TABLE II. *DTA and dehydration data on okenite from India*

| Locality | Endothermic reaction (°C) | Exothermic reaction (°C) | Dehydration | |
|---|---|---|---|---|
| | | | 0–200 °C | 0–500 °C |
| Bombay | 100, 197, 376 | 890 | 35.3 | 88 |
| Nasik | 98, 188, 368 | 890 | 39.65 | 88.23 |
| Poona | 100, 190, 370 | 890 | 42.66 | 93 |

In conclusion it may therefore be remarked that the DTA curves of okenite may serve as excellent identification characteristics, and that the precise range of temperature of transformation of okenite to wollastonite and cristobalite is from 855 °C to 915 °C.

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# Further evidence for the instability of LiMnSi$_2$O$_6$ at low pressure

SPODUMENE and spodumenes with Al replaced by Fe, Cr, V, Sc, In, and Ga have been synthesized at various temperatures and pressures. Brown (1971) synthesized Fe, Cr, V, and Sc spodumenes by firing pelletized silica, lithium carbonate, and metal oxide mixes at 850 to 1000° but failed to produce Al, Mn, or Ga spodumenes. He suggested no LiMnSi$_2$O$_6$ exists because spontaneous distortion caused by the pyroxene structure does not correspond to that required by Mn$^{3+}$ due to the Jahn–Teller effect. This follows the argument presented by Strens (1965) to account for failure to hydrothermally synthesize Ca$_3$Mn$_2$Si$_3$O$_{12}$ garnet at 2–3 kb and 530–600°, and is supported by the occurrence of non-cubic henritermierite with hydrogarnet composition Ca$_3$(Mn$_{1.5}$Al$_{0.5}$)(SiO$_4$)$_2$

(OH)$_4$ (Gaudefroy et al., 1969) and by the doubtful validity of blythite.

However, reviewing garnets, Geller (1967) noted germanate garnets Ca$_3$Mn$_2$Ge$_3$O$_{12}$ and Cd$_3$Mn$_2$Ge$_3$O$_{12}$ had been synthesized and Mn$^{3+}$ had been substituted for Fe$^{3+}$ to Y$_3$ (Mn$_{0.1}$ Fe$_{1.9}$) Fe$_3$O$_{12}$ in YlG, suggesting Mn$^{3+}$ may enter sites lacking suitable distortion. For spodumene, Leckebusch et al. (1974) found Mn$^{3+}$ in reddish violet varieties but Mn$^{2+}$ in reddish yellow spodumenes.

These and other reports on Mn$^{3+}$ in blanfordites suggest Mn$^{3+}$ may enter the pyroxene structure, and successful syntheses of Al spodumene hydrothermally (reviewed by Stewart, 1978) indicate Brown's failure to obtain LiMnSi$_2$O$_6$ may be because of the technique and conditions used and

not because of its instability. Drysdale (1975) synthesized Cr, Fe, V, In, and Sc spodumenes hydrothermally at 2kb $P_{H_2O}$ from gels within the stability fields of the $\alpha$ oxyhydroxides or $\alpha$ oxides and $CM_2O_3$ oxides respectively, a synthesis route in which near densest packing is maintained throughout to provide a favourable structural environment for spodumene nucleation, and this technique has now been applied to synthesis of $LiMnSi_2O_6$. Because the manganese oxyhydroxides and oxides are not exactly analogous to those of Fe, Cr, V, In, and Sc, a precisely similar Mn gel could not be prepared and three varieties of starting material were used, each likely to be suitable for spodumene synthesis by analogy with other successful syntheses of substituted spodumenes.

Material A: Manganite based. $\gamma$ MnOOH has a deformed InOOH structure, with anions in a near hexagonal close-packed array. The material was prepared by solution of silica gel ($<$ 300 mesh) in $2N$ LiOH to produce a sol. This was added to a 0.1 M solution of manganese sulphate containing 10% hydrogen peroxide with vigorous agitation, and a slight excess of ammonia. The suspension was boiled briefly, filtered and washed on a Buchner funnel, and the co-precipitated silica and manganese oxyhydroxide dispersed in a solution of lithium carbonate to produce the desired Li:Mn:Si ratio. The mix was evaporated to dryness at 80° under reduced pressure.

Material B: Groutite based. No reliable groutite synthesis is known so a sample of natural groutite kindly donated by Mr R. Phillips from the Durham University collection was used. This was dispersed in a silica sol, which was then precipitated, and the preparation completed as in A.

Material C: Partridgeite based. Partridgeite has a distorted $CM_2O_3$ structure. A $LiMnSi_2O_6$ composition was prepared following the procedure of Frondel and Ito (1968).

All experiments were carried out with the charges in sealed capsules contained in externally heated, cold seal, test tube pressure vessels. Weighing of capsules before and after runs detected leaks and these capsules were discarded. Temperatures were measured by chromel-alumel thermocouples located externally in wells in the vessel walls alongside charges and are accurate to $\pm$ 10°. Pressures were measured on Bourdon gauges rate accurate to 50 bars. All runs were carried out at 2 kb $P_{H_2O}$. Water and a 5% hydrogen peroxide solution were variously used as hydrothermal fluid. Some runs were buffered using the technique described by Abs-Wurmback and Langer (1975). Vessels were

first brought up to pressure cold and then up to temperature in 10 to 20 minutes, maintaining pressure constant at 2 kb. At the end of a run vessels were quenched, reaching less than 100° in under 1 minute. Phase identification was by X-ray diffraction and optical microscopy.

Runs carried out with the three materials at 440° to 700° yielded various assemblages in which partridgeite and quartz were the only phases definitely identified. No $LiMnSi_2O_6$ was found.

In the absence of known experiment design factors inhibiting synthesis it is concluded that $LiMnSi_2O_6$ is not stable under these conditions. Other structures containing $Mn^{3+}$ in octahedral coordination with appropriate distortion have been synthesized under similar conditions, e.g. kentrolite was prepared by Ito and Frondel (1969) and has $Mn^{3+}$ octahedrally coordinated in a trigonal prismatic arrangement with four short and two long Mn-O bonds. Nishizawa and Koizumi (1975) found $Ca_3Mn_2Si_3O_{12}$ garnet was not formed at 600° 2 kb $P_{H_2O}$, wollastonite and partridgeite crystallizing from this bulk composition. They did, however, produce cubic garnet of this composition at 1100° and 30 to 60 kb. The structure has distorted $SiO_4$ tetrahedra strongly effected by the Jahn-Teller distortion of $MnO_6$ octahedra. They suggest silicate garnets with $Mn^{+++}$ on 'a' may occur naturally as a relatively high-pressure mineral. Possibly $LiMnSi_2O_6$ also becomes stable at pressures very much higher than 2 kb. This is under further investigation here.

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