

Microwave-assisted selective preparation and characterization of $\text{Li}_{21}\text{Si}_5$ and $\text{Li}_{17}\text{Sn}_4$

Gen-Tao Zhou,^{a,b} Oleg Palchik,^a Israel Nowik,^c R. Herber,^c Yuri Koltypin,^a and Aharon Gedanken^{a,*}

^aDepartment of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

^bSchool of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, People's Republic of China

^cRacah Institute of Physics, Hebrew University, Jerusalem 91904, Israel

Received 25 December 2003; received in revised form 22 April 2004; accepted 24 April 2004

Available online 24 June 2004

Abstract

Two types of intermetallic lithium alloys, $\text{Li}_{21}\text{Si}_5$ and $\text{Li}_{17}\text{Sn}_4$ (previously $\text{Li}_{22}\text{Si}_5$ and $\text{Li}_{22}\text{Sn}_5$), were prepared for the first time using microwave-assisted solid-state reaction. The optimum oven power for their preparation is 80–60%, and the irradiation times are 5 min for $\text{Li}_{21}\text{Si}_5$ or 10 min for $\text{Li}_{17}\text{Sn}_4$. A cheap alumina crucible was found to be the most suitable container in quick (less than 10 min) microwave reactions for Li-containing alloys. The synthesized compounds were characterized by PXRD. Mössbauer spectroscopy was used to characterize $\text{Li}_{17}\text{Sn}_4$ under different conditions. The hyperfine interaction parameters of ^{119}Sn in $\text{Li}_{17}\text{Sn}_4$ show a typical Li–Sn alloy Sn isomer shift (1.88 mm/s). The oxidization processes of the two intermetallic lithium alloys in air were investigated. The microwave method was found to be simple, fast and efficient, with high selectivity for the preparation of these compounds.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Intermetallic alloy; Microwave radiation; Solid-state reaction

1. Introduction

There is a great deal of interest in the development of new anode and cathode materials for Li batteries. The search for the new Li-containing anode has continued for more than a few decades. The use of Li-alloys as an anode material was found to be very advantageous due to its higher gravimetric and volumetric theoretical capacity and extra safety relative to the carbonaceous anodes [1–4]. Unfortunately, poor cycling performance was associated with the use of these anodes, due to the mechanical defects that develop during volume expansion (up to 200%) of the alloys through lithium insertion [5,6]. Recently, it was found that using nanoparticles of these alloys could prevent the mechanical failure of the anode [7–9]. The nanoparticles were easily prepared by ball-milling techniques. However, the preparation of the

bulk alloys is not an easy process and that could prevent the commercialization of these materials. There are a few reasons for the difficulty in the fabrication of the Li-alloys: (1) Li-alloys are currently prepared by a classical high temperature method, which demands a very high reaction temperature ($\leq 1000^\circ\text{C}$) and prolonged heating (days); (2) due to the highly corrosive nature of the molten Li, special reaction containers like expensive tantalum are needed. These drawbacks motivated the development of a new synthetic method that overcomes these problems and facilitates product formation. The microwave-assisted reaction method is presented. This method does not suffer from the disadvantages of the classical preparation technique.

Microwave-assisted chemical reactions have only recently been developed, but they have already been shown to be superior to other synthetic techniques in the fields of organic and analytical chemistry [10–18]. Its extension to inorganic chemistry was much slower, but there are already a few examples of the application of microwave heating to inorganic synthesis [19–34]. We

*Corresponding author. Fax: 972-3-535-1250.

E-mail address: gedanken@mail.biu.ac.il (A. Gedanken).

URL: <http://www.biu.ac.il/ESC/ch/faculty/gedanken/gedint.html>.

recently developed a microwave-assisted solid-state synthesis for the Zintl compounds from the Alkali-Sn–Se series [19]. The current work is a continuation of this effort towards the application of microwave heating to solid-state chemistry.

This report describes the synthesis and characterization of an attractive group of Li-alloys: $\text{Li}_{21}\text{Si}_5$ and $\text{Li}_{17}\text{Sn}_4$, which were previously regarded as $\text{Li}_{22}\text{Si}_5$ and $\text{Li}_{22}\text{Sn}_5$. Recently, their composition and structure were modified by Nesper et al. [35] and Nazar et al. [36]. This study was motivated by the fact that these two alloys contain the highest quantities of Li relative to other intermetallic phases in the Li–Sn and Li–Si systems. This will result in the highest volumetric capacity for these two compounds. The application of the microwave method is especially advantageous for these compounds, because it allows the use of cheap alumina (Al_2O_3) containers even for the very Li-rich phases such as $\text{Li}_{21}\text{Si}_5$ and $\text{Li}_{17}\text{Sn}_4$.

Since Fuji Film Co. announced the development of lithium batteries employing an amorphous tin-based composite oxide as a negative electrode [37], a group of new anode materials was born. The basic idea is that at near-equilibrium conditions these oxides are converted to lithium alloys and Li_2O during the first charging cycle. It is known that Li_2O is a solid electrolyte, and thus can serve as a current collector and maintain the electrode microstructure in further cycles. However, the initial Li_2O formation represents a significant initial capacity loss, analogous to what is generally found in lithium–carbon electrodes. If one can prepare a homogeneous composite material that consists of metal and Li_2O instead of simple oxides, the initial capacity loss can be avoided due to the formation of initial Li_2O . In this context, oxidization of a Li-containing alloy was investigated.

2. Experimental section

2.1. Reagents

Chemicals were used as obtained: (1) tin powder, 99.5% purity, –100 mesh; silicon powder, 99% purity, –325 mesh (Aldrich). Lithium foil, 99.9% purity and Alumina-23 crucibles (Alfa Aesar). Tantalum tubes (OD 8 mm \times WT 0.4 mm) were from MaTeck. Because of the high sensitivity of the lithium to N_2 , and of the resulting products to moisture and oxygen, all manipulations were conducted in an Ar-filled glove box, with less than 1 ppm of O_2 and H_2O .

2.2. Synthesis

A typical procedure was as follows: For the preparation of $\text{Li}_{17}\text{Sn}_4$, 0.4 g of tin powder was placed in the

alumina crucible with 0.12 g of lithium (a slight excess of lithium). The lithium foil was cut in the Ar-filled glove box into the small rectangular pieces (approx. $2 \times 2 \text{ mm}^2$). Then the Sn (or Si) powder was mixed with these Li pieces in the crucible. This mixture was gently pressed by hand using a spatula. Pressing is a very important part of the procedure in order to obtain a smooth preparation of Li–Si or Li–Sn alloys by our method. On the one hand, it prevents the Li metal from “jumping” out of the crucible during the microwave reaction, and also increases the contact area between lithium and silicon or tin. On the other hand, it makes the surface of the lithium foil rough, and according to our observations, the lithium foil with a rough surface better absorbs the microwave irradiation. The crucible with reactants was carefully placed in a quartz ampoule. The quartz ampoule was evacuated up to 5×10^{-5} Torr, and after that sealed by an oxygen-gas flame. The sealed quartz ampoule was placed in a microwave cavity and was exposed to microwave irradiation for a given time (shown in Table 1). After completion of the synthesis the ampoule was opened inside an argon-filled glove box. In the case of $\text{Li}_{21}\text{Si}_5$, similar procedures were adopted. A typical reagent ratio was 0.1 g of silicon and 0.12 g of lithium, again with the lithium in small excess. Only a minor reaction between Li, the quartz ampoule, and the alumina crucible was detected. It is important to emphasize that all of the reactions were reproducible.

The high temperature solid-state reaction was carried out in the alumina crucible in the following way: the reaction mixture contained the two elements with the same elemental ratio as in the microwave reaction. The solid mixture was also pressed inside the alumina crucible, and then the crucible was sealed in a quartz ampoule. This ampoule was heated to 750°C at a heating rate of $10^\circ\text{C}/\text{min}$ in a programmed heating vertical-tube furnace, and held at this temperature for 24 h. This temperature, 750°C , was selected based on the phase diagrams of the compound of $\text{Li}_{21}\text{Si}_5$ and $\text{Li}_{17}\text{Sn}_4$ [38].

2.3. Equipment

The Microwave oven was a modified Kenwood 900 W. At 70% power the oven works in a cycling mode: 15 sec-on, 5 sec-off. The high-temperature reaction was carried out in a vertical-tube oven. The X-ray diffraction patterns of the products were recorded with a Bruker AXS D8 Advance Powder X-ray Diffractometer (using $\text{CuK}\alpha$ $\lambda = 0.15418 \text{ nm}$ radiation) operating at 40 kV/40 mA, with a graphite reflected beam monochromator and variable divergence slits. During measurements, compounds were sealed in a home-built, air-free PXRD cell. Mössbauer spectrum analysis was conducted on the compound $\text{Li}_{17}\text{Sn}_4$. Three samples of $\text{Li}_{17}\text{Sn}_4$ were studied using the 23.88 keV

Table 1
Microwave-assisted preparation conditions and some experimental observations

Reaction	MW parameters ^a	XRD results	Observations
(1) Li _(excess) + Si	80%, 20 min	Pure Li ₂₁ Si ₅	Sparks for 3 min
	80%, 10 min	Pure Li ₂₁ Si ₅	Sparks for 3 min
	80%, 5 min	Pure Li ₂₁ Si ₅	Sparks for 3 min
	60%, 5 min	Pure Li ₂₁ Si ₅	Sparks for 4 min
	50%, 10 min	Li ₂₁ Si ₅ + Si	Sparks for 9 min
	30%, 10 min	Li ₂₁ Si ₅ + Si	Sparks for 10 min
(2) Li + Si (stoichiometric)	80%, 20 min	Li ₂₁ Si ₅ + Si	Sparks for 3 min
(3) Li _(excess) + Sn	80%, 20 min	Pure Li ₁₇ Sn ₄	Sparks for 8 min
	80%, 10 min	Pure Li ₁₇ Sn ₄	Sparks for 8 min
	60%, 20 min	Pure Li ₁₇ Sn ₄	Sparks for 8 min
	50%, 20 min	Li ₁₇ Sn ₄ + Sn	Sparks for 20 min
	30%, 20 min	Li ₁₇ Sn ₄ + Sn	Sparks for 20 min
(4) Li + Sn (stoichiometric)	80%, 20 min	Li ₁₇ Sn ₄ + Sn	Sparks for 10 min

^a Microwave power and reaction time.

Mössbauer transition of ¹¹⁹Sn, employing a Ba^{119m}SnO₃ source, a 2 mm thick NaI scintillation counter and a conventional constant acceleration Mössbauer drive. The three samples were put into sealed plastic holders, faced with a palladium foil as a critical X-ray absorber. The absorber of sample I was prepared immediately after the preparation of the material, under an argon atmosphere. An absorber of sample II was prepared under normal atmospheric conditions within several minutes. Absorber III was prepared from material kept in a sealed bottle, a month after it was prepared. Sample II was measured at temperatures over the interval of 90–400 K, inside a variable temperature cryostat with vacuum of 10⁻³ Torr.

3. Results and discussions

It has been found that a large number of oxides (e.g., NiO, V₂O₅, WO₃, Cr₂O₃ and CuO) and a few halides (e.g., AgI and CuI) absorb microwave energy very efficiently and can be heated to 1000 K or more. Carbon powder (in both graphitized and amorphous forms) and some metals (e.g., Fe, Co, V, Zn) are also known to be good microwave susceptors and heat up rapidly [22]. However, the application of microwaves is not possible when none of the reactants is a good microwave susceptor. Thus, the first step is to check the interaction of the microwave irradiation with the reagents (Li, Sn, and Si). We exposed them individually to microwave irradiation (the elements were inside evacuated ampoule, and the lithium foil was roughened, as mentioned above). Flashes of sparks are seen only for Li and Sn, and Li foil shows stronger microwave coupling than Sn powders. Silicon powders remained inert, which is

consistent with the observation of Vaidhyanathan and Rao for Si under microwave irradiation [30]. The microwave absorbing ability is found to vary in the order Li > Sn >> Si.

The microwave reaction between lithium and silicon or tin is very forceful. After few seconds, an intense flash appeared inside the ampoule while the oven was in the “on” part of the cycle. The intensity of this glow at the beginning of the reaction was very high. As the reaction proceeded, the intensity of the light dropped. When the oven was in the “off” part of its cycle, the glow disappeared. We summarize the results of different reactions with the visual observations in Table 1. When the reactions were conducted at 100% microwave power, the “jumping” of the lithium from the crucible was observed, which results in ampoule failure. The temperature of the reactions is estimated to be around 700°C for 60% power, based on the color of the glow (for both prepared compounds). The sparks at low power levels, such as 50% and 30%, were less intense than at high power levels. The approximate temperatures during these reactions were 450°C and 350°C, respectively. Table 1 shows that under the lower oven powers (50% and 30%) microwave irradiation cannot initiate a complete reaction of metal Li with Si or Sn. Therefore, the optimum oven power is 80–60% for the preparation of Li₂₁Si₅ or Li₁₇Sn₄, and the irradiation times for Li₂₁Si₅ are shorter than those for Li₁₇Sn₄. This is possible because semi-metallic Si has a higher reactivity with metallic Li relative to metallic Sn.

Furthermore, we found that the disappearance of the sparks (discharge) could be an indication of the completion of the reaction. The samples obtained at different irradiation times did not result in hard, self-sintered bulk products. This shows that no further

solidification occurs at elevated temperatures either for $\text{Li}_{21}\text{Si}_5$ or $\text{Li}_{17}\text{Sn}_4$. This indicates that the compounds of $\text{Li}_{21}\text{Si}_5$ or $\text{Li}_{17}\text{Sn}_4$ are not good microwave susceptors, even at high temperatures.

The PXRD patterns of $\text{Li}_{21}\text{Si}_5$ and $\text{Li}_{17}\text{Sn}_4$ prepared by microwave heating are shown in Fig. 1. The comparison of the diffractograms with the calculated values for these compounds shows excellent matching (for $\text{Li}_{21}\text{Si}_5$ and $\text{Li}_{17}\text{Sn}_4$ the Powder XRD patterns were calculated using the “Powder Cell 1.0 program” (<http://www.ccp14.ac.uk/tutorial/powdcell/>) from the single crystal data published by Nesper et al. [35] and Nazar et al. [36]. The lattice parameters calculated from the diffractograms for $\text{Li}_{21}\text{Si}_5$ were equal to 18.79 Å (18.71 Å in the literature [35]) and for $\text{Li}_{17}\text{Sn}_4$ were equal to 19.7952 Å (19.6902 Å in the literature [36]). Their space group is $F\bar{4}3m$.

All our attempts to prepare these compounds in a quartz container were unsuccessful, due to the very rapid reaction of the lithium with the quartz. The use of a tantalum container for these microwave reactions was also unsuccessful. In this instance, the failure was due to

the very rapid heating of the tantalum to very high temperatures, which led to the melting of the bottom of the quartz ampoule. In contrast, the alumina (Al_2O_3) crucibles were used very successfully. Almost no reaction was observed with these crucibles, and the same container could be used many times. When alumina containers were used for regular, prolonged high temperature reactions (750°C for 24 h), liquid lithium reacted with alumina, resulting in the failure of the crucible and the ampoule.

The high temperature reaction with volatile compounds such as Sn and Li are generally conducted in the closed (welded) containers of tantalum. This precaution hinders the evaporation of the reacting elements during prolonged heating and, as a result, prevents the shift in the desired stoichiometry. Because open alumina containers were used in our microwave reactions, it was especially important to control the stoichiometry of the desired compounds. The comparison of the different ratios of the elements before and after reaction shows that very little evaporation of the volatile elements occurs, especially lithium (<2%). We attribute this result to the very quick heating of microwave irradiation. Despite the high temperatures that are achieved, because of the very short reaction times, the volatile elements hardly evaporate. In order to receive the ~21/5 and 17/4 stoichiometric ratios in the prepared compounds, a slight excess of the lithium must be used. This result proves that in microwave reactions open containers could be used.

The Li–Si or Li–Sn phase diagrams show the existence of several intermetallic phases [38]. An attempt was therefore made to prepare the other Li–Si or Li–Sn alloy compounds through changing the elemental ratios of Li/Si or Li/Sn, and/or microwave oven power. Our experimental results show that the intermetallic compound of $\text{Li}_{21}\text{Si}_5$ or $\text{Li}_{17}\text{Sn}_4$ is always the preferential phase. This indicates the high selectivity of microwave-assisted synthesis for the preparation of $\text{Li}_{21}\text{Si}_5$ and $\text{Li}_{17}\text{Sn}_4$. In the microwave-assisted deoxygenation reactions, Vaidhyanathan et al. [34] have found that the oxides with layer- and chain-structures can be reduced by graphite carbon under microwave irradiation, whereas non-layered oxides, such as WO_3 , anatase TiO_2 , and SnO_2 can not, also indicating the high selectivity of deoxygenation.

The oxidation processes of both $\text{Li}_{21}\text{Si}_5$ and $\text{Li}_{17}\text{Sn}_4$ compounds in air were studied. The compounds were left for various times under open air and the PXRD was measured for these samples (see Fig. 2). Both compounds were found to be sensitive to oxidation. For the $\text{Li}_{21}\text{Si}_5$ (Fig. 2a), the PXRD pattern of the compound exposed to air for 5 h showed more complex peaks, which can be indexed as SiO_2 and lithium silicon oxides. The decomposed products of the compound $\text{Li}_{17}\text{Sn}_4$ exposed to air for 5 h are Li_7Sn_2 , Li_8SnO_6 , and the main

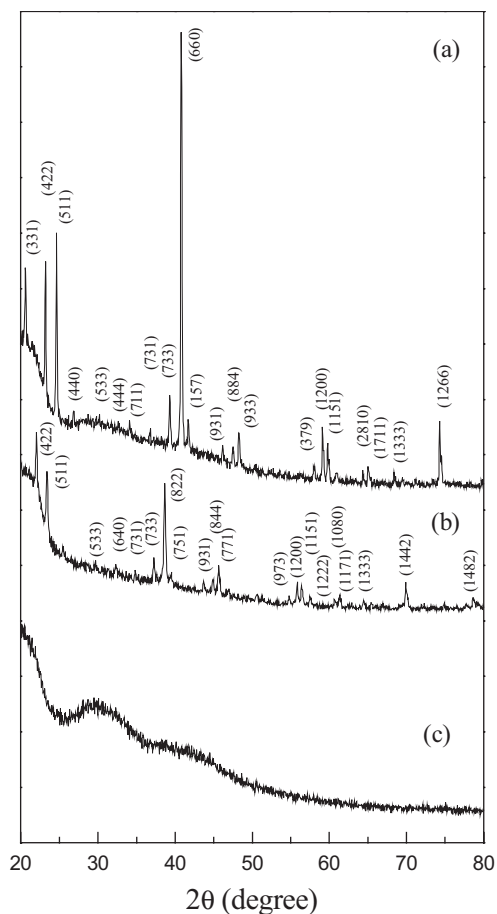


Fig. 1. Typical PXRD patterns of the as-prepared $\text{Li}_{21}\text{Si}_5$ (a) and $\text{Li}_{17}\text{Sn}_4$ (b), as well as the PXRD pattern of the empty sample cell (c).

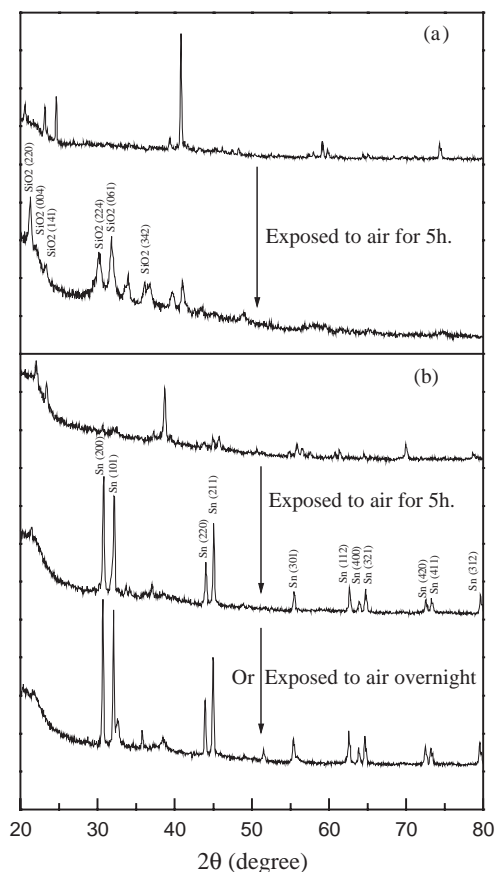


Fig. 2. PXRD patterns of the as-prepared $\text{Li}_{21}\text{Si}_5$ (a) and $\text{Li}_{17}\text{Sn}_4$ (b) before and after exposing to air.

phase is β -tin, but the same compound exposed to air overnight is completely oxidized to Li_8SnO_6 , Li_2SnO_3 , and main phase is β -tin. No SnO_2 and SnO can be detected (Fig. 2b).

^{119}Sn Mössbauer effect studies of three samples of $\text{Li}_{17}\text{Sn}_4$ were carried out. Many of the Li–Sn systems have been studied in the past by Mössbauer spectroscopy [39,40]. Some of the spectra of the three samples studied by us are shown in Fig. 3. The parameters obtained from the analysis of the spectra are given in Table 2. The spectra were analyzed by assuming that they are composed of two sub-spectra, one corresponding to pure $\text{Li}_{17}\text{Sn}_4$ and the second a product of the disintegration of the pure material, which is identified as metallic β -Sn. Since in $\text{Li}_{17}\text{Sn}_4$ there are at least five inequivalent Sn sites [36,39], leading to a distribution of possible quadrupole interactions (QS), the QS values were taken into account by assuming a continuous Gaussian distribution. The solid lines in the figures are the theoretical least square fits to the experimental spectra, yielding the parameters given in Table 2. An attempt to fit the spectra with a single quadrupole interaction, like in Ref. [40], yields a worse fit and

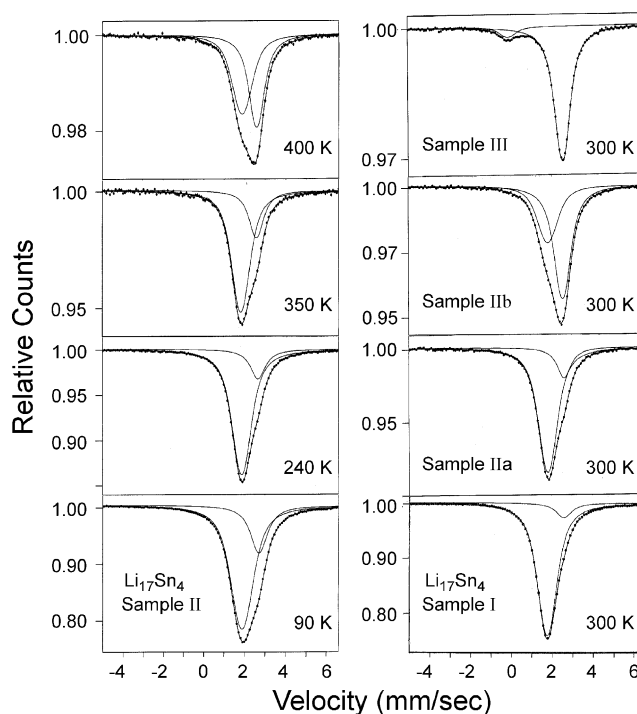


Fig. 3. ^{119}Sn Mössbauer spectra of three samples of $\text{Li}_{17}\text{Sn}_4$ at 300 K after different thermal histories, and sample II at various temperatures.

quadrupole splittings similar to those obtained from our distribution fit (see Table 2).

The results of the Mössbauer studies show that when exposed to air, the $\text{Li}_{17}\text{Sn}_4$ compound disintegrates, extremely rapidly into Li compounds and β -Sn. This disintegration occurs even under low pressure (10^{-3} Torr) when the samples are heated to several tens of degrees above room temperature. Surprisingly, very little SnO_2 is formed in the disintegration process, even after a long period of time (sample III contains some SnO_2). The formation of SnO either in its red or black modification during this decomposition can be excluded on the basis of its characteristic Mössbauer signature ($\text{IS} \sim 2.6\text{--}2.7$ mm/s, $\text{QS} \sim 1.31\text{--}1.33$ mm/s), which is not observed in any of the spectra of the present study. All of these are in agreement with the PXRD results of the compound exposed to air for a given time (see Fig. 2b). The $\text{Li}_{17}\text{Sn}_4$ compound has a much higher Debye temperature than β -Sn, due to the strong bonds to the many first nearest neighbors of Li. The hyperfine interaction parameters of ^{119}Sn in $\text{Li}_{17}\text{Sn}_4$ indicate a typical Sn–Li alloy isomer shift [40] (1.88 mm/s). The distribution of quadrupole interactions around an average zero value reflects the distortions of the high symmetry location of Sn in this compound [36,39]. The average of the absolute value of the quadrupole splitting, relevant to the Mössbauer spectra, can be obtained from the standard deviation, as shown in Table 2.

Table 2
Hyperfine interaction parameters of the Mössbauer spectra of $\text{Li}_{17}\text{Sn}_4$ samples^a

Sample	Temp. (K)	Inten. I (%)	I.S. I (mm/s)	σ_q (mm/s)	QS I (mm/s)	QSS (mm/s)	Inten.II (%)	I.S. II (mm/s)	QS II (mm/s)	Γ_{fwhm} (mm/s)
I	300	92(2)	1.88(2)	0.50(3)	0.40(3)	0.35(5)	8	2.72(3)	0.18(2)	0.90(2)
II	90	77	1.88	0.64	0.51	0.42	23	2.71	0.20	0.93
II	140	79	1.88	0.61	0.49	0.39	21	2.70	0.19	0.89
II	190	82	1.88	0.57	0.45	0.37	18	2.69	0.19	0.85
II	240	84	1.87	0.49	0.39	0.34	16	2.65	0.10	0.86
II	270	86	1.87	0.49	0.39	0.33	14	2.66	0.10	0.83
II	300	84	1.85	0.50	0.40	0.34	16	2.64	0.10	0.82
II	350	75	1.82	0.50	0.40	0.33	25	2.58	0.20	0.78
II	400	51	1.88	0.60	0.48	0.40	49	2.58	0.25	0.78
II	300 ^b	37	1.86	0.58	0.46	0.45	69	2.60	0.30(3)	0.83
III	300	7	-0.05(5)	QS=0.32			93	2.60	0.28	0.78

^aI.S. are isomer shifts (relative to BaSnO_3) of the two subspectra, Γ_{fwhm} is the full line width at half-maximum, QS is the quadrupole splitting and σ_q is the root of mean square deviation of the Gaussian quadrupole splitting distribution, around an average value of 0.0(1) mm/s. The average of the absolute value of the quadrupole splitting (QS I), relevant to the Mössbauer spectra, is derived from the standard deviation, $\text{QS I} = \sqrt{2/\pi}\sigma_q \approx 0.8\sigma_q$. For comparison, the value of the quadrupole splitting obtained from a single quadrupole doublet fit (QSS) is also given.

^bSample II after cooling from 400 K.

4. Conclusions

The two Li-containing alloys, $\text{Li}_{21}\text{Si}_5$ and, were successfully prepared by the fast, high selective microwave-assisted solid-reaction method. The PXRD patterns confirm that the two compounds have phase purity. The hyperfine interaction parameters of ^{119}Sn in $\text{Li}_{17}\text{Sn}_4$ show a typical intermetallic Sn^{4+} isomer shift (1.88 mm/s).

Acknowledgments

Dr. G.-T. Zhou thanks the Fred and Barbara Kort Postdoctoral Fellowship Foundation for financial support and the China Scholarship Council for its support. Prof. A. Gedanken thanks the EC for a research grant ENK6-CT-1999-00006, awarded through the 5th Program to a consortium entitled NanoBatt.

References

- [1] J. Wolfenstine, J. Powder Source 79 (1999) 111.
- [2] K.M. Abraham, Electrochim. Acta 38 (1993) 1233.
- [3] R.A. Huggins, J. Power Source 26 (1989) 109.
- [4] D. Fauteux, R. Koksang, J. Appl. Electrochem. 23 (1993) 1.
- [5] J.O. Besenhard, P. Komenda, A. Paxions, E. Wudy, Solid State Ionics 18–19 (1986) 823.
- [6] J.O. Besenhard, M. Hess, P. Komenda, Solid State Ionics 40–44 (1990) 525.
- [7] G.X. Wang, L. Sun, D.H. Bradhurst, S. Zhong, S.X. Dou, H.K. Liu, J. Alloys Compounds 306 (2000) 249.
- [8] J. Yang, Y. Takeda, N. Imanishi, T. Ichikawa, O. Yamamoto, J. Power Sources 79 (1999) 220.
- [9] J. Yang, M. Wachtler, M. Winter, J.O. Besenhard, Electrochem. Solid-State Lett. 2 (1999) 161.
- [10] A. de la Hoz, A. Diaz-Ortiz, A. Moreno, F. Langa, Eur. J. Org. Chem. 22 (2000) 3659.
- [11] A. Loupy, Mod. Solvents Org. Synth. 206 (1999) 153.
- [12] Q.H. Jin, F. Liang, H.Q. Zhang, L.W. Zhao, Y.F. Huan, D.Q. Song, TRAC Trends Anal. Chem. 18 (1999) 479.
- [13] C.R. Strauss, Austral. J. Chem. 52 (1999) 83.
- [14] S.A. Galema, Chem. Soc. Rev. 26 (1997) 233.
- [15] R. VanEldik, C.D. Hubbard, New J. Chem. 21 (1997) 825.
- [16] D.A.C. Stuerger, P. Gaillard, J. Microwave Power Electromagn. Energy 31 (1996) 87.
- [17] C.R. Strauss, R.W. Trainor, Austral. J. Chem. 48 (1995) 1665.
- [18] A. Zlotorzynski, Crit. Rev. Anal. Chem. 25 (1995) 43.
- [19] O. Palchik, A. Gedanken, V. Palchik, M.A. Slifkin, A.M. Weiss, J. Solid State Chem. 165 (2002) 125.
- [20] M.H. Bhat, B.P. Chakravarthy, P.A. Ramakrishnan, A. Levasseur, K.J. Rao, Bull. Mater. Sci. 23 (2000) 461.
- [21] P.S. Whitfield, I.J. Davidson, J. Electrochem. Soc. 147 (2000) 4476.
- [22] K.J. Rao, B. Vaidyanathan, M. Ganguli, P.A. Ramakrishnan, Chem. Mater. 11 (1999) 882.
- [23] A.G. Whittaker, D.M.P. Mingos, J. Chem. Soc. Dalton Trans., 1995, 2073.
- [24] C.C. Landry, J. Lockwood, A.R. Barron, Chem. Mater. 7 (1995) 699.
- [25] R. Kerner, O. Palchik, A. Gedanken, Chem. Mater. 13 (2001) 1413.
- [26] O. Palchik, R. Kerner, A. Gedanken, A.M. Weiss, M.A. Slifkin, V. Palchik, J. Mater. Chem. 11 (2001) 874.
- [27] D.M.P. Mingos, Res. Chem. Intermed. 20 (1994) 85.
- [28] B. Vaidyanathan, P. Raizada, K.J. Rao, J. Mater. Sci. Lett. 16 (1997) 2022.
- [29] K.J. Rao, P.D. Ramesh, Bull. Mater. Sci. 18 (1995) 447.
- [30] B. Vaidyanathan, K.J. Rao, J. Mater. Res. 12 (1997) 3225.
- [31] A.G. Whittaker, D.M.P. Mingos, J. Chem. Soc. Dalton Trans., 1992, 2751.
- [32] C.C. Landry, A.R. Barron, Science 260 (1993) 1653.
- [33] R.E. Douthwaite, M.L.H. Green, J. Rosseinsky, Chem. Mater. 8 (1996) 394.
- [34] B. Vaidyanathan, M. Ganguli, K.J. Rao, J. Mater. Chem. 6 (1996) 391.
- [35] R. Nesper, H.G.V. Schnering, J. Solid-State Chem. 70 (1987) 48.

- [36] G.R. Goward, N.J. Taylor, D.C.S. Souza, L.F. Nazar, *J. Alloys Compounds* 329 (2001) 82.
- [37] P. Hubberstey, T. Sample, M.J. Capaldi, M.G. Barker, *J. Nucl. Mater.* 217 (1–2) (1994) 93.
- [38] T.B. Massalski (Ed.), *Binary Alloy Phase Diagrams*, 2nd Edition. Vol. 3, ASM International, 1990.
- [39] (a) V.V. Chekin, A.P. Vinnikov, I. Burakhoich, *Soviet Phys.-Solid State* 10 (1968) 225;
(b) J. Chouvin, J. Olivier-Fourcade, J.C. Jumas, B. Simon, O. Godiveau, *Chem. Phys. Lett.* 308 (1999) 413.
- [40] R.A. Dunlap, D.A. Small, D.D. MacNeil, M.N. Obrovac, J.R. Dahn, *J. Alloys Compounds* 289 (1999) 135.