

BRIEF COMMUNICATIONS

Li₂ZnI₄: A Neutron Powder Study

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The crystal structure of Li₂ZnI₄ was determined by means of neutron powder diffraction studies at 298 K. The olivine-type structure (space group *Pnma*, $Z = 4$, $a = 1480.3(9)$, $b = 856.0(2)$, $c = 701.2(1)$ pm) was refined by the Rietveld method to a final $R_1 = 5.48\%$. In a nearly ideal hexagonal close-packed iodide ion arrangement, Li is located in octahedral, and Zn, in tetrahedral voids, respectively. Apart from the Zn-I distances, which are significantly shortened, the bond lengths obtained are as expected from the crystal radii. © 1990 Academic Press, Inc.

Introduction

Ternary lithium halides Li₂MCl₄ ($M = \text{Mg, V, Cr, Mn, Fe, Co, Cd}$) and Li₂MBr₄ ($M = \text{Mg, Mn, Cd}$) belong to the best lithium ion conductors known (1-4). The unusually high ionic conductivity of these compounds is connected with order-disorder phase transitions (5). Furthermore it has been proven that in the case of ternary chlorides with inverse spinel structure the mobility of tetrahedrally coordinated lithium ions is larger than that of lithium in octahedral voids (6). Therefore, we tried to synthesize new lithium halides with tetrahedrally coordinated lithium ions. The only ternary lithium iodide of the A₂BX₄ type obtained is

Li₂ZnI₄ oP28 (7), which likewise exhibits high ionic conductivity. In this paper, we present the results of our neutron powder diffraction studies.

Experimental

Li₂ZnI₄ was obtained by fusing stoichiometric amounts of anhydrous LiI and ZnI₂ in evacuated sealed borosilicate glass ampoules. Details are given elsewhere (7). The sample was characterized by X-ray Guinier photographs [Huber Guinier 600 system].

Neutron diffraction data (at 298 K) were collected on the powder diffractometer D2B with twofold collimation of 5' at the Institut Laue-Langevin (ILL) in Grenoble. A thin-walled vanadium can of 16 mm in diameter was used as sample container. The neutron

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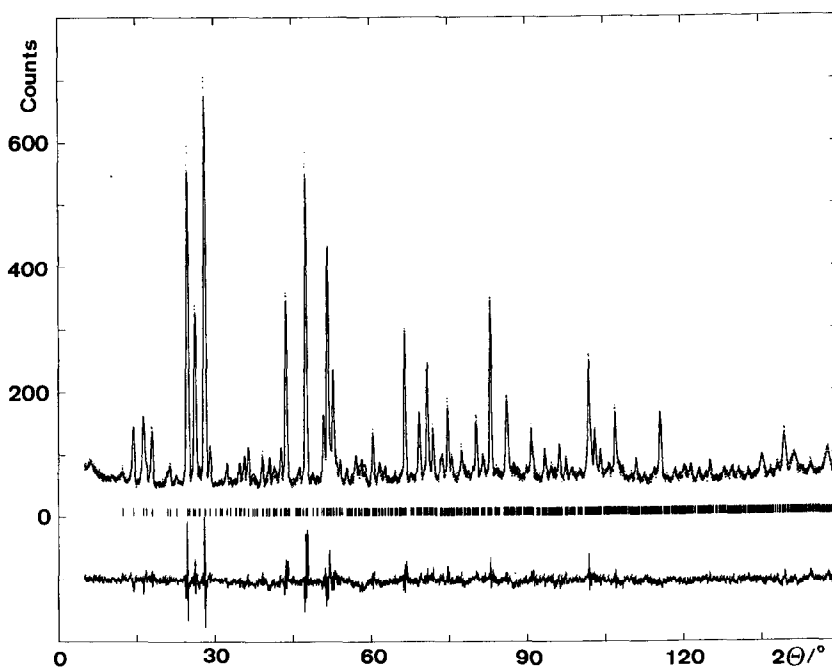


FIG. 1. Observed (···), fitted (---), and difference profiles for Li_2ZnI_4 . Calculated 2θ values indicated by vertical bars (|).

TABLE I

DATA OF STRUCTURE REFINEMENT AND STRUCTURAL PARAMETERS OF Li_2ZnI_4

Lattice constants: $a = 1480.3(9)$ pm

$b = 856.0(2)$ pm

$c = 701.2(1)$ pm

Space group: $Pnma$

$Z = 4$

Number of structural parameters: 18

Halfwidth parameters ($^{\circ 2}$) $U = 0.128(9)$

$V = -0.300(13)$

$W = 0.287(4)$

Atom	Position	Occupation	x	y	z	$B/10^4 \text{ pm}^2$
Li(1)	4a	4	0	0	0	3.6(6)
Li(2)	4c	4	0.269(2)	0.25	0.000(6)	4.9(10)
Zn	4c	4	0.0858(9)	0.25	0.4037(7)	2.4(1)
I(1)	4c	4	0.0918(8)	0.25	0.769(1)	2.1(3)
I(2)	4c	4	0.4228(10)	0.25	0.252(1)	2.1(3)
I(3)	8d	8	0.1700(7)	0.0063(9)	0.248(2)	2.6(2)

$R_{\text{wp}} = 13.25\%$ (expected 7.71%)

$R_1 = 5.48\%$

TABLE II
SELECTED INTERATOMIC DISTANCES (pm) AND ANGLES (°) OF OLIVINE-TYPE
Li₂ZnI₄ (esd's IN PARENTHESES)

		ZnI ₄ tetrahedron	
Zn-I(1)	256.3(9)	I(1)-Zn-I(2)	116.3(5)
Zn-I(2)	264.8(19)	2 × I(1)-Zn-I(3)	113.2(4)
		2 × I(2)-Zn-I(3)	104.9(3)
2 × Zn-I(3)	266.4(12)	I(3)-Zn-I(3)	103.1(5)
		LiI ₆ octahedra	
2 × Li(1)-I(1)	300.8(7)	I(1)-Li(1)-I(1)	180.0
2 × Li(1)-I(2)	298.5(7)	2 × I(1)-Li(1)-I(2)	91.3(2)
2 × Li(1)-I(3)	305.9(12)	2 ×	88.7(2)
		2 × I(1)-Li(1)-I(3)	94.5(3)
		2 ×	85.5(3)
		I(2)-Li(1)-I(2)	180.0
		2 × I(2)-Li(1)-I(3)	88.4(3)
		2 ×	91.7(3)
		I(3)-Li(1)-I(3)	180.0
Li(2)-I(1)	308.3(35)	I(1)-Li(2)-I(2)	173.9(15)
Li(2)-I(2)	288.2(37)	2 × I(1)-Li(2)-I(3)	83.8(7)
2 × Li(2)-I(3)	295.8(29)	2 × I(1)-Li(2)-I(3)	86.9(9)
2 × Li(2)-I(3)	308.6(30)	2 × I(2)-Li(2)-I(3)	91.7(10)
		2 × I(2)-Li(2)-I(3)	97.2(8)
		2 × I(3)-Li(2)-I(3)	169.4(11)
		2 × I(3)-Li(2)-I(3)	88.9(3)
		I(3)-Li(2)-I(3)	85.1(10)
		I(3)-Li(2)-I(3)	95.7(12)
I(1)-I(2)	418.8(14)-442.8(14)		
I(1)-I(3)	412.0(14)-445.5(14)		
I(2)-I(3)	421.2(16)-438.1(14)		

wavelength used was 159.4 pm. The 2θ range was 5–150°, the step-width being 0.025°. Background points were determined graphically.

Structural refinement was performed by means of a modified Rietveld program (8, 9) using the scattering lengths $b(\text{Li}) = -2.03$, $b(\text{Zn}) = 5.68$, and $b(\text{I}) = 5.28$ fm (10). The fractional coordinates of the isostructural Na₂ZnCl₄ (11) were used as starting parameters.

The R factors obtained are defined as $R_{\text{wp}} = 100\% \cdot [\sum w(Y_{\text{obsd}} - Y_{\text{calcd}})^2 / \sum wY_{\text{obsd}}^2]^{1/2}$, $R_{\text{exp}} = 100\% \cdot [(N - P + C) / \sum wY_{\text{obsd}}^2]^{1/2}$, $R_1 = 100\% \cdot \sum |I_{\text{obsd}} - I_{\text{calcd}}| / \sum I_{\text{obsd}}$ with $w = 1/\sigma_Y$ and $N - P + C =$ degrees of freedom.

Results and Discussion

The observed and fitted diffraction patterns of olivine-type Li₂ZnI₄ are shown in Fig. 1. The refinement converged to a final $R_1 = 5.48\%$, based on 1702 observations, containing 696 reflections and 1676 degrees of freedom. The final profile and structural parameters are given in Table I, selected interatomic distances and angles, in Table II. As described by Cockcroft and Fitch (12) the relatively large R_{wp} factor results from a non-Gaussian peak shape due to a defective monochromator on D2B, but does not affect the refinements in any way. The quality of the fit may be judged from Fig. 1.

The site occupancy of both lithium posi-

tions was found to be 100%. Attempts to refine the structure, assuming disorder, e.g., interchange of lithium and zinc, failed.

Li_2ZnI_4 crystallizes with a nearly hexagonal close-packed arrangement of iodide ions. The lithium ions are located in octahedral voids, the zinc ions in tetrahedral ones.

The I-I interatomic distances (412.0(14)–445.5(14) pm) correspond to the sum of the crystal radii, viz. 412 pm (13). The Zn-I distances (256.3(9)–266.4(12) pm) are significantly shorter than the sum of the crystal radii (280 pm), but resemble those in ZnI_2 (14). The Li-I distances (295.8(29)–308.6(30) pm) are as expected from the sum of the crystal radii (296 pm).

The high ionic conductivity of Li_2ZnI_4 (7) compared especially to that of LiI may be due to the great number of empty octahedral sites. However, partial occupation of these sites could not be observed.

Acknowledgments

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