

On lithium and sodium trivalent-metal pyroxenes and crystal-field effects

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SUMMARY. Of the metals in the series Sc, V, Cr, Mn, Fe, and Ga pyroxenes of the type $\text{LiM}^{3+}\text{Si}_2\text{O}_6$ were obtained only from Sc, V, Cr, and Fe in dry synthesis experiments near 1000 °C. Ga and Al gave keatite derivatives (so-called ' β -spodumenes') by dry heating; α -Ga-eucryptite was obtained from Ga hydrothermally at pressures between 4.5 and 6.5 kb. Mn gave Mn_2O_3 . The lattice parameters of the pyroxenes vary irregularly with atomic number. This variation and the failure to produce a Mn^{3+} -pyroxene can be explained by the crystal-field theory. At high temperatures Al and Ga are too small to stabilize a silicate pyroxene phase even at moderately high pressures and form less dense tectosilicates. The octahedral stabilization energy for Cr^{3+} ensures that Cr, which has the same size as Ga, forms a pyroxene.

THE lithium pyroxene spodumene has only been synthesized at high pressures (Munoz, 1968, 1969), even though its geological occurrences do not suggest that it is a high-pressure mineral. On the other hand, $\text{LiAlGe}_2\text{O}_6$ crystallizes as a pyroxene at atmospheric pressure (Hahn and Behruzi, 1968). It was thought (Brown, 1968) that a study of lithium trivalent-metal pyroxenes might shed light on the crystal chemistry of the pyroxenes in general and spodumene in particular.

Experimental. The trivalent metals used in this study were $_{13}\text{Al}$, $_{21}\text{Sc}$, $_{23}\text{V}$, $_{24}\text{Cr}$, $_{25}\text{Mn}$, $_{26}\text{Fe}$, and $_{31}\text{Ga}$. Mixes were made up from lithium carbonate, silica, and oxides of the metals by grinding for 30 min in an agate mortar. In the dry-heating experiments the powders were pressed at 20 ton/in² for 1 min to ensure good contact, and then heated at a temperature corresponding to the stability of the trivalent state of the metal in air—Cr 24 h at 980 °C, Mn 24 h at 850 °C, and Fe 24 h at 1000 °C. In the case of vanadium, V_2O_3 was produced from V_2O_5 by reduction with H_2 at 1000 °C for 3 h, and the mixture then heated for 5 h under the same conditions. The mixtures containing Al, Sc, and Ga were heated for 24 h at temperatures between 950 and 1000 °C. Hydrothermal experiments were only carried out in the case of Ga.

The microcrystalline products were examined on a diffractometer using Si as internal standard, and the lattice parameters refined by the method of least squares. In some cases lines corresponding to unreacted materials were seen, especially in the cases of scandium and manganese. The times were probably too short in these cases for reaction to go to completion, so it is possible that the products differ slightly from the ideal composition. Single crystals were not available for any of the synthetic pyroxenes, so it was not possible to determine whether their space groups departed from $C2/c$ or not (Appleman and Stewart, 1966; Hahn and Behruzi, 1968).

Monoclinic pyroxenes were obtained with trivalent vanadium, chromium, iron, and scandium, though for the latter there were many extra peaks and the parameters did not refine well. The lattice parameters for the first three are given in table I along with those obtained by Ito and Frondel (1968) for synthetic $\text{LiScSi}_2\text{O}_6$.

TABLE I. *Lattice constants of synthetic and natural pyroxenes of type $\text{LiM}^{3+}\text{Si}_2\text{O}_6$ (the figures in brackets are the probable errors in the last figure shown)*

	<i>a</i>	<i>b</i>	<i>c</i>	β	Vol.
<i>Synthetic pyroxenes</i>					
$_{21}\text{Sc}^*$	9·83 (2) Å	8·98 (2) Å	5·37 (1) Å	110·4° Å (1)	444·4 Å ³
$_{23}\text{V}$	9·642 (13)	8·581 (8)	5·314 (9)	109·73° (11)	413·8 (11)
$_{24}\text{Cr}$	9·546 (3)	8·583 (1)	5·255 (1)	110·04° (3)	404·5 (2)
$_{26}\text{Fe}$	9·682 (1)	8·679 (1)	5·299 (1)	110·14° (1)	418·03 (6)
$_{31}\text{Ga}^\dagger$	9·58 (5)	8·52 (3)	5·29 (1)	110·2° (5)	405·2
<i>Natural spodumenes</i>					
No.					
I	9·471 (1)	8·385 (1)	5·220 (1)	110·32° (1)	388·79 (9)
97‡	9·468 (2)	8·384 (1)	5·212 (2)	110·31° (2)	388·04 (12)
684‡	9·470 (4)	8·386 (1)	5·219 (2)	110·33° (4)	388·7 (3)
1200‡	9·477 (2)	8·390 (1)	5·227 (1)	110·38° (2)	389·58 (17)

* Ito and Frondel (1968).

† Neuhaus and Meyer (1965).

‡ Same material as studied by Edgar (1968).

It proved impossible to obtain a pyroxene with Ga either in the dry-heating or hydrothermal experiments tried. Neuhaus and Meyer (1965) were successful at high pressure using Ga (table I), as was Munoz (1968) using Al. No pyroxene was obtained using Mn, only cubic Mn_2O_3 .

With both Al and Ga mixes, no pyroxenes were obtained by dry heating at atmospheric pressure. In the case of Al a stuffed keatite-type phase $\beta\text{-LiAlSi}_2\text{O}_6$ (' β -spodumene') was obtained. With Ga mixes the phases obtained were $\beta\text{-LiGaSi}_2\text{O}_6$ (' β -Ga-spodumene') and a minor amount of a phase with the same structure as $\alpha\text{-LiAlSi}_2\text{O}_6$, α -eucryptite. This latter phase was obtained with only a small amount of glass in the two hydrothermal experiments (3 days at 600 °C, 6·5 kb and 4 days at 715 °C, 4·5 kb), the lattice parameters for the well-crystallized material in the second experiment being a $13\cdot642 \pm 0\cdot002$ and c $9\cdot100 \pm 0\cdot002$ Å. Presumably, the composition of the α -Ga-eucryptite type solid solution can extend towards the $\text{LiGaSi}_2\text{O}_6$ composition (as found by Munoz, 1968, for the ' β -eucryptite' form of $\text{LiAlSi}_2\text{O}_6$) but the limit of solubility is not known.

Discussion. In fig. 1 the lattice parameters for the lithium pyroxenes are plotted against the atomic number of the trivalent metal from $_{21}\text{Sc}$ to $_{31}\text{Ga}$. For Sc, Fe, and Ga the values for the axial lengths and the volume (the uncertainty in the angle β for $\text{LiGaSi}_2\text{O}_6$ is too large to be sure) decrease smoothly as would be expected from the

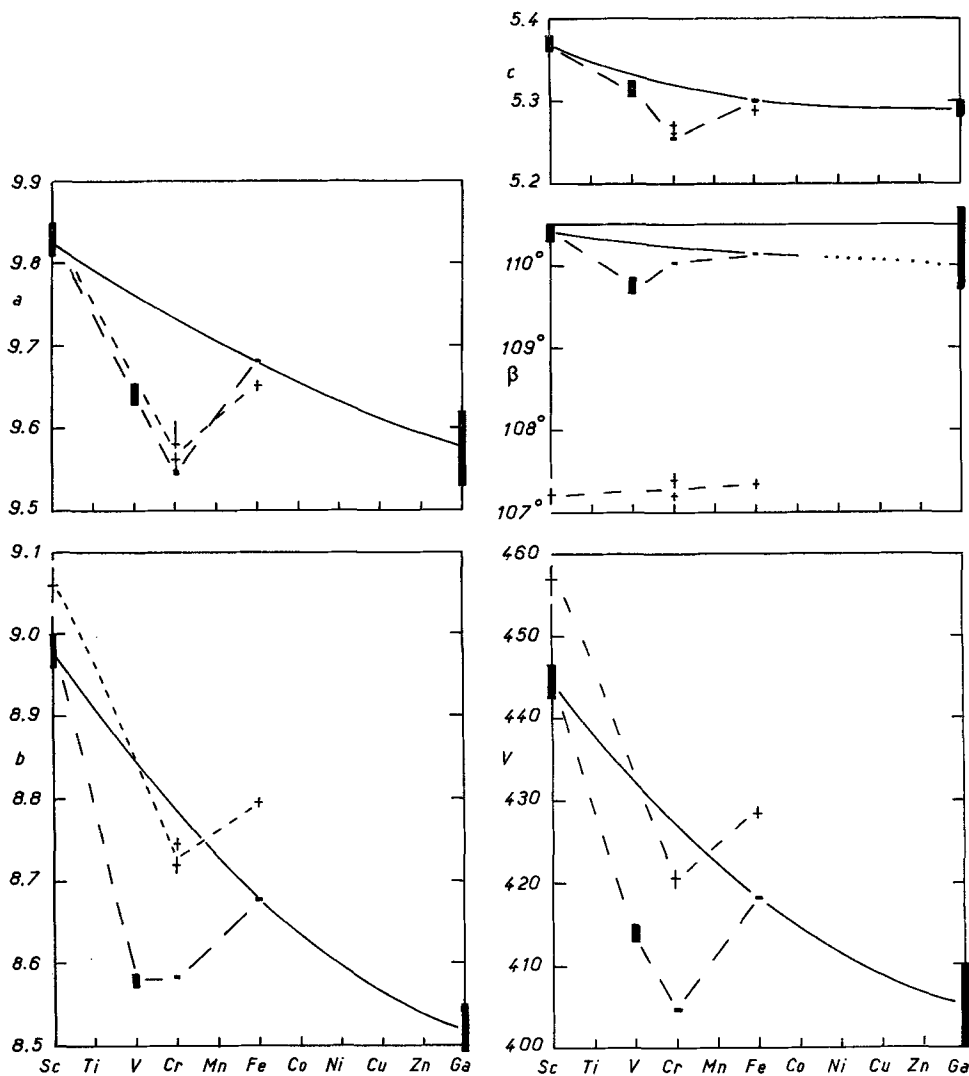


FIG. 1. Plot of the lattice parameters of lithium and sodium pyroxenes against atomic number of the trivalent cation. The filled symbols are for lithium pyroxenes and the crosses for sodium pyroxenes; the sizes of the symbols in the vertical direction indicate the probable error (in some cases estimated for the cell volumes). The volume is for the conventional C-centred cell. Data from table I and from Ito and Frondel (1968), Clark *et al.* (1968), and Frondel and Klein (1965).

increased nuclear charge. The values for ${}_{23}\text{V}$ and ${}_{24}\text{Cr}$ are smaller than those for iron and lie below the smooth curve through the points for the first three.

These discrepancies can be explained by crystal-field theory. The trivalent cations occupy the M1 site in Li-pyroxenes, which is a slightly distorted octahedron. The contraction from Sc^{3+} to Cr^{3+} can be explained by the fact that the $3d$ electrons in

V^{3+} and Cr^{3+} occupy t_{2g} orbitals, which are directed between the ligands in the distorted octahedral field. In the case of Fe^{3+} two further electrons occupy the two e_g orbitals, which are directed towards the six ligands and repel them slightly giving longer metal-oxygen bonds (Orgel, 1960; Burns and Fyfe, 1967), and hence larger lattice parameters. The same situation occurs in the sodium pyroxenes, where the Cr^{3+} pyroxene cosmochlore has smaller parameters than the Fe^{3+} pyroxene aegirine (fig. 1).

The failure to synthesize a Mn^{3+} pyroxene may perhaps be explained by the crystal-field theory. Clark *et al.* (1969) have published bond lengths for two lithium and four sodium pyroxenes (two from the literature). In all six cases the M1 octahedron at room temperature is deformed, the intermediate bond length being always slightly closer to the largest than to the smallest. Only in the cases of spodumene, cosmochlore, and $NaInSi_2O_6$ does the deformation of the octahedron approach a squat tetragonal configuration with four longer and two shorter bonds. The ratio of the length of the two shortest bonds to the average length of the other four is 0.92 for spodumene. For $LiFeSi_2O_6$ the deformation is more nearly orthorhombic, the intermediate bonds being only slightly larger than the average of the shortest and longest. The pyroxene structure clearly accommodates itself to the size of the cations in the M1 site.

The Mn^{3+} ion has only one electron in the e_g orbital and generally occurs in elongate octahedra in crystals with four short and two long bonds. Strens (1966) has shown that the octahedron should have a deformed tetragonal configuration with $c > a$. The configuration with $c < a$ should only be stable if the energy required to distort the crystal as a whole is not great. The Mn^{3+} ion is probably nearer in 'size' to Fe^{3+} than to Al^{3+} . If the same distortions in the pyroxene occur at high as at low temperatures, it is possible that an Mn^{3+} ion cannot accommodate itself in a Li-pyroxene as the spontaneous distortion caused by the rest of the structure in such pyroxenes does not correspond to that required by Mn^{3+} .

In both the Li- and Na-pyroxenes the effect of increasing the size of the cation in the M1 site is to increase the volume and the b , a , and c -axes in that order, β changing less (fig. 2). Compared with lithium pyroxenes the effect of substituting the larger Na^+ ion in the M2 site is to increase the b -axis and to reduce β ; the effect on β increases and on b decreases when the size of the cation in M1 is increased in the series Al, Cr, Fe, Sc (fig. 2); the a and c -axes remain virtually unchanged. The effect of replacing Si in tetrahedral co-ordination by larger cations is not yet clear. In the case of germanium, the Al and Ga germanate pyroxenes have apparently different Space groups (or at least different pseudogroups) and differ markedly in their parameters (Hahn and Behrzi, 1968). In $CaAlAlSiO_6$ 'Tschermak's molecule', the replacement of Si by Al in the tetrahedra is complicated by the simultaneous presence of Al in the octahedral site M1 and of Ca in the site M2.

As predicted by Whittaker (1960) the angle β is largely determined by the cation in M2 with only minor influence of the cation in M1; this influence increases as the size of the cation in M2 increases from Li to Ca (fig. 2). The empirical relation deduced by Clark *et al.* (1968) between the b -axis and the average M1-O distance in eightfold co-ordinated Na- and Ca-pyroxenes would have to be modified for sixfold co-ordinated Li-pyroxenes by reducing the constant by about 0.14 Å. It may not apply to inter-

mediate substitutions (Clark *et al.*, 1969) nor to complex substitutions as the cations in the M1, M2, and Z sites modify the *b*-axis.

In conclusion, it would appear that both Al and Ga ions are too small to form a silicate pyroxene structure at atmospheric pressure at high temperatures and prefer

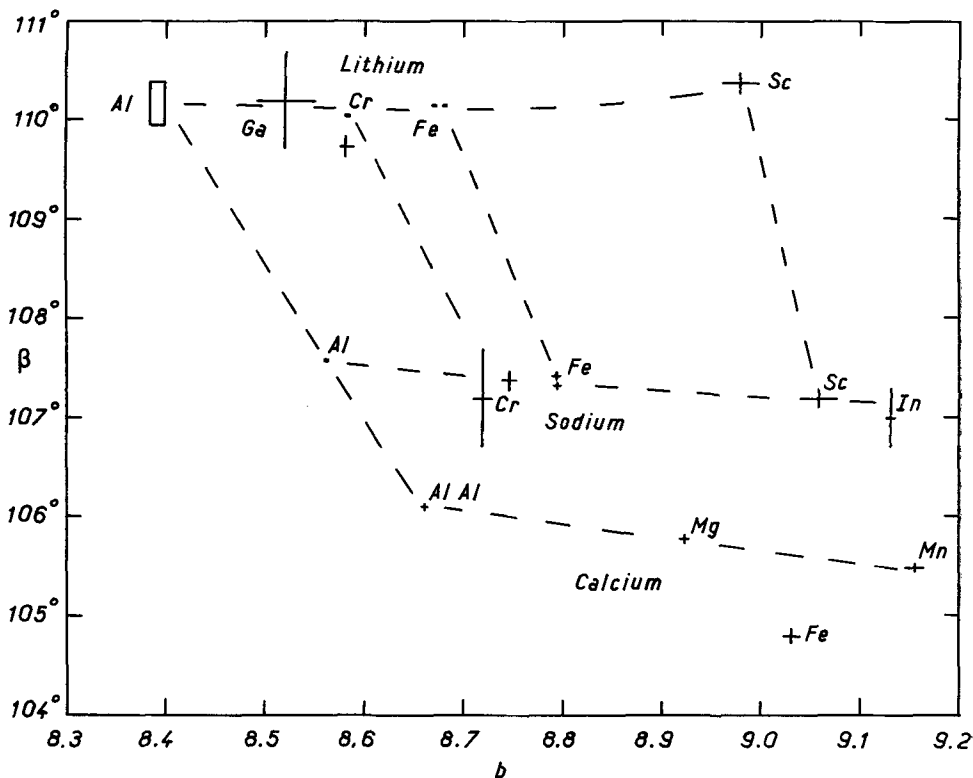


FIG. 2. Plot of b against β for lithium, sodium, and calcium pyroxenes. The crosses indicate the probable errors in the lattice parameters; the open rectangle for spodumene contains six such crosses. Data from table I and from Appleman and Stewart (1966), Munoz (1968), Prewitt and Burnham (1966), Frondel and Klein (1965), Clark *et al.* (1968), Nolan and Edgar (1963), Ito and Frondel (1968), Christensen and Hazell (1967), Hays (1966), Nolan (1969), and Freed and Peacor (1967).

tetrahedral co-ordination in framework silicates; if Munoz's (1968) data represent stable equilibrium, the extrapolated maximum temperature for the existence of spodumene at atmospheric pressure is in the range 400–500 °C. This temperature should be higher in the case of gallium because of its larger ionic radius. On the other hand, the octahedral site stabilization or preference energies for Cr^{3+} and for V^{3+} are sufficiently great, especially in the case of Cr^{3+} , to ensure that they enter into octahedral co-ordination.

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