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Solid Solubility between Uvarovite and Spessartite

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Abstract

Powdered mixtures of synthetic uvarovite [a = 12.010(1)Å; n = 1.855(5)] and synthetic spessartite [a = 11.615(1)Å; n = 1.800(5)] held at 27.5 kbar and 1450°C for 48 hours yielded continuous solid solutions for which the cell edge and refractive index varied linearly with composition. At one atmosphere pressure in air, partial solubilities were found up to 20 mole percent from each end member. In air uvarovite is stable up to 1375(5)°C, spessartite to 1160°C, and a 50-50 percent mixture breaks down at 1050°C, the minimum melting temperature in the solid solution series. The partial solubility observed at one atmosphere in air might be caused by the instability of Mn^{2+} and the low temperature of reaction.

Introduction

The minerals of the garnet group are divided into two series, pyralspite and ugrandite. Among the garnets in the same series, complete and continuous solubility has been found, but no continuous solubility appears between the garnets belonging to the two different series (Winchell and Winchell, 1951; Deer, Howie, and Zussman, 1962). However, continuous solid solubility between pyralspite and ugrandite can be expected because of natural occurrences of calcian pyrope, calcian almandite, and calcian spessartite (Němec, 1967), manganoan grossularite (Frondel and Ito, 1965), and chromian pyrope (knorringite; Nixon and Hornung, 1968).

Magnesian uvarovite and magnesian or manganoan andradite were synthesized under high pressure (Coes, 1955; Roy and Tuttle, 1956). Up to 20 percent Fe^{3+} can be substituted for Al^{3+} in synthetic spessartite (Geller and Miller, 1959b). Recently a continuous solid solution between almandite and grossularite was formed under high pressure (Hariya and Nakano, 1972).

In the binary system of uvarovite and spessartite, solid solubility has not yet been reported (Gentile and Roy, 1960). In the present work, however, complete and continuous formation of solid solution at all compositions between uvarovite and spessartite was found under high pressure. Even at one atmosphere air pressure, partial solid solutions were obtained.

Experimental

The raw materials were $CaCO_3$, $MnCO_3$, Cr_2O_3, α-Al_2O_3, and amorphous SiO_2. α-Al_2O_3 was prepared by heating 99.99 percent pure γ-Al_2O_3 for 2 hours, and amorphous SiO_2 by hydrolysis of silicon ethoxide and heating at 1200°C for 2 hours. Other materials were reagent grade chemicals.

Sample disks 10 mm in diameter and 1 mm thick were placed in a platinum boat and heated in a SiC furnace at one atmospheric air pressure, pure oxygen pressure, and pure nitrogen pressure. Temperatures of the heat treatments were kept constant within ± 2°C. Heat treatments under high pressure were carried out in sealed platinum capsules by using the girdle type high pressure apparatus (Naka, Ito, and Inagaki, 1972).

After heat treatment, the phases formed were identified by X-ray powder technique and optical microscopy. The lattice constants of the garnets were determined from *640* and *642* diffractions, referenced to internal standards of silicon and sodium chloride. The refractive index was measured by oil immersion. Melting was detected by the deformation of the sample disks after heat treatment.

Synthesis and Stability of Uvarovite and Spessartite

From the mixture of $CaCO_3$, Cr_2O_3, and SiO_2, the single phase of uvarovite was synthesized by heating at 1150° to 1300°C for a few hours under atmospheric pressure of pure oxygen. In air, uvarovite was formed from oxides mixture by reheating at 1100° to 1350°C with intermediate grinding, but it always coexisted with $CaSiO_3$ and Cr_2O_3, as reported by many authors (Geller and Miller, 1959a; Isaacs, 1965; Pyatikop and Karyakin, 1968; and Arnould, Kabbani, and Phan, 1969). In nitrogen no uvarovite was formed.

The uvarovite obtained is light green. Its lattice constant is a = 12.010(1)Å, a little higher than the a = 12.000(1) reported by Pyatikop and Karyakin (1968). Its X-ray powder data is presented in Table 1. The refractive index, n = 1.855(5), is similar to that of natural uvarovite (Deer *et al,* 1962).

At 1375(5)°C, uvarovite broke down to pseudowollastonite and Cr_2O_3 in air. No change in lattice constant was observed even after heating to 1370°C.

Spessartite was prepared by heating the mixture of $MnCO_3$, Al_2O_3, and SiO_2 at 700°C for 1 hour in a vacuum of 10^{-3} torr and then at 1160° to 1200°C for 2 hours under atmospheric pressure of pure nitrogen. The melting point of spessartite in nitrogen was determined as 1195(5)°C, which agrees well with the reported congruent melting point, 1195(2)°C (Yoder and Keith, 1951). The lattice constant, a = 11.615(1)Å, and refractive index, n = 1.800(5), are almost the same as those—a = 11.621(1)Å and n = 1.800(2)—reported by Skinner (1956). The crystal is pale pink. Spessartite melts at 1160°C in air and breaks down to glass and galaxite. No change in lattice constant was observed even after heating to 1100°C in air.

In order to synthesize uvarovite and spessartite, the control of atmosphere is necessary. Uvarovite could be synthesized only in oxygen, probably because of the reactivity of Cr_2O_3. On the other hand, spessartite could be obtained only in nitrogen because of the necessity of maintaining the manganese in the manganous state (Snow, 1943; Yoder and Keith, 1951). The manganous ion is relatively stable in silicate minerals (Muan, 1959). Single phases of uvarovite and spessartite have been used as starting materials for formation of garnet solid solution under high pressure as well as under one atmosphere air pressure.

TABLE 1. X-Ray Powder Data for Uvarovite

hkl	d_{obs}	d_{calc}	I/I_1
220	4.250	4.246	15
321	3.205	3.210	6
400	3.005	3.003	70
420	2.688	2.686	100
332	2.561	2.561	20
422	2.452	2.452	55
431	2.355	2.355	16
521	2.194	2.193	11
611	1.947	1.948	20
620	1.900	1.899	10
631	1.776	1.771	1
444	1.734	1.734	6
640	1.666	1.666	23
642	1.6055	1.6049	61
800	1.5016	1.5013	10
741	1.4786	1.4783	1
653	1.4346	1.4356	< 1
822	1.4157	1.4154	1
840	1.3432	1.3428	11
842	1.3106	1.3104	11
921	1.2955	1.2951	1
664	1.2805	1.2803	8
930	1.2664	1.2660	1
844	1.2265	1.2258	1
941	1.2132	1.2132	2
1040	1.1153	1.1151	9
880	1.0619	1.0615	6
1200	1.0009	1.0008	3
1220	0.9874	0.9872	2
1222	0.9741	0.9744	7
1163	0.9322	0.9323	< 1
1260	0.8951	0.8953	4
1262	0.8854	0.8854	3
888	0.8667	0.8668	2

Cu Kα radiation
Synthesized at 1150°C for 3 hours in oxygen.

Synthesis of Solid Solution between Uvarovite and Spessartite

Under High Pressure

The garnet solid solution was synthesized at 27.5 kbar and 1450°C from powdered mixtures of uvarovite and spessartite. Formation of the solid solution was so slow that complete and continuous solubility between them was observed only after 48 hours' heating under high pressure. The lattice constant and refractive index of the solid solution vary linearly with composition (Figs. 1, 2). The lattice constants observed coincide with the calculated values of those obtained from the regression formula of Novak and Gibbs (1971) using Shannon and Prewitt's ionic radii (1969).

In the process of formation of the solid solution, the diffraction peaks of spessartite broadened and shifted to the low diffraction angle side (uvarovite spacing side) with heating. However, the peaks of uvarovite neither shifted nor broadened, but their relative intensities decreased with heating. This indicates that uvarovite diffused into spessartite more quickly than spessartite into uvarovite.

In Air

Mixtures of uvarovite and spessartite in various ratios were heated under one atmosphere air pressure. The results are summarized in Table 2. The solid solubilities are found up to about 20 percent on both sides of the end members. A single phase of gar-

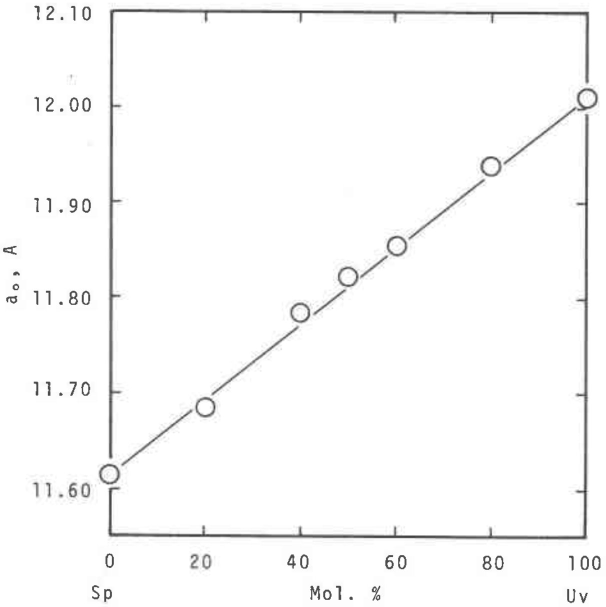

FIG. 1. Change of lattice constant for the system spessartite-uvarovite. Sp, spessartite; Uv, uvarovite.

net solid solution was formed from the mixture of 90 percent spessartite and 10 percent uvarovite at 1050°C; its lattice constant agreed both with the calculated value and with the value obtained from the high pressure experiments described above. This solid solution began to melt and to break down at 1100°C, though pure spessartite was stable up to 1160°C in air. In mixtures with the amount of spessartite varying between 80 and 40 percent, no single-phase garnet was obtained, even after long-term heating. In these samples, galaxite solid solution and/or a glassy phase, indicating a breaking-down and melting of the samples, were detected at 1100°C and, in the sample with 50 percent spessartite, at 1050°C. In this latter sample, the identified pseudowollastonite might have been formed by breakdown of uvarovite in a non-equilibrium reaction at 1050°C.

The sample with 20 percent spessartite changed to a garnet solid solution at 1150°C after 100 hours' heating. Its lattice constant coincides exactly with that of the one synthesized under high pressure. From the sample with 10 percent spessartite, a single phase was obtained at 1180°C, but its lattice constant was a little lower than the expected value. This might have been caused by the high temperature of reaction, 1180°C, which was higher than the decomposition temperature of spessartite in air. Some of manganous ion in this solution might have been oxidized to manganic state.

Synthesis of garnet solid solutions from the corresponding mixtures of the raw materials under one atmosphere pressure of nitrogen was tried but was not successful except in the case of the sample with 90 percent spessartite. Galaxite solid solution and pseudowollastonite were identified as the main products in these experiments. The garnet solid solution with 90 percent spessartite had the same lattice constant as that of the one synthesized from the garnet mixture in air and also agreed with the calculated value.

Conclusion

In the chemical formula of garnet, $\{X_3\}$ $[Y_2]$ $(Z_3)O_{12}$, $\{X\}$ represents the dodecahedral site, $[Y]$ the octahedral site, and (Z) the tetrahedral site. It is reasonably assumed that Mn^{2+} and Ca^{2+} substitute in the dodecahedral site, and Al^{3+} and Cr^{3+} in the octahedral site and, therefore, that complete and continuous solubility between uvarovite and spessartite may be expected (Novak and Gibbs, 1971). However, this solid solubility has not been previously reported.

In the present work, complete solubility has been shown to be possible under a pressure of 27.5 kbar at 1450°C. The lattice constants and refractive indices of these solid solutions vary linearly with the composition. The lattice constants observed for the solid solutions agree with those calculated using the regression formula of Novak and Gibbs (1971).

Only partial solubility was found at one atmosphere pressure. This was most likely caused by the instability of Mn^{2+} in air and also by the low temperature of the reaction because one of the reac-

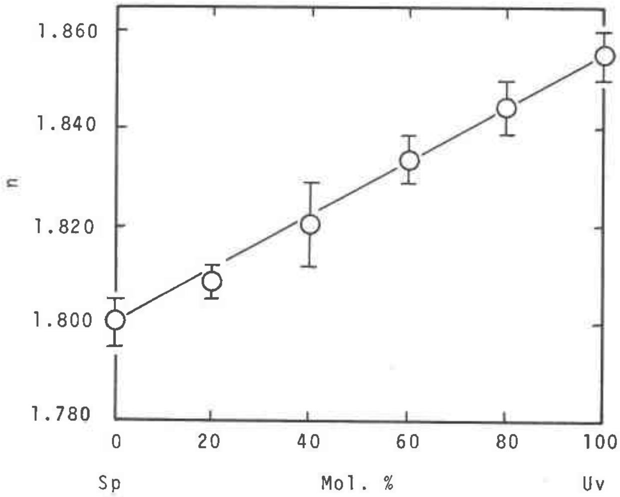

FIG. 2. Change of refractive index for the system spessartite-uvarovite.

TABLE 2. Heating Results for the Mixtures of Spessartite and Uvarovite at Atmospheric Pressure of Air

Starting Materials Composition (mole%) spessartite	: uvarovite	Heating conditions T(°C)	t(hrs)	Products	Cell dimension of garnet a_o (Å)
100	0	1160	2	glass, Gl	
		1100	2	Sp	11.621(5)
90	10	1150	3	glass, Glss	
		1100	8	Gss ≫ Glss	
		1050	8	Gss	11.653(5)
80	20	1150	3	glass, Glss, SiO_2	
		1100	8	Gss, Sp, Glss, SiO_2	
		1075	20	Gss ≫ Sp, Glss, SiO_2	11.69(1)
60	40	1100	8	glass, Glss	
		1060	95	Uv, Sp, Glss ≫ Gss	
		1055	93	Uv, Sp Gss	11.65(3)
50	50	1100	8	glass, Glss Uv, Cr_2O_3, Pw	
		1055	20	Sp, Uv, Glss, glass ≫ Pw, Cr_2O_3	
		1040	100	Uv, Sp ≫ Gss	
		1015	45	Sp, Uv	
40	60	1100	8	Uv, Glss, glass	
		1060	95	Uv, Sp ≫ Glss	
		1055	93	Sp, Uv	
20	80	1155	100	Gss	11.942(5)
		1055	15	Uv, Sp	
10	90	1180	95	Gss	11.945(5)
0	100	1400	2	Pw, Cr_2O_3	
		1380	5	Uv, Pw, Cr_2O_3	12.008(2)
		1380	25	Pw, Cr_2O_3 Uv	
		1370	25	Uv,	12.006(1)

Abbreviations: Gl, galaxite; Glss, galaxite solid solution; Gss, garnet solid solution; Pw, pseudowollastonite.
Heat treatments above 25 h were carried out by reheating with intermediate grinding.
Underlined represents the garnet which has the lattice constant present in last column.

tants, spessartite, melted and broke down at 1160°C in air.

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