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Low-Temperature Structural Determination of Anhydrous Li_2SeO_4

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Anhydrous Li_2SeO_4 crystallizes in the trigonal space group $R\bar{3}$ with $a = 13.931(2)$, $c = 9.304(3)$ Å, $V = 1563.7$ Å^3, $Z = 18$, $D_c = 2.988$ g cm^{-3}. The unit cell transforms to the rhombohedral coordinate system as $a = 8.620$ Å, $\alpha = 107.81(2)°$, $V = 521.2$ Å^3, $Z = 6$. The structure contains selenate anions bridged by Li in the phenacite structural type. Data collection was performed at low temperature for precise placement of the Li cations which are tetrahedrally surrounded by oxygen atoms. Some problems with secondary extinction were apparent and a correction was made. The structure refined to an R value of 0.034.

Introduction

Certain compounds containing tetrahedral oxyanions have been the focus of recent interest since their high-temperature cubic phases exhibit anomalously high ionic conductivity. Examples of these include Li_2SO_4 (*1*), $LiNaSO_4$ (*2*), and $LiAgSO_4$ (*3*). In addition, these cubic phases have been described as plastic phases, characterized by extensive orientational disorder of the sulfate ions. There has been speculation that the ionic conductivity of these phases is dynamically enhanced through the (hindered) rotational motion of the sulfate ions (*4*).

In the context of an extensive spectroscopic study of these related crystals, it was decided to consider other ionic crystals containing tetrahedral oxyanions and lithium cations. An obvious choice is lithium selenate, Li_2SeO_4, for which no spectroscopic data are available. A set of complete, symmetry-based vibrational mode assignments requires that the distribution of normal modes over the irreducible representations of the crystal factor group be calculated, and this in turn requires that the sites occupied by the atoms in the crystal be known. Therefore detailed structural information about a crystal is a prerequisite for a complete analysis of the vibrational spectrum. To this purpose an X-ray structural study of anhydrous Li_2SeO_4 has been performed.

Experimental

Single crystals of Li_2SeO_4 cannot be grown from aqueous solution in the temperature range 25–90°C since only the monohydrate form is the stable phase. This is the same difficulty encountered in attempts to grow single crystals of Li_2SO_4 from water solution. However, in the case of Li_2SO_4 it has been found (*5*) that anhydrous single crystals can be grown from aqueous solutions containing H_2SO_4 over a narrow com-

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position range. This behavior (6) is seen not only in the Li_2SO_4 system but also in other systems (7) of the form inorganic salt/strong acid of common anion/water. In these systems it is often observed that the hydration of the inorganic salt in the solid phase is decreased with respect to hydration of the solid phase found in the salt/water system without any acid present.

Therefore, the phases present in the system $Li_2SeO_4/H_2SeO_4/H_2O$ at approximately 30°C were investigated. This system was found to be similar to the corresponding sulfate system. Three solid phases were present: $Li_2SeO_4 \cdot H_2SeO_4$, Li_2SeO_4, and $Li_2SeO_4 \cdot H_2O$. No attempt was made to quantitatively determine the phase relationships in this system. The approximate solution composition range for the formation of Li_2SeO_4 was found to be (in weight percentage) 71% H_2SeO_4 and 14% Li_2SeO_4 to 53% H_2SeO_4 and 17% Li_2SeO_4. Li_2SeO_4 and H_2SeO_4 were purchased from Gallard–Schlesinger Chemical Corporation. The Li_2SeO_4 was recrystallized twice and stored in a desiccator. The H_2SeO_4 (96%) was not further purified. Solutions in the middle of the Li_2SeO_4 composition range were made using distilled water and heated to 70°C. These solutions were then slowly cooled to 30°C over a period of 2 to 3 days resulting in the formation of good quality single crystals of Li_2SeO_4. Two different crystal habits were observed: small rods of hexagonal cross section (used in this study), and larger hexagonal plates. These crystals are not stable at room temperature in ordinary atmosphere due to the formation of the hydrate which destroys the surface of the crystal after one to several hours of exposure.

The diffraction study was conducted on colorless hexagonal cylindrically shaped crystals of Li_2SeO_4. Under stringent anhydrous conditions, a crystal of approximate size 0.16 × 0.15 × 0.10 mm was sealed in a thin-walled capillary for data collection. A total of 1835 reflections were collected at low temperature (138 ± 2 K) in the range $3° \leq 2\theta \leq 50°$ using a CAD-4 automated diffractometer with Mo$K\alpha$ radiation and a graphite monochromator. A total of 603 unique reflections were obtained. All were used in the subsequent refinement. A sample data set indicated systematic absences of the form $-h + k + l \neq 3n$ and disproved the Laue group $\bar{3}m$. Possible space groups therefore were $R\bar{3}$ and $R3$. The cell parameters were obtained by precisely centering upon 25 intense reflections. Other details of data collection were as follows: scan method, $\theta/2\theta$; scan rate, variable up to 45 sec per scan; scan range, calculated by $0.85 + 0.20 \tan\theta$ with 25% extension on each side for backgrounds. Three intensity monitors were checked every 2 hr of X-ray time and varied randomly 2% over the entire data collection. Three orientation standards were centered after every 200 observations. The hexagonal representation of the unit cell was chosen for data collection and refinement.

The centrosymmetric space group $R\bar{3}$, No. 148 (8), was assumed and gave satisfactory refinement.[1] The position of the Se atom was obtained from a Patterson synthesis. All other atoms were located from subsequent Fourier maps and occupy general positions in the unit cell. Least-squares refinement was particularly difficult due to large correlation coefficients and significant secondary extinction effects. In order to successfully refine the structure, 50 reflections that were obviously seriously affected by secondary extinction were removed while the atomic positional and thermal parameters were refined. The 50 omitted reflections were then restored and an empirical systematic secondary extinction

[1] All computations were performed using local modifications of the programs of SHELX-76: G. M. Sheldrick, University Chemical Laboratory, Cambridge, England, 1976.

TABLE I

ATOMIC POSITIONAL COORDINATES

	Hexagonal axes			Rhombohedral axes		
	x	y	z	x	y	z
Se	.19794(3)	−.01470(3)	.25046(5)	.03782	.44840	.26516
O1	.2154(3)	.1104(3)	.2492(3)	.1442	.4646	.1388
O2	.3198(3)	−.0043(2)	.2485(4)	−.0756	.5683	.2528
O3	.1299(3)	−.0786(3)	.3957(3)	.1872	.5256	.4743
O4	.1277(3)	−.0816(3)	.1072(3)	−.1021	.2349	.1888
Li1	.1905(7)	−.0169(6)	.5858(10)	.3784	.7763	.6027
Li2	−.0202(6)	−.2115(6)	.0847(10)	−.1066	.0645	.2962

correction was applied. The corrected F_c values were of the form

$$F_c(\text{corr}) = F_c(1 - 0.001 * x * F_c^2/\sin\theta)$$

which is the usual SHELX correction. All atomic, overall scale, and secondary extinction parameters were then allowed to vary in a full matrix least-squares calculation. The final value of x in the equation above was 0.00575.

Because it was difficult to visually distinguish the crystal faces through the capillary, absorption corrections were not made even though $\mu(\text{Mo}K\alpha) = 114\ \text{cm}^{-1}$. The inability to correct for absorption is unfortunate in an otherwise accurate study.

Full matrix least-squares varying Se and O atoms anisotropically and Li atoms isotropically yielded $R_w = 0.034$.[2] The maximum shift in the last cycle was $<0.01\sigma$. In a final difference map the largest peak represented 1.0 e Å^{-3} in the vicinity of O4. Neutral atom scattering factors and corrections for anomalous dispersion were obtained from Ref. (*9*).

Final atomic positional parameters for both the hexagonal and rhombohedral unit cells are presented in Table I. Interatomic distances and bond angles are listed in Table II. Thermal parameters relative to the hexagonal unit cell are given in Table III. Observed and calculated structure factors are contained in Table A.[3]

Discussion

Anhydrous Li_2SeO_4 at room temperature crystallizes in the phenacite structural type which also includes Li_2CrO_4 (*10*) and Li_2WO_4 (*11*). Since the crystal data for Li_2SeO_4 at 138 K agreed with information from powder patterns at room temperature (*12*), there was apparently no phase change between 138 and 300 K. It was anticipated that low-temperature data would facilitate the precise placement of the Li atoms.

The selenium atoms are located within regular tetrahedra of oxygen atoms with an average Se–O length of 1.636(3) Å. This value is in accordance with Se–O bond lengths in other selenate complexes, e.g., 1.65(2) Å in Na_2SeO_4 (*13*); 1.64(1) Å in K_2SeO_4 (*14*); 1.643(8) Å in $Cu(NH_3)_4SeO_4$ (*15*).

The Li–O bond distances range from 1.919 to 1.987 Å and average 1.952(22) Å.

[2] $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2]^{1/2}$; $w = 1/\sigma^2(F)$.

[3] See NAPS document No. 4155 for 3 pages of supplementary material. Order from NAPS Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance in U.S. funds only $7.75 for photocopies or $4.00 for microfiche. Outside the U.S. and Canada add postage of $4.50 for the first 20 pages and $1.00 for each page thereafter. $1.50 for microfiche postage.

TABLE II

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG.)[a]

Se–O1 = 1.637(3)	Li1–O1[b] = 1.934(9)	Li2–O1[e] = 1.919(9)
Se–O2 = 1.632(3)	Li1–O2[c] = 1.945(8)	Li2–O2[f] = 1.969(8)
Se–O3 = 1.635(3)	Li1–O3 = 1.962(9)	Li2–O4 = 1.960(8)
Se–O4 = 1.640(3)	Li1–O3[d] = 1.942(8)	Li2–O4[g] = 1.987(10)
O1–Se–O2 = 108.2(2)	O1[b]–Li1–O2[a] = 112.0(4)	
O1–Se–O3 = 108.9(2)	O1[b]–Li1–O3 = 116.8(4)	
O1–Se–O4 = 109.2(2)	O1[b]–Li1–O3[d] = 109.3(4)	
O2–Se–O3 = 110.6(2)	O2[c]–Li1–O3 = 105.2(4)	
O2–Se–O4 = 109.9(2)	O2[c]–Li1–O3[d] = 102.6(4)	
O3–Se–O4 = 110.0(2)	O3–Li1–O3[d] = 110.0(4)	
O1[e]–Li2–O2[f] = 108.4(4)	Li1[d]–O1–Se = 126.1(3)	
O1[e]–Li2–O4 = 106.9(4)	Li2[h]–O1–Se = 126.9(3)	
O1[e]–Li2–O4[g] = 116.9(4)	Li1[d]–O1–Li2[h] = 105.5(4)	
O2[f]–Li2–O4 = 109.6(4)	Li1[i]–O2–Se = 126.4(4)	
O2[f]–Li2–O4[g] = 104.7(4)	Li2[j]–O2–Se = 120.7(3)	
O4–Li2–O4[g] = 110.2(4)	Li2[j]–O2–Li1[i] = 112.8(3)	
	Li1[g]–O3–Se = 129.4(3)	
	Li1–O3–Se = 120.0(3)	
	Li1–O3–Li1[g] = 110.5(4)	
	Li2[k]–O4–Se = 118.1(3)	
	Li2–O4–Se = 131.8(3)	
	Li2–O4–Li2[k] = 109.8(4)	

[a] All transformations are relative to the hexagonal axes and are listed below.

[b] $y, 1 + y - x, 1 - z$.
[c] $\frac{2}{3} + y - x, \frac{1}{3} - x, \frac{1}{3} + z$.
[d] $x - y, x, 1 - z$.
[e] $1 + y - x, 1 - x, z$.
[f] $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{1}{3} - z$.
[g] $1 + y, 1 + y - x, 1 - z$.
[h] $-y, x - y, z$.
[i] $\frac{1}{3} - y, \frac{2}{3} + x - y, z - \frac{1}{3}$.
[j] $\frac{2}{3} + y, \frac{1}{3} + y - x, \frac{1}{3} - z$.
[k] $x - y, 1 + x, \bar{z}$.

The O–Li–O bond angles indicate a roughly tetrahedral arrangement of the oxygen atoms. Tetrahedra of oxygen atoms about a central Li are also found in lithium stannate (*16*) (Li–O = 1.88–2.00 Å), lithium tellurate (*17*) (Li–O = 1.95–2.06 Å), lithium sulfate (*18*) (Li–O = 1.91–1.99 Å), and lithium tungstate (*11*) (Li–O = 1.80–2.10 Å) illustrating Li–O bond distances equivalent to those in the title structure within experimental error.

TABLE III

THERMAL PARAMETERS[a]

	U or U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Se	.0030(3)	.0031(3)	.0015(3)	.0000(2)	.0001(2)	.0012(2)
O2	.012(2)	.004(2)	.006(2)	.001(1)	.000(1)	.005(1)
O2	.004(2)	.007(2)	.010(2)	.000(1)	.000(1)	.004(1)
O3	.006(2)	.008(2)	.002(2)	.001(1)	.003(1)	.001(1)
O4	.005(1)	.008(2)	.005(1)	−.001(1)	.000(1)	.001(1)
Li1	.011(2)					
Li2	.012(2)					

[a] Thermal parameters are relative to the hexagonal axes. Anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*)]$. Isotropic thermal parameters are of the form $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$.

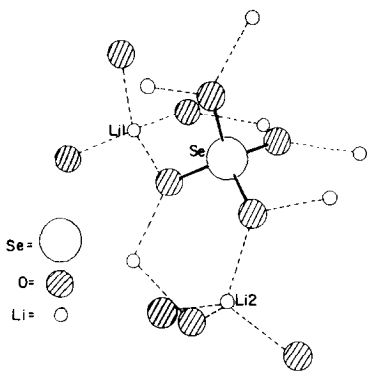

FIG. 1. A portion of the Li_2SeO_4 array. Tetrahedral coordination is evident for the labeled Se and Li sites.

Each oxygen atom is bonded by one selenium and two lithium atoms in a distorted trigonal arrangement. The Li–O–Li bond angles are compressed from an ideal 120° to an average of 110(3)° while the Li–O–Se angles are opened to a mean 125(5)°. The geometry of a portion of the Li_2SeO_4 array is illustrated in Fig. 1.

Although strictly speaking, the structures of Li_2SeO_4 and monoclinic Li_2SO_4 (*18*) (room temperature, phase II structure) are not isomorphous, they are closely related. In each structure, the chalcogen atoms and the Li atoms are tetrahedrally coordinated. The coordination sphere about Li is described by four oxygen atoms each of which is bound to a different Se atom, and of these four oxygen atoms, two are in symmetry-related positions. The difference between the chalcogen–oxygen bond lengths (S–O = 1.472(4) Å and Se–O = 1.636(3) Å) is 0.164 Å which is close to the value of the simple difference in covalent radii (ΔR_{cov} = 0.15 Å) (*19*) between sulfur and selenium.

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