JOURNAL OF SOLID STATE CHEMISTRY **104**, 391–396 (1993)

A Single-Crystal X-Ray Diffraction Study of Lithium Zirconate, $Li_6Zr_2O_7$, a Solid-State Ionic Conductor

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Received May 14, 1992; in revised form September 21, 1992; accepted November 2, 1992

The structure of lithium zirconate ($Li_6Zr_2O_7$) has been solved by the single-crystal X-ray method. $Li_6Zr_2O_7$ is monoclinic, space group *C*2/*c* and cell parameters a = 10.440(4), b = 5.991(1), c = 10.204(2) Å, β = 100.25(3)°, Z = 8 (for the asymmetric unit $Li_3ZrO_{7/2}$). A least-squares refinement gave conventional and weighted R factors of 0.041 and 0.052, respectively. The structure is of the NaCl type and is characterized by an ordered anionic deficiency. As a consequence the coordination number of the Li atoms is 5, with the coordination geometry of a distorted square pyramid. Also, the oxygen octahedron around each Zr atom is significantly distorted. A comparison between $Li_6Zr_2O_7$ and Li_2ZrO_3, another phase of the NaCl type, shows that the structure of the former compound is more "open" than that of Li_2ZrO_3 and, for this reason, a higher mobility of both the Li^+ and O^{2-} ions can be expected for the former phase. These results are in agreement with conductivity measurements.

Introduction

The system Li_2O-ZrO_2 has recently drawn attention and has been widely investigated due to the interesting physical properties of many of its phases, possible candidates in applications as solid-state ionic conductors and ceramics in thermonuclear fusion reactors.

Several well-defined compounds, such as Li_2ZrO_3, $Li_{5.52}Zr_{2.62}O_8$, $Li_6Zr_2O_7$, and Li_8ZrO_6, have been identified by X-ray powder diffraction in this system. However, the crystal structure was determined only in the former three cases (Refs. *1*, *2*, and *3*, respectively). The powder pattern of $Li_6Zr_2O_7$ was found to be identical to that reported in the JCPDS file under the title "Li_4ZrO_4." In fact no evidence for the existence of this phase was ever found and a new JCPDS card (N.34-312) is labeled as "$Li_6Zr_2O_7$." As shown in Ref. (*3*) and in the present paper the latter phase is monoclinic. An apparently metastable polymorph of $Li_6Zr_2O_7$ was also investigated by Enriquez *et al.* (*4*) and by Wyers and Cordfunke (*5*), and was found to be triclinic by X-ray powder diffraction. The single-crystal X-ray diffraction study of $Li_6Zr_2O_7$ was carried out because of the interesting properties of the phases in the Li_2O–ZrO_2 system and of the relative paucity of structural information about them.

Experimental Procedures

The crystals of monoclinic $Li_6Zr_2O_7$ were grown during attempts to prepare Li_4ZrO_4

0022-4596/93 $5.00

TABLE I

ATOMIC POSITIONAL AND THERMAL PARAMETERS

Atom	*x*	*y*	*z*	B(Å^2)	Mult.
Zr	0.18351(1)	−0.12161(3)	0.36469(1)	0.224(1)	1.0
Li(1)	0.2064(5)	0.3682(8)	0.3946(5)	0.88(5)*	1.0
Li(2)	0.4349(6)	0.1410(9)	0.4163(6)	1.39(8)*	1.0
Li(3)	0.0654(5)	0.0973(8)	0.1019(5)	0.84(6)*	1.0
O(1)	0.2499(2)	0.1119(2)	0.2453(2)	0.71(2)	1.0
O(2)	0.1333(1)	−0.3664(2)	0.5018(1)	0.43(1)	1.0
O(3)	0.1218(1)	0.1227(2)	0.4775(1)	0.48(1)	1.0
O(4)	0.000	−0.1486(4)	0.250	0.87(3)	0.5

Note. Site multiplicities are given in the last column. Starred atoms were refined isotropically. The anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, defined as $\frac{4}{3} \cdot [a^2 \cdot B(1, 1) + b^2 \cdot B(2, 2) + c^2 \cdot B(3, 3) + ab(\cos \gamma) \cdot B(1, 2) + ac(\cos \beta) \cdot B(1, 3) + bc(\cos \alpha) \cdot B(2, 3)]$. $R = 0.041$, $R_w = 0.052$. Space group $C2/c$, $Z = 8$ (for the asymmetric unit $Li_3ZrO_{7/2}$). Calculated density $d = 3.870$ g cm^{-3}. Lattice parameters: $a = 10.440(4)$, $b = 5.991(1)$, $c = 10.204(2)$ Å, $\beta = 100.25(3)°$.

in an effort to clarify the phase diagram of the Li_2O–ZrO_2 system. No phase with the composition Li_4ZrO_4 was ever obtained.

A specimen of the composition $2Li_2O : ZrO_2$ was heated in a sealed Pt tube to approximately 1400°C, slow cooled at ~3°/hr to 800°C, and removed from the furnace. The crystals in this specimen proved to be the new phase $Li_6Zr_2O_7$.

$Li_6Zr_2O_7$ crystallizes in space group $C2/c$ with $a = 10.440(4)$, $b = 5.991(1)$, $c = 10.204(2)$ Å, $\beta = 100.25(3)°$. The intensities of 4229 Bragg reflections were measured with a Nonius CAD-4 diffractometer using monochromated Mo*Kα* radiation ($\lambda = 0.71073$ Å) and empirically corrected for absorption. The structure was solved by Patterson and Fourier methods and refined by least squares to conventional and weighted R factors of 0.041 and 0.052 respectively, for the 2966 reflections with $I \geq 3\sigma(I)$. All calculations were performed with standard Nonius programs. The structural parameters are given in Tables I and II.

Results and Discussion

The rock-salt type structure is characterized by an ordering of the cations with sequences $(O{-}Zr)_2{-}(O{-}Li)_6$ along a direction parallel to one of the edges of a face-centered pseudocubic cell ($a_c = 4.28$ Å) which can be obtained from the monoclinic cell with the transformation

$$(-\tfrac{1}{8}\ \tfrac{1}{2}\ \tfrac{1}{4},\ -\tfrac{1}{8}\ -\tfrac{1}{2}\ \tfrac{1}{4},\ \tfrac{3}{8}\ 0\ \tfrac{1}{4})$$

(Fig. 1). In fact one of the oxygen ions (O(4)) in the asymmetric unit ($Li_3ZrO_{7/2}$) is in a

TABLE II

TABLE OF GENERAL TEMPERATURE FACTORS—*B*

Atom	$B(1, 1)$	$B(2, 2)$	$B(3, 3)$	$B(1, 2)$	$B(1, 3)$	$B(2, 3)$
Zr	0.087(3)	0.277(3)	0.306(3)	0.017(3)	0.030(2)	0.012(4)
O(1)	0.93(3)	0.53(3)	0.75(3)	−0.20(2)	0.34(2)	0.12(2)
O(2)	0.22(2)	0.48(3)	0.58(2)	−0.06(2)	0.04(2)	0.03(3)
O(3)	0.34(2)	0.49(2)	0.65(2)	0.03(3)	0.17(2)	−0.05(3)
O(4)	0.29(4)	1.26(6)	0.92(5)	0	−0.28(4)	0

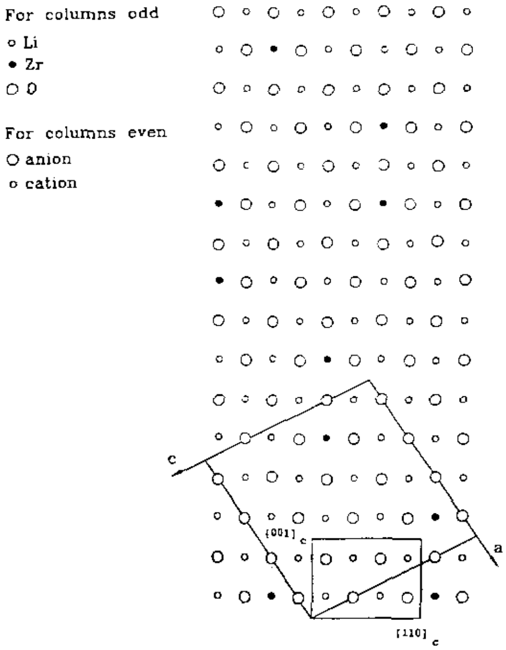

FIG. 1. Orthogonal projection on the (1$\bar{1}$0) plane of the NaCl structure (idealized structure for $Li_6Zr_2O_7$). Ordering of the cations in $Li_6Zr_2O_7$ is indicated by the different representations of Zr(●) and Li(○) ions. In this representation, for the sake of clarity, only atoms at $y \cong 0.9$ are given.

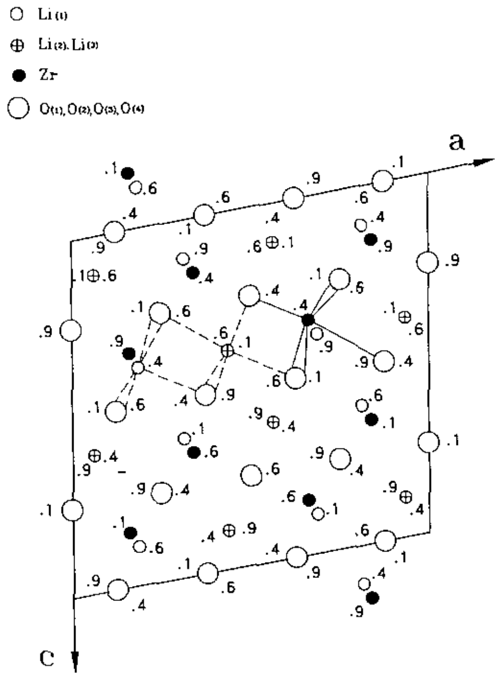

FIG. 2. Orthogonal projection of the $Li_6Zr_2O_7$ structure on the (010) plane of the monoclinic cell.

special position (on a twofold axis) and therefore the structure is characterized by an ordered anionic deficiency, with 32 cations and 28 oxygen ions in the unit cell. Indeed on the twofold axes of the monoclinic cell every other anionic site, expected for the idealized NaCl structure, is empty and, as a consequence, the coordination number of the lithium ions is five, with coordination geometries of distorted square pyramids (Fig. 2). Indeed a Fourier difference map calculated at the end of the refinement does not show significant peaks in the region of the empty anionic sites. The Zr coordina-

TABLE III

SELECTED INTERATOMIC DISTANCES (IN Å)

Zr–O(1)	2.055(1)	Li(1)–O(1)	2.265(4)
O(1)	2.138(1)	O(1)	2.147(4)
O(2)	2.155(1)	O(2)	2.146(4)
O(2)	2.143(1)	O(3)	1.981(4)
O(3)	2.037(1)	O(3)	2.022(4)
O(4)	2.066(0)		
Li(2)–O(1)	2.367(6)	Li(3)–O(1)	2.204(4)
O(2)	2.100(5)	O(2)	2.098(4)
O(2)	2.031(4)	O(3)	1.990(4)
O(3)	1.938(4)	O(3)	1.983(4)
O(4)	2.311(5)	O(4)	2.299(4)

TABLE IV

Selected Interatomic Bond Angles (in °)

O1–Zr–O1	91.24(1)	O1–Li(1)–O1	85.53(14)
O1–Zr–O2	174.23(4)	O1–Li(1)–O2	167.75(21)
O1–Zr–O2	92.44(4)	O1–Li(1)–O3	86.68(15)
O1–Zr–O3	91.14(4)	O1–Li(1)–O3	101.02(17)
O1–Zr–O4	95.40(5)	O1–Li(1)–O2	88.40(15)
O1–Zr–O2	88.39(4)	O1–Li(1)–O3	162.26(23)
O1–Zr–O2	88.40(4)	O1–Li(1)–O3	98.15(17)
O1–Zr–O3	177.22(4)	O2–Li(1)–O3	96.10(16)
O1–Zr–O4	89.97(5)	O2–Li(1)–O3	90.35(16)
O2–Zr–O2	81.79(4)	O3–Li(1)–O3	98.98(18)
O2–Zr–O3	89.09(4)		
O2–Zr–O4	90.36(5)		
O2–Zr–O3	90.06(4)		
O2–Zr–O4	172.02(5)		
O3–Zr–O4	91.25(5)		
O1–Li(2)–O2	156.85(24)	O1–Li(3)–O2	87.80(15)
O1–Li(2)–O2	86.79(18)	O1–Li(3)–O3	97.28(16)
O1–Li(2)–O3	100.13(19)	O1–Li(3)–O3	161.70(22)
O1–Li(2)–O4	78.88(16)	O1–Li(3)–O4	85.16(13)
O2–Li(2)–O2	101.75(20)	O2–Li(3)–O3	91.97(16)
O2–Li(2)–O3	99.19(23)	O2–Li(3)–O3	97.81(16)
O2–Li(2)–O4	85.37(16)	O2–Li(3)–O4	167.89(20)
O2–Li(2)–O3	101.39(21)	O3–Li(3)–O3	99.91(18)
O2–Li(2)–O4	154.14(26)	O3–Li(3)–O4	98.68(15)
O3–Li(2)–O4	99.86(17)	O3–Li(3)–O4	86.09(15)

tion number is six and the oxygen octahedron is significantly distorted (Fig. 2). As can be easily verified in Fig. 2, the coordination polyhedra share corners and edges. In particular O(3) is a common corner to the three oxygen square pyramids of Li(1), Li(2), and Li(3) and to the Zr octahedron. In all cases the lithium atoms are significantly shifted from the centers of gravity of their coordination polyhedra toward positions opposite to those of the empty anionic sites.

The most relevant bond distances and angles are given in Tables III and IV, respectively. Calculations based on the bond-valence method (*6*) give the valence values reported in Table V. These values are in reasonable agreement with those expected.

In Table V the average Zr–O and Li–O distances are also reported. The indices of distortion of the various coordination polyhedra, defined as the standard deviation $\sigma(\overline{M\text{–}O})$ of the average $\overline{M\text{–}O}$ distances, are also given. The $\sigma(\overline{M\text{–}O})$'s of the oxygen polyhedra about the Li atoms are greater than those of the Zr octahedra by one order of magnitude. For Li(1), Li(2), and Li(3), the values of those indices are 0.11, 0.18, and 0.14, respectively. The higher values are related to the square pyramids having a corner occupied by O(4), the oxygen atom

TABLE V

Selected Interatomic Distances

M–O	$\overline{M\text{–}O}$	$\sigma(\overline{M\text{–}O})$	Valence
Zr–O	2.099	0.052	3.98(1)
Li(1)–O	2.112	0.113	0.93(1)
Li(2)–O	2.149	0.183	0.89(1)
Li(3)–O	2.115	0.137	0.93(1)

Note. Calculated valences for M are given in the last column. Calculated valency values for the four independent oxygen atoms are 1.89, 1.88, 1.98, and 1.92, respectively.

TABLE VI

Compound	Ref.	Li	C.N.	$(Li–O)_{min}$	$(Li–O)_{max}$	$(\overline{Li–O})$	$\sigma(\overline{Li–O})$
Li_2WO_4(ii)	(*7*)	Li(1)	4	1.82(4)	2.22(5)	2.02	0.23
		Li(2)	6	1.76(4)	2.44(5)	2.10	0.30
Li_2WO_4(iv)	(*8*)		4	1.62(5)	2.32(5)	1.98	0.31
Li_2SnO_3	(*1*)	Li(1)	6	2.141(10)	2.297(10)	2.208	0.06
		Li(2)	6	2.127(5)	2.247(3)	2.202	0.06
		Li(3)	6	2.170(3)	2.21(4)	2.189	0.02
Li_2ZrO_3	(*1*)	Li(1)	6	2.06(1)	2.418(3)	2.215	0.16
		Li(2)	6	2.15(1)	2.257(1)	2.208	0.05
α-Li_3TaO_4	(*9*)		6	—	—	2.162[a]	0.09[a]
β-Li_3TaO_4	(*9*)	Li(1)	6	—	—	2.162	0.045
		Li(2)	6	—	—	2.176	0.048
		Li(3)	6	—	—	2.138	0.066

Note. Distances are given in Å. C.N. is the coordination number. $(Li–O)_{min}$, $(Li–O)_{max}$, and $(\overline{Li–O})$ are respectively the smallest, greatest, and averaged Li–O distances. $\sigma(\overline{Li–O})$ is the standard deviation on the $(\overline{Li–O})$ values.

[a] Average on 12 different Li atoms.

located on a twofold axis. In this connection, it is interesting to note that the *B*(2, 2) and *B*(3, 3) thermal parameters of O(4) are larger than *B*(1, 1). For O(4), while the equivalent isotropic thermal parameter B_{eq} (Table I) is 0.87(3), the general temperature parameters *B*(2, 2) and *B*(3, 3) are 1.26(6) and 0.92(5), respectively (Table II). These results may indicate some degree of positional disorder for this oxygen atom.

It may be interesting to compare the structure of $Li_6Zr_2O_7$ with that of Li_2ZrO_3 (*1*), looking for possible correlations with their ionic conduction properties.

Both structures are of the NaCl type. However, the distribution of the cations is different in the two phases, and for this reason they cannot be considered isostructural.

In Li_2ZrO_3, all cations have octahedral coordination and the structure has to be considered as close packed, and only the relatively large Li–O average distance of 2.212 Å may explain the small conductivity shown by this phase.

In $Li_6Zr_2O_7$ the average (Li(2)–O) distance is greater than the average distances of two 6-coordinated Li ions in Li_2WO_4 (*7*) and β-Li_3TaO_4 (*9*). Moreover, the maximum (Li(2)–O) distance is higher than four of six $(Li–O)_{max}$ distances reported in Table VI for the 6-coordinated Li ions. Thus the structure of $Li_6Zr_2O_7$ is more "open" than that of Li_2ZrO_3, and for this reason both the Li^+ and the O^{2-} ions may have a higher mobility in $Li_6Zr_2O_7$ than in Li_2ZrO_3. These results are in agreement with conductivity measurements (*10*). The measured ionic conductivity of $Li_6Zr_2O_7$, identified as "Li_4ZrO_4" in Ref. (*10*), is higher than that of Li_2ZrO_3 by one order of magnitude.

Whether the conductivity in $Li_6Zr_2O_7$ is cationic or anionic or both is not clear. Hellstrom and Van Gool (*10*) do not take into consideration the possibility of a significant mobility of the oxygen ions. However, in view of the high values of the thermal parameters for O(1) and O(4) (see Table II), one cannot exclude a mechanism of anionic conduction being, at least partially, active in $Li_6Zr_2O_7$. Further conductivity experiments, with a variable partial pressure of oxygen at the anode, may give an answer to this question.

Acknowledgment

Three of us (M. Z., I. N. S., and L. E. D.) acknowledge financial support by the Progetto Finolizzato Materiali Speciali per Tecnologie Avanzate, Consiglio Nazionale delle Ricerche, Rome, Italy.

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