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Neutron Profile Refinement of the Structures of Li_2SnO_3 and Li_2ZrO_3

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The crystal structures of the compounds Li_2SnO_3 and Li_2ZrO_3 have been refined with the Rietveld method [H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969)] using neutron powder diffraction data collected at room temperature. Both compounds crystallize with the symmetry of space group $C2/c$. For Li_2SnO_3, $Z = 8$, and the lattice parameters obtained from the refinement are $a = 5.2889(2)$, $b = 9.1872(3)$, $c = 10.0260(3)$ Å, and $\beta = 100.348(2)°$. For Li_2ZrO_3, $Z = 4$, and $a = 5.4218(2)$, $b = 9.0216(4)$, $c = 5.4187(2)$ Å, and $\beta = 112.709(2)°$. Both compounds have NaCl-type structures in which the oxygen anions, as well as the cations, form a distorted cubic close-packed network. The order among the lithium and the tetravalent cations is different in the two compounds. In Li_2SnO_3, there are two types of layers perpendicular to c^*, one with Li^+ only and one with Li^+ and Sn^{4+} in the ratio 1 : 2. In Li_2ZrO_3, the layers perpendicular to c^* are all the same with Li^+ and Zr^{4+} ions in the ratio 2 : 1. The different arrangement of the cations in the two structures can be explained in terms of the difference in size of Sn^{4+} and Zr^{4+}.

Introduction

Compounds of the type Li_2BO_3 (B Ti, Mo, Pd, etc.) are of interest as possible Li^+ ion conductors if nonstoichiometry can be introduced into their structures (*1*). Li_2SnO_3 and Li_2ZrO_3 are important representatives of this class of compounds.

The structure of Li_2SnO_3 was determined by X-ray single-crystal and powder techniques (*2*). Lattice parameters and space group were determined from Weissenberg, precession, and Guinier photographs. The compound is monoclinic with space group $C2/c$. There are eight molecules per unit cell. The atomic positions of all the Sn^{4+} and O^{2-} ions and those of $12Li^+$ were determined from Patterson and difference Fourier maps, but the remaining four Li^+ ions were not located from the maps, and their position was assumed on the basis of chemical and lattice energy considerations.

The structure of Li_2ZrO_3 was also determined by X-ray methods (*3*). The symmetry, again, is monoclinic. The lattice parameters a, b, and β of this compound are similar to the corresponding ones of Li_2SnO_3, but the c parameter is about half that of the tin compound. There are four molecules per unit cell. The atomic positions of the metal and oxygen ions were determined from Patterson and difference

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Fourier syntheses, and on the basis of these positions it was decided that the structure does not have a center of symmetry and belongs to space group *Cc*. Because of strong absorption and anomalous dispersion effects it was not possible to determine the positional parameters of any of the Li^+ ions, and a number of possible models were discussed.

A knowledge of the location of all the atomic species in the unit cells of the two compounds is essential for a meaningful comparison of the two structures. The powder neutron diffraction study was carried out in order to confirm or reject the assignment of the Li^+ positions in Li_2SnO_3 and to decide where the Li^+ ions are located in the structure of Li_2ZrO_3.

Experimental

The specimens of Li_2SnO_3 and Li_2ZrO_3 were prepared for neutron diffraction examination by mixing and grinding together the appropriate quantities of Li_2CO_3 and the corresponding oxides to give a final 30-g batch. All materials were of commercial grade and were designated chemically pure. The mixtures were first calcined at 700°C for 24 hr to obtain preliminary reaction and to release most of the CO_2, then reground and reheated repeatedly, first at 1000°C for 16 hr and then at 1400°C for several hours in a tightly covered Pt crucible. After each hour at 1400°C, the material was removed from the furnace and a portion was examined by X-ray diffraction to determine crystallinity and the degree of combination.[1] When all of the peaks of the oxide and/or other phases had disappeared and the diffraction peaks of the desired phase were strong and sharp with distinct α_1–α_2 doublets at 30–40° 2θ, the specimens were deemed ready for final study. Studies on the system Li_2O–ZrO_2 have shown that the phase Li_2ZrO_3 can exist as a nonstoichiometric solid solution and that unit cell dimensions vary considerably with the Li_2O content (R. S. Roth, unpublished results). Lattice parameter measurements indicate that the composition of the sample used in this study is very close to Li_2ZrO_3. No problems of composition exist in the Li_2O–SnO_2 system, since no measurable region of nonstoichiometry has been found for the phase Li_2SnO_3.

Neutron diffraction data were collected, for both compounds, at room temperature with a five-detector diffractometer at the National Bureau of Standards Reactor. The conditions used in the experiments are summarized in Table I. The neutron intensities were analyzed with the Rietveld method (*4*), modified by Prince (*5*) to simultaneously process the data from the five counters of the diffractometer. The background was assumed to be a straight line of finite slope and was refined for each of the five channels of the diffractometer together with the profile and structural parameters. The initial values of the lattice parameters were determined by X-ray powder diffraction, and the profile parameters *U*, *V*, and *W*, which define the full-width at half-maximum of the Bragg reflections, were calculated with the formulas derived by Caglioti *et al.* (*6*). The neutron-scattering amplitudes used in the calculations were $b(O) = 0.58$, $b(Sn) = 0.62$, $b(Zr) = 0.71$, and $b(Li) = -0.214 \times 10^{-12}$ cm (*7*). In all cases a refinement was considered complete when the factor R_w[2] did not change by more than one part in a thousand in two successive cycles.

For Li_2SnO_3, the space group was as-

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[1] Cu$K\alpha$ radiation and a high-angle diffractometer equipped with a graphite monochromator were used in these measurements.

[2] The *R* factors used in profile analysis are defined in a number of publications. See, for example, Hewat (*8*).

TABLE I

EXPERIMENTAL CONDITIONS USED TO COLLECT THE NEUTRON POWDER INTENSITY DATA FOR Li_2SnO_3 AND Li_2ZrO_3

Monochromatic beam:	Reflection 220 of a Cu monochromator	
Wavelength:	1.5416(3) Å	
Horizontal divergences:	(a) in-pile collimator:	10′ arc
	(b) monochromatic beam collimator:	20′ arc
	(c) diffracted beam collimator:	10′ arc
Monochromator mosaic spread:	~15′ arc	
Sample container:	Vanadium can ~10 mm in diameter	
Angular ranges scanned by each detector:	5–40, 25–60, 45–80, 65–100, 85–120	
Angular step: 0.05°		

sumed to be $C2/c$ and the initial positions of all atoms were those given by Kreuzburg *et al.* (*2*). At first the isotropic thermal parameters assigned to the atoms were kept fixed during the refinement, while the profile and positional parameters were allowed to change. The R factors obtained in these calculations are $R_N = 6.04$, $R_p = 6.93$, $R_w = 8.96$, and $R_E = 6.73$. These values show that the assignment of the Li^+ positions is correct. A subsequent refinement in which the occupancies of the Li^+ ions were allowed to vary showed that the occupancy parameter of Li(1), located in the eightfold position of space group $C2/c$, is not significantly different from one, while those of the Li^+ ions in the fourfold positions $4d\bar{1}$ and $4e2$ are significantly lower than 0.5 (~0.4). It is conceivable that tin ions may replace some Li^+ ions with the formation of cationic vacancies. However, such substitution, if present, would almost certainly involve Sn^{2+} ions rather than Sn^{4+} ions because the electrostatic charge unbalance, and the consequent structural distortions, caused by Sn^{2+} would be much smaller than those introduced by the Sn^{4+} ions. Our results are therefore compatible with a model containing, in positions $4d\bar{1}$ and $4e2$, about 4% Sn^{2+}, 4% vacancies, and 92% Li^+. A choice between the two models, however, is difficult, because the values of χ obtained in the

TABLE II

RESULTS OF THE PROFILE REFINEMENT OF THE STRUCTURE OF Li_2SnO_3

Atom	Position	x	y	z	B (Å^2)	Multiplicity
Sn(1)	$4e2$	0	0.418(1)	$\frac{1}{4}$	0.2	0.5
Sn(2)	$4e2$	0	0.750(1)	$\frac{1}{4}$	0.2	0.5
O(1)	$8f1$	0.1387(7)	0.2610(7)	0.1339(3)	0.48(8)	1.0
O(2)	$8f1$	0.1118(6)	0.5853(7)	0.1340(2)	0.19(6)	1.0
O(3)	$8f1$	0.1343(6)	0.9078(7)	0.1322(3)	0.15(6)	1.0
Li(1)	$8f1$	0.231(2)	0.073(1)	−0.0006(7)	1.5	1.0
Li(2)	$4d\bar{1}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	1.5	0.41(1)
Li(3)	$4e2$	0	0.083(6)	$\frac{1}{4}$	1.5	0.394(8)

Note. $R = 5.27$, $R_p = 6.68$, $R_w = 8.67$, $R_E = 6.73$. Space group $C2/c$, $Z = 8$. $a = 5.2889(2)$, $b = 9.1872(3)$, $c = 10.0260(3)$ Å, $\beta = 100.348(2)°$. Number of observations: 3273. Number of independent Bragg reflections: 358.

TABLE III

RESULTS OF THE PROFILE REFINEMENT OF THE STRUCTURE OF Li_2ZrO_3

Atom	Position	x	y	z	B (Å²)	Multiplicity
Zr	$4e2$	0	0.0916(5)	$\frac{1}{4}$	0.16(5)	0.5
O(1)	$4d\bar{1}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	0.40(5)	0.5
O(2)	$8f1$	0.2721(4)	0.5754(3)	0.4863(4)	0.31(4)	1.0
Li(1)	$4e2$	0	0.423(2)	$\frac{1}{4}$	1.4(3)	0.45(1)
Li(2)	$4e2$	0	0.742(2)	$\frac{1}{4}$	1.1(3)	0.46(1)

Note. $R = 5.01$, $R_p = 6.35$, $R_w = 8.82$, $R_E = 5.09$. Space group $C2/c$, $Z = 4$. $a = 5.4218(2)$, $b = 9.0216(4)$, $c = 5.4187(2)$ Å, $\beta = 112.709(2)°$. Number of observations: 2505. Number of independent Bragg reflections: 186.

two cases are too close to the limit imposed by the Gaussian approximation.[3] The positional parameters are practically unaffected by the structural model. In fact, the atomic coordinates obtained in the two refinements differ, on the average, by less than two standard deviations, and only for the y coordinate of the Li(3) ion is the difference almost 5σ. To avoid the uncertainties associated with the choice of the model, we will therefore consider in what follows only those conclusions which depend on the positions of the atoms in the unit cell. In Table II, the results of the second refinement are shown.

The refinement of Li_2ZrO_3 was based on space group Cc. The initial positional parameters were those determined by Dittrich and Hoppe (*3*). The results of these calculations, in which both positional and thermal parameters were allowed to vary, showed that the final atomic coordinates were consistent, to within one standard deviation, with a center of symmetry. A second refinement based on space group $C2/c$ and starting with the same initial parameters was therefore carried out. The centrosymmetric model refined to R factors equal to those obtained previously and the thermal parameters were more reasonable than those obtained for the acentric structure [for example, $B(O2) = -0.12(40)$ in Cc and $B(O2) = 0.25(4)$ Å² in $C2/c$]. We would like to note at this point that the choice of the space group was initially made by Dittrich and Hoppe (*3*) on the basis of the oxygen positions determined from a difference Fourier map. The atomic coordinates refined by these authors (with a final $R = 6.8\%$, based on structure factors) were shifted from the centrosymmetrical positions by as much as 9σ. These results, however, are not necessarily significant, because the model considered in the calculations was incomplete (all the Li^+ ions were missing), and the measured intensities were strongly affected by absorption. No such shortcomings exist in the neutron experiment, and it seems more likely that the structure of Li_2ZrO_3 has symmetry $C2/c$ rather than Cc. All subsequent refinements were therefore based on the centric space group. A difference Fourier map calculated after the neutron refinement in $C2/c$ showed three small bumps in correspondence to the positions of Li(2) in the ab plane and slightly above and below one-fourth along the c axis. This feature could be interpreted as due to disorder, i.e., to a very small departure of Li(2) from the arrangement dictated by space group $C2/c$. (The cations involved move toward the

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[3] Least-squares fits of single peaks of standard materials, such as Al_2O_3, analyzed with the same experimental conditions used in this work give, for the Gaussian approximation, an average value of χ between 1.15 and 1.30.

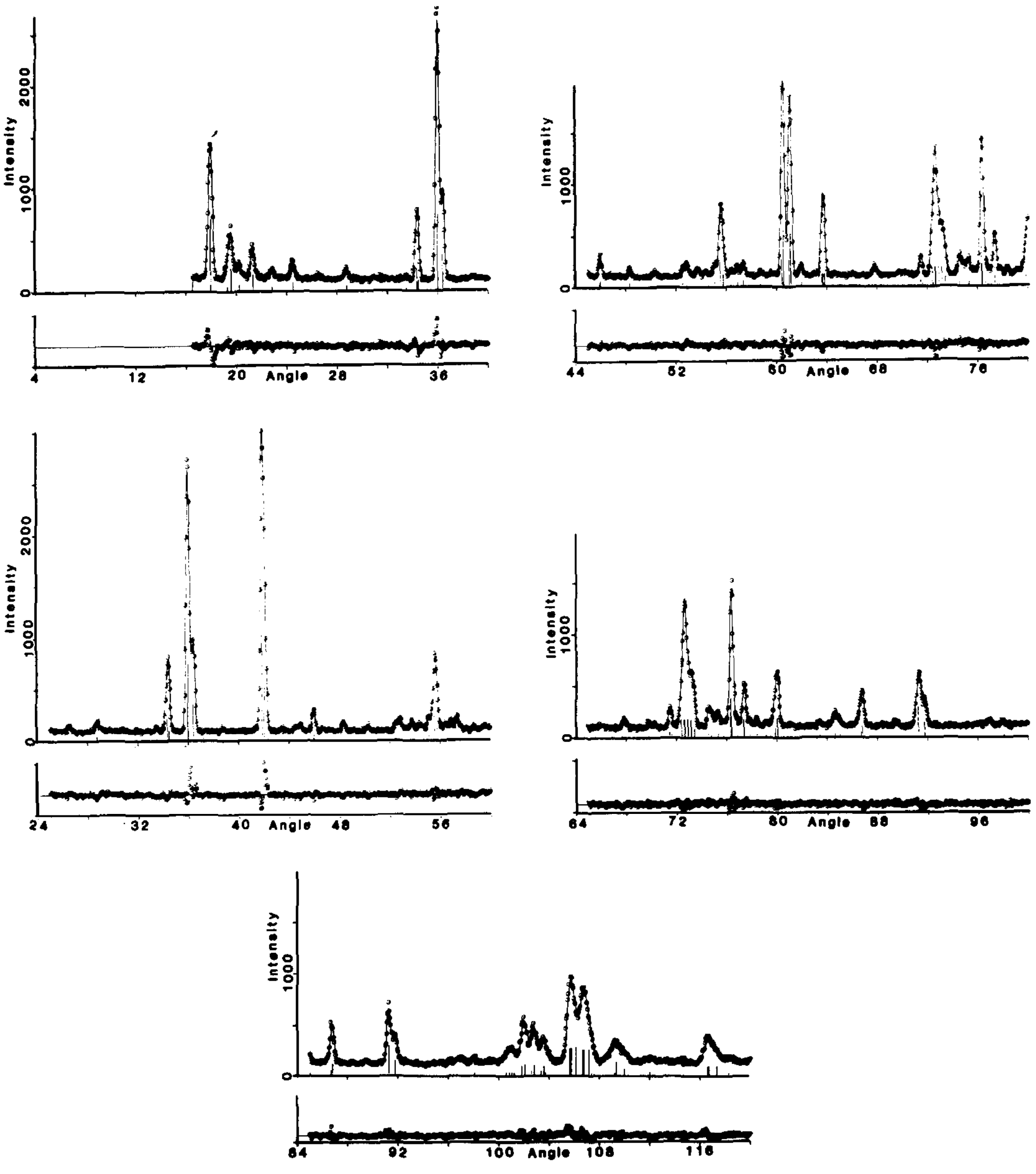

FIG. 1. Observed (circles), calculated (continuous line), and difference profiles for Li_2SnO_3.

O–O octahedral edges shared with three Zr-occupied octahedra.) The inclusion in the refinement of the occupancy parameters of Li(1) and Li(2) gave values lower than 0.5. These differences, however, do not seem significant. This result may be an indication that the substitution of Li^+ by Zr^{4+}, if present, is less important than that of Li^+ by Sn^{2+} in Li_2SnO_3. As in the previous case, a choice of the model is not possible. The final parameters for the disordered configuration of Li_2ZrO_3 are given in Table III.[4] Figures 1 and 2 show the calculated and

[4] Tables of observed and calculated intensities for Li_2SnO_3 and Li_2ZrO_3 can be obtained from the authors.

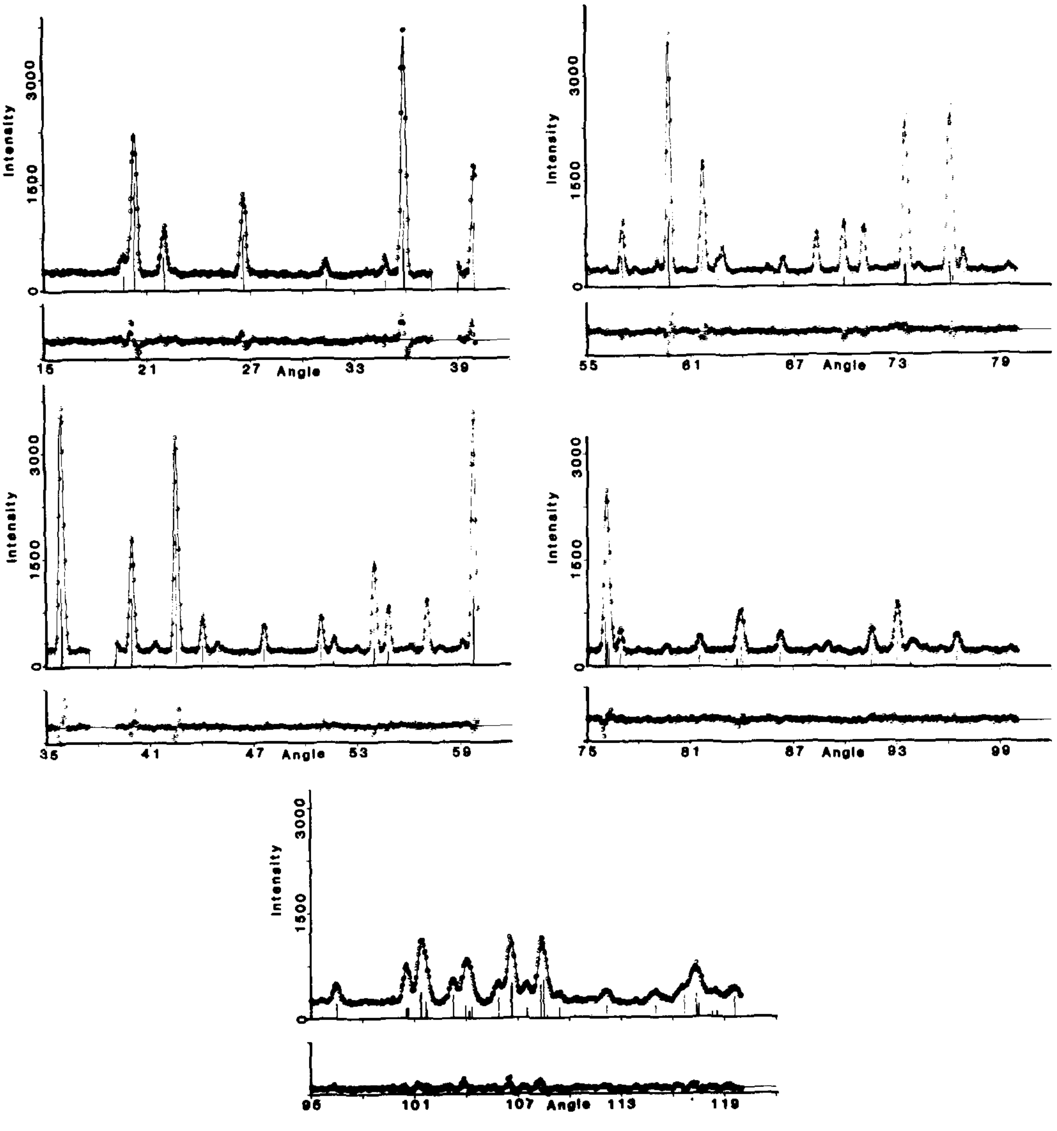

FIG. 2. Observed (circles), calculated (continuous line), and difference profiles for Li_2ZrO_3. The small angular region at $2\theta \approx 38°$ was excluded because a small peak, attributed to impurities in the sample, was present.

observed profiles and the difference profiles for Li_2SnO_3 and Li_2ZrO_3, respectively.

Discussion

The structural arrangement of Li_2ZrO_3 and Li_2SnO_3 is NaCl-like. In both compounds, therefore, the oxygen atoms form a distorted cubic close-packed network, and the cations occupy, in an ordered fashion, all octahedral sites present in this network. Consequently, the cations also form a cubic close-packed network. The distribution of the lithium and of the tetravalent cations is different in the two compounds, and for this reason, these cannot be considered isostructural.

Figures 3 and 4 show the orthogonal projections on the *ab* monoclinic plane of the

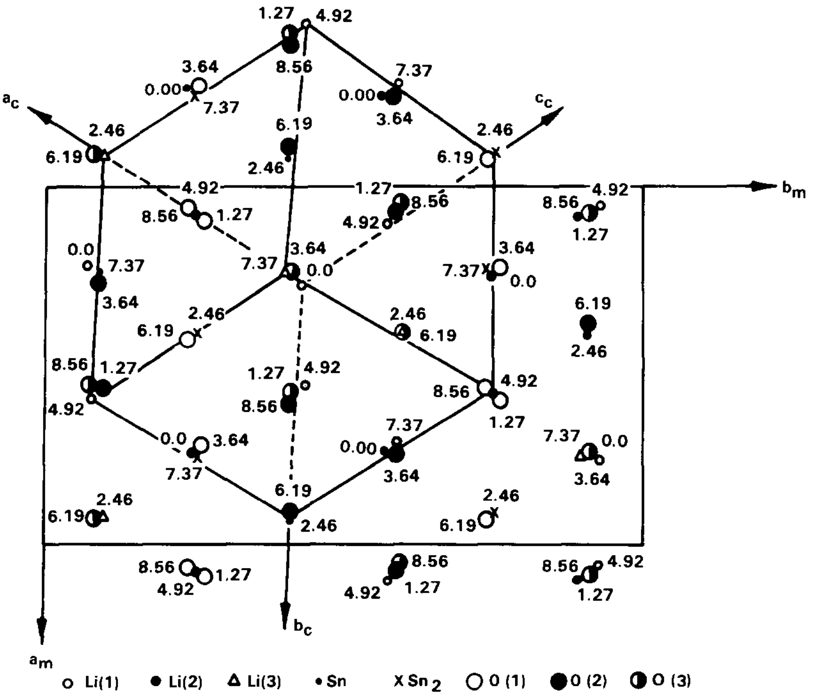

FIG. 3. Orthogonal projection on the (001) plane of the structure of Li_2SnO_3. The heights are given in angstroms.

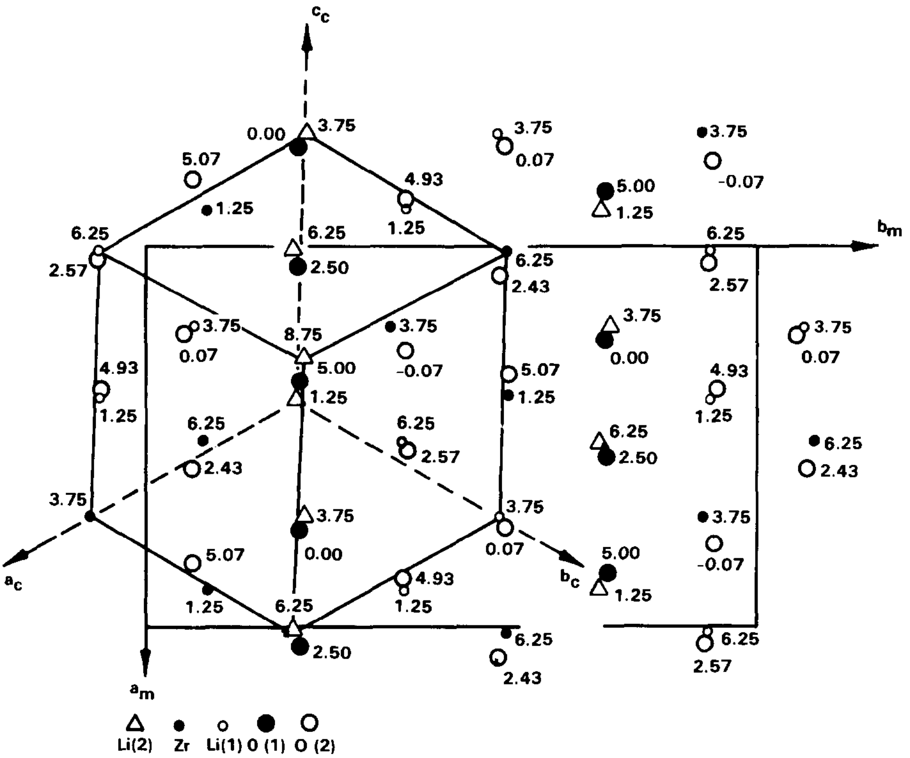

FIG. 4. Orthogonal projection on the (001) plane of the structure of Li_2ZrO_3. The heights are given in angstroms.

Li_2SnO_3 and Li_2ZrO_3 structures, respectively. The pseudo-NaCl subcells are outlined. The transformation matrices relating the monoclinic unit cells to the pseudocubic subcells are

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_M = \begin{pmatrix} -\frac{1}{2} & 1 & -\frac{1}{2} \\ -\frac{3}{2} & 0 & \frac{3}{2} \\ \frac{3}{2} & 1 & \frac{3}{2} \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_c ,$$

$\Delta = 6$, for Li_2SnO_3, and

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_M = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & \bar{1} \\ \overline{\frac{3}{2}} & \frac{3}{2} & 0 \\ \frac{1}{2} & \frac{1}{2} & 1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_c ,$$

$\Delta = 3$, for Li_2ZrO_3. In each compound, the *ab* monoclinic plane is almost perpendicular to one of the four ⟨111⟩ axes of the pseudocubic subcell; therefore there exist close-packed layers of oxygen octahedra parallel to this plane. Since the distribution of cations in the layers parallel to *ab* is different from the distributions in the octahedral layers perpendicular to the other three ⟨111⟩ axes, we will use it to describe the cation ordering.

In the structure of Li_2SnO_3, if we disregard the difference between Li(1), Li(2), and Li(3) and that between Sn(1) and Sn(2), there exist two types of layers, one composed of lithium-occupied octahedra only and the other composed of lithium- and tin-occupied octahedra in a 1 : 2 ratio, stacked alternately along the perpendicular to the *ab* plane. The cations of the mixed layers are ordered in such a way that they form hexagonal close-packed planes in which the tin atoms occupy the vertices of the hexagons and the lithium atoms the centers. A given layer repeats every six levels, namely, after a double cubic close-packed sequence AB′CA′BC′ (where B′A′C′ refer to lithium-occupied octahedron layers).

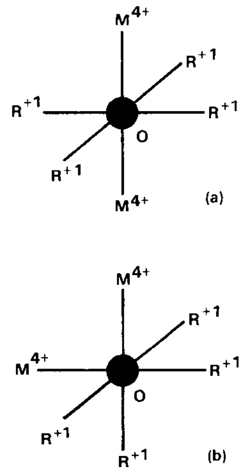

FIG. 5. Possible coordinations of the oxygen atoms in $R_2^{+1}M^{4+}O_3$ structures.

In the structure of Li_2ZrO_3, if we disregard the difference between Li(1) and Li(2), all the layers parallel to the *ab* monoclinic plane have the same cation distribution; namely, they are composed of lithium- and zirconium-occupied octahedra in a 2 : 1 ratio. The cations belonging to one octahedral layer form hexagonal close-packed planes as in the previous case. However, in Li_2ZrO_3, the lithium atoms occupy the vertices of the hexagons while the zirconium atoms occupy the centers. As in the case of Li_2SnO_3, a given octahedral layer repeats every six layers and is related to the next one above by a shift equivalent to either ($\frac{1}{2}$, 0, $\frac{1}{2}$) or (0, $\frac{1}{2}$, $\frac{1}{2}$), where the indices refer to the pseudocubic subcell.

As pointed out by Dorrian and Newnham (*9*) in the $R_2^{+1}M^{4+}O_3$ compounds with the NaCl structure, there are two types of coordination (Fig. 5) for the oxygen atoms. Of the two configurations, only (b) can be consistent with full three-dimensional order; on the contrary, it would be geometrically impossible to construct NaCl-like superstructures with the (a) configuration. In the structure of Li_2SnO_3, all the oxygen atoms have the (b) configuration. In that of Li_2ZrO_3, two-thirds of the oxygen atoms have the (b) configuration, whereas one-third have the (a) configuration.

Tables IV and V give the important interatomic distances together with their standard deviations in the two structures. The

TABLE IV

INTERATOMIC DISTANCES (Å) WITH THEIR STANDARD DEVIATIONS IN Li_2SnO_3

	Sn1-Sn2	3.05(1)	2×	Sn2-Li1	3.048(9)
2×	Sn1-Sn2	3.062(6)	2×	Sn2-Li1	3.114(9)
2×	Sn1-Li1	3.013(9)	2×	Sn2-Li2	3.037(1)
2×	Sn1-Li1	3.092(9)		Sn2-Li3	3.06(6)
2×	Sn1-Li2	3.037(5)	2×	Sn2-Li3	3.06(3)
	Sn1-Li3	3.08(6)	2×	Sn2-O1	2.053(3)
2×	Sn1-Li3	3.05(3)	2×	Sn2-O2	2.059(8)
2×	Sn1-O1	2.069(8)	2×	Sn2-O3	2.074(8)
2×	Sn1-O2	2.076(8)	Average	Sn2-O	2.062
2×	Sn1-O3	2.079(3)	Index of distortion		0.01
Average	Sn1-O	2.075			
Index of distortion		0.005	2×	O1-O2	2.978(6)
			2×	O1-O2	2.943(6)
	O1-O1	2.966(9)	2×	O1-O3	2.951(6)
2×	O1-O2	2.983(9)	2×	O1-O3	2.784(6)
2×	O1-O3	2.987(6)		O2-O2	2.792(8)
2×	O1-O3	2.784(6)	2×	O2-O3	2.965(9)
	O2-O2	2.792(8)		O3-O3	2.967(8)
2×	O2-O3	2.971(6)	Average	O-O	2.917
2×	O2-O3	3.004(6)	Index of distortion		0.08
Average	O-O	2.935			
Index of distortion		0.09			
2×	Li1-Li1	3.14(2)	2×	Li2-Li3	3.03(3)
2×	Li1-Li1	2.79(2)	2×	Li2-O1	2.247(3)
2×	Li1-Li1	3.26(2)	2×	Li2-O2	2.232(5)
2×	Li1-Li2	2.969(9)	2×	Li2-O3	2.127(5)
2×	Li1-Li2	3.189(10)	Average	Li2-O	2.202
2×	Li1-Li2	3.020(10)	Index of distortion		0.06
2×	Li1-Li3	2.986(9)			
2×	Li1-Li3	2.95(3)	2×	O1-O2	3.112(5)
			2×	O1-O2	3.221(6)
	Li1-O1	2.297(10)	2×	O1-O3	3.197(6)
	Li1-O1	2.218(10)	2×	O1-O3	2.987(6)
	Li1-O2	2.217(9)	2×	O2-O3	3.197(4)
	Li1-O2	2.235(10)	2×	O2-O3	2.965(9)
	Li1-O3	2.141(10)	Average	O-O	3.113
	Li1-O3	2.142(9)	Index of distortion		0.11
Average	Li1-O	2.208			
Index of distortion		0.06	2×	Li3-O1	2.21(4)
			2×	Li3-O2	2.170(3)
	O1-O1	3.126(9)	2×	Li3-O3	2.19(4)
	O1-O2	3.112(5)	Average	Li3-O	2.189
	O1-O2	2.978(6)	Index of distortion		0.02
	O1-O2	2.983(9)			
	O1-O3	3.245(9)		O1-O1	2.966(9)
	O1-O3	2.951(6)	2×	O1-O2	3.221(6)
	O1-O3	3.197(6)	2×	O1-O2	2.943(6)
	O2-O2	3.152(8)	2×	O1-O3	3.245(9)
	O2-O3	3.004(6)	2×	O2-O3	3.212(6)
	O2-O3	3.197(4)	2×	O2-O3	2.971(6)
	O2-O3	3.212(6)		O3-O3	2.967(8)
	O3-O3	3.250(8)	Average	O-O	3.093
Average	O-O	3.117	Index of distortion		0.14
Index of distortion		0.11			

indices of distortion of the various octahedra are also given. They are defined as the standard deviation of the average of the twelve oxygen–oxygen distances.

The average Sn–O and Li–O distances in Li_2SnO_3 are 2.069 and 2.202 Å, respectively. The Sn(1)- and Sn(2)-occupied octahedra have a similar index of distortion: 0.09 for Sn(1) and 0.08 for Sn(2). Similarly, the indices of distortion of Li(1)- and Li(2)-occupied octahedra are 0.11 for both cations. A somewhat higher value, 0.14, is obtained for Li(3)-occupied octahedra. This is not surprising because Li(3), together with Sn(1) and Sn(2), forms the mixed cation octahedral layers and, being monovalent, causes the majority of the distortion in the oxygen octahedron around it. The average octahedral distortion of the mixed octahe-

TABLE V

INTERATOMIC DISTANCES (Å) WITH THEIR STANDARD DEVIATIONS IN Li_2ZrO_3

2×	Zr-Zr	3.174(3)	2×	Li1-Li1	3.04(1)
	Zr-Li1	2.99(2)		Li1-Li2	2.88(3)
2×	Zr-Li1	3.109(9)	2×	Li1-Li2	3.09(1)
2×	Zr-Li1	3.006(1)	2×	Li1-Li2	3.16(1)
	Zr-Li2	3.15(2)	2×	Li1-O1	2.17(1)
2×	Zr-Li2	3.098(9)	2×	Li1-O2	2.06(1)
2×	Zr-Li2	3.032(8)	2×	Li1-O2	2.418(3)
2×	Zr-O1	2.073(3)	Average	Li1-O	2.215
2×	Zr-O2	2.100(3)	Index of distortion		0.16
2×	Zr-O2	2.116(4)			
Average	Zr-O	2.096		O1-O1	3.003(1)
Index of distortion		0.02	2×	O1-O2	2.940(3)
			2×	O1-O2	3.241(2)
	O1-O1	3.003(1)	2×	O1-O2	3.265(2)
2×	O1-O2	3.009(2)	2×	O2-O2	3.032(5)
2×	O1-O2	2.940(3)	2×	O2-O2	3.304(5)
2×	O1-O2	3.033(2)		O2-O2	3.071(5)
2×	O2-O2	3.032(5)	Average	O-O	3.137
2×	O2-O2	2.774(5)	Index of distortion		0.15
	O2-O2	2.970(5)			
Average	O-O	2.962		Li2-Li2	2.88(3)
Index of distortion		0.09	2×	Li2-Li2	3.09(1)
			2×	Li2-Li2	3.16(1)
			2×	Li2-O1	2.257(1)
			2×	Li2-O2	2.15(1)
			2×	Li2-O2	2.22(1)
			Average	Li2-O	2.208
			Index of distortion		0.05
			2×	O1-O2	3.033(2)
			2×	O1-O2	3.265(2)
			2×	O1-O2	3.009(2)
			2×	O1-O2	3.241(2)
				O2-O2	3.071(5)
			2×	O2-O2	3.167(5)
				O2-O2	2.970(5)
			Average	O-O	3.123
			Index of distortion		0.11

dral layers is the same as that of the lithium octahedral layers.

The average Zr–O and Li–O distances in Li_2ZrO_3 are 2.096 and 2.212 Å, respectively. The Zr-occupied octahedra have a distortion (0.09) which is comparable to that of the Sn-occupied octahedra (0.085) in Li_2SnO_3. As expected, the Li-occupied octahedra are more distorted than the zirconium counterparts. The index of distortion of Li(1) octahedra is 0.15, while that of Li(2) octahedra is 0.11. No explanation can be found for this difference. However, if the Li(2) cations do not obey the $C2/c$ arrangement, the drastic increase of the distortion has to be expected.

The reason why the cation arrangement is different in the two structures seems to be related to the difference in size between Sn^{4+} and Zr^{4+}. All $Li_2M^{4+}O_3$ compounds reported so far, with the exception of Li_2ZrO_3, have a cation ordering similar to that of Li_2SnO_3. Of all the tetravalent cations forming these compounds, Zr^{4+} has the largest ionic radius, and therefore it is logical to surmise that the factor deciding the cation ordering is the $r(Li^{+1})/r(M^{4+})$ ratio. The cation order found in Li_2ZrO_3 can be regarded as a three-dimensional order, whereas that found in Li_2SnO_3 is of a lower dimensionality since it contains layers of lithium-occupied octahedra alternating with layers composed of lithium- and tin-occupied octahedra. The ratios of the radii for Li_2SnO_3 and Li_2ZrO_3 are 1.10 and 1.06, respectively (*10*). Any one given A_2MO_3 compound assumes the Li_2SnO_3 ordering when the radii ratio is larger than 1.06 and assumes the Li_2ZrO_3 ordering when the radii ratio is smaller than 1.06. This rule is verified by all the $Li_2M^{4+}O_3$ compounds reported by Lang (*11*).

References

1. E. E. Hellstrom and W. Van Gool, *Solid State Ionics* **2**, 59 (1981).
2. G. Kreuzburg, F. Stewner, and R. Hoppe, *Z. Anorg. Allg. Chem.*, Band 379, 242 (1970).
3. G. Dittrich and R. Hoppe, *Z. Anorg. Allg. Chem.*, Band 371, 306 (1969).
4. H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969).
5. E. Prince, "National Bureau of Standards U.S. Technical Note 1117," edited by F. J. Shorten (1980).
6. G. Caglioti, A. Paoletti, and F. P. Ricci, *Nucl. Instrum.* **3**, 223 (1958).
7. G. E. Bacon, *Acta Crystallogr. Sect. A* **28**, 357 (1972).
8. A. W. Hewat, "ILL Report 74H62S," Grenoble, France (1974).
9. J. F. Dorrian and R. E. Newnham, *Mater. Res. Bull.* **4**, 179 (1969).
10. R. D. Shannon, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
11. G. Lang, *Z. Anorg. Allg. Chem.*, Band 348, 246 (1966).