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Synthesis and Structural Characterization of Lithium Iron Diarsenate, $LiFeAs_2O_7$

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A new iron(III) diarsenate, $LiFeAs_2O_7$, was synthesized hydrothermally at 230°C and characterized by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group *C*2 (No. 5) with $a = 6.676(2)$ Å, $b = 8.285(2)$ Å, $c = 4.744(2)$ Å, $\beta = 103.96(2)°$, $Z = 2$, and $R = 0.0192$. SHG measurements on a powder sample confirm the absence of center of symmetry in the structure. The structure consists of intersecting tunnels running along the [001] and ⟨110⟩ directions, and the Li^+ ions are located at the intersection of these tunnels. The framework is built up from corner-sharing FeO_6 octahedra and As_2O_7 groups. The structure is discussed along with the phosphate analog $LiFeP_2O_7$. © 1994 Academic Press, Inc.

INTRODUCTION

Ferric diphosphates of the stoichiometry $AFeP_2O_7$ (A = alkali metals) exhibit three different structure types. $A'FeP_2O_7$ (A' = Cs, Rb, K) (1, 2) and the low-temperature form of the sodium compound I-$NaFeP_2O_7$ (3) are isostructural. The high-temperature form, II-$NaFeP_2O_7$ (4), and $LiFeP_2O_7$ (5, 6) adopt the other two structure types. The frameworks of these phases are built up from corner-sharing FeO_6 octahedra and P_2O_7 groups. Since we have been studying the structural chemistry of transition metal arsenates (7–9), it would be interesting to know whether the arsenate analogs of the above-mentioned phosphates adopt the same structure types. To our knowledge, no corresponding arsenates have been reported. In this work we present the synthesis and single-crystal X-ray structure of the first member in this family, $LiFeAs_2O_7$. It adopts a structure related to that of $LiFeP_2O_7$, but crystallizes in a different space group.

EXPERIMENTAL

Synthesis. Reagent-grade LiOH, Fe_2O_3, and 80% H_3AsO_4, obtained from Merk, were used as received. Colorless crystals of $LiFeAs_2O_7$ were obtained by heating a mixture of LiOH (0.15 g), Fe_2O_3 (0.5 g), 80% H_3AsO_4 (2 ml), and H_2O (10 ml) (molar ratio of Li : Fe = 1 : 1) in a Teflon-lined autoclave (23 ml) at 230°C for 5 days before slow cooling at 5°C h^{-1} to room temperature. The product was filtered off, washed with water, rinsed with ethanol, and dried in a desiccator at ambient temperature. Visual microscopic inspection showed that in addition to the colorless crystals of the title compound the product also contained a small amount of red-brown material, which was not further characterized due to the limited amount of sample. An optimum reaction condition to eliminate the side product has not been found. Powder X-ray diffraction analysis using a Scintag powder diffractometer on a powdered sample of manually selected colorless crystals compared very well with that calculated from the single-crystal data. The Li content was analyzed by using an ICP-AE spectrometer after dissolving the sample in dilute nitric acid (found, 2.38%; calculated for $LiFeAs_2O_7$, 2.14%). The same sample was used for subsequent second harmonic generation (SHG) measurements.

Single-crystal X-ray diffraction. A colorless crystal of dimensions 0.14 × 0.14 × 0.08 mm was used for indexing and intensity data collection on a Nicolet R3m/V four-circle diffractometer. Unit cell parameters and orientation matrix were determined by a least-squares fit of 13 peak maxima with $5° < \theta < 25°$. Axial oscillation photographs were taken to check the unit cell parameters and symmetry properties. Octants collected were $\pm h$, $+k$, $+l$. The intensity data were corrected for Lorentz polarization and absorption effects. Absorption correction was based on ψ scans of a few suitable reflections with χ values close to 90° using the program XEMP of the SHELXTL-PLUS program package (10). Based on systematic absences, statistics of intensity distribution, and successful solution and refinement of the structure, the space group was determined to be *C*2. The Patterson method was used to locate heavy atoms and a few O atoms, and the remainder of atoms were found from succesive difference maps.

The absolute configuration of the structure was established by adding to the least-squares refinement one additional parameter, η. Refinement of η tended strongly to +1, indicating that the configuration was correct. The

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TABLE 1
Crystal Data and Intensity Collection Parameters for $LiFeAs_2O_7$

Formula	$LiFeAs_2O_7$
M	324.6
Crystal symmetry	Monoclinic
Space group	$C2$ (No. 5)
a (Å)	6.676(2)
b (Å)	8.285(2)
c (Å)	4.744(2)
β (°)	103.96(2)
V (Å^3)	254.6(1)
Z	2
D_c (g cm^{-3})	4.234
$\mu(MoK\alpha)$ (cm^{-1})	15.83
T (°C)	24
Scan rate (° min^{-1})	Variable; 2.93–14.65° min^{-1} in ω
Scan mode	θ–2θ
Scan width (°)	1.0° plus $K\alpha$ separation
$2\theta_{max}$(°)	55
No. of reflections collected	380
Unique observed reflections	315 [$I > 3\sigma(I)$]
Refined parameters	50
R^a	0.0192
R'^b	0.0190
GOF	0.922
$(\Delta\rho)_{max,min}$(e Å^{-3})	0.89, −0.77

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

TABLE 2
Positional and Thermal Parameters (Å^2 × 100) for $LiFeAs_2O_7$

Atom	x	y	z	U_{eq}[a,b]
As	0.78358(8)	0.46144	0.5920(1)	0.56(2)
Fe	0.5	0.6252(3)	0	0.62(3)
O(1)	0.7503(7)	0.6055(7)	0.8223(9)	1.1(1)
O(2)	0.8322(8)	0.2821(8)	0.747(1)	1.3(1)
O(3)	0.6068(6)	0.4418(7)	0.2744(9)	0.7(1)
O(4)	0	0.540(1)	0.5	1.4(2)
Li	0	0.747(4)	0	3.6(6)

Anisotropic thermal parameters[c]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As	0.46(3)	0.61(3)	0.65(3)	0.06(2)	0.21(2)	0.06(3)
Fe	0.49(6)	0.65(6)	0.70(6)	0	0.13(4)	0
O(1)	1.1(2)	1.0(2)	1.4(2)	−0.5(1)	0.6(1)	−0.0(2)
O(2)	1.5(3)	0.7(2)	1.6(2)	0.6(2)	−0.0(2)	0.4(2)
O(3)	0.3(2)	0.9(3)	0.7(2)	0.1(2)	0.2(1)	0.0(2)
O(4)	0.4(3)	1.3(3)	2.6(3)	0	0.6(2)	0

[a] The lithium atom was refined with the isotropic thermal parameter.
[b] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.
[c] Anisotropic temperature factors are of the form Temperature = $\exp[-2\pi^2 (h^2U_{11}a^{*2} + \cdots + 2hkU_{12}a^*b^* + \cdots)]$.

multiplicity for Li was allowed to refine, but did not deviate significantly from full occupancy. Therefore, the Li was considered fully occupied in the final cycles of refinement. The structure was refined by full-matrix least-squares refinement based on F values. The Li atom was refined with the isotropic thermal parameter, and all other atoms were refined anisotropically. Corrections for anomalous dispersion and secondary extinction were made (coefficient = 0.027(1)). Neutral-atom scattering factors were used. Structure determination and refinement were performed on DEC MicroVAX computer system using the SHELXTL-PLUS programs. Tables of bond angles and observed and calculated structure factors are submitted as supplementary materials.

SHG measurements. The second harmonic generation response of powder $LiFeAs_2O_7$ was measured on an apparatus similar to that described by Dougherty and Kurtz in reflection mode (11). A Q-switched pulsed Nd : YAG laser operating at 1064 nm was used as the radiation source. The sample was loaded in a capillary of 1-mm inner diameter. The sample had an SHG signal about 9 times that of quartz, confirming the absence of a center of symmetry in the structure.

RESULTS AND DISCUSSION

The crystallographic data are listed in Table 1. The atomic coordinates, selected bond distances, and bond-valence sums are given in Tables 2 and 3. Atoms Li, Fe, and O(4) sit on twofold axes, and all other atoms are at general positions. The iron and arsenic atoms are six- and four-coordinated, respectively. A perspective view of the structure along the [001] direction is shown in Fig. 1. The framework consists of corner-sharing FeO_6 octahedra and AsO_4 tetrahedra. Lithium atoms are located in the infinite tunnels with heptagonal windows, each of which is formed by the edges of three octahedra and four tetrahedra. Each tunnel shows lateral pentagonal windows, which form straight tunnels parallel to the [110], [$\bar{1}$10], [1$\bar{1}$0], and [$\bar{1}\bar{1}$0] directions (Fig. 2). Therefore, the structure consists of intersecting tunnels running along the [001] and ⟨110⟩ directions, and the lithium ions are located at the intersection of these tunnels. In $LiFeP_2O_7$ lateral hexagonal windows are observed, but they do not form straight tunnels.

TABLE 3
Selected Bond Lengths (Å) and Bond-Valence Sums (Σs) for $LiFeAs_2O_7$

Li–O(1)	2.05(2)(2×)	Li–O(3)	2.09(2)(2×)
Σs(Li–O) = 0.80			
Fe–O(1)	2.052(5)(2×)	Fe–O(2)	1.931(6)(2×)
Fe–O(3)	2.016(5)(2×)		
Σs(Fe–O) = 3.16			
As–O(1)	1.668(6)	As–O(2)	1.657(6)
As–O(3)	1.683(4)	As–O(4)	1.735(3)
Σs(As–O) = 5.05			

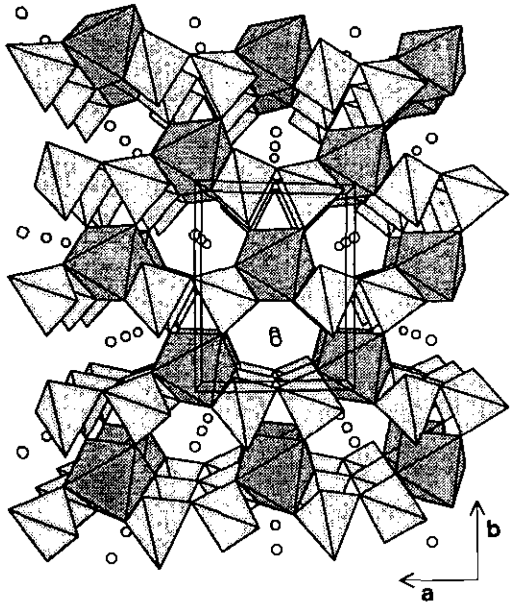

FIG. 1. Perspective view of the $LiFeAs_2O_7$ structure along the [001] direction. In this representation the corners of octahedra and tetrahedra are O atoms and the Fe and As atoms are at the center of each octahedron and tetrahedron, respectively. Open circles are Li atoms.

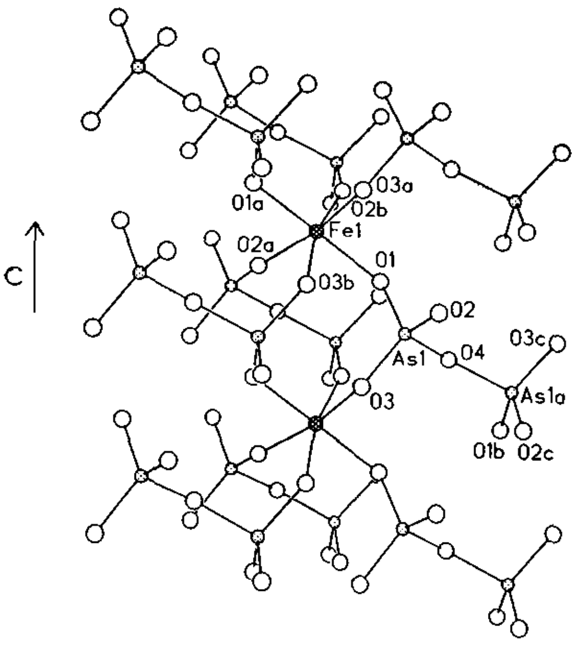

FIG. 3. Section of an infinite chain in the $LiFeAs_2O_7$ structure showing the coordination of As_2O_7 ligands around Fe atoms.

In $LiFeAs_2O_7$ each FeO_6 octahedron shares corners with six different As_2O_7 octahedra to form ${}^1_\infty[Fe(As_2O_7)_{6/2}]$ infinite chains along the [001] direction (Fig. 3). Each diarsenate group shares its six corners with six different FeO_6 octahedra belonging to three different ${}^1_\infty[Fe(As_2O_7)_{6/2}]$ chains. Thus, a three-dimensional architecture with the stoichiometry ${}^3_\infty[Fe(AS_2O_7)_{6/6}]$ is formed. In $LiFeP_2O_7$, each FeO_6 octahedron is linked to five different P_2O_7 groups. Each P_2O_7 group shares its six corners with five different FeO_6 octahedra and is bonded to one of the octahedra through bidentate bonding. The FeO_6 octahedron in $LiFeAs_2O_7$ is distorted as shown by the O · · · O distances (2.650–3.095 Å) and O–Fe–O bond angles (82.2–102.0°). The shortest O · · · O distance involves two O(3) atoms which are coordinated to the same Li atom. Namely, the FeO_6 octahedron and Li–O polyhedron share a common edge. The two O^{2-} anions forming the common edge are drawn closer together so that the two anions better shield the positive charges on the cations. The octahedral distortion can also be estimated by using the equation $\Delta = (1/6)\Sigma[(R_i - \bar{R})/\bar{R}]^2$, where R_i = individual bond length and $\bar{R}$ = average bond length (12). The calculation results show that FeO_6 in $LiFeAs_2O_7$ ($10^4 \times \Delta = 38.6$) is more distorted than that in $LiFeP_2O_7$ ($10^4 \times \Delta = 16.6$). The PO_4 tetrahedra of a P_2O_7 group in $LiFeP_2O_7$ point in the same direction and are in a nearly eclipsed configuration. In contrast, the two AsO_4 tetrahedra of a As_2O_7 group in $LiFeAs_2O_7$ point in opposite directions and are in a staggered configuration (Fig. 4). In the AsO_4 tetrahedra belonging to each diarsenate group the As atoms are displaced away from the bridging oxygen, O(4), so that one longer and three shorter As–O bonds are formed. Both the AsO_4 tetrahedra are distorted as shown by the O · · · O distances (2.576–2.883 Å) and O–As–O bond angles (98.4–118.7°). The As–O–As bond angle involving the bridging oxygen is 135.7°.

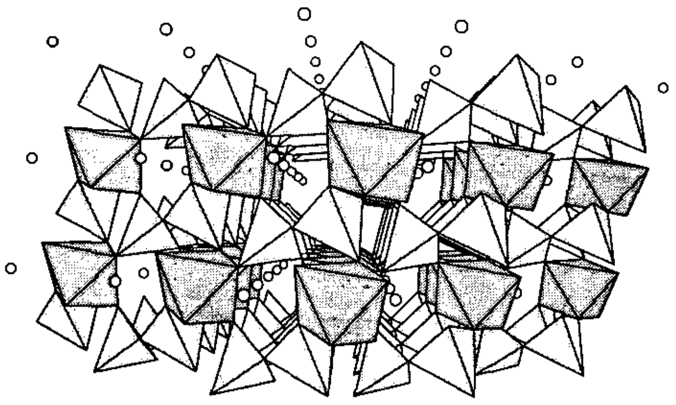

FIG. 2. Perspective view of the $LiFeAs_2O_7$ structure along the [110] direction.

The coordination number of the Li^+ ion was determined on the basis of the maximum gap in the Li–O distances ranked in increasing order. The maximum cation–anion distance according to Donnay and Allmann (13) was also

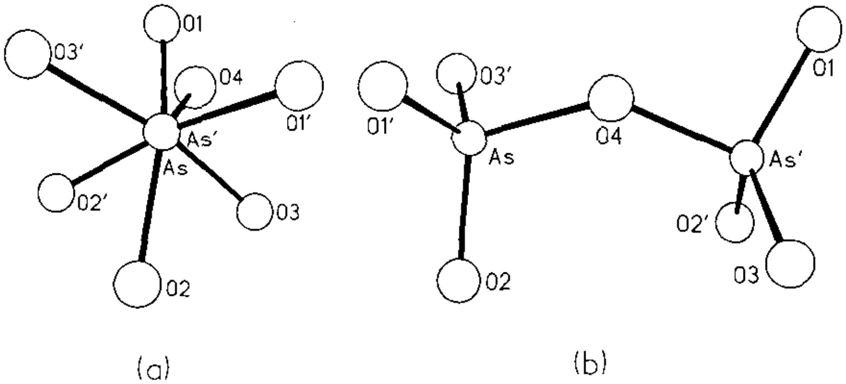

FIG. 4. View of a As_2O_7 group (a) parallel and (b) perpendicular to the As ··· As vector.

considered. Therefore, the Li+ ion is coordinated by four oxygen atoms and the fifth Li–O distance is 2.778 Å. The four Li–O bond lengths have an average value of 2.07 Å, which is shorter than the expected value of 2.12 Å predicted by Shannon (12) for ^{VI}Li–O, but longer than that for ^{IV}Li–O (1.95 Å). The bond valence sum for Li is somewhat lower than +1, indicative of a loosely bound Li atom. The four oxygen neighbors define a distorted tetrahedron (Fig. 5). In $LiFeP_2O_7$ the Li^+ ion is coordinated by four oxygen atoms in a geometry similar to SF_4.

This structural study shows that the As_2O_7 group is very adaptive to the bonding requirements of other groups in the structure by adjusting the As–O–As bond angle and the configuration of two AsO_4 tetrahedra. The size of the alkali metal cation should also play an important role in the crystal structure. Further research to synthesize alkali metal iron diarsenates is in progress.

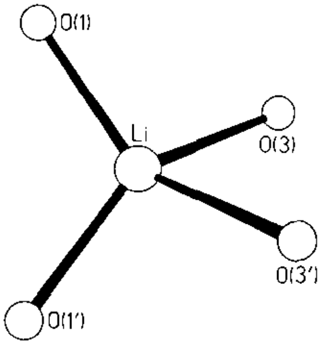

FIG. 5. View along [001] showing the environment of the Li^+ ion.

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