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Dilithium Magnesium Zirconium Tetraoxide with an α-$LiFeO_2$ Structure

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Abstract. Li_2MgZrO_4. Formed by solid-state reaction of Li_2ZrO_3 and MgO; isostructural with α-$LiFeO_2$ [Posnjak & Barth (1931). *Phys. Rev.* **38**, 2234–2239] but with Mg, Zr disordered over Fe sites. $M_r = 193{\cdot}41$, tetragonal, $I4_1/amd$, $a = 4{\cdot}209\,(1)$, $c = 9{\cdot}145\,(2)$ Å, $V = 162{\cdot}010$ Å^3, $Z = 2$, $D_x = 3{\cdot}964$ g cm^{-3}, Cu $K\alpha_1$, $\lambda = 1{\cdot}5405$ Å, $\mu = 27{\cdot}1$ mm^{-1}, $F(000) = 180$, powdered sample, room temperature, $R = 0{\cdot}033$ for 16 unique reflections. Li—O bond lengths are 2·110 (1) and 2·441 (15) Å, the latter being abnormally long, and Mg, Zr—O are 2·110 (1) and 2·132 (15) Å.

Introduction. In the family of oxides that have rock-salt and ordered rock-salt structures, various cation-ordering sequences are possible with phases containing >1 cation. We are interested in the synthesis of new ordered and partially ordered structures, their solid solutions and phase transitions and describe here the synthesis and structure of one such phase, Li_2MgZrO_4.

Experimental. Li_2MgZrO_4 prepared by solid-state reaction of Li_2ZrO_3 and MgO. Li_2ZrO_3 first prepared by reaction of equimolar amounts of Li_2CO_3 and ZrO_2 (Analar grade) in a Pt crucible in a muffle furnace. Reaction mixture heated initially at 870 to 970 K for a few hours to expel CO_2 followed by 1 to 2 d at 1170 K. For the reaction of Li_2ZrO_3 and MgO to produce Li_2MgZrO_4, higher temperatures were found to be necessary, ~1370 K; at these temperatures loss of lithia by volatilization was a serious problem that could not be overcome simply by placing a lid on the crucible. The method that was adopted, successfully, to avoid lithia loss was to carry out reaction in pelleted samples and to have pellets immersed completely in pre-sintered powder of the same composition. The pellets, with covering powder, were fired in covered Pt crucibles at 1320 K for 24 h.

Reaction product(s) analysed by X-ray powder diffraction, Philips Hägg Guinier camera, Cu $K\alpha_1$ radiation, KCl as internal standard for accurate *d*-spacing measurements, Philips PW 1050/25 diffractometer for intensity measurements, flat sample, Cu $K\alpha$ radiation, scan speed $\frac{1}{8}°$ 2θ min^{-1}. Powder pattern of Li_2MgZrO_4 fairly simple with relatively few peaks; a search through the X-ray powder diffraction file, treating it as an unknown, showed its pattern to be very similar to those of phases such as $LiScO_2$ and α-$LiFeO_2$. These have ordered rock-salt structures with a tetragonal unit cell. X-ray powder pattern of Li_2MgZrO_4 was indexed by analogy with that of α-$LiFeO_2$ and accurate unit-cell dimensions obtained by least-squares refinement using 16 unique reflections.

As a starting hypothesis for the structure of Li_2MgZrO_4, it was assumed to be derived from the

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α-$LiFeO_2$ structure by the replacement mechanism $2Fe^{3+} \rightleftharpoons Mg^{2+} + Zr^{4+}$. Since there was no evidence of any extra lines in the X-ray pattern that could possibly have arisen from a superstructure, it was assumed that the Mg^{2+}, Zr^{4+} ions were disordered over the Fe^{3+} sites.

The essential correctness of this structural model was confirmed by refinement of X-ray powder intensity data. For this, intensities were taken as proportional to peak areas, determined by the method of counting squares. Intensities were corrected for multiplicity and Lp factors, converted to F_{obs} values and these F_{obs} values used for structure refinement. The starting coordinates were those reported for α-$LiFeO_2$ (Posnjak & Barth, 1931; Wyckoff, 1964); the origin was taken at centre ($2/m$), at 0, $-\frac{1}{4}$, $\frac{1}{8}$ from $\bar{4}m2$. Scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1962). Computer programs for structure refinement by Ahmed, Hall, Pippy & Huber (1973). Variables in structure refinement were oxygen z parameter and isotropic temperature factors for Li, (Mg, Zr) and O. All allowed to refine simultaneously giving final R of 0·033 using 16 unique reflections. The final atomic coordinates are listed in Table 1, bond lengths and angles in Table 2.*

Discussion. The structure of Li_2MgZrO_4 is shown in Fig. 1 as a projection of the unit-cell contents down **b**. It consists, basically, of two rock-salt-like unit cells placed together to give a doubled c axis. The reason for the doubling of c to give a tetragonal unit cell is associated with the particular way that the cations – Li^+ and Mg^{2+}/Zr^{4+} – order themselves over the octahedral sites of the essentially cubic close-packed array of oxide ions.

The structure is, however, somewhat distorted in that (i) it is elongated along **c** by ~8%, (ii) the shapes of the LiO_6 and $(Mg,Zr)O_6$ octahedra are somewhat distorted, (iii) two of the Li–O bond lengths are abnormally long, 2·44 Å, Table 2, and (iv) the close-packed oxide layers are slightly buckled. These distortions occur because, in the three-dimensional array of edge-sharing octahedra, some of the $(Mg,Zr)O_6$ octahedra share common edges and the large electrostatic repulsion between the associated pairs of Mg^{2+}/Zr^{4+} ions results in an effective elongation in the **c** direction.

From an inspection of Fig. 1, each $(Mg,Zr)O_6$ octahedron shares common edges with twelve other octahedra: eight LiO_6 octahedra and four $(Mg,Zr)O_6$ octahedra. The centres of the pairs of edge-sharing $(Mg,Zr)O_6$ octahedra are 3·107 (1) Å apart whereas the centres of pairs of edge-sharing $(Mg,Zr)O_6/LiO_6$ octahedra are separated by 3·107 (1) Å (4×) and 2·976 (1) Å (4×). The latter distance is related to the unit-cell a parameter by $a/\sqrt{2} = 2{\cdot}976$ (1) Å. The former two distances are given by $[(c/4)^2 + (a/2)^2]^{1/2} = 3{\cdot}107$ (1) Å. Hence, repulsion between (Mg^{2+}, Zr^{4+}) ions occupying pairs of edge-sharing octahedra is responsible for the elongation of the structure in the **c** direction. It also accounts for the distorted shapes of the octahedra. The more polarizing nature of the (Mg^{2+},

Table 1. *Atomic parameters for* Li_2MgZrO_4 *with e.s.d.'s in parentheses*

	Wyckoff position	x	y	z	B_{iso}(Å^2)
O	8(e)	0	$\frac{1}{4}$	0·108 (2)	1·20 (32)
Zr, Mg	4(a)	0	$\frac{3}{4}$	$\frac{1}{8}$	1·79 (11)
Li	4(b)	0	$\frac{1}{4}$	$\frac{3}{8}$	0·02 (106)

Table 2. *Bond lengths* (Å) *and angles* (°)

	Bond length	e.s.d.	Number of equivalent bonds
Li–O	2·110	0·001	4
	2·441	0·015	2
Zr, Mg–O	2·110	0·001	4
	2·132	0·015	2

		e.s.d.	Number of equivalent angles
O–Li–O and O–Mg, Zr–O	94·20	0·31	4
	90·31	0·33	4
	85·80	0·31	4
Li–O–Li	85·80	0·31	2
Zr–O–Zr	94·20	0·31	2
Zr–O–Li	85·80	0·31	2
	94·20	0·31	2
	90·31	0·33	4

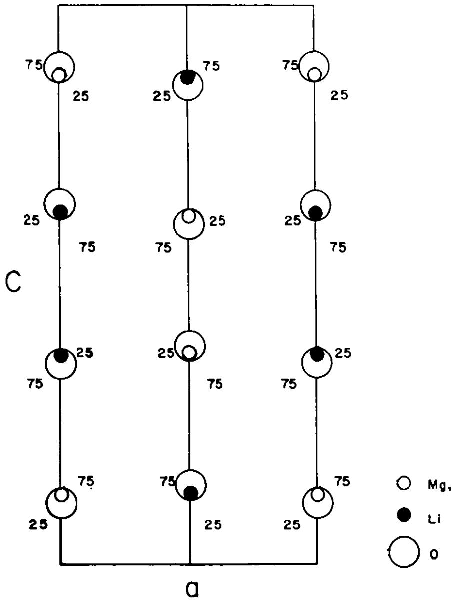

Fig. 1. Projection of the structure of Li_2MgZrO_4.

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* The powder data, including calculated intensity data at lower d spacings than were obtained experimentally, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42374 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Zr^{4+}) ions gives rise to essentially equal (Mg,Zr)—O bond distances of 2·12 (1) Å. This constraint of constant bond distance coupled with the net electrostatic repulsion between (Mg^{2+},Zr^{4+}) ions in the **c** direction causes the oxygens to be displaced from their ideal value of 0·125 (Table 1). Consequently, the less-polarizing Li^+ ions are forced to accept two abnormally long Li—O bonds of 2·44 (2) Å in the **c** direction. As further evidence of the repulsion between edge-sharing $(Mg,Zr)O_6$ octahedra, the oxide ions that form these common edges are separated by only 2·888 Å, giving a reduced O—(Mg,Zr)—O angle of 85·8 (3)°. For undistorted $(Mg,Zr)O_6$ octahedra with angles of 90° and the same $(Mg,Zr)O_6$ bond length, the oxygen–oxygen edges would be 3·107 Å. This closer approach of the oxide ions in the edge-sharing $(Mg,Zr)O_6$ octahedra serves both to push apart the (Mg^{2+}/Zr^{4+}) cations on either side and partially to shield their positive charges from each other.

The isotropic temperature factor for lithium (Table 1) is anomalously low. This may be an artefact associated with the limited data set that was available; also the e.s.d. is relatively large.

Various oxides $LiMO_2$, M = trivalent ion, form the α-$LiFeO_2$ structure but Li_2MgZrO_4 is the first to contain three cations. This is made possible by the similar size/coordination requirements of Mg^{2+} and Zr^{4+}, which typically have octahedral bond distances to oxygen of ~2·12 Å (Shannon & Prewitt, 1969, 1970) and which allows them to be disordered over the Fe^{3+} sites, without incurring additional major structural distortions.

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The Structures of Trithallium Tetraselenophosphate and Trithallium Tetrathioarsenate at 65 K

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Abstract. Low-temperature (65 K) single-crystal neutron structure determinations were performed on the isostructural materials Tl_3PSe_4 and Tl_3AsS_4 using a newly designed single-crystal diffractometer at the Los Alamos National Laboratory Pulsed Neutron Facility. For Tl_3PSe_4: $M_r = 959{\cdot}92$, $Pcmn$, $a = 9{\cdot}291\ (2)$, $b = 10{\cdot}991\ (3)$, $c = 9{\cdot}041\ (2)$ Å, $V = 923{\cdot}30$ Å^3, $Z = 4$, $D_x = 6{\cdot}905$ Mg m^{-3}, $\lambda_{\rm neutron} = 0{\cdot}75 \rightarrow 4{\cdot}2$ Å, $F(000) = 252{\cdot}5$ fm. For Tl_3AsS_4: $M_r = 816{\cdot}29$, $Pcmn$, $a = 9{\cdot}089\ (2)$, $b = 10{\cdot}803\ (2)$, $c = 8{\cdot}867\ (2)$ Å, $V = 870{\cdot}60$ Å^3, $Z = 4$, $D_x = 6{\cdot}227$ Mg m^{-3}, $\lambda_{\rm neutron} = 0{\cdot}75 \rightarrow 4{\cdot}2$ Å, $F(000) = 177{\cdot}2$ fm. For Tl_3PSe_4 (Tl_3AsS_4) 2335 (2678) reflections were measured with $I > 3\sigma(I)$ and refined by full-matrix least squares to $R(F) = 0{\cdot}049$ (0·053). Results of atomic-parameter refinement from this study yield an increase in precision by a factor of two over a previous single-crystal neutron structural study at room temperature (293 K). Deviation of the PSe_4^{3-} (AsS_4^{3-}) group from an idealized tetrahedral arrangement is significant and one Tl^+ ion

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