

MIX-CRYSTALS OF Ca_2SiO_4 AND Mn_2SiO_4 *

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INTRODUCTION

Former investigators have suggested that Ca_2SiO_4 (shannonite) and Mn_2SiO_4 (tephroite) are isomorphous, but little optical and no x -ray data have been obtained to support this view. The present writer has prepared a series of artificial minerals containing measured proportions of Ca_2SiO_4 and Mn_2SiO_4 and subjected the series to optical and x -ray study. The work was aided by many valuable suggestions and criticisms offered by Dr. A. N. Winchell. Thanks are also due Dr. R. C. Emmons for assistance in the use of the high temperature equipment and double variation apparatus required in attacking the problem.

HISTORICAL REVIEW

Both end members of the series were prepared years ago, but it was not until 1914 that St. Kallenberg¹ synthesized a series of melts containing various proportions of Ca_2SiO_4 and Mn_2SiO_4 . More recently Tokody² published an account of a similar research. Both investigators concluded, on the basis of fusion temperatures, densities, molecular weights, and molecular volumes, that Mn_2SiO_4 is isomorphous with the γ -phase of Ca_2SiO_4 . Day and Shepherd³ have shown that Ca_2SiO_4 exists in three phases, viz., the α -phase, stable only above 1410°C ., the β -phase, stable between 1410° and 675°C ., and the γ -phase, which exists below 675°C .. A 10 per cent volume increase occurs when inversion to the γ -phase takes place. Wright⁴ states that the α -phase is monoclinic, the β -phase orthorhombic, and the γ -phase probably monoclinic.

THE SERIES IN NATURE

Mn_2SiO_4 is represented in nature by the rare mineral tephroite. Glaucocroite, corresponding to CaMnSiO_4 , is found at the same

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¹ St. Kallenberg: *Zeits. f. Anorg. Chemie*, **88**, (1914), pp. 355-359.

² L. Tokody: *Zeits. f. Anorg. Chemie*, **169**, (1928), pp. 51-56.

³ A. L. Day and E. S. Shepherd, with optical study by F. E. Wright: *Am. Jour. Sci.*, **22**, (1906), pp. 265-302.

⁴ *Op. cit.*

locality, i.e., Franklin, N. J. The lime orthosilicate is exceedingly rare, but the β -phase has been reported from Tasmania⁵ and Quebec.⁶

PROCEDURE

Melts containing MnO are difficult to produce since this substance takes on more oxygen very readily at temperatures well below its fusion point. Previous workers have overcome this difficulty by heating in a stream of nitrogen. This practice was not feasible in the present investigation: instead, heating was carried on in a vacuum, an electric furnace devised by R. C. Emmons⁷ being used. In this furnace a strong electric current is passed through a pair of carbon electrodes, one being hollow and functioning as a crucible.

Molecular proportions of ordinary C.P. quality CaCO_3 , MnCO_3 and SiO_2 were carefully weighed, mixed, and packed into the crucible which is approximately 1 inch long and 1/8 inch in diameter. Before heating was commenced the air in the furnace was evacuated. A temperature of 800–1000°C. was maintained for a few moments to drive off the CO_2 . The carbon electrodes and transit framework of the furnace contain much absorbed air, which is given off as the temperature rises. For this reason the air pump was kept in operation during the entire procedure. When the sintering was complete the current was increased until the temperature exceeded the theoretical melting point by 50–100°C. The current was then decreased slowly. Since MnO oxidizes so readily and a little air is always being given off from the electrodes and the transit framework, cooling is allowed to proceed rapidly, seldom for more than five minutes. The crystals so formed were small, but optical data could usually be obtained from them with accuracy. Not infrequently strain effects precluded precise orientation. The crystals were then heated for approximately 10 minutes at a temperature not more than 200° below their melting point. This operation eliminated the strain effects and caused crystal enlargement. In the case of the lime-rich melts such procedure was found inadvisable for two reasons. In the first place the melting temperatures are so high that air was released more abundantly from the system and combined more readily with the MnO. Secondly, the MnO con-

⁵ F. P. Paul: *Tsch. Min. Pet. Mit.*, **25**, (1906), p. 309.

⁶ N. L. Bowen: *Am. Jour. Sci.*, **3**, (1922), p. 30.

⁷ R. C. Emmons: *Science*, **73**, (1931), pp. 499–500.

tent of these mixtures was so small that a very small amount of air was sufficient to convert it entirely to MnO_2 .

DESCRIPTION OF THE ARTIFICIAL CRYSTALS

Tephroite is greyish and glaucochroite bluish-green, but all of the artificial minerals which contain 30 per cent or more of Mn_2SiO_4 are marked by a decided greenish coloration. With less Mn_2SiO_4 the crystals crumble to a white powder. Tokody suggests that the crumbling is due to the 10 per cent volume increase which $\beta\text{-Ca}_2\text{SiO}_4$ undergoes when inverting to the stable γ -phase. In thin section the crystals are colorless to light-brown and show high relief. Tiny dark inclusions are common in the manganese-rich minerals. Their identity was not determined. Possibly they are hausmannite which forms readily when MnO is oxidized.

OPTICAL STUDIES

The optical work consisted chiefly in obtaining three indices of refraction and the optic angle for crystals of each melt. The double variation method of R. C. Emmons⁸ was used in conjunction with a Leitz universal stage modified by Emmons.⁹ An error of $\pm .0005$ for the refractive indices, and 2° to 3° for the observed optic angle may be expected in sodium light; indices are accurate to $\pm .001$ for other wave lengths. For indices up to 1.74 the liquids recommended by Emmons were used. By dissolving sulphur in methylene iodide a maximum of 1.79 could be obtained. The further addition of iodoform brought the liquid to 1.83.

The results (see Table 1 and Fig. 1) show a progressive and rather regular decrease in indices of refraction from 100 per cent Mn_2SiO_4 to 100 per cent Ca_2SiO_4 (Wright's¹⁰ figures for $\gamma\text{-Ca}_2\text{SiO}_4$ have been used.) Apparently there is no regular change in the optic angle. Mn_2SiO_4 is orthorhombic and might be expected to be isomorphous with the orthorhombic $\beta\text{-Ca}_2\text{SiO}_4$. This does not appear to be the case for the indices of $\beta\text{-Ca}_2\text{SiO}_4$ are definitely higher than those of any melt containing less than 60 per cent Mn_2SiO_4 . Furthermore, the optical character of $\beta\text{-Ca}_2\text{SiO}_4$ is positive, whereas the optic sign is negative in all the preparations studied by the writer. It appears inescapable that it is the *supposedly* monoclinic

⁸ R. C. Emmons: *Am. Min.*, 13, (1928), pp. 504-515. *Am. Min.*, 14, (1929), pp. 414-426

⁹ R. C. Emmons: *Am. Min.*, 14, (1929), pp. 441-461.

¹⁰ F. E. Wright: *Op. cit.*

γ -Ca₂SiO₄ which is isomorphous with Mn₂SiO₄. The evidence for placing γ -Ca₂SiO₄ in the monoclinic system is admittedly weak. Wright's indices are those of a positive mineral, whereas he states that the optic sign is negative. The limits of error stated for the indices are sufficient however to account for this discrepancy.

TABLE I

Comp.		N _g	N _m	N _p	N _g -N _p	2V Calc.	2V Obs.	Pleochroism
100% Mn ₂ SiO ₄	F	1.8369	1.8258	1.7920	.0449	60° 30'	60°	X = Brown Y = Brownish-red Z = Blue
	D	1.8143	1.8038	1.7720	.0423	61° 20'		
	C	1.8102	1.7997	1.7681	.0421	60° 15'		
80% Mn ₂ SiO ₄ 20% Ca ₂ SiO ₄	F	1.7854	1.7750	1.7415	.0439	58° 40'	59°	X = Brown Y = Brownish-red Z = Blue
	D	1.7717	1.7592	1.7257	.0460	62° 40'		
	C	1.7678	1.7547	1.7206	.0472	64°		
70% Mn ₂ SiO ₄ 30% Ca ₂ SiO ₄	F	1.7685	1.7594	1.7335	.0350	60° 30'	not obs.	X = Brown Y = Brownish-red Z = Blue
	D	1.7570	1.7463	1.7180	.0390	63°		
	C	1.7538	1.7428	1.7138	.0400	64°		
60% Mn ₂ SiO ₄ 40% Ca ₂ SiO ₄	F	1.7518	1.7460	1.7212	.0306	53°	not obs.	X = Brown Y = Brownish-red Z = Blue
	D	1.7352	1.7248	1.6980	.0372	64°		
	C	1.7304	1.7196	1.6917	.0387	65°		
50% Mn ₂ SiO ₄ 50% Ca ₂ SiO ₄	F	1.7342	1.7253	1.7010	.0332	62°	67°	X = Pale Brown Y = Pale Brown Z = Pale Bluish
	D	1.7205	1.7105	1.6850	.0355	64°		
	C	1.7178	1.7072	1.6810	.0368	65°		
40% Mn ₂ SiO ₄ 60% Ca ₂ SiO ₄	F	1.7166	1.7076	1.6930	.0236	76°	not obs.	Not observed
	D	1.6998	1.6945	1.6798	.0200	62°		
	C	1.6979	1.6928	1.6780	.0199	60°		
30% Mn ₂ SiO ₄ 70% Ca ₂ SiO ₄	F	1.6992	1.6954	1.6878	.0114	64°	not obs.	X = Pale Brown Y = Pale Brown Z = Faint Blue
	D	1.6842	1.6800	1.6704	.0138	68°		
	C	1.6802	1.6759	1.6647	.0155	64°		
20% Mn ₂ SiO ₄ 80% Ca ₂ SiO ₄	F	1.6874	1.6843	1.6797	.0077	79°	not obs.	Not Observed
	D	1.6747	1.6714	1.6638	.0109	64°		
	C	1.6705	1.6671	1.6598	.0107	65°		
10% Mn ₂ SiO ₄ 90% Ca ₂ SiO ₄	F	1.6738	1.6730	1.6633	.0105	22° (?)	62°	X = Pale Brown Y = Pale Brown Z = Colorless
	D	1.6607	1.6580	1.6505	.0102	62°		
	C	1.6584	1.6549	1.6475	.0109	67°		

Unfortunately the reaction $\text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO}$ commences at 1620°C. whereas the fusion point of γ -Ca₂SiO₄ is about 2080°. Accordingly this mineral cannot be synthesized in a carbon crucible. Day and Shepherd¹¹ state that γ -Ca₂SiO₄ can be prepared in platinum, but the equipment necessary was not available to the writer.

¹¹ *Op. Cit.*, p. 280.

It was therefore impossible to check the optical and crystallographic data on the lime end-member. It would be extremely desirable to do this.

X-RAY STUDIES

To throw more light on the problem *x*-ray powder photographs of the series were made. It will be noted (see plate 1) that the pat-

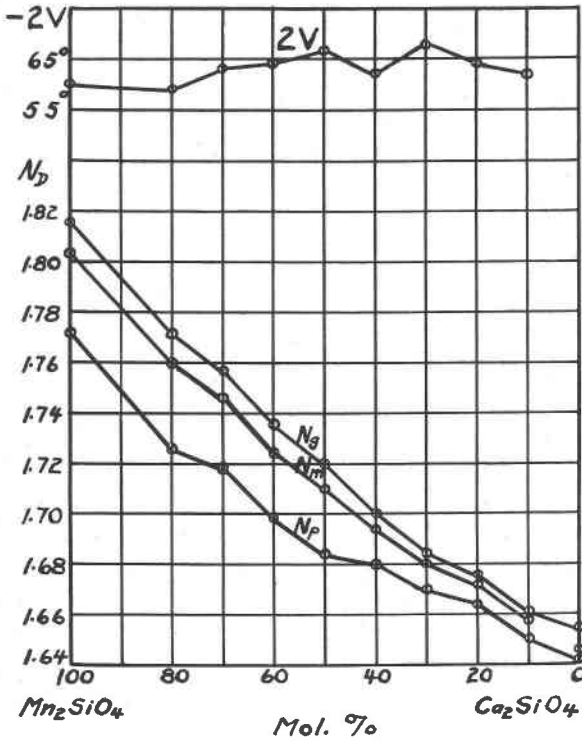


Fig. 1. Variation in Refractive Indices and Optic Angle.

terns of natural and artificial tephroite are identical except that the entire pattern of the former is offset to the left with respect to that of the latter. An inspection of all of the photographs indicates that the amount of offsetting is a function of the amount of non-manganese content. Natural and artificial glaucochroite display interesting similarities. The patterns of the minerals containing between 100 and 50 per cent Mn_2SiO_4 are in excellent accord. The

PLATE I. X-RAY PATTERNS OF THE $\text{Ca}_2\text{SiO}_4\text{-Mn}_2\text{SiO}_4$ SERIES% Ca_2SiO_4

0

0

10

30

40

50

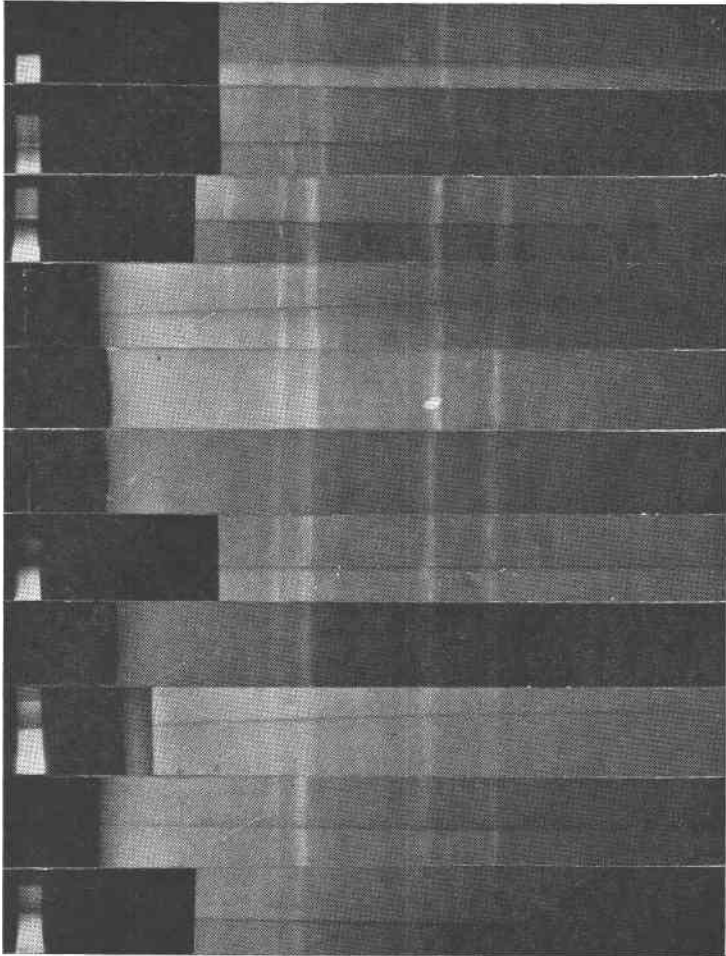
50

60

70

80

90

% Mn_2SiO_4 100 (Approx.)
Nat. Tephroite100
Art. Tephroite

90

70

60

50
Art. Glaucochroi50
Nat. Glaucochro

40

30

20

10

patterns of the lime-rich varieties, while similar in that the principal lines are offset to the left, also show some lines which do not correspond with any in the patterns of the manganese-rich minerals. Considerable difficulty was encountered with the 50, 60, and 70 per cent Ca_2SiO_4 minerals. The first photographs obtained from them showed a number of rather faint lines which failed to check with those of the high-manganese types. Practically every line of the manganese-rich minerals was represented more or less distinctly however. Accordingly, three new mixtures were prepared and photographed. The resultant patterns of the 50 and 70 per cent Ca_2SiO_4 minerals were then found to fit much better, but that of the mineral containing 60 per cent Ca_2SiO_4 was still anomalous. Next, four minerals, all containing 60 per cent Ca_2SiO_4 —40 per cent Mn_2SiO_4 were synthesized, two being sintered at 1100°C . for 10 minutes after fusion, the other pair not so treated. Both of the former gave more satisfactory patterns, while both of the latter yielded anomalous results. Comparison under the microscope was then made. The product which had been sintered proved to be made up of crystals showing good extinction. The unsintered product showed a few grains which could be oriented on the universal stage and which yielded optical values very close to that of the sintered material. The remaining grains however were made up of a confused mass of tiny crystals on which no accurate optical study could be made. Nevertheless it was possible to determine that the refractive indices of this material are probably not far removed from those of the sintered mineral.

The reason for the anomalous behavior of the lime-rich species is not clear. The x -ray evidence seems to indicate that two substances are present in some of the unsintered material and only one in the sintered variety. The inference is that sintering changes one of the substances to the other and since there is no evidence of chemical change the process must be that of inversion. Considering that pure Ca_2SiO_4 exists in three phases such inversion is not untoward.

CONCLUSIONS

1. Optical data appear to indicate that Mn_2SiO_4 and $\gamma\text{-Ca}_2\text{SiO}_4$ form mix-crystals in all proportions.
2. X -ray evidence shows clearly that calcium may replace manganese at least up to 50 per cent in the orthosilicates. Replacement

to an even greater extent is indicated but not proved. The lime-rich members of the series probably crystallize in two forms one of which can invert to the other.

3. Manganese and calcium may proxy for one another, at least at high temperatures, more completely than has been suspected previously.

4. It has generally been held that two substances belonging to different crystal systems cannot form an isomorphous series. It will be necessary to prove definitely that γ - Ca_2SiO_4 is monoclinic before concluding that a broader conception of isomorphism is required to explain the results obtained by the writer.