Other products were $(CF_3)_2PSH$ (0.022 g, 0.11 mmole), excess $(CF_3)_2PH$ (0.209 g, 1.23 mmoles), both identified by their infrared spectra, and a small amount of H_2S, identified by mass spectrometry and the characteristic reaction with lead acetate.

(b) Reaction of $(CF_3)_2PSH$ with Sulfur. The mercaptophosphine (0.311 g, 1.54 mmoles) reacted with sulfur (1 g) after 36 hr at 160° to give a small amount (0.06 mmole) of a volatile material (shown not to be H_2S), unreacted $(CF_3)_2PSH$ (0.012 g, 0.06 mmole), and the phosphinic acid, $(CF_3)_2P(S)SH$ (0.313 g, 1.34 mmoles), which was trapped at −63°. *Anal.* Calcd for $C_2HF_6PS_2$: *m/e* (mass spectrometer), 233.9161; CF_3 liberated on alkaline hydrolysis, 29.5%; mol wt, 234. Found: *m/e*, 233.9159; CF_3, 29.6%; mol wt, 237. The main bands in the infrared spectrum were at 2580 w, 2565 (sh) w, 1280 w, 1208 vs, 1178 vs, 846 m, 760 m, 730 s, 573 m, 519 m, 472 m cm^{-1}. Samples of the dithiophosphinic acid prepared from the reaction of $(CF_3)_2PSH$ and sulfur were examined by fluorine nmr for $(CF_3)_2PSP(CF_3)_2$ which is readily identified by its strong and characteristic spectrum.[25] At the highest gain only resonances due to the phosphinic acid were observed indicating that there was certainly less than 0.25% of the bis(phosphino) sulfide impurity present.

Preparation of $CF_3PF(S)N(CH_3)_2$. The dimethylaminophosphine, $CF_3PFN(CH_3)_2$ (0.460 g, 2.82 mmoles), prepared from CF_3PF_2 and $(CH_3)_2NH$,[28] was sealed in an evacuated tube with sulfur (1 g) and heated at 180° (6 days). The phosphine sulfide, $CF_3PF(S)N(CH_3)_2$ (0.235 g, 1.21 mmoles), was isolated by vacuum fractionation. *Anal.* Calcd for $C_3H_6F_4NPS$: *m/e* (mass spectrometer), 194.9895; mol wt, 195. Found: *m/e*, 194.9891; mol wt, 192. No CF_3H was liberated on alkaline hydrolysis, as expected. The infrared spectrum showed absorption at 3020 w, 2950 m, 2915 (sh) w, 2870 w, 2825 w, 1455 w, 1318 m, 1212 vs, 1166 vs, 1149 vs, 1078 w, 1010 vs, 890 vs, 786 s, 750 (sh) w, 653 s, 474 m cm^{-1}.

Preparation of $F_2P(S)N(CH_3)_2$. $PF_2N(CH_3)_2$ (0.116 g, 1.03 mmoles) and sulfur (1 g) were allowed to react for 5 days at 150°. Vacuum fractionation gave $F_2P(S)N(CH_3)_2$ (0.131 g, 0.90 mmole), identified by its infrared, nmr, and mass spectra.[12] A more volatile fraction was shown by infrared spectroscopy to contain PF_3, $F_3P{=}S$, and a trace of SiF_4.

Acknowledgment. We thank Dr. A. Hogg and Mr. A. Budd for assistance with the mass spectral measurements and The National Research Council of Canada and The Defence Research Board of Canada for financial support.

(28) J. F. Nixon and R. G. Cavell, *J. Chem. Soc.*, 5893 (1964).

High-Pressure–High-Temperature Syntheses. III. Direct Syntheses of New High-Pressure Forms of $LiAlO_2$ and $LiGaO_2$ and Polymorphism in $LiMO_2$ Compounds (M = B, Al, Ga)[1a]

C. H. Chang and J. L. Margrave

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. *Received July 21, 1967*

Abstract: New high-pressure polymorphs, β-$LiAlO_2$ and β-$LiGaO_2$, have been synthesized in an opposed-anvil press at 18 kbars, 370° and 18 kbars, 420°, respectively. These new high-pressure forms are isostructural. Debye–Scherrer powder patterns have been indexed on the basis of monoclinic structures and indicate the lattice parameters a = 8.147 Å, b = 7.941 Å, c = 6.303 Å, β = 93.18° for β-$LiAlO_2$ and a = 8.110 Å, b = 8.065 Å, c = 6.422 Å, β = 94.56° for β-$LiGaO_2$. Infrared absorption spectra suggest that aluminum and gallium in these new phases have both coordination numbers four and six. A consistent nomenclature for the system $LiMO_2$ (M = B, Al, Ga) is proposed and used.[1b] The polymorphs of $LiMO_2$ include three phase types: (1) the α phases, prepared at normal pressures (M^{3+} exhibits a low coordination number: three for boron or four for aluminum); (2) the γ forms synthesized at high pressures and temperatures (M^{3+} has a high coordination number: four for boron and six for aluminum); and (3) the β forms, prepared at intermediate pressures and temperatures (M^{3+} exhibits both coordination numbers).

Two crystalline forms of $LiAlO_2$ have been reported. The first form (α-$LiAlO_2$) was prepared at normal pressure,[2] and it is tetragonal with a = 5.169 Å and c = 6.268 Å with all cations tetrahedrally coordinated.[3–5] The second crystalline form of $LiAlO_2$ was obtained first by Lehmann and Hesselbarth[6] at 600°, and recently by Marezio and Remeika,[7] at 35 kbars and 850°. This hexagonal form, γ-$LiAlO_2$, has a = 2.801 Å and c = 14.214 Å and all cations are octahedrally bonded.[8]

There are also two crystalline forms of $LiGaO_2$ which have been synthesized at normal pressure and temperature; α-$LiGaO_2$ crystallizes in an orthorhombic structure with a = 5.402 Å, b = 6.372 Å, and c = 5.007 Å.[9,10] By subjecting the low-pressure form to a pressure of 30 kbars and a temperature of 850°, Marezio and Remeika[11] obtained a high-pressure phase, γ-$LiGaO_2$, with a hexagonal unit cell of a = 2.9113 Å and c = 14.466 Å. The most important difference between these two phases is that, in the low-pressure form, the coordination number of Ga, paralleling that of Al in

---

(1) (a) Extracted, in part, from the Ph.D. thesis of C. H. Chang, submitted to the faculty of Rice University, May 1967. (b) The new nomenclature described in the abstract is used throughout the paper.

(2) (a) R. A. Hatch, *Am. Mineralogist*, **28**, 471 (1953); (b) F. A. Hummel, *J. Am. Ceram. Soc.*, **34**, 235 (1951).

(3) J. Thery, A. M. Lejus, D. Bariancon, and R. Collonges, *Bull. Soc. Chim. France*, 973 (1961).

(4) E. F. Bertaut, A. Delapalme, G. Bassi, A. Durif-Varambon, and J. C. Joubert, *Bull. Soc. Franc. Mineral. Crist.*, **88**, 103 (1965).

(5) M. Marezio, *Acta Cryst.*, **59**, 396 (1965).

(6) H. A. Lehmann and H. Hesselbarth, *Z. Anorg. Allgem. Chem.*, **313**, 117 (1961).

(7) M. Marezio and J. P. Remeika, *J. Chem. Phys.*, **44**, 3143 (1966).

(8) A. M. Lejus and R. Collongues, *Compt. Rend.*, **254**, 2005 (1962).

(9) R. Hoppe, *Angew. Chem.*, **71**, 457 (1959).

(10) M. Marezio, *Acta Cryst.*, **18**, 481 (1965).

(11) M. Marezio and J. P. Remeika, *J. Phys. Chem. Solids*, **26**, 1277 (1965).

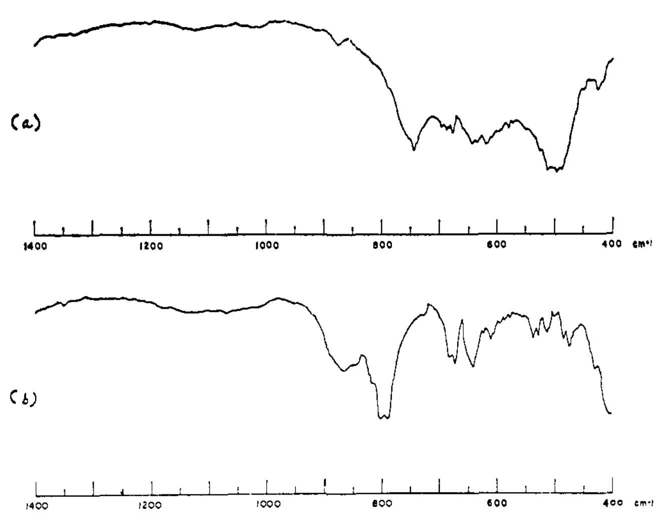

Figure 1. Infrared spectra of (a) γ-$LiAlO_2$, (b) β-$LiAlO_2$.

low-pressure $LiAlO_2$, is four while in the high-pressure form it is six.

Since the coordination number of Ga^{3+} [11] or Al^{3+} [12] can be a mixture of four and six in oxide compounds, it is quite reasonable to speculate that a third form with mixed coordination, paralleling β-$LiBO_2$,[13] may exist for both $LiAlO_2$ and $LiGaO_2$.

Experimental Section

Syntheses of these new phases were performed in a Tem-press SJ-100 opposed-anvil device.[14] Various mixtures of lithium peroxide, Li_2O_2, and M_2O_3 (M = Al, Ga) were prepared. Samples were contained in the pyrophyllite high-pressure cell and covered with Ta foils to separate them from the anvils. By subjecting the mixtures to a pressure of 18 kbars and temperatures of 370 and 420° for Al_2O_3 and Ga_2O_3, respectively, for a period of 10 hr, two new high-pressure phases were obtained after quenching.

The new high-pressure phases of $LiAlO_2$ could also be synthesized by pressing a 2:1 molar mixture of Li_2O_2 and aluminum nitride, AlN, at 22 kbars and 550° for 11 hr. It was found that, when the mixture of Li_2O_2 and Al_2O_3 was allowed to react at 25 kbars and 530°, the γ-$LiAlO_2$ was synthesized directly. Instead of the γ form of $LiGaO_2$, however, $LiGa_5O_8$ was obtained after heating the mixure of Li_2O_2 and Ga_2O_3 at 34 kbars and 820° for 4 hr.

Results and Discussions

$LiAlO_2$. The X-ray powder photographs of various $LiAlO_2$ phases were taken at room temperature in a Norelco 114.6-mm camera with Ni-filtered, Cu Kα radiation at 35 kV and 18 mA. The patterns of the low-pressure (α) and the high-pressure (γ) $LiAlO_2$ forms are the same as obtained previously,[2,6,7] while the new β-phase pattern indicates a less symmetrical lattice. The β pattern has been indexed on the basis of a monoclinic structure with cell dimensions a = 8.147 Å, b = 7.941 Å, c = 6.303 Å, and β = 93.18° as shown in Table I. This behavior parallels the HBO_2 and $LiBO_2$ systems,[13] and suggests the presence of Al in sites with different coordination numbers.

Infrared absorption spectra were obtained on a Beckman IR9 infrared spectrophotometer by using the KBr-disk technique. As show in Figure 1, the distinctive band at 740 cm^{-1} for γ-$LiAlO_2$ corresponds to an Al–O stretching frequency with Al octahedrally coordinated, and no absorption in the range 800–900 cm^{-1}, characteristic of the AlO_4 group,[15,16] is seen. This is consistent with the conclusions obtained from X-ray data[8] that all aluminum ions are octahedrally coordinated in γ-$LiAlO_2$.

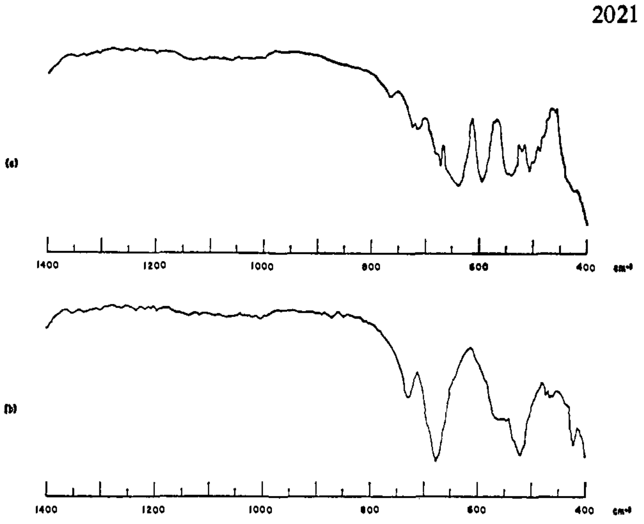

Figure 2. Infrared spectra of (a) $LiGa_5O_8$, (b) β-$LiGaO_2$.

Table I. X-Ray Diffraction Pattern of Newly Synthesized β-$LiAlO_2$[a]

hkl	Rel intensity[b]	2θ	d_{obsd}	d_{calcd}
200	s	21.92	4.05	4.068
020	s	22.98	3.87	3.914
002	w	28.57	3.12	3.146
300	s	33.10	2.706	2.712
030	m	33.97	2.639	2.647
022	s	36.65	2.452	2.467
212	w	38.00	2.368	2.344
230	vvw	41.46	2.178	2.129
003	vw	43.17	2.096	2.097
023	w	50.17	1.8183	1.8553
240	vw	50.78	1.7979	1.7844
340	vw	57.45	1.6040	1.6023
004	w	58.56	1.5762	1.5730
014	m	60.14	1.5385	1.5449
$44\underline{0}$	w	66.72	1.4019	1.4213
$30\bar{4}$	vw	67.34	1.3905	1.3951
304	w	72.55	1.3029	1.3004

[a] a = 8.147 Å, b = 7.941 Å, c = 6.303 Å, β = 93.18°. [b] s, strong; m, medium; w, weak; v, very; vv, very very.

The occurrence of absorption bands from 725 to 900 cm^{-1} in the spectrum of the new phase, in contrast with γ-$LiAlO_2$, suggests a mixture of octahedral and tetrahedral coordination of the aluminum ions. On this basis, the new phase indeed parallels β-$LiBO_2$ with the group III element showing two coordination numbers in the crystal.

Marezio and Remeika[17] reported the $\gamma \rightarrow \alpha$ transition in their sample after heating overnight at 600° in the air. In this work, both γ-$LiAlO_2$ and the new β phase were heated in platinum crucibles at 710° for 3 days, but no low-pressure phase was found. Thus, the reverse transition appears to be slow.

$LiGaO_2$. The new β form of $LiGaO_2$ is isostructural with the β-$LiAlO_2$. Debye–Scherrer powder pat-

---

(12) P. Tarte and R. Collongues, *Ann. Chim.*, **9**, 135 (1964).
(13) C. H. Chang and J. L. Margrave, *Mater. Res. Bull.*, **2**, 929 (1967).
(14) C. H. Chang, Ph.D. Thesis, Rice University, 1967.
(15) V. A. Kolesova, *Opt. i Spektroskopiya*, **10**, 414 (1961).
(16) V. A. Kolesova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2082 (1962).
(17) M. Marezio and J. P. Remeika, *J. Chem. Phys.*, **44**, 3348 (1966).

Table II. X-Ray Diffraction Pattern of Newly Synthesized β-$LiGaO_2$[a]

hkl	Rel intensity[b]	2θ	d_{obsd}	d_{calcd}
200	s	21.78	4.08	4.042
020	s	22.83	3.90	4.032
002	w	28.25	3.16	3.201
300	m	32.77	2.73	2.695
030	w	33.32	2.69	2.688
022	s	35.98	2.50	2.507
$20\bar{2}$	m	37.49	2.399	2.396
131	w	37.95	2.371	2.390
230	vw	40.63	2.220	2.239
003	m	42.28	2.138	2.134
401	vw	45.96	1.9746	1.9732
140	vw	46.47	1.9541	1.9562
331	w	49.27	1.8494	1.8518
$41\bar{1}$	w	49.63	1.8368	1.8352
402	w	51.87	1.7627	1.7730
033	vw	54.99	1.6698	1.6714
422	m	56.18	1.6372	1.6239
430	vw	57.01	1.6153	1.6154
004	w	57.83	1.5944	1.6005
014	m	58.88	1.5684	1.5698
$10\bar{4}$	vw	59.59	1.5514	1.5468
143	w	64.18	1.4511	1.4562
304	m	65.42	1.4266	1.4269
$41\bar{3}$	vw	67.45	1.3885	1.3912
134	vw	68.33	1.3727	1.3714
600	w	69.83	1.3469	1.3473
$30\bar{4}$	m	70.83	1.3303	1.3305

[a] a = 8.110 Å, b = 8.065 Å, c = 6.422 Å, β = 94.56°. [b] See footnote *b*, Table I.

terns of both of the high-pressure forms of $LiGaO_2$ were obtained, and the β-$LiGaO_2$ pattern could be indexed on the basis of a monoclinic structure with a = 8.110 Å, b = 8.065 Å, c = 6.422 Å, and β = 94.56° as shown in Table II. The absorption spectrum (Figure 2) bears a resemblance to that of β-$LiAlO_2$. The absorption from 625 to 750 cm^{-1} is from GaO_4 groups, while that in the region 475–600 cm^{-1} is from GaO_6 groups. Also shown in Figure 2 is the spectrum of $LiGa_5O_8$ in which Ga occupies both tetrahedral and octahedral sites.[18]

Nomenclature. The nomenclature presently in the literature for $LiMO_2$ compounds does not have a unique basis; therefore, it is quite easy to be confused and misled. For example, the low-pressure form of $LiBO_2$ was called the α phase, that of $LiAlO_2$ was labeled the γ form, while the corresponding $LiGaO_2$ polymorph was originally called β-$LiGaO_2$,[11] following the nomenclature used in the $NaFeO_2$ system.

Since the polymorphism of $LiMO_2$ species is analogous to that of HBO_2 as will be discussed in the next section, a nomenclature similar to that of HBO_2, as suggested by Marezio and Remeika[17] for $LiBO_2$, should be used for all $LiMO_2$ compounds. On the basis of this new nomenclature, the new phases reported are β-$LiAlO_2$ and β-$LiGaO_2$, the other two high-pressure forms are γ-$LiAlO_2$ and γ-$LiGaO_2$, and the normal pressure forms are α-$LiAlO_2$ and α-$LiGaO_2$.

Thus, the polymorphs of $LiMO_2$ compounds (M = B, Al, Ga) include three structures: an α form prepared at normal pressures and temperatures, in which all metal ions M^{3+} show trigonal (B) or tetrahedral (Al, Ga) coordination; a γ form, prepared at highest pressures, in which all metal ions M^{3+} show tetrahedral (B) or octahedral (Al, Ga) coordination; and a β form, prepared under intermediate conditions, in which the metal ions show both types of coordination, analogous to the β-HBO_2 system.

Because of the complexity arising from the metal ions occupying two types of coordination sites, the lattices of the β forms have lower symmetry than those of the corresponding α and γ forms, as shown in Table III. The high-pressure γ forms crystallize in the lattices of highest symmetries.

The various forms of $LiMO_2$ can be synthesized directly through the following general reaction

$$Li_2O_2(s) + M_2O_3(s) \longrightarrow 2LiMO_2(s) + 0.5O_2(g)$$

under conditions of high pressure and high temperature as summarized in Table IV.

Table III. Polymorphism of HBO_2 and $LiMO_2$ Compounds

	α phases		β phases		γ phases		
Compound	Lattice structure	CN[a]	Lattice structure	CN[a]	Lattice structure	CN[a]	Ref
HBO_2	Orthorhombic	3	Monoclinic	3, 4	Cubic	4	13
$LiBO_2$	Monoclinic	3	Unknown, probably triclinic	3, 4	Tetragonal	4	13
$LiAlO_2$	Tetragonal	4	Monoclinic	4, 6	Hexagonal	6	This work
$LiGaO_2$	Orthorhombic	4	Monoclinic	4, 6	Hexagonal	6	This work

[a] CN = coordination number.

Table IV. The Direct Syntheses of High-Pressure $LiMO_2$ Phases

$LiMO_2$	β phase	γ phases	Ref
$LiBO_2$	15 kbars, 230°	18 kbars, 370°	13
$LiAlO_2$	18 kbars, 370°	25 kbars, 530°	This work
$LiGaO_2$	18 kbars, 420°	30 kbars,[a] 850°	This work

[a] $\alpha \rightarrow \gamma$ transition reported by Marezio and Remeika;[11] in this work, the compound $LiGa_5O_8$ was found at 34 kbars and 820°.

Acknowledgment. This work was supported financially by funds administered through the office of Dr. George Wyman of the Chemistry Division of the U. S. Army Research Office, Durham.

---

(18) J. C. Joubert, M. Brunel, A. Waintal, and A. Durif, *Compt. Rend.*, 256, 5324 (1963).