JOURNAL OF MATERIALS SCIENCE 11 (1976) 1607–1614

Flux growth of crystals of some magnetic oxide materials: Mn_7SiO_{12}, CuO, MCr_2O_4, $MTiO_3$, Ni_2NbBO_6, $MMoO_4$ and $Li_2M_2(MoO_4)_3$, (M = Mn, Co, Ni)

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The flux growth of crystals of a number of compounds of Mn, Co and Ni is reported. The crystals have been characterized by X-ray powder patterns and electron probe microanalysis (EPMA). Empirical formulae are given. Two of the materials occur as minerals: Mn_7SiO_{12}, Braunite, and CuO, Tenorite.

1. Introduction

This paper reports the flux growth of some oxides containing transition metal ions. In growth from fluxed melts, the compound which crystallizes first should be that having the highest thermodynamic stability under the prevailing conditions; but, unless reliable phase diagrams or the results of previous experimental work are available, it is rarely possible to predict what phases will crystallize. Moreover, a single melt may yield three or more different crystalline phases during cooling; and in exploratory work unexpected compounds are often obtained as crystals. Most compounds containing transition metals are likely to have interesting magnetic properties, and those occurring in the present work were, therefore, characterized by their X-ray powder patterns and by electron probe microanalysis (EPMA). The latter enabled empirical formulae to be calculated, but such formulae can only be regarded as preliminary until the crystal structures are fully worked out. The crystals reported here include two that occur as minerals: Braunite, Mn_7SiO_{12} and Tenorite, CuO. Table I summarizes available information on

TABLE I Magnetic transition temperatures and melting points of the compounds

Formula	T_N(K)	Reference	Melting point (°C)	Reference
CuO	230	[1–3]	decomposes above 1000	
$MnCr_2O_4$	43	[4]		
	55	[5]		
$NiCr_2O_4$	60	[6]		
$CoTiO_3$	38	[7]	1470	[8]
	42	[9]		
$MnTiO_3$	41	[10]	1360, incongruently	[11]
	62	[12]		
Ni_2NbBO_6	25	[13]		
$NiMoO_4$	19	[9]	1475	[14]
$MnMoO_4$	13	[9]	1100	[14]
$CoMoO_4$	5	[9]	1300	[14]
$Li_2Mn_2(MoO_4)_3$	tends ferromag.	[9]		
$Li_2Co_2(MoO_4)_3$	tends ferromag.	[9]		
$Li_2Ni_2(MoO_4)_3$	tends ferromag.	[9]		

magnetic transition temperatures and melting points for some of the materials studied [1–14].

2. Chemicals

The following chemicals were used: BDH Analar grade CuO, PbO, Na_2CO_3, MoO_3 and PbO_2; BDH Laboratory Reagent grade CuF_2, $PbCl_2$, NH_4HF_2, $MnCO_3$, Li_2CO_3, Cr_2O_3, NiO, CoO, TiO_2, V_2O_5, B_2O_3 and $Na_2B_4O_7$; BDH Optran grade Nb_2O_5; Johnson Matthey Grade II PbF_2 and Koch-Light SiO_2.

3. Experimental

Since small crystals about 0.5 mm on edge were required for initial measurements of magnetic susceptibility, no attempt has been made to optimise crystal growth conditions. The starting materials were weighed out to ± 0.05 g, mixed together and put into platinum crucibles. The lids were closely fitted and the crucibles were placed in D-shaped sillimanite muffles [15], inside furnaces with crusilite elements at each side [16]. The muffle entrance was blocked with refractory brick and the furnace was heated at $100\,K\,h^{-1}$ to the desired temperature. After a suitable soak period the slow cooling programme was begun. Each crucible was then situated in a temperature gradient such that the base of each crucible was about 5° C cooler than the top.

At the end of the experiment, "hot draining" was frequently used to separate flux from crystals, especially when the crystals were fragile or soluble in acid. After each crucible had cooled to room temperature, it was inverted on a bed of alumina powder and the temperature was raised at $176\,K\,h^{-1}$ to an estimated 50 to 100 K above that at which the flux would liquefy. The crucible was then cooled to room temperature at the same rate. Because growth had occurred in a temperature gradient, the crystals were located chiefly near the crucible base, from which it was easy to detach them after the lid and the disc of solidified flux had been removed. The flux formed a high melting compound with alumina at the junction of lid and crucible and so prevented further escape.

Alternatively, the crucible and contents were soaked in water or dilute acid solution for several days. This sometimes softened the flux sufficiently to allow washing by decantation, drying and visual or magnetic separation of the crystals. The crystals were finally cleaned with hot water or very dilute nitric acid.

Materials which contain transition metal ions are either ferromagnetic, ferrimagnetic or highly paramagnetic at room temperature; thus a first test was to determine whether a small piece of the crystal, approximately $0.5\,mm^3$, was attracted by a magnet. If the test was positive, an X-ray powder pattern was made, for identification or characterization purposes. EPMA indicated the contents of the main constituents (excepting Boron) and of possible impurities and enabled empirical formulae to be calculated. These are provisional until such time as crystal structures are finalized. Examination of transparent crystals with a polarizing microscope showed whether extinction occurred or crystallographic domains were present.

The following section describes the preparation of each crystal material, its examination and characterization.

The starting compositions and furnace programmes are given in Table II.

4. Notes on the crystals

4.1. Mn_7SiO_{12}, Braunite

The mineral Braunite, Mn_7SiO_{12} or 3 Mn_2O_3.-$MnSiO_3$, occurs in many localities as black to steel-grey crystals up to 5 cm in length. Impurities such as Ba, Fe, Ca and Mg are invariably present in the mineral specimens [17].

Black, shiny, faceted crystals which gave an X-ray powder pattern in close agreement with published data for the mineral [18] were produced from a fluxed melt containing $MnCO_3$ and SiO_2, with $Na_2CO_3 + MoO_3$ as solvent (Table II). The crystals were attacked by dilute NaOH or HNO_3 solution and were therefore separated from the flux by hot draining at 800° C. The crystals, attached to the crucible base and sides, were cleaned by soaking in warm water. Prisms up to $(2 \times 1 \times 0.3)\,mm^3$ were obtained as shown in Fig. 1.

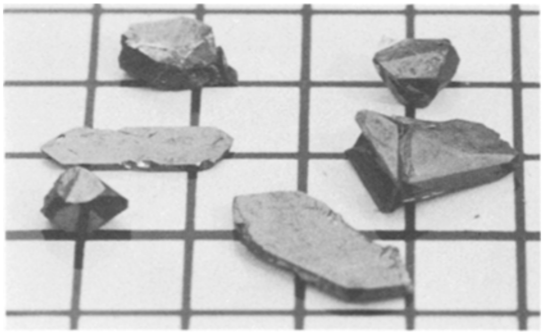

Figure 1 Prisms and platelets of Mn_7SiO_{12} (1 mm grid).

TABLE II Starting compositions, cooling programmes and crystal products

Formula	Starting compositions	Crucible volume (cm^3)	Initial temp. (°C)	Holding time (h)	Cooling rate ($K h^{-1}$)	Final temp. (°C)	Crystal products
Mn_7SiO_{12}	9.1 g $MnCO_3$, 2.4 g SiO_2, 9.6 g Na_2CO_3, 19.5 g MoO_3	50	1270	20	1	800	Black prisms up to (2 × 1 × 0.3) mm^3, shown in Fig.1
CuO (1)	5 g CuF_2, 12.3 g PbF_2, 14 g $PbCl_2$, 2.5 g NH_4HF_2	20	1000	9	1.2	600	Black rods and platelets, (1.5 × 1 × 1) mm^3, shown in Fig. 2
(2)	5 g CuF_2, 18 g PbO, 36 g PbF_2, 1 g PbO_2	40	1000	9	1.2	600	Crystals 1 to 2 mm on edge, less well-formed than above
$Mn_xCr_{3-x}O_4$	23 g $MnCo_3$, 23 g Cr_2O_3, 74 g PbF_2, 72 g PbO, 5 g PbO_2	50	1260	26	2	900	Black octahedra up to 2.5 mm on edge, shown in Fig. 3
$NiCr_2O_4$	11.2 g NiO, 22.8 g Cr_2O_3, 74 g PbF_2, 3.3 g PbO_2, 76 g PbO	100	1260	26	2	900	Black octahedra up to 2.5 mm on edge
$CoTiO_3$	2.8 g CoO, 3 g TiO_2, 25.7 g PbO, 11.2 g V_2O_5	50	1290	24	2	800	Black plates of $CoTiO_3$, (4 × 3 × 0.6) mm^3, red by transmitted light, and rods of rutile. $CoTiO_3$ is shown in Fig. 4
$MnTiO_3$	2.6 g $MnCO_3$, 1.8 g TiO_2, 45 g PbF_2, 1 g PbO_2	50	1285	144	–		Black platelets up to (3 × 2 × 0.5) mm^3
Ni_2NbBO_6	6.6 g NiO, 20 g Nb_2O_5, 33 g $Na_2B_4O_7$	50	1250	9	2 after 3 days, 4	500	Orange $NiNb_2O_6$ prisms and green Ni_2NbBO_6 up to about (3 × 2 × 2) mm^3
$CoMoO_4$	3 g CoO, 6.5 g Na_2CO_3, 27 g MoO_3	20	1260	15	2 after 3 days, 3	500	Crystals up to 15 mm edge which broke up into pieces about 3 mm on edge
$MnMoO_4$	3.4 g MnO_2, 6.5 g Na_2CO_3, 27 g MoO_3	20	1260	15	2 after 3 days, 3	500	Crystals over 10 mm on edge which cleaved into pieces approx. 4 mm on edge as shown in Fig. 5
$NiMoO_4$	6 g NiO, 12.9 g Na_2CO_3, 54 g MoO_3	50	1250	9	2 after 3 days, 3	500	Crystals over 10 mm on edge yielded fragments less than 2 mm on edge
$Li_2Ni_2(MoO_4)_3$	2 g NiO, 1.8 g Li_2CO_3, 10.8 g MoO_3	20	1295	9	1.5	650	Gold needles of $Li_2Ni_2(MoO_4)_3$, about (2.5 × 0.2 × 0.1) mm^3
$Li_2Mn_2(MoO_4)_3$	6 g $MnCO_3$, 5 g SiO_2, 3.7 g Li_2CO_3, 21 g MoO_3	50	1290	20	2	800	Small black rods of $Li_2Mn_2(MoO_4)_3$ about (6 × 0.5 × 0.3) mm^3
$Li_2Co_2(MoO_4)_3$	3 g CoO, 0.8 g SiO_2, 1.8 g Li_2CO_3, 10.8 g MoO_3	20	1290	20	2	800	Larger black shiny rods of $Li_2Co_2(MoO_4)_3$ shown in Fig. 6

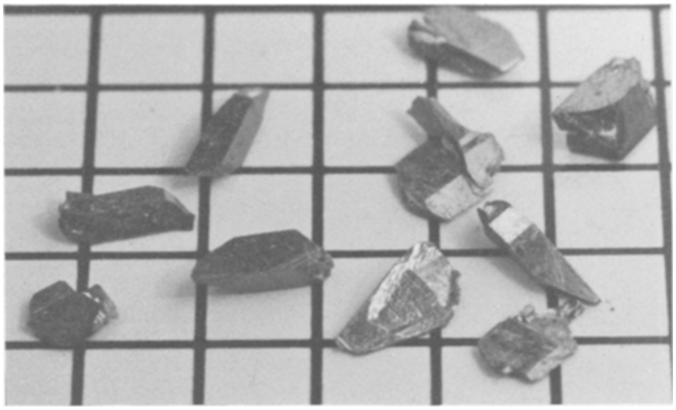

Figure 2 Crystals of CuO (1 mm grid).

EPMA indicated that the empirical formula of the crystals was Mn_7SiO_{12}:

	Formula requires (%)	EPMA indicates (%)
Mn	63.6	63.7
Si	4.6	4.5
Na	–	< 0.05

Although X-ray powder pattern data corresponded closely to published data [18], in the present work the four stronger lines of the pattern were broad, indicating splitting. Three of these had multiple indices and were not analysed, but the line profile of the strongest peak, $h\,k\,l = 2\,2\,4$, was plotted and showed two $K\alpha_1$, $K\alpha_2$ doublets with an angular separation of $2\theta = 0.05°$. Thus it seems that a more exact study of the structure is needed.

4.2. CuO, Tenorite

Tenorite occurs in nature as paper-thin twinned aggregates, curved plates or thin shiny scales. It has a monoclinic structure, and is steel-grey to black.

CuO begins to decompose above 1000° C, limiting the choice of fluxes to those with low melting points. Both $PbO + PbF_2$, and $PbF_2 + PbCl_2$, were successful as fluxes for CuO, and black shiny prisms were produced. The latter flux mixture was the most effective, and since Cu^{2+} was introduced as CuF_2 into a melt of chlorides and fluorides, the crystals evidently grew by hydrolysis of the melt. The X-ray powder pattern corresponded closely to published data [19]. Some crystals are shown in Fig. 2.

4.3. $NiCr_2O_4$ and $MnCr_2O_4$

The Jahn–Teller transition exhibited by the chromium spinels makes them of special interest. Several papers refer to crystals grown from Bi_2O_3 as flux [20–22] and platinum crucibles of 1.5 litre capacity have been used [6], but no details of starting compositions and growth conditions are given. Kunmann *et al.* [23] published detailed descriptions of their growth from ($Na_2W_2O_7 + Na_2WO_4$).

Nevriva investigated flux growth methods for $Mn_xCr_yO_4$ [24]. He found that the system reported by Kunmann *et al.* [23] for MCr_2O_4 crystals yielded only crystals of MWO_4. Nevriva concluded that $PbO + PbF_2$ produced the best $Mn_xCr_yO_4$ crystals.

In the present work, $Mn_xCr_yO_4$ and $NiCr_2O_4$ crystals were required, and a survey was made of the reported methods as applied to both compounds. Like Nevriva [24], we found that experiments with $Na_2W_2O_7 + Na_2WO_4$ as flux yielded only metal tungstate crystals. Because of its severe attack on platinum, Bi_2O_3 alone was not used as a flux, but with $Bi_2O_3 + V_2O_5$ [25] small $NiCr_2O_4$ crystals were produced. With $PbO + PbF_2$, crystals of $NiCr_2O_4$ and of $Mn_xCr_yO_4$ over 2.5 mm on edge were obtained from 50 cm^3 crucibles; some are shown in Fig. 3. Complete solution was not achieved, and a layer of solute floated at the melt

Figure 3 Octahedra of $Mn_xCr_yO_4$ (1 mm grid).

surface while crystals grew at the crucible base as the result of combined evaporation and slow cooling. The X-ray powder pattern was in good agreement with published data [26].

4.4. $CoTiO_3$ and $MnTiO_3$

The phase diagram of $MnTiO_3$ indicates that it melts incongruently at 1360° C [11], thus the melt-grown crystals are described as inhomogeneous [12]. Since large $NiTiO_3$ crystals were produced from $Pb_2V_2O_7$ as flux [25], this appeared the most suitable method for preparing crystals of the related $MTiO_3$ compounds. However, several attempts to use $Pb_2V_2O_7$ as flux for $MnTiO_3$, using different ratios of $MnO:TiO_2$, resulted only in TiO_2. Slow cooling of a solution of the components in PbF_2 and also evaporation of this solution at 1150° C produced only Mn_3O_4. Evaporation of PbF_2 from the solution at 1285° C finally produced platelets of $MnTiO_3$, up to $(3 \times 2 \times 0.5)\,mm^3$. Very thin fragments were orange by transmitted light. The crystals were cleaned in hot 1 : 10 HNO_3 solution.

Crystals of $CoTiO_3$ grew as platelets about $(3 \times 2)\,mm^2$ and up to 1 mm thick from $Pb_2V_2O_7$ as flux, which was separated by hot draining at 1000° C. Much rutile crystallized with thin platelets of $CoTiO_3$, which were dark red by transmitted light. Some are shown in Fig. 4. $CoTiO_3$ was also grown by evaporation of PbF_2 from its solution with CoO and TiO_2. The X-ray powder patterns were in good agreement with published data [27, 28].

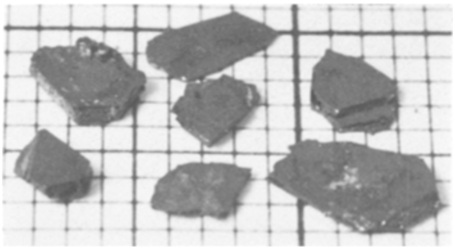

Figure 4 Platelets of $CoTiO_3$.

4.5. Ni_2NbBO_6

In the course of experiments intended to produce $NiNb_2O_6$ from $Na_2B_4O_7 + Nb_2O_5$ as flux, it was found that when the ratio $NiO:Nb_2O_5$ was about 1 : 3 by weight, a new phase besides $NiNb_2O_6$ and $NaNbO_3$ was obtained. This was bright emerald green in thin section (about 1 mm); thicker crystals were very dark green, translucent, and showed uniform extinction. Well-formed platelets up to $(2 \times 3 \times 0.3)\,mm^3$ often formed at the surface of the melt, while thicker crystals grew at the crucible base.

The crystals were recovered by hot draining at 1000° C and cleaned by soaking in hot water to which a few drops of 1 : 5 HNO_3 solution had been added.

EPMA showed good agreement with the formula Ni_2NbBO_6:

	Formula requires (%)	EPMA indicates (%)
Ni	37.0	37.1
Nb	29.3	29.8
Na	–	<0.05

Sintering the stoichiometric mixture was complicated by the tendency of B_2O_3 to sublime. However, the X-ray powder pattern of the sinter prepared by heating for 17 h at 1200° C showed all the lines of the crystal, plus a few weak lines which were not identified.

The X-ray powder pattern of the crystals is given in Table III. The structure of Ni_2NbBO_6 is the subject of a current investigation.

TABLE III X-ray powder pattern data for Ni_2NbBO_6

d_{obs}	$I_{estimated}$	d_{obs}	$I_{estimated}$
5.05	VW	2.352	VW
4.34	W	2.276	VW
3.70	MS	2.244	VW
3.27	VW	2.186	W
3.13	VW	1.985	VW
2.973	VS	1.960	VW
2.686	W	1.906	W
2.564	S	1.848	VW
2.494	M	1.812	VW
2.411	W	1.742	VW

4.6. $MMoO_4$ (M = Ni, Co, Mn)

These materials have been shown to become antiferromagnetic below 20 K [9] but measurements on single crystals have not been reported. It has been remarked that a phase change occurred in boules pulled from the melt and rapidly cooled. This resulted in sub-millimetre particles of $CoMoO_4$, and a fine powder of $NiMoO_4$ [14]. The phase change was noted earlier in a study by differential thermal analysis which showed that in the compounds $MMoO_4$ ($M = Ba^{2+}$, Zn^{2+}, Ni^{2+}, Co^{2+}), heated at $8\,K\,min^{-1}$, an endothermic reaction occurred between 300 and 450° C. When

$CoMoO_4$ was heated, then cooled at 8 K min^{-1}, no corresponding reaction was noted, and on immediate reheating the endothermic reaction was absent, but after a lapse of 24 h a slight endothermic reaction was again observed on heating. This indicated that the phase change was reversible after a time lapse. With $NiMoO_4$, the reaction on cooling was explosive [29].

Crystal structure studies show that $CoMoO_4$ and $NiMoO_4$ are isostructural and monoclinic [30–32], whereas $\alpha MnMoO_4$ (the room temperature form) has a different monoclinic structure, isostructural with $MgMoO_4$ [33]. The only orthorhombic form of cobalt molybdate is in fact $Co_2Mo_3O_{12}$, according to Smith [30].

Flux growth experiments were undertaken in the hope that slowly cooling $MMoO_4$ through the crystallographic transition might result in less damage to the crystals. $Li_2MoO_4 + MoO_3$ as flux resulted in $Li_2M_2(MoO_4)_3$, but $Na_2MoO_4 + MoO_3$ yielded large shiny crystals of $MMoO_4$ about $(10 \times 10 \times 6)\,mm^3$ which grew at the crucible base, and which were seen after softening the flux in hot water.

$NiMoO_4$: The large crystals broke up at once into a mass of powdery smaller particles. All were dull green, and under the polarizing microscope most did not transmit light. Small pieces, e.g. $(0.7 \times 0.3 \times 0.3)\,mm^3$, showed simultaneous extinction.

$CoMoO_4$: The crystal material was less fragile than $NiMoO_4$, but cleaved very readily into pieces about $(4 \times 3 \times 1)\,mm^3$ with shiny faces. The crystals appeared black, but were red by transmitted light. Only small fragments (approx. 0.1 mm thick) were translucent.

The X-ray powder pattern of this material closely resembled that of $NiMoO_4$ and agreed with published data [31].

$MnMoO_4$: These crystals were less fragmented. Cleaved pieces are shown in Fig. 5, and simultaneous extinction was observed in platelets approximately $(1.2 \times 1.2 \times 2)\,mm^3$. Their colour was scarlet by transmitted light.

4.7. $Li_2M_2(MoO_4)_3$ (M = Mn, Co, Ni)

Attempts to use $(Li_2MoO_4 + MoO_3)$ as a solvent for $MMoO_4$ or M_2SiO_4 resulted in crystals which had similar, unidentified X-ray powder patterns. A crystal from the batch with M = Co was analysed; the result was in agreement with the empirical formula $Li_2Co_2(MoO_4)_3$:

	Formula requires (%)	EPMA indicates (%)
Co	19.3	19.7
Mo	47.1	47.1
Si	–	<0.02

Crystals having this formula were referred to by van Uitert *et al.* [9], but no data as to characterization were given.

A stoichiometric mixture of the component oxides was accordingly held at 1000° C for 24 h. The X-ray powder pattern of the sinter was in good agreement with that of the crystals. Since the crystals with Ni and Mn had similar X-ray powder patterns to $Li_2Co_2(MoO_4)_3$, it was deducted that they had similar empirical formulae. X-ray powder pattern data are given in Table IV.

The crystals were all brittle, translucent, and showed simultaneous extinction parallel to the axis.

$Li_2Co_2(MoO_4)_3$: These occurred as black, shiny rods up to $(12 \times 1 \times 1.3)\,mm^3$, blue by transmitted light. Some are shown in Fig. 6.

$Li_2Mn_2(MoO_4)_3$: The rods were black, shiny, red by transmitted light, and up to $(6 \times 0.5 \times 0.3)\,mm^3$.

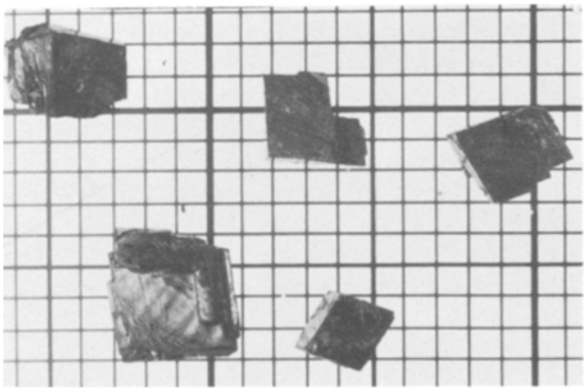

Figure 5 Cleaved pieces of $MnMoO_4$ (1 mm grid).

TABLE IV X-ray powder pattern data for $Li_2M_2(MoO_4)_3$, (M = Mn, Co, Ni)

$I_{\text{estimated}}$	$Li_2Mn_2(MoO_4)_3$ d_{obs}	$Li_2Co_2(MoO_4)_3$ d_{obs}	$Li_2Ni_2(MoO_4)_3$ d_{obs}
W	5.24	5.24	5.19
MS	4.46	4.42	4.40
W	3.47	3.42	3.38
VS	3.41	3.37	3.34
S	3.37	3.33	3.30
W	3.041	3.006	2.971
W	2.976	2.943	2.901
W	2.867	2.838	2.810
VW	2.654	2.618	2.592
M	2.618	2.587	2.558
MS	2.576	2.550	2.530
VW	2.503	2.480	2.457
VW	2.338	2.305	2.293
W	2.291	2.254	2.231
VW	2.239	2.206	2.195
W	2.088	2.054	2.041
W	1.968	1.942	1.929
W	1.952	1.924	1.908
W	1.938	1.888	1.874
VW	1.865	1.839	1.827
W	1.847	1.826	1.811
M	1.829	1.803	1.790
M	1.650	1.625	1.612
M	1.614	1.588	1.578

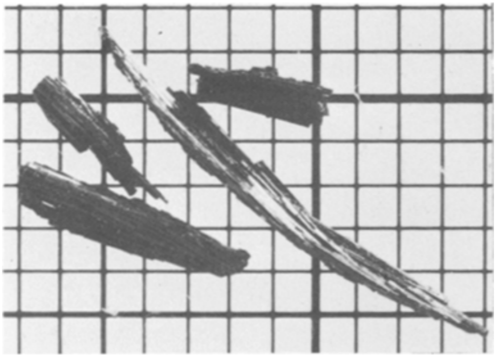

Figure 6 Rods of $Li_2Co_2(MoO_4)_3$ (1 mm grid).

$Li_2Ni_2(MoO_4)_3$: These grew as gold coloured needles about (2.5 × 0.2 × 0.1) mm^3.

Acknowledgements

The authors are grateful to Dr. G. Garton and Dr. S. H. Smith for helpful comments and to the latter also for technical assistance. This work was supported in part by the Science Research Council.

References

1. B. N. BROCKHOUSE, *Phys. Rev.* **94** (1954) 781.
2. R. D. SPENCE and R. EWING, *ibid* **112** (1958) 1544.
3. M. O'KEEFFE and F. S. STONE, *J. Phys. Chem. Solids* **23** (1962) 261.
4. J. M. HASTINGS and L. M. CORLISS, *J. Phys. Soc. Japan* **17** Suppl. B3 (1962) 43.
5. S. FUNAHASHI, K. SIRATORI and Y. TAMONO, *ibid* **29** (1970) 1179.
6. T. TSUSHIMA, *ibid* **18** (1963) 1162.
7. R. E. NEWNHAM, J. H. FANG, and R. P. SANTORO, *Acta Cryst.* **17** (1964) 240.
8. J. H. STRIMPLE, Doctoral Thesis, Rutger's University, State University of New Jersey, May 1957.
9. L. G. VAN UITERT, R. C. SHERWOOD, H. J. WILLIAMS, J. J. RUBIN and W. A. BONNER, *J. Phys. Chem. Solids* **25** (1964) 1447.
10. R. J. JOENK, *J. Appl. Phys.* **34** (1963) 1097.
11. J. GRIEVE and J. WHITE, *J. Roy. Tech. Coll. (Glasgow)* **4** (1940) 661.
12. J. J. STICKLER and G. S. HELLER, *J. Appl. Phys.* **33** (1962) 1302.
13. Private communication, M. R. WELLS and J. F. A. DA SILVA, Clarendon Laboratory, Oxford.
14. L. G. VAN UITERT, J. J. RUBIN and W. A. BONNER, *J. Amer Ceram. Soc.* **46** (1963) 512.
15. B. M. WANKLYN and Z. HAUPTMAN, *J. Mater. Sci.* **9** (1974) 1078.
16. G. GARTON, S. H. SMITH and B. M. WANKLYN, *J. Crystal Growth* **13/14** (1972) 588.
17. C. PALACHE, H. BERMAN and C. FRONDEL, "Dana's Mineralogy" 7th Edn. (Wiley, 1946).
18. ASTM 14–195.
19. ASTM 5–661.
20. T. TSUSHIMA, Y. KINO and S. FUNAHASHI,

J. Appl. Phys. 39 (1968) 626.
21. Y. KINO, B. LÜTHI and M. E. MULLEN, *J. Phys. Soc. Japan* 33 (1972) 687.
22. T. TSUSHIMA, *ibid* **17** Suppl. B 1 (1962) 189.
23. W. KUNMANN, A. FERRETTI, R. J. ARNOTT and D. B. ROGERS, *J. Phys. Chem. Solids* **26** (1965) 311.
24. M. NEVRIVA, *Kristall und Technik* **6** (1971) 517.
25. B. M. WANKLYN, *J. Crystal Growth* **7** (1970) 368.
26. ASTM 4–763.
27. ASTM 2–846.
28. ASTM 15–866.
29. Y. TRAMBOUZE, Y. COLLEUILLE and T. H. THE, *Compt. Rend.* **242** (1956) 497.
30. G. W. SMITH, *Nature* **188** (1960) 306.
31. *Idem, Acta Cryst.* **15** (1962) 1054.
32. G. W. SMITH and J. A. IBERS, *ibid.* **19** (1965) 269.
33. S. C. ABRAHAMS and J. N. REDDY, *J. Chem. Phys.* **43** (1965) 2533.

Received 5 February and accepted 1 March 1976.