Pressure-supported crystal growth and single-crystal structure determination of Li$_2$SiF$_6$

Abstract: High-pressure/high-temperature conditions of 5.5 GPa and 750 °C applied to a powder of Li$_2$SiF$_6$ led to a pressure-supported crystal growth of Li$_2$SiF$_6$ maintaining single crystals of sufficient quality for a single-crystal structure determination. The compound crystallizes in the space group $P\overline{3}21$ (No. 150) with 3 formula units and the lattice parameters $a = 8.219(2)$, $c = 4.5580(9)$ Å, $V = 266.65(8)$ Å$^3$, $R_1 = 0.0178$, and $wR_2 = 0.0391$ (all data). This work verified the published powder diffraction data of Li$_2$SiF$_6$ and the predicted space group. Additionally, powder-FT-IR and Raman-spectroscopic investigations on single-crystals of Li$_2$SiF$_6$ were performed for the first time.

Keywords: high-pressure, hexafluorosilicate, crystal structure

1 Introduction

Lithium salts with large near-spherical polyatomic anions arouse great interest in the research field of lithium ion accumulators. In 1954, the compound Li$_2$SiF$_6$ was synthesized by Cox for the first time [1]. Cox provided only unit cell constants based on X-ray powder diffraction, but he was not able to perform a structure refinement. Li$_2$SiF$_6$ can be prepared by neutralizing H$_2$SiF$_6$ with a lithium hydroxide solution. This route led solely to a powder sample with low crystallinity, wherefore the structure determinations were merely performed on the basis of powder diffraction data. In 2005, Liivat et al. [2] used Molecular Dynamics simulations to determine the correct space group ($P\overline{3}21$ or $P\overline{3}m1$) of Li$_2$SiF$_6$. The calculations led to the result that $P\overline{3}21$ is probably the correct space group. The capability as battery electrolyte and the uncertainty of the correct space group made a single-crystal structure determination important. The pressure-induced crystallization is a possible method to get crystals of compounds, which prefer the amorphous state. In the case of powders with a low degree of crystallinity, high-pressure/high-temperature conditions can improve the size and the quality of the crystals. E.g., the use of high-pressure conditions led to the first crystalline tin borate $\beta$-SnB$_4$O$_7$ [3], the new borates $\beta$-MB$_2$O$_5$ ($M$ = Hf, Zr) [4, 5] and enabled the synthesis of single-crystals of $\pi$-ErB$_6$O$_3$ [6] with a high quality for a single-crystal structure determination. In this paper, we report the pressure-supported crystal growth of Li$_2$SiF$_6$ in crystals with sufficient quality for single-crystal structure determination for the first time. We report the single-crystal structure determination of Li$_2$SiF$_6$, a comparison of the single-crystal data with the powder data of Cox et al., a comparison with the isotypic phase Na$_2$SiF$_6$ [7], and IR- and Raman-spectroscopic investigations.

2 Experimental section

2.1 Synthesis

The pressure-induced crystallization of Li$_2$SiF$_6$ was achieved under high-pressure/high-temperature conditions of 5.5 GPa and 750 °C in a modified Walker-type multianvil apparatus. For the experiment, a powder of Li$_2$SiF$_6$ was finely ground and filled into a boron nitride crucible (Henze BNP GmbH, HeBoSint® S100, Kempten, Germany). The crucible was placed into an 18/11-assembly and compressed by eight tungsten carbide cubes (TSM-10, Ceratizit, Reutte, Austria). To apply the pressure, a 1000 t multianvil press with a Walker-type module (both devices from the company Vogenreiter, Mainleus, Germany) was used. The assembly and its preparation are described in Refs. [8–12]. The mixture of the starting materials was compressed to 5.5 GPa within 160 min and kept at this pressure. During the heating period, the temperature was increased to 750 °C in 10 min, kept for 10 min, and lowered to 350 °C within 25 min, followed by quenching to room temperature. The decompression of the assembly required nine hours. The recovered pressure medium
(MgO octahedron, Ceramic Substrates & Components Ltd., Newport, Isle of Wight, UK) was broken apart and the sample was separated from the surrounding boron nitride crucible. The compound Li2SiF6 was found in the form of colorless air-stable crystals.

At ambient pressure, Li2SiF6 decomposes into LiF and SiF4 at temperatures above 250 °C [13]. Under the applied pressure of 5.5 GPa, it is possible to enhance the temperature to a value of 750 °C without decomposition of the sample. Therefore, the mobility of the Li cations and SiF62− anions is dramatically enhanced leading to a preferred crystallisation process in contrast to the crystallisation starting from a lower temperature at ambient pressure conditions.

### 2.2 Crystal structure analysis

The powder diffraction pattern was obtained in transmission geometry, using a Stoe Stadi P powder diffractometer with Ge(111)-monochromatized MoKα (λ = 0.7093 Å) radiation. Figure 1 shows the diffraction pattern of Li2SiF6 (top), as well as reflections of compressed hexagonal boron nitride from the crucible, marked with a ring. The experimental powder pattern well reproduces the theoretical pattern simulated from single-crystal data (bottom). Indexing the reflections of Li2SiF6, we obtained the lattice parameters \( a = 8.2190(1) \) Å, \( c = 4.5580(1) \) Å and a unit-cell volume of 266.65(1) Å³. This confirms the similar lattice parameters, obtained from the single-crystal X-ray diffraction study (Table 1) and the powder data of Cox [1]. Small single-crystals of Li2SiF6 were isolated by mechanical fragmentation. The single crystal intensity data were collected at room temperature using a Nonius Kappa-CCD diffractometer with graphite-monochromatized MoKα radiation (λ = 0.71073 Å). A semiempirical absorption correction based on equivalent and redundant intensities (Scalepack [14]) was applied to the intensity data. All relevant details of the data collection and evaluation are listed in Table 1. According to the systematic extinctions and the structure determination, the trigonal space group \( \text{P} \overline{3}21 \) was derived. The structure solution and refinement (full-matrix least-squares against \( F^2 \)) were performed using the SHELX-97 software suite [15, 16] with anisotropic atomic displacement parameters for all atoms. The crystal was merohedrally twinned and the refinement was carried out with the twin correction \([100, 010, 001]\), improving the \( R_1 \)-value from 0.133 (without matrix) to 0.017. The twin ratio was 3:2. Checking of a possible higher symmetry by using the program PLATON [17] was unsuccessful. The final difference Fourier syntheses did not reveal any significant peaks. Tables 2–5 list the positional parameters, anisotropic displacement parameters, and interatomic distances.

![Fig. 1: Top: experimental powder pattern of Li2SiF6 (space group: P321); one reflection of compressed hexagonal BN is marked with a ring. Bottom: theoretical powder pattern of Li2SiF6 based on single-crystal diffraction data.](image)
Table 1: Crystal data and structure refinement of Li₂SiF₆ (standard deviations in parentheses).

| Property                           | Value                  |
|------------------------------------|------------------------|
| Empirical formula                  | Li₂SiF₆                |
| Molar mass, g · mol⁻¹               | 155.97                 |
| Crystal system                     | trigonal               |
| Space group                         | P₃2₁ (No. 150)         |
| Lattice parameters from powder data |                        |
| Powder diffractometer              | STOE Stadi P           |
| Radiation                           | MoKα (λ = 0.7093 Å)   |
| a, Å                               | 8.219(2)               |
| c, Å                               | 4.5580(1) (4.560)      |
| V, Å³                              | 266.65(1) (266.8)      |
| Single crystal data                |                         |
| Single crystal diffractometer      | Enraf-Nonius CCD       |
| Radiation                           | MoKα (λ = 0.71073 Å)  |
| a, Å                               | 8.219(2)               |
| c, Å                               | 4.5580(9)              |
| V, Å³                              | 266.65(8)              |
| Formula units per cell, Z          | 3                      |
| Calculated density, g · cm⁻³       | 2.914                  |
| Crystal size, mm³                   | 0.06 × 0.06 × 0.02     |
| Temperature, K                      |                        |
| Absorption coefficient, mm⁻¹       | 0.702                  |
| F(000)                              | 222                    |
| θ range, °                         | 2.9–34.9               |
| Range in hkl                        | ±13, ±13, ±7           |
| Total no. of reflections           | 4647                   |
| Independent reflections            | 792 (Rint = 0.0299)    |
| Reflections with | ≥ 2σ(I)          | 776 (Rw = 0.0167)     |
| Data/parameters                     | 792/45                 |
| Absorption correction              | multi-scan (Scalepack [14]) |
| Goodness-of-fit on F²              | 1.103                  |
| Final R indices [I ≥ 2σ(I)]        | R₁ = 0.0171            |
|                                  | wR₂ = 0.0391           |
| R indices (all data)               | R₁ = 0.0178            |
|                                  | wR₂ = 0.0392           |
| Largest diff. peak and hole, e · Å⁻³ | 0.32/−0.19            |
| Twin Matrix                         | 100, 010, 001          |
| BASF                                | 0.4:0.6                |
| Flack parameter x                   | 0.1(3)                 |

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-425923.

Table 2: Atomic coordinates, Wyckoff positions and equivalent isotropic displacement parameters Ueq (Å²) of Li₂SiF₆ (space group: P321) with standard deviations in parentheses. Ueq is defined as one third of the trace of the orthogonalized Uij tensor.

| Atom | Wyckoff | x    | y    | z    | Ueq  |
|------|---------|------|------|------|------|
| Li1  | 3f      | 0.2945(5) | 0    | ½    | 0.0174(6) |
| Li2  | 3e      | 0.6287(5) | 0    | 0    | 0.0219(7) |
| Si1  | 1a      | 0     | 0    | 0    | 0.0076(2) |
| Si2  | 2d      | ½     | ½    | 0.4839(2) | 0.00802(9) |
| F1   | 6g      | 0.1026(2) | 0.2948(2) | 0.2098(2) | 0.0130(2) |
| F2   | 6g      | 0.1391(2) | 0.5579(2) | 0.2719(2) | 0.0129(2) |
| F3   | 6g      | 0.4718(2) | 0.2452(2) | 0.3051(2) | 0.0120(2) |

Table 3: Anisotropic displacement parameters of Li₂SiF₆ (space group: P321) with standard deviations in parentheses.

| Atom | U₁₁   | U₁₂   | U₁₃   | U₂₂   | U₂₃   | U₃₃   | U₁₂   | U₁₃   | U₂₃   |
|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Li1  | 0.0166(9) | 0.0112(2) | 0.0232(2) | ½ U₂₂ | ½ U₁₃ | −0.001(2) |
| Li2  | 0.0212(2) | 0.0252(2) | 0.0202(2) | ½ U₂₂ | ½ U₁₃ | 0.0042(2) |
| Si1  | 0.0069(2) | U₁₁   | 0.0090(2) | ½ U₁₁ | 0     | 0     |
| Si2  | 0.0076(2) | U₁₁   | 0.0089(2) | ½ U₁₁ | 0     | 0     |
| F1   | 0.0122(4) | 0.0104(4) | 0.0147(3) | 0.0044(4) | −0.0028(5) | −0.0048(3) |
| F2   | 0.0091(4) | 0.0154(5) | 0.0128(3) | 0.0052(4) | −0.0031(2) | −0.0026(4) |
| F3   | 0.0097(3) | 0.0129(4) | 0.0132(2) | 0.0055(4) | −0.0032(3) | −0.0014(4) |

2.3 Vibrational spectra

The FTIR-ATR (Attenuated Total Reflection) spectra of powders were measured with a Bruker Alpha-P spectrometer with a diamond ATR-crystal (2×2 mm), equipped with a DTGS detector in the spectral range of 400–4000 cm⁻¹ (spectral resolution 4 cm⁻¹). 24 scans of the sample were acquired. A correction for atmospheric influences using the OPUS 7.0 software was performed.

The single-crystal Raman spectra of Li₂SiF₆ were measured in the spectral range of 100–1500 cm⁻¹ with a Raman micro-spectrometer LabRAM HR-800 (HORIBA Jobin Yvon GmbH, Bensheim/Germany) and hundredfold magnification. As excitation source, a Nd:YAG laser (λ = 532.22 nm) was used. The Raman-scattered light was detected through an optical grid with 1800 lines/mm. Four ranges were measured with a spectral resolution better than 2 cm⁻¹. The measurement time per step was 80 s. A background correction was applied.
3 Results and discussion

3.1 Crystal structure of Li$_2$SiF$_6$

The primitive trigonal cell with the lattice parameters $a = 8.219(2)$ and $c = 4.5580(9)$ Å of this compound contains three formula units Li$_2$SiF$_6$. Figure 2 shows the crystal structure down [001]. The structure of Li$_2$SiF$_6$ is composed of two independent octahedral SiF$_6^{2-}$ groups and two crystallographically independent lithium cations. The Si(1)F$_6^{2-}$ polyatomic anion is built up by six identical Si–F distances of 168.5(2) pm and the values of the intramolecular F–Si–F angles reveal an octahedral configuration. The second hexafluorosilicate anionic group Si(2)F$_6^{2-}$ contains two different Si–F bonds with bond lengths of 169.0(2) and 169.0(8) pm possessing also an octahedral configuration.

Each of the two crystallographically independent lithium cations is located in an octahedral coordination with six fluorine neighbours. Figure 3 shows the corner-linked [LiF$_6$]$^{5-}$ octahedra.

The bond-valence sums of the individual cations and anions of Li$_2$SiF$_6$ were calculated from the crystal structure. Table 4 shows the interatomic distances (pm) in Li$_2$SiF$_6$ (space group: P321) calculated with the single-crystal lattice parameters (standard deviations in parentheses).

Table 4: Interatomic distances (pm) in Li$_2$SiF$_6$ (space group: P321) calculated with the single-crystal lattice parameters (standard deviations in parentheses).

|          | Li1–F1 195.5(2) (2×) | Li2–F2 196.1(2) (2×) | Si1–F1 168.5(2) (6×) | Si1–F3 200.9(2) (2×) | Li2–F1 214.5(3) (2×) | Li2–F3 216.6(4) (2×) | Si2–F2 169.0(2) (3×) | Si2–F3 169.0(8) (3×) |
|----------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Li1–F2  | 195.5(2) (2×)        | F1–Li1–F1 101.2(2)   | F1–Li1–F3 99.63(6) (2×) | F1–Li1–F3 99.63(6) (2×) | F3–Li1–F3 154.2(2)   | F1–Li1–F2 166.4(2) (2×) | F1–Li1–F2 88.35(4) (2×) | F3–Li1–F2 69.36(7) (2×) |
| Li2–F1  | 200.9(2) (2×)        | F2–Li2–F2 108.0(2)   | F2–Li2–F3 93.427(2) (2×) | F2–Li2–F3 93.427(2) (2×) | F3–Li2–F3 174.3(2)   | F2–Li2–F1 93.71(5) (2×) | F2–Li2–F1 88.35(4) (2×) | F3–Li2–F1 74.2(2) |
| Li2–F3  | 213.2(2) (2×)        | F3–Li3–F3 170.3(2)   | F3–Li3–F1 169.0(8) (3×) | F3–Li3–F1 169.0(8) (3×) | F1–Li3–F1 177.08(7) (3×) | F1–Li3–F2 84.0(2)   | F1–Li3–F2 90.69(6) (6×) | F1–Li3–F2 90.69(6) (6×) |
| Si1–F1  | 168.5(2) (6×)        | F1–Si1–F1 177.08(7) (3×) | F2–Si2–F3 179.33(6) (3×) | F2–Si2–F3 179.33(6) (3×) | F3–Si3–F3 90.80(5) (3×) | F3–Si3–F1 91.15(7) (3×) | F3–Si3–F1 91.15(7) (3×) | F3–Si3–F1 91.15(7) (3×) |
| Si1–F2  | 169.5(2) (6×)        | F1–Si1–F1 90.96(4) (6×) | F2–Si2–F2 90.55(4) (3×) | F2–Si2–F2 90.55(4) (3×) | F3–Si3–F2 89.79(5) (3×) | F3–Si3–F2 89.79(5) (3×) | F3–Si3–F2 89.79(5) (3×) | F3–Si3–F2 89.79(5) (3×) |
| Si1–F3  | 200.9(2) (2×)        | F1–Si1–F1 86.99(7) (3×) | F2–Si2–F3 88.87(5) (3×) | F2–Si2–F3 88.87(5) (3×) | F3–Si3–F3 90.80(5) (3×) | F3–Si3–F3 90.80(5) (3×) | F3–Si3–F3 90.80(5) (3×) | F3–Si3–F3 90.80(5) (3×) |

Table 5: Interatomic angles (deg) in Li$_2$SiF$_6$ (space group: P321) calculated with the single-crystal lattice parameters (standard deviations in parentheses).

|          | F1–Li1–F1 101.2(2) | F2–Li2–F2 108.0(2) | F1–Li1–F3 99.63(6) (2×) | F2–Li2–F3 93.427(2) (2×) | F1–Li1–F3 99.63(6) (2×) | F2–Li2–F3 93.427(2) (2×) | F3–Li1–F2 166.4(2) (2×) | F2–Li2–F1 93.71(5) (2×) | F2–Li2–F1 88.35(4) (2×) | F3–Li1–F2 88.35(4) (2×) | F2–Li2–F1 158.2(2) (2×) | F1–Li3–F1 177.08(7) (3×) | F2–Si2–F3 179.33(6) (3×) | F1–Si1–F1 90.96(4) (6×) | F2–Si2–F2 90.55(4) (3×) | F1–Si1–F1 86.99(7) (3×) | F2–Si2–F3 88.87(5) (3×) | F1–Si1–F1 91.15(7) (3×) | F3–Si3–F3 90.80(5) (3×) |
|----------|--------------------|--------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|

Fig. 2: Projection of the crystal structure of Li$_2$SiF$_6$ viewed down [001].

Fig. 3: Crystal structure of Li$_2$SiF$_6$ with a view down [001], showing the corner-linked [LiF$_6$]$^{5-}$ octahedra.
re, using the bond-length/bond-strength-concept (∑V) [18, 19] and the CHARDI-(Charge Distribution in Solids, ∑Q) concept [20, 21]. The values of both calculations are shown in Table 6. The calculations led to values which fit well for the formal ionic charges.

The comparison of the lattice parameters $a$ and $c$ ($a = 8.219(2)$, $c = 4.5580(9)$ Å for Li$_2$SiF$_6$ and $a = 8.859(2)$ and $c = 5.038(2)$ Å for Na$_2$SiF$_6$ [7]) reveals the typical rise from lithium to sodium isotypic compounds corresponding to the larger ionic radius of Na$^+$ compared to Li$^+$. The main $M$–$F$ ($M = Li, Na$) distance in Na$_2$SiF$_6$ (233 pm) is about 27 pm larger than in Li$_2$SiF$_6$ (206.1 pm). The comparison of the $F$–$M$–$F$ ($M = Li, Na$) angles shows that the sodium-fluorine polyhedra are more deformed than the lithium-fluorine polyhedra. No significant deviations of the bond lengths and angles of the SiF$_6^{2–}$ group are observed. The coordination numbers of the alkaline ions are equivalent.

### 3.2 Vibrational spectroscopy

The FTIR-ATR spectrum and the single-crystal Raman spectrum of Li$_2$SiF$_6$ is shown in Fig. 5 and 6, respectively. The powder-FTIR-ATR spectrum shows strong bands at 705, 510 and 460 cm$^{-1}$. The position and the intensity of these bands fit well with the published data of Li$_2$SiF$_6$ $\cdot$ H$_2$O [22]. The highest peak in the spectrum is the $v_3$ band of the SiF$_6^{2–}$ group at 705 cm$^{-1}$. The $v_4$ band is split into two sharp peaks of equal intensity at 510 and 460 cm$^{-1}$. Furthermore, no OH or water bands could be detected in the range of 3000 to 3600 cm$^{-1}$. The single-crystal Raman spectrum shows one very strong peak at 660 cm$^{-1}$ and three weaker peaks at 420, 500 and 1100 cm$^{-1}$. The highest peak can be assigned to the $v_1$ Raman band of SiF$_6^{2–}$. The weak band at about 400 cm$^{-1}$ was also observed by Badachhape et al. [22] in an aqueous solution of Li$_2$SiF$_6$. Couture-Mathieu et al. [23] observed in the Raman spectrum of a single crystal of (NH$_4$)$_2$SiF$_6$ the Raman-active fundamentals $E_g$ ($v_9$) at 466 cm$^{-1}$ and $F_{2g}$ ($v_5$) at 403 cm$^{-1}$ beside the $A_{1g}$ fundamental ($v_1$) of the SiF$_6^{2–}$ group. The observed peaks at 500 and 420 cm$^{-1}$

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**Table 6:** Charge distribution in Li$_2$SiF$_6$ (space group: P321) calculated with VaList (∑V) [17, 18] and the CHARDI concept (∑Q) [19, 20].

|        | Li1 | Li2 | Si1 | Si2 |
|--------|-----|-----|-----|-----|
| ∑V     | 0.98| 0.87| 4.52| 4.46|
| ∑Q     | 1.00| 1.00| 4.00| 4.00|
| F1     | −1.07| −1.06| −1.04|
| F2     | −1.00| −1.01| −0.99|

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**Fig. 5:** Powder-FT-IR reflectance spectrum of Li$_2$SiF$_6$ (space group: P321) in the range of 400–1800 cm$^{-1}$.

**Fig. 6:** Single-crystal Raman spectrum of Li$_2$SiF$_6$ (space group: P321) in the range of 100–1500 cm$^{-1}$.
in the spectrum of Li$_2$SiF$_6$ are probably the $\nu_2$ and the $\nu_5$-bands.

4 Conclusions

The pressure-supported crystal growth of the hexafluorosilicate compound Li$_2$SiF$_6$ at 5.5 GPa and 750 °C enabled a single-crystal structure determination, for the first time verifying the correct space group $P321$. The powder data of Cox et al. [1] and the theoretical calculations of Liivat et al. [2] are now confirmed by more accurate data, containing a more precise set of atomic coordinates, including anisotropic displacement parameters. In addition, spectroscopic data for this compound, powder-FTIR-ATR- and Raman-measurements on single-crystal were performed.

Acknowledgements: The research was funded by the Austrian Science Fund (FWF): P 23212-N19.

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Received March 14, 2013; accepted May 23, 2013
Published online February 5, 2014