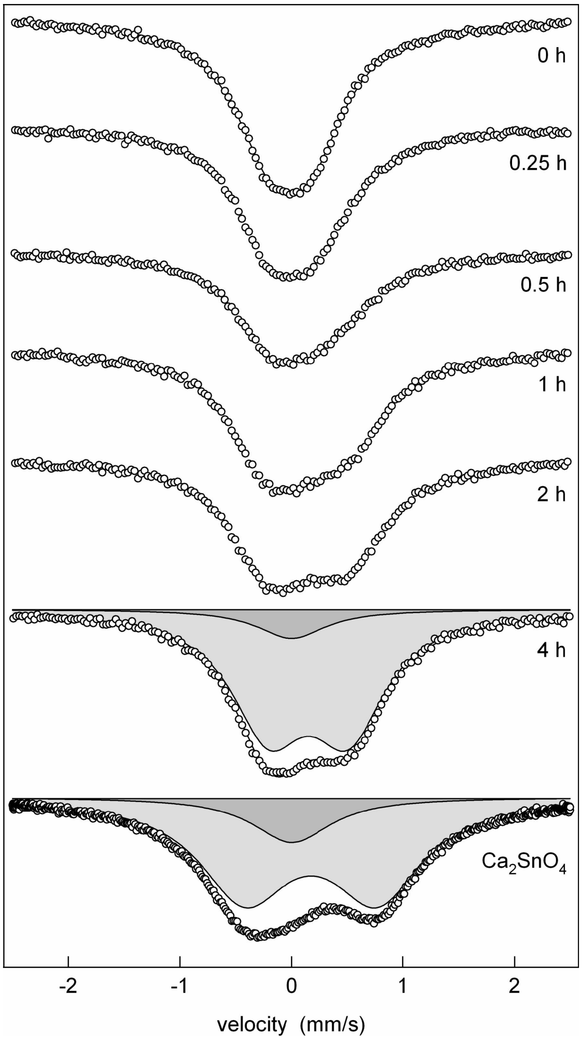

Figure 6. Mössbauer spectra of the 2 CaO + SnO_2 mixture milled for various times. The spectrum at the bottom corresponds to Ca_2SnO_4 prepared by the conventional ceramic route.

An interesting observation is that the average quadrupole splitting for the mechanochemically synthesized Ca_2SnO_4 (QS = 0.722(4) mm/s) is significantly smaller than that estimated for the conventionally prepared Ca_2SnO_4 (QS = 1.192(2) mm/s), see Figure 6. This reflects the presence of smaller electric field gradients acting on Sn nuclei in the nanomaterial in comparison to those experienced by Sn nuclei in bulk Ca_2SnO_4. Taking into account the coordinates of tin and oxygen atoms in the orthorhombic structure of bulk Ca_2SnO_4 [Sn ≡ (0/0/0), O_I ≡ (0.228/0.049/0.5), O_{II} ≡ (0.36/0.31/0)] as determined by XRD,[11a] the relatively large QS value (i.e., large electric field gradients) for bulk Ca_2SnO_4 can be explained by a highly asymmetric charge distribution around Sn nuclei originating from the different bond lengths of $d(Sn-O_I) = 2.15$ Å and $d(Sn-O_{II}) = 2.01$ Å in SnO_6 octahedra. This is clearly shown in Figure 7, where the orthorhombic structure of Ca_2SnO_4 is projected on the (001) plane.[11a] Consequently, the smaller QS value for mechanosynthesized Ca_2SnO_4 can be explained by the presence of distorted but more symmetric SnO_6 octahedra in its structure,

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(26) (a) Bergmann, I.; Šepelák, V.; Feldhoff, A.; Heitjans, P.; Becker, K. D. *Rev. Adv. Mater. Sci.* **2008**, *18*, 375. (b) Šepelák, V.; Indris, S.; Heitjans, P.; Becker, K. D. *J. Alloys Compd.* **2007**, *434−435*, 776. (c) Šepelák, V.; Indris, S.; Bergmann, I.; Feldhoff, A.; Becker, K. D.; Heitjans, P. *Solid State Ionics* **2006**, *177*, 2487. (d) Šepelák, V.; Tkáèová, K.; Boldyrev, V. V.; Steinike, U. *Mater. Sci. Forum* **1996**, *228−231*, 783.

(27) Sreeja, V.; Smitha, T. S.; Nand, D.; Ajithkumar, T. G.; Joy, P. A. *J. Phys. Chem. C* **2008**, *112*, 14737.

(28) Nordhei, C.; Ramstad, A. L.; Nicholson, D. G. *Phys. Chem. Chem. Phys.* **2008**, *10*, 1053.

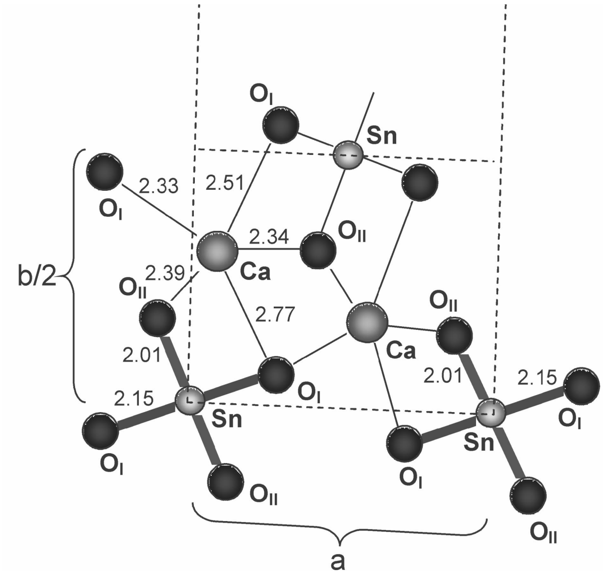

Figure 7. Projection of orthorhombic structure of Ca_2SnO_4 on the (001) plane emphasizing different lengths of $Sn-O_I$ and $Sn-O_{II}$ bonds in SnO_6 octahedra. Interatomic distances are given in angstroms.[11a]

i.e., octahedra with bond lengths for which $d(Sn-O_I) - d(Sn-O_{II}) < 0.14$ Å. This is in line with the present NMR investigations revealing a broad distribution of local environments around the Sn nuclei in the mechanosynthesized Ca_2SnO_4. From the present Mössbauer data it cannot be ascertained whether the $Sn-O_I$ and $Sn-O_{II}$ bonds in the nanomaterial are longer or shorter than those in the bulk Ca_2SnO_4. In conclusion, the short-range structural information obtained from NMR and Mössbauer measurements can be summarized in stating that the surface shell regions of mechanosynthesized stannate nanoparticles are disordered due to broadly distorted but symmetric octahedral environments around Sn nuclei (SnO_6 octahedra with more converging $Sn-O_I$ and $Sn-O_{II}$ bond lengths). Note that because of the relatively structureless Mössbauer spectrum of the mechanosynthesized product, no attempt was made to separate the surface effects from the bulk effects in nanoparticles and to quantitatively estimate the fraction of the $CaSnO_3$ phase.

Conclusions

The present study demonstrates that nanostructured Ca_2SnO_4 with an average crystallite size of about 15 nm can be synthesized from binary oxide precursors in a relatively short reaction time (4 h) 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 present work contributes to the search for novel sustainable production routes of functionally tailored nanomaterials.

On the basis of the results of high-resolution TEM studies, it is concluded that the mechanosynthesized Ca_2SnO_4 nanoparticles possess a nonuniform configuration consisting of an ordered core with orthorhombic structure surrounded by a disordered surface shell region. The observed lattice fringes crossing the whole particle core demonstrate the single-crystalline character of the stannate nanoparticles. The thickness of the disordered surface shell is found to be about 1.5 nm. Assuming a spherical shape of nanoparticles and taking both their average size and the thickness of their surface shell as determined experimentally by XRD and TEM, the volume fraction of surfaces shell regions in the mechanosynthesized nanomaterial is estimated to be about 50%.

In addition to the XRD method being sensitive to medium- and long-range structural order, the mechanically induced evolution of the 2 CaO + SnO_2 mixture submitted to high-energy milling was also followed by ^{119}Sn MAS NMR and ^{119}Sn Mössbauer spectroscopy. The well-resolved ^{119}Sn MAS NMR spectra of the Sn-containing educt and product phases enables us to monitor the single-step mechanosynthesis route and to accurately determine the degree of conversion of the mechanochemical reaction, reaching 100% after 4 h of milling. It is also evidenced that the NMR active ^{119}Sn nuclei provide a very sensitive probe for the concurrent quantitative identification of nanostructured Ca_2SnO_4 (93%) and $CaSnO_3$ (7%) present in the mechanosynthesized product.

Because of the ability of both solid-state ^{119}Sn MAS NMR and ^{119}Sn Mössbauer spectroscopies to probe the local environment of Sn nuclei, valuable complementary insight into the local structural disorder in mechanosynthesized Ca_2SnO_4 is obtained. The comparative NMR study of bulk and nanocrystalline Ca_2SnO_4 reveals the presence of a considerably broader distribution of local environments around the Sn nuclei in the mechanosynthesized material. This variation may be explained by mechanically induced deformations of SnO_6 octahedra. On the other hand, the comparative Mössbauer investigation of the bulk and nanosized Ca_2SnO_4 clearly shows that Sn nuclei in the nanomaterial experience smaller electric field gradients, indicating a more symmetric charge distribution around Sn nuclei in nanostannate. This finding hints to the appearance of more symmetric SnO_6 octahedra in the nanomaterial in comparison to those present in the bulk Ca_2SnO_4. Taking into account the core−shell configuration of mechanosynthesized stannate nanoparticles evidenced by HR-TEM, it can be assumed that the distorted but more symmetric SnO_6 octahedra are located in the near-surface regions of the nanomaterial.

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