The Al–Li–Si System

1. A New Structure Type Li$_8$Al$_3$Si$_5$ and the Ternary Solid-State Phase Equilibria

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Solid-state phase equilibria of the ternary Al–Li–Si system were studied by arc-melted and levitation-melted samples in the as-cast state and annealed at 250°C up to 1 month. Phase analysis was done with X-ray powder diffractometry. The ternary phase diagram at 250°C is established. Three virtually stoichiometric ternary phases exist: LiAlSi (τ_1), Li$_{5.3}$Al$_{0.7}$Si$_2$ (τ_2), Li$_8$Al$_3$Si$_5$ (τ_3). The phase τ_3 is a new compound, whereas τ_1 and τ_2 have also been reported in previous works. Other phases claimed in the literature do not exist in the stable phase diagram. The single crystals of the new ternary τ_3 compound were studied to determine their compositions by SEM/EDX. The crystal structure of the τ_3 compound was resolved using its similarities to LiAlSi structure and refined using Rietveld analysis. It is found that the Li$_8$Al$_3$Si$_5$ compound constitutes a new structure type with space group $P\bar{4}3m$ and Pearson symbol cP16. Its unique features compared to closely related structure types are discussed. © 2001 Academic Press

INTRODUCTION

Lithium is an important alloying element for further reducing the density of the light metals magnesium and aluminum. Lithium additions increase the strength and elasticity of aluminum. Silicon additions increase the hardness of alloys. Development and improvement of the physical properties of new Li-containing multicomponent alloys requires understanding of the thermodynamic phase relations. In the framework of the generation of a multicomponent database for magnesium alloys the ternary Li–Al–Si systems is needed as an important subsystem for Mg–Li–Al–Si–*X* alloys. Controlling the precipitation of phases from the Al–Li–Si edge system in the (Mg) matrix requires a precise knowledge of the stability and structure of these phases. In spite of that, the knowledge of the ternary Li–Al–Si system is very limited. The few experimental investigations published in literature deal mainly with the Al-rich corner, technically interesting for aluminum alloys. Several ternary phases were reported. However, there was no final conclusion which phases are really stable or possibly metastable. Additional experimental work was found necessary to solve these problems. The experimental work of this study was supported and complemented by a thermodynamic analysis of the phase equilibria over a wide temperature range, presented in Part 2 of this paper (1).

THE Li–Al–Si SYSTEM IN LITERATURE

Al-Rich Corner

The first investigations in the Li–Al–Si system were published by Boom (2, 3). A ternary eutectic reaction at 569°C was found, 8 K lower than the binary Al–Si eutectic. Kadaner *et al.* (4) examined the solidification of Al-rich alloys by thermal analysis. The alloys were prepared in alumina crucibles using a eutectic salt mixture of potassium chloride and lithium chloride as flux. The thermal analysis was performed with cooling and heating rates of 2 K/min. The microstructures of slowly and rapidly cooled alloys were examined by metallographic analysis. Based on these results several vertical phase diagram sections in the Al-rich corner were also published (4). From the results they also derived the phase relations and the liquidus surface in the Al-rich corner. A quasibinary section between Al and the ternary τ_1 phase (LiAlSi) with a eutectic maximum temperature of 635°C was found. Two ternary eutectic equilibria were proposed, one occurring at 595°C (liquid at 1.5 at.% Si, 28.3 at.% Li) and the other at 565°C (liquid at 11.1 at.% Si, 0.2 at.% Li). The same group published isothermal sections of the Al-rich corner using metallographic analysis of alloys annealed at 550, 500, and 200°C (5). An equilibrium of a ternary phase τ, based on the composition Li$_3$Al$_2$Si$_2$, with (Al) is shown.

More recently Hanna *et al.* (6) determined the same part of the liquidus surface. Forty alloys were prepared from binary samples melted together in alumina crucibles under argon. These binary alloys were chill casted under argon. Thermal analyses were carried out with constant cooling and heating rates of 4 K/min. Metallographic examination of the alloys completed this investigation. Using these

results a liquidus surface of the Al-rich corner was constructed. The temperature of the eutectic maximum $L + (Al) + \tau_1$ was found at 632°C but at much lower Al content compared to (4). Two ternary eutectic equilibria were derived (6): E_1 at 592°C (liquid at 0.8 at.% Si, 31.6 at.% Li) and E_2 at 575°C (liquid at 12.8 at.% Si, 5.3 at.% Li). Compared to the results of (4) their liquidus surface is much more flat.

An extensive review of the experimental data is given by (7) and (8). They found large discrepancies in the data reported in the literature partly caused by differences in the assumed binary phase diagrams. Due to the contradictions in the published data, only few pieces of solid information about the ternary phase diagram can be extracted from these experimental data:

- (Al) solid solution is in equilibrium with τ_1, LiAl, and (Si).
- $L + (Al) + \tau_1$ forms a eutectic maximum in the range of 632 to 635°C.
- One ternary eutectic is $E_1 : L = (Al) + LiAl + \tau_1$ at 595°C (4,5) or 592°C (6).
- Other ternary eutectic is $E_2 : L = (Al) + (Si) + \tau_1$ at 565°C (4,5) or 575°C (6).
- The ternary solubility of Li and Si in (Al) is between 1 and 3 at.%

Ternary Solid Phases

An Al-rich ternary phase was first observed by (3) and (4) and assumed to be close to $Li_3Al_2Si_2$ composition. Later detailed crystallographic investigations (9, 10) established the composition of τ_1 as LiAlSi with cubic structure and $a = 594$ pm. Thirty alloys were prepared by heating in sealed Fe crucibles at 900–1000°C for 2 h by (9). They found an extended homogeneity range of τ_1 toward the binary LiAl phase with a similar crystal structure. At the composition Li_2Al_2Si a cubic phase with $a = 612$ pm was mentioned. At 13 at.% Si a cubic phase with $a = 613$ pm was detected in a heterogeneous sample. This phase was interpreted (9) as ternary solid solution of τ_1 even though it shows the same crystal structure and lattice parameter as the binary LiAl phase. Blessing (11) reported a separate cubic phase Li_2AlSi with $a = 606.1$ pm, which was shown previously (9) within the homogeneity range of τ_1. Attempts to produce a single phase with this composition by (12) and (13) were unsuccessful. In a cast alloy with 16.1 at.% Li and 6.6 at.% Si the primary phase was found (14) with a composition $Li_3Al_2Si_2$.

In alloys containing more than 50 at.% Li another ternary phase $Li_{5.3}Al_{0.7}Si_2$ (τ_2) was detected (11). A hexagonal phase with the composition Li_3AlSi was also reported (11) without solving the crystal structure. Pavlyuk *et al.* (13) prepared several ternary alloys by arc melting in purified Ar atmosphere and annealed the alloys for 240 h at 200°C in Ta containers. Four stoichiometric ternary phases were found: LiAlSi (τ_1), $Li_{5.3}Al_{0.7}Si_2$ (τ_2), Li_3AlSi, and a new ternary phase with the composition $Li_{12}Al_3Si_4$. As result of their investigation an isothermal section at 200°C is given, including the phase relations of the four ternary phases.

All published data were derived from X-ray diffraction analysis. Experimental difficulties by handling of Li-rich alloys were stated by several authors. No thermal analysis and metallographic techniques were performed. The questions regarding composition and homogeneity range of τ_1 and the stability of the ternary phases are still unsettled.

EXPERIMENTAL INVESTIGATION

Sample Preparation and Analysis

To solve the questions about the relations among ternary phases of the Al–Li–Si system three series of samples were prepared in the present study. Starting materials were aluminum powder (99.8 mass%, Alfa), lithium bulk material (99.9 mass%, Chemetall, Frankfurt), and silicon chips (99.9998 mass%, Wacker). The elements were weighed and mixed in glove-box with Ar atmosphere and pressed under a pressure of 100 MPa into small pellets of around 0.5 g. The first samples were prepared by arc-melting in purified argon atmosphere. Due to high weight losses (5–10 mass%) by arc-melting, levitation melting under purified argon was performed with most of the alloys. Heating power was controlled carefully to avoid evaporation. Weight loss was found less than 1 mass% by levitation melting. Repeating of levitation melting for the Si-rich alloys was not possible since the formed alloys show no electrical conductivity after cooling. Samples were packed into Ta containers and sealed in silica ampoules. The annealing was carried out at 250°C for up to 1 month.

Alloys were powdered in a hand mill and investigated using an X-ray powder diffractometer Siemens D-5000 with $CoK\alpha$ radiation. The routine measurements were performed with a step 0.02° of 2θ and 3 s exposition time in the point. The obtained diffraction patterns were analyzed quantitatively using the program PowderCell 2.1 (15). Further refinement of the X-ray pattern to identify the crystal structure of the ternary compounds was performed using the Rietveld program WinRietveld 3.01 (16).

The mechanically extracted single crystals of the new ternary phase were also investigated using electron microscope Leitz-AMR 1600T with EDX-detector for the determination of composition.

RESULTS

Phase Diagram Analysis

Three series of samples were prepared and investigated. All sample compositions with the identified phases are given in Table 1. The first series of samples was prepared by

TABLE 1
Sample Compositions and Identified Phases

Composition (at.%)			
Al	Li	Si	Phases identified by XRD
			Set 1
38	31	31	τ_1 + (Al)
28	48	24	τ_1 + τ_3 + LiAl
19	54	27	τ_3 + (?)
10	65	25	τ_2 + (?)
			Set 2
35	31	34	τ_1 + (Al) + Si
28	44	28	τ_1 + τ_3 + LiAl
31	48	21	τ_1 + τ_3 + LiAl
20	60	20	τ_2 + τ_3 + LiAl
16	63	21	τ_2 + τ_3 + LiAl
			Set 3
13	37	50	τ_3 + Si
10	55	35	τ_3 + $Li_{12}Si_7$ (+ Si)
16	47	37	τ_3 + Si (+ $Li_{12}Si_7$)
19	43	38	τ_3 + τ_1 + Si
10	50	40	τ_3 + $Li_{12}Si_7$ + Si
20	48	32	τ_3 + τ_1

Note. Phase order indicates observed peak intensities. Annealing conditions: set 1, 250°C, 13 days; set 2, 250°C, 1 month; set 3, as cast.

FIG. 1. Experimental isothermal section of the Al–Li–Si phase diagram at 250°C; dots represent the compositions of the investigated samples (also reported in Table 1); for the two- and three-phase alloys, arrows point to the identified phases.

arc-melting to check the ternary intermetallic phase compositions reported in the literature (see Table 1, set 1). Four samples were prepared and annealed for 13 days at 250°C. Only two ternary phases LiAlSi (τ_1) and $Li_{5.3}Al_{0.7}Si_2$ (τ_2) could be confirmed in our samples. Additionally a new ternary compound (τ_3) was detected with a similar diffraction pattern to LiAlSi compound. This phase was formed in the region with more Li content and had larger cell parameters. It was supposed that composition of this compound is near to Li_2AlSi.

The second series of samples was prepared to detect stable phases and their homogeneity ranges and to prove composition of τ_3-phase. Five samples were prepared by levitation melting and annealed for 1 month at 250°C. Longer annealing was used to check if there is an influence of annealing time. The compositions Li_3AlSi and $Li_{12}Al_3Si_4$ were also annealed for longer time to examine the phases in equilibrium. Again, only three ternary phases were detected. All the compounds show no detectable ranges of homogeneity. XRD phase analysis showed that an alloy with the composition Li_2AlSi contains three phases: τ_1 + "τ_3" + LiAl. EDX analysis of τ_3 phase in this sample showed the ratio of Al:Si = 0.369:0.631.

No difference in the phases content was observed in the arc or levitation melted alloys. The various time of annealing also showed no significant differences between series. The Si-rich samples showed the equilibrium phases even in the as-cast state.
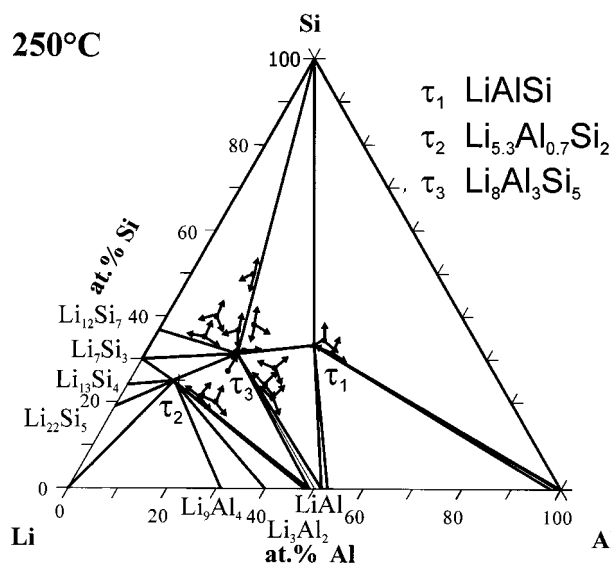
The third series of samples was prepared to detect composition of τ_3-phase and the phase relations in the Si-rich part. This series was examined as-cast. Six samples with compositions around the supposed composition of τ_3-phase were prepared and investigated by XRD. The largest content of the new phase was found in the two alloys with the compositions $Li_{48}Al_{20}Si_{32}$ and $Li_{54}Al_{19}Si_{27}$. The refinement of the crystal structure gave the composition $Li_8Al_3Si_5$ for τ_3 as described below.

The results of the present XRD investigation of the solid-state phase equilibria are summarized in the Al–Li–Si phase diagram in Fig. 1. This isothermal section is given at 250°C but is presumably valid down to room temperature. Three ternary compounds were detected (see Table 2). All phases have negligible ranges of homogeneity. No ternary solubility of binary compounds was detected.

Crystal Structure Refinement of the τ_3 ($Li_8Al_3Si_5$) Phase

A single phase sample with a composition $Li_8Al_3Si_5$ was prepared by levitation melting to solve the crystal structure of τ_3 compound. A small amount of Si was added for the calibration of pattern. To avoid an oxidation of the sample the powder was mixed with an indifferent oil and the scanning time was limited to 20 s in each point. The X-ray pattern for the crystal structure refinement of the τ_3 phase was collected on the X-ray powder diffractometer (Siemens D-5000) from 25° to 95° of 2θ in a $\theta/2\theta$ scan (see Fig. 2). The CoKα radiation was used with a step size 0.02° of 2θ and 20 s scanning time in the point.

TABLE 2
Ternary Solid Phases of the Al–Li–Si System

Compound	Strcuture type	Pearson symbol	Space group	Lattice parameters (nm)		
				a	b	c
τ_1, LiAlSi	LiAlSi	cF12	$F\bar{4}3m$	0.59282		
τ_2, $Li_{5.3}Al_{0.7}Si_2$	$Li_{5.3}Al_{0.7}Si_2$	hP8	$P6_3/mmc$	0.43410		0.81052
τ_3, $Li_8Al_3Si_5$	$Li_8Al_3Si_5$	cP16	$P\bar{4}3m$	0.61146		

The crystal structure of $Li_8Al_3Si_5$ was supposed to be related to the *fcc* structure of LiAlSi compound, because of similarities in the X-ray patterns. These two phases, however, can be clearly separated as shown in the XRD spectrum of a two-phase as-cast sample with a composition in the middle between $Li_8Al_3Si_5$ and LiAlSi phases (see Fig. 3). Since the arrangement of atoms with a composition $Li_8Al_3Si_5$ was impossible in the $F\bar{4}3m$ space group, the primitive space group $P\bar{4}3m$ was used for the refinement. Some small peaks in the powder pattern, which should be absent for the *fcc* structure, supported the choice of the primitive space group.

The refinement of the $Li_8Al_3Si_5$ crystal structure was carried out using the Rietveld program WinRietveld 3.01 (16). No corrections of the experimental pattern were made as long as peaks of Si showed practically no deviations from theoretical values. Ten reflections of Si and 31 reflections of $Li_8Al_3Si_5$ were refined to the $R = 6.97$, $R_w = 9.25$, Fitness quality = 1.57. The calculated and experimental patterns are presented in Fig. 2.
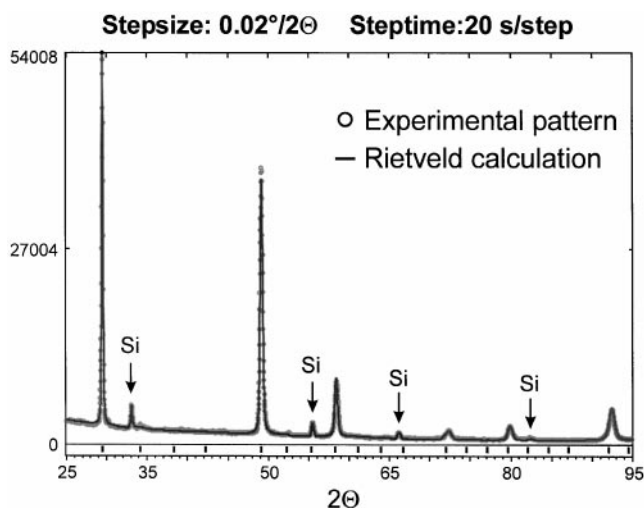

FIG. 3. XRD spectrum of a $Li_8Al_3Si_5$ and LiAlSi two-phase as cast sample.

The $Li_8Al_3Si_5$ compound crystallizes in the new structure type (space group $P\bar{4}3m$, Pearson symbol cP16) with only 16 atoms in the unit cell. The crystallographic parameters of $Li_8Al_3Si_5$ are presented in Table 3. The resulting crystal structure model is illustrated in Fig. 4.

DISCUSSION

Three ternary phases were found during the investigation of the Al–Li–Si system. All these phases show only very slight shifts of the X-ray diffraction patterns in the variety of samples and have therefore negligible ranges of homogeneity. For two ternary phases LiAlSi (τ_1) and $Li_{5.3}Al_{0.7}Si_2$ (τ_2) the literature data are confirmed. A new ternary compound $Li_8Al_3Si_5$ (τ_3) was found and its structure was refined. The phases τ_1 and τ_3 with high Si content appear to be brittle and show no electrical conductivity at room

FIG. 2. Experimental X-ray powder pattern of the single-phase $Li_8Al_3Si_5$ sample and refined pattern by Rietveld method. Small amount of Si was added for the calibration of pattern.

TABLE 3
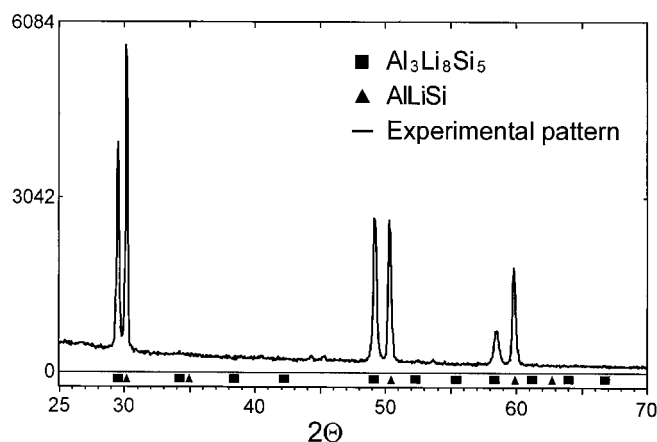### Crystallographic Parameters of the $Li_8Al_3Si_5$ Compound

Composition	$Li_8Al_3Si_5$
Structure type	$Li_8Al_3Si_5$
Space group	$P\bar{4}3m$
Pearson symbol	cP16
Cell parameters	$a = 0.61147(1)$ nm

Atom	Wyckoff position	x	y	z	B_{iso}
Al	3d	0.5	0	0	1.4(1)
Li1	1a	0	0	0	2.1(8)
Li2	3c	0	0.5	0.5	2.3(6)
Li3	4e	0.751(4)	0.751(4)	0.751(4)	2.1(5)
Si1	1b	0.5	0.5	0.5	0.9(2)
Si2	4e	0.248(2)	0.248(2)	0.248(2)	0.93(6)

FIG. 4. Crystal structure of the $Li_8Al_3Si_5$ compound.

temperature, whereas the τ_2 compound is more ductile and shows electrical conductivity. Two other ternary compounds, "Li_3AlSi" and "$Li_{12}Al_3Si_4$," reported in literature,
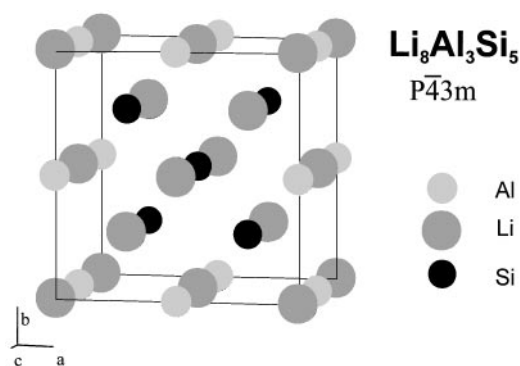
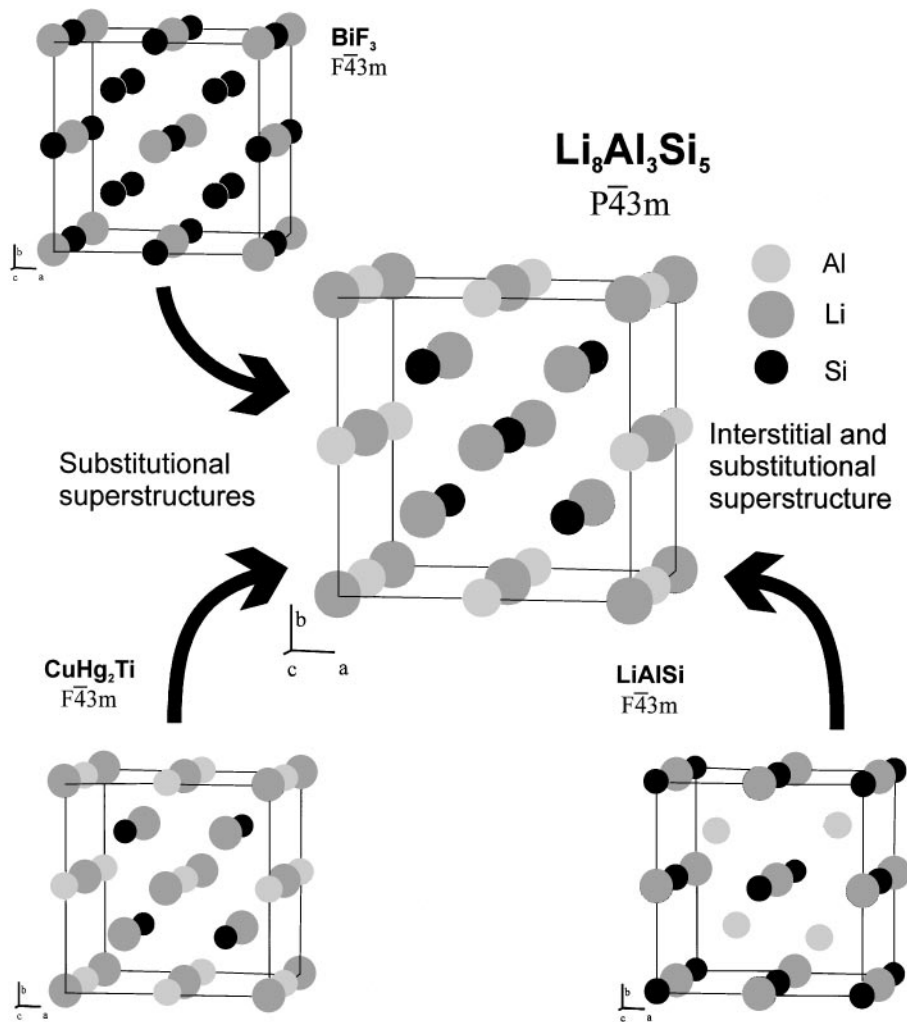were not found. These compositions have been specifically decked, they are located in the three phase field $\tau_1 + \tau_3 + LiAl$, and are detailed in Table 1. They are possibly metastable phases. The triangulation at 250°C reported by (13) is confirmed considering the change of the composition of the ternary phases. This further supports Fig. 1 with the phase relations obtained at 250°C.

No ternary solid solutions on the base of binary phases were found. Reported ones by (9) may result from problems by interpretation of their X-ray diffraction pattern. Confusion may result from similarities in the diffraction pattern among $Li_8Al_3Si_5$, $LiAlSi$, and $LiAl$ phases, which are different only with respect to intensities and have small variation in the d-values. An example is given in Fig. 3 for the comparison of $Li_8Al_3Si_5$ and $LiAlSi$.

The new $Li_8Al_3Si_5$ compound crystallizes in a new structure type with space group $P\bar{4}3m$, Pearson symbol cP16, detailed in Table 3. The $Li_8Al_3Si_5$ structure type is closely

FIG. 5. Crystal structure of the $Li_8Al_3Si_5$ compound and closely related structures.

TABLE 4
Bond Lengths of $Li_8Al_3Si_5$ Compared to Closest Bond Lengths of AlLiSi, AlLi, $Li_{12}Si_7$, and Li_7Si_3

atom1	$Al_3Li_8Si_5$ atom2	Distance, nm
Al	Li1	0.306
Al	Li2	0.306
Al	Li3	0.264
Al	Si2	0.264
Li1	Li3	0.264
Li2	Li3	0.265
Li1	Si2	0.263
Li2	Si1	0.306
Li2	Si2	0.265
Li3	Si1	0.266
Li3	Si2	0.308
Si1	Si2	0.267

		Closest distance, nm			
atom1	atom2	AlLiSi	AlLi	$Li_{12}Si_7$	Li_7Si_3
Al	Al		0.276		
Al	Li	0.257	0.276		
Al	Si	0.257			
Li	Li		0.276	0.261	0.261
Li	Si	0.297		0.259	0.261
Si	Si			0.237	0.234

related to the *fcc* structure types of $CuHg_2Ti$, BiF_3, and LiAlSi. It can be interpreted as substitutional superstructure to $CuHg_2Ti$ and BiF_3 structure types or as a substitutional and interstitial superstructure to LiAlSi structure type. These relations are sketched in Fig. 5. The most similar structure is $CuHg_2Ti$. The difference is that the position $4b:\frac{1}{2},\frac{1}{2},\frac{1}{2}$ in the *fcc* $CuHg_2Ti$ structure is split into two positions $1b:\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and $3d:\frac{1}{2},0,0$ in the $Li_8Al_3Si_5$ structure, which are occupied by different sorts of atoms. This causes the change from face-centered $CuHg_2Ti$ structure to primitive $Li_8Al_3Si_5$ structure. The same change takes place also in BiF_3 and LiAlSi. Additional differences in BiF_3 and AlLiSi structure types occur in the occupation of the $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ and $\frac{3}{4},\frac{3}{4},\frac{3}{4}$ positions. The vacant position $\frac{3}{4},\frac{3}{4},\frac{3}{4}$ in the LiAlSi is filled in the $Li_8Al_3Si_5$ structure. The $8c:\frac{1}{4},\frac{1}{4},\frac{1}{4}$ position in the BiF_3 structure is split into two positions $4e:x,x,x$ ($x = 0.248(2)$ and $0.751(4)$) in the $Li_8Al_3Si_5$ structure, which are occupied by different sorts of atoms.

The bond lengths of the $Li_8Al_3Si_5$ phase compared to closest bond lengths of some related compounds are presented in Table 4. These compounds have very high packing density if metallic radii are used. This could be interpreted by the covalent character of bonding. This is supported by the fact that $Li_8Al_3Si_5$, as well as other LiAlSi compounds, shows no electrical conductivity at room temperature.

CONCLUSION

The ternary Al–Li–Si solid-state phase relations in isothermal section at 250°C were established using the X-ray diffraction methods and EDX analysis. Three ternary phases were found in this system. Two of them τ_1 and τ_2 were reported in previous works. The third one, τ_3 ($Li_8Al_3Si_5$) phase is a new compound. In addition it was found that it crystallizes in the new $Li_8Al_3Si_5$ structure type with a space group $P\bar{4}3m$ and Pearson symbol cP16. All ternary phases have negligible homogeneity ranges.

Other ternary phases reported in the literature were not found in this work. Contradictory information about compositions and crystal structures of these compounds presented in literature support the conclusion that they are not stable phases.

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