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ORTHOPYROXENE AND CLINOPYROXENE POLYMORPHS OF $CoGeO_3$

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ABSTRACT

Solid-state reaction of CoO with GeO_2 has yielded two cobalt metagermanate ($CoGeO_3$) phases. *X*-ray diffraction shows an orthorhombic form analogous to the orthopyroxene enstatite: $a=18.77$Å, $b=8.99$, $c=5.35$, *Pbca*; and a monoclinic phase analogous to the diopside-augite clinopyroxenes: $a=9.64$Å, $b=8.99$, $c=5.15$, $\beta=101°10'$, $C2/c$. Monoclinic single crystals were grown from the melt. The orthorhombic structure is stable below 1351° C. and the monoclinic form is stable above this temperature. A minor amount of the monoclinic phase coexists metastably down to 1241° C. The orthorhombic form transforms to the monoclinic rapidly and completely above 1351° C. Lengthy runs were unsuccessful in bringing about the reverse transition. $CoGeO_3$ melts congruently at 1377° C.

INTRODUCTION

In a recent study (Tauber *et al.*, 1963), the formation of an enstatite phase was reported in the system GeO_2-$MnGeO_3$. The present work extends the investigation of $MeGeO_3$ compounds, where Me is a divalent first transition metal cation. Syntheses were undertaken with $Me=Fe^{2+}$, Ti^{2+}, Ni^{2+}, and Co^{2+}. Attempts to prepare the Fe and Ti analogues have thus far been unsuccessful, principally due to the failure of the method to maintain the cations divalent. A stable ferrous germanate analogous to enstatite had been expected on the basis of ionic size. A monoclinic $FeGeO_3$ phase has recently been reported by Royen and Forwerg (1963), who used an HCl gaseous transport reaction in a sealed quartz tube. In the present study Ni^{2+} was found to yield a spinel consistently. In the case of Co^{2+}, however, cobalt metagermanate ($CoGeO_3$) phases were obtained with unit cells and space groups corresponding to both enstatite and the diopside-augite clinopyroxenes. Royen and Forwerg (1963) mentioned a $CoGeO_3$ phase and inferred monoclinic symmetry. Preparation and phase relation studies are described for the cobalt metagermanates found in the present study; *x*-ray diffraction data and some morphological measurements are given.

EXPERIMENTAL PROCEDURES

Starting materials for $CoGeO_3$ synthesis were GeO_2 (Eagle-Picher electronic grade) and CoO. The latter was prepared from $CoCO_3$ (Fisher C.P. reagent) by two sequences of heating to 1200° C., grinding, and sieving, monitored by *x*-ray diffraction and loss-in-weight measurements. Five-gram batches of 50:50 intimately mixed oxides were pelletized, fired at 1000° C. for two hours in air, quenched in air, ground and sieved.

This sequence was repeated to ensure homogeneity, which was checked microscopically and by powder x-ray diffraction.

The resulting $CoGeO_3$ served as starting material for most of the single-crystal preparation and was also used to determine phase transitions by quench furnace experiments. For the latter, samples were sealed in small Pt tubes, heated, and quenched in air or water. Results were independent of the quench method. Temperature was measured with a calibrated Pt-Pt 10% Rh thermocouple and held to better than $\pm 1°$ C. with a proportional controller for periods of four hours or less; for runs exceeding four hours, a maximum drift of $\pm 3°$ C. was noted. All samples were examined with a binocular microscope and by powder x-ray diffraction; some thin sections were prepared. Having established conditions for single-phase preparation, repeated syntheses were made to accumulate sufficient material for the determination of diffraction intensities and spacings on a powder x-ray diffractometer. The same material was subsequently used for wet chemical analyses, in which Co was determined electrolytically and Ge gravimetrically as Mg_2GeO_4 (Hillebrand *et al.*, 1953). Within the accuracy of the procedures, approximately 0.1%, observed stoichiometry coincided with $CoGeO_3$.

The GeO_2:CoO 50:50 material was used to grow single crystals by heating in sealed Pt tubes to 30° C. above the melting point and cooling at 1–4°/hr to below the liquidus. Zero- and upper-level Weissenberg and precession x-ray patterns were obtained using FeK radiation. When GeO_2:CoO 60:40 and 70:30 materials were used in an attempt to grow single crystals, only glass and polycrystalline material were obtained.

Results and Discussion

Phase relations. Samples were quenched, in the manner described above, from temperatures in the range 1200 to 1450° C. Results are summarized in Table 1. Up to $1241 \pm 2°$ C., powder x-ray patterns showed a single orthorhombic phase with cell dimensions (Table 2) and diffraction data (Table 3) descriptive of the orthopyroxene enstatite. Above $1351 \pm 3°$ C., a single monoclinic phase was found, bearing an analogous relationship to the diopside-augite clinopyroxenes. From 1241 to 1351° C., the major phase by far was the orthorhombic compound. A small amount of the monoclinic phase, however, beginning with a trace and reaching no more than minor proportions, persisted throughout this temperature range, as noted by powder x-ray diffraction. The minor amount of monoclinic phase, and the relatively large temperature interval (110° C.) over which it is found to coexist with the orthorhombic form, indicate that the monoclinic compound forms metastably in this temperature region.

All samples of the orthorhombic phase, when heated above 1351° C.,

TABLE 1. QUENCH FURNACE DATA FOR $CoGeO_3$

Temp. (°C)	Time at Temp. (hrs.)	Phases[1] and Remarks
1200	3	E
1233	4	E
1238	3	E
1244	4	E+trace CP
1247	4	E+trace CP
1259	4	E+trace CP
1288	18	E+minor CP
1300	30	E+minor CP+spinel; tube leaked, 10% loss in wt.
1326	14	E+minor CP
1349	20	CP
1350	1	E+minor CP
1354	48	E+minor CP
1362	25	CP; chips removed from tube crumbled to powder
1368	70	CP; chips removed from tube crumbled to powder
1371	2	CP; partially melted
1375	2	CP; almost completely melted
1379	2	CP; melted
1380	4	CP; melted
1395	1	CP; melted
1424	1	CP+spinel; melted, tube leaked
1441	4	CP; melted

[1] E=enstatite; CP=clinopyroxene.

rapidly transformed into the monoclinic modification. Attempts to perform the reverse transformation were all unsuccessful. In addition to samples heated for shorter periods, two specimens of the monoclinic phase were heated in sealed Pt tubes at 900° and 1300° C., each for 65 days. X-ray powder patterns showed only the monoclinic modification.

TABLE 2. UNIT CELL DATA FOR ENSTATITIC $CoGeO_3$, $MnGeO_3$, $MgGeO_3$ AND $MgSiO_3$

	$CoGeO_3$	$MnGeO_3$[1]	$MgGeO_3$[2]	$MgSiO_3$[3] (enstatite)
a	18.77Å	19.29	18.661	18.22
b	8.99	9.25	8.954	8.829
c	5.35	5.48	5.346	5.192
Space group	*Pbca*	*Pbca*	*Pbca*[4]	*Pbca*

[1] Tauber *et al.* (1963).
[2] Roth (1957).
[3] Swanson *et al.* (1956); setting transformed for comparison purposes.
[4] Based on Roth's (1955) statement, "isostructural with enstatite."

TABLE 3. *X*-RAY POWDER DIFFRACTION DATA FOR ENSTATITIC $CoGeO_3$[1]

hkl	$d_{obs.}$	$d_{calc.}$	I/I_1
020	4.50 Å	4.50 Å	6
211	4.13	4.13	3
121	3.38	3.39	33
411	3.28	3.28	6
420, 221	3.23	3.24, 3.23	100
321	3.02	3.02	42
610	2.955	2.955	94
511	2.908	2.908	19
421	2.778	2.775	36
131	2.592	2.590	44
202	2.579	2.573	53
112, 521	2.539	2.540, 2.537	28
231	2.519	2.519	19
212	2.465	2.473	22
312	2.376	2.372	17
402, 711, 621	2.319	2.324, 2.316, 2.315	17
040	2.248	2.248	6
222	2.235	2.233	6
240	2.185	2.186	19
512	2.120	2.117	14
811	2.093	2.090	11
422, 141	2.061	2.064, 2.060	14
440, 241	2.027	2.027, 2.023	25
631	2.006	2.006	17
341	1.969	1.967	8
821	1.941	1.939	8
332, 911, 441	1.900	1.901, 1.899, 1.896	11
712	1.855	1.853	6
10, 1, 0, 432	1.838	1.837, 1.836	8
541	1.816	1.814	11
802, 532	1.763	1.764, 1.762	6
831, 722	1.749	1.746, 1.745	19
10, 1, 1	1.736	1.738	19
313	1.687	1.685	17
342	1.657	1.659	19
123, 10, 2, 1	1.650	1.651, 1.648	14
223	1.634	1.632	22
840, 912	1.620	1.623, 1.618	6
323, 451, 732, 11, 1, 1	1.602	1.602, 1.602, 1.601, 1.600	11
542, 12, 0, 0, 423	1.562	1.564, 1.564, 1.563	44
10, 0, 2	1.533	1.536	31
11, 2, 1, 133, 613	1.529	1.529, 1.527, 1.527	47
	1.500		47

[1] Filtered FeK radiation

In the case of $MgGeO_3$, Robbins and Levin (1959) found that a transition from the monoclinic phase to the orthorhombic form was possible but that the conversion was sluggish.

Upon melting, $CoGeO_3$ always crystallized in the monoclinic form, whether slow-cooled or quenched. When heated in air or when a sealed Pt tube failed, a red spinel phase was also detected. Absence of the spinel phase, as determined by x-ray diffraction and thin section analysis, was taken as evidence for congruent melting. The melting point is $1377 \pm 5°$ C. (Table 1).

In several instances, when quench furnace reaction products in the form of chips were removed from their platinum tubes, the samples quickly disintegrated into powder. All attempts to rapidly record an x-ray diffraction pattern showed only the monoclinic phase already identified. Nevertheless, since protoenstatite is metastable at room temperature and behaves in a similar manner, it is interesting to consider the possibility of a protoenstatite analogue. A high-temperature x-ray diffraction study might clarify such phase relations.

Crystallography. The lower temperature, orthorhombic phase was obtained only as a deep violet powder. Attempts to prepare orthorhombic single crystals by using non-stoichiometric mixtures to lower the melting point into a temperature range where the phase is stable were unsuccessful. The x-ray diffraction powder pattern, obtained with unfiltered FeK radiation, is clearly analogous to that for enstatitic $MnGeO_3$ (Tauber *et al.*, 1963) and was indexed accordingly. The resultant cell dimensions are compared in Table 2 with those for several similar phases. No reflections were noted on the powder pattern which would alter the space group from that previously found for enstatitic $MnGeO_3$, *Pbca* (Tauber *et al.*, 1963). The indexed powder pattern, showing good agreement between calculated and observed d values, is given in Table 3.

The higher temperature monoclinic phase was obtained in both powder and small single-crystal form. The powder, light violet in color, gave an x-ray pattern analogous to clinopyroxene and led to the cell dimensions shown in Table 4; comparison is made with the cells of other clinopyroxenes. Indexed powder data appear in Table 5.

Single crystals of the monoclinic form are pale violet to pink violet in color and lath-shaped along c; average dimensions are $1 \times 0.25 \times 0.1$ mm. The lath form is {110}. Specimens are brittle and display an easy prismatic cleavage. All crystals showed polysynthetic twinning on (100).

Morphological data were obtained on two specimens using a two-circle optical goniometer. Three forms were identified: the front (ortho) and

TABLE 4. UNIT CELL DATA FOR MONOCLINIC $GoGeO_3$, $FeGeO_3$, $MgGeO_3$, $CaMg(SiO_3)_2$ AND $MgSiO_3$

	$CoGeO_3$	$FeGeO_3$[1]	$MgGeO_3$[2]	$CaMg(SiO_3)_2$[3] (diopside)	$MgSiO_3$[4] (clino-enstatite)
a	9.64Å	9.58	9.60	9.750	9.618
b	8.99	9.16	8.92	8.930	8.828
c	5.15	5.21	5.16	5.249	5.186
β	101°10′	102°20′	100°49′	105°50′	108°22′
Space Group	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$P2_1/c$

[1] Royen and Forwerg (1963)
[2] Robbins and Levin (1959)
[3] Kuno and Hess (1953); actual composition is $Ca_{.49}Mg_{.47}Fe_{.04}SiO_3$
[4] Kuno and Hess (1953)

side (clino) pinacoids, {100} and {010}, respectively, and the prism {110}. Interfacial angles are given in Table 6.

Single-crystal x-ray patterns confirmed monoclinic symmetry and showed the following systematic absences:

$$\begin{aligned} &hkl, && h + k = 2n + 1 \\ &h0l, && l = 2n + 1 \end{aligned}$$

This conforms to the centrosymmetric space group $C2/c$.

All the clinopyroxenes were considered for some time to have the diopside structure, with end-centered symmetry, $C2/c$. Atlas (1952), however, was apparently the first to discern primitive symmetry for clinoenstatite, and subsequently Morimoto (1956) and Bown and Gay (1957) established the space group $P2_1/c$ for pigeonite. Morimoto *et al.* (1960) refined the structures of clinoenstatite and pigeonite and showed that the small size of divalent Mg or Mg+Fe causes a displacement of these cations from their special diopside structure positions. Thus two kinds of silicate chains are produced, and the space group becomes $P2_1/c$. Structurally, then, one differentiates the end-centered diopside-augite clinopyroxenes from the primitive clinoenstatite-pigeonite clinopyroxenes. An excellent summary of structural relations among the pyroxenes is presented by Deer *et al.* (1963).

Since the end-centered space group was found in the present study for monoclinic $CoGeO_3$, the latter is considered analogous to the diopside-augite clinopyroxenes. The presence of Ge apparently favors this structure, since the other reported clinopyroxene metagermanates also have the same space group (Table 4). However, the diopside-augite clinopyroxenes differ from their analogous metagermanates in that the former

TABLE 5. *X*-RAY POWDER DIFFRACTION DATA FOR MONOCLINIC $CoGeO_3$[1]

hkl	$d_{obs.}$	$d_{calc.}$	I/I_1
020	4.48 Å	4.49 Å	8
021	3.36	3.36	31
220	3.26	3.26	56
310	2.98	2.97	100
$\bar{2}21$	2.92	2.92	78
$\bar{3}11$	2.81	2.80	50
221	2.59	2.59	94
$\bar{1}31$	2.55	2.55	83
002	2.53	2.53	61
$\bar{1}12$	2.47	2.47	3
311	2.38	2.38	14
040	2.24	2.25	19
$\bar{3}12$	2.13	2.13	25
202	2.069	2.068	19
041	2.055	2.053	19
240	2.028	2.030	25
222	1.878	1.879	19
$\bar{5}11$, 510	1.854	1.855, 1.851	22
241	1.831	1.832	25
312	1.772	1.772	19
042	1.679	1.679	19
$\bar{2}42$, $\bar{5}12$, 151	1.651	1.651, 1.650, 1.649	22
$\bar{5}31$	1.606	1.602	64
402	1.580	1.580	22
350	1.563	1.562	56
$\bar{3}51$	1.534	1.534	6
242	1.524	1.522	11
060	1.498	1.498	72
$\bar{1}52$	1.475	1.473	22
$\bar{4}42$, 531	1.460	1.461, 1.458	67
$\bar{4}23$, 061	1.438	1.438, 1.436	3
260, $\bar{3}33$, 152	1.425	1.428, 1.427, 1.424	25
	1.391		28
	1.339		25
	1.290		31
	1.276		22

[1] Filtered FeK radiation

TABLE 6. MORPHOLOGICAL DATA FOR MONOCLINIC $CoGeO_3$

Face	No. of Times Observed	Range	Weighted Average	Calculated Value
			Angle with *b*	
(110)	7	42°54′–43°46′	43°33′	43°33′
(100)	3	88°59′–90°16′	89°58′	90°00′
			Angle with *a**	
(110)	7	46°05′–47°29′	46°32′	46°27′

show no orthopyroxene (enstatite) equivalents, while Mg, Co and Mn metagermanates have enstatite phases (Table 2). Although not yet reported, enstatitic $FeGeO_3$ should also be obtainable. Synthesis of end-member ferrosillites ($FeSiO_3$), with powder patterns "roughly similar to those of monoclinic and orthorhombic enstatite," has recently been reported (Lindsley *et al.*, 1964) by high-pressure, high-temperature reaction. The position of these phases in the overall metasilicate structural scheme awaits positive determination of their space groups, if not their complete structures.

SUMMARY

The metagermanate $CoGeO_3$ has been synthesized below 1241° C. in a single-phase orthorhombic form analogous to enstatite, and above 1351° C. as a single-phase monoclinic variety analogous to the diopside-augite clinopyroxenes. From 1241 to 1351° C., a minor amount of the monoclinic form coexists with the orthorhombic phase. The orthorhombic to monoclinic transformation was easily accomplished, but the reverse transition could not be obtained. Only the monoclinic form could be prepared as single crystals. $CoGeO_3$ melts congruently at 1377° C. Attempts to prepare $FeGeO_3$, $TiGeO_3$, and $NiGeO_3$ by analogous solid-state reactions were unsuccessful.

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Note added in proof: Since submission of this paper, two references in $CoGeO_3$ have appeared:

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