

Contributions to the synthesis of spessartine analogues

RENATA HŘÍCHOVÁ

Department of Mineralogy, Institute of Chemical Technology, Prague

SUMMARY. Many syntheses have been carried out in order to establish the possibility of replacing manganese in spessartine, $Mn_3Al_2(SiO_4)_3$, by various elements (Be, Mg, Ca, Sr, Ba, Pb, Cu, Ni, Co, Fe^{2+} , Sc, Yt, Zn, Cd) as well as aluminium by Sc, Yt, Zr, Ti, Cr, Fe^{3+} by a solid state reaction. The syntheses were done by sintering pellets of the desired composition at about 1100 °C for 5–10 hours under normal pressure. It has been found that an inert atmosphere creates more favourable conditions for the syntheses of spessartine analogues, compared to the results obtained in the open-air reaction, where often spinel was obtained. All the reaction products were submitted to X-ray and chemical analysis and to IR spectroscopical examination.

THE garnet lattice, built up from metal ions in four, six, and eight coordinated sites, provides an excellent model for the investigation of the coordination tendencies of different ions, for which reason it has become a subject of interest to many authors. The crystal chemistry of garnets has been recently studied by Gentile and Roy (1960), Strens (1965), Ito and Frondel (1967), and Geller (1967).

The object of the present paper is an investigation of the participation of ions in the spessartine lattice as well as of the role of manganese in garnets. Spessartine represents a link between ugrandites and pyralspites and in addition to that offers good stability in a relatively large *PT* field. For this reason it has been used as a model substance for this investigation.

Experimental. Garnets were prepared as microcrystalline powders by sintering pellets of the desired composition. Mixtures in stoichiometric proportions were prepared, usually from nitrates, carbonates, or acetates, and then thoroughly ground in alcoholic suspension. The samples were then dried and heated to 700 °C for at least 5 hours, re-ground in an agate mortar and the mixture was compacted into pellets, sealed in a Pt vessel, and brought to 1000 to 1200 °C under normal pressure for a period of about 5–10 hours either in air or in an argon atmosphere. About 250 syntheses have been carried out. The progress of the spessartine synthesis was examined by X-rays, which showed that the reaction proceeds without intermediate crystalline phases. The crystallization rate of spessartine as a function of heating time was also examined by chemical analysis, by determining the decrease of the amount of free (acid-soluble) manganese. The results are illustrated in fig. 1 and are in full correspondence with those obtained by X-rays for Ca-garnets by Ito and Frondel (1967).

The reaction products of all experiments were examined by X-rays; the unit cell

dimensions a (table I) were computed by averaging the values obtained from the reflections 400, 420, 444, 521, 611, 640, 642, and 842. The precision is not high because of poor line quality of some samples (Mn-Sr, Mn-Sc, Mn-Ti) and is estimated at $\pm 0.02 \text{ \AA}$.

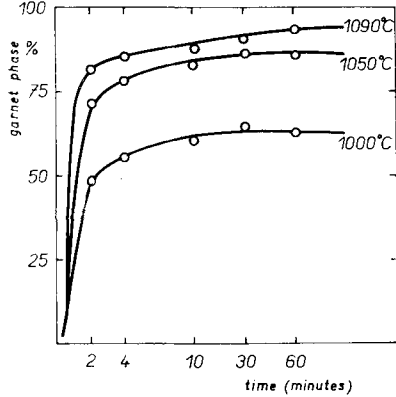


FIG. 1. Crystallization of spessartine as a function of time.

The homogeneity of the samples was tested: by X-rays and electron microscopy for all samples, microscopically (for phases detectable at magnification $100\times$), by fractioned dissolution in acids for phases significantly differing in dissolution rates, and by IR spectroscopy for all garnets synthesized. Under the microscope, the garnets (at magnification $200\times$) were found to consist of dendritic crystals. The IR spectra of the garnets were obtained with a UR-10 Model spectrometer using the KBr pellet technique in the region from 400 to 1200 cm^{-1} (table II). All the samples exhibit intense absorption bands in the region from 800 to 1100 cm^{-1} , assigned to the SiO_4 tetrahedra (Siebert, 1966) as well as from 500 to 710 cm^{-1} , these

TABLE I. Synthetic garnets in the spessartine series

	Air	Argon	Temp.	a
Substitutions in the eight-coordinated sites				
$\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$	+	+	1100 °C	11.63 Å
$(\text{Mn}_{1.5}\text{Ca}_{1.5})\text{Al}_2(\text{SiO}_4)_3$	+	+	1150	11.70
$(\text{Mn}_2\text{Cu})\text{Al}_2(\text{SiO}_4)_3$	+	+	1000	11.60
$(\text{Mn}_2\text{Be})\text{Al}_2(\text{SiO}_4)_3$	+	+	1150	11.54
$(\text{MnCd}_2)\text{Al}_2(\text{SiO}_4)_3$	+	+	1050†	11.78
$\text{Cd}_2\text{Al}_2(\text{SiO}_4)_3$	+	+	1000†	11.80
$(\text{Mn}_2\text{Yt})\text{Al}_2(\text{Si, Al})\text{O}_4)_3$	+	+	1150	11.70
$(\text{Mn}_2\text{Sc})\text{Al}_2(\text{Si, Al})\text{O}_4)_3$	+	+	1150	11.63
$(\text{Mn}_{2.8}\text{Mg}_{0.2})\text{Al}_2(\text{SiO}_4)_3$	—	+	1100	11.61
$(\text{Mn}_{2.9}\text{Pb}_{0.1})\text{Al}_2(\text{SiO}_4)_3$	—	+	1050	11.62
$(\text{Mn}_{1.2}\text{Fe}_{1.8})\text{Al}_2(\text{SiO}_4)_3$	—	+	1050	11.60
$(\text{Mn}_{2.4}\text{Co}_{0.6})\text{Al}_2(\text{SiO}_4)_3$	—	+	1100	11.58
$(\text{Mn}_{2.6}\text{Ni}_{0.4})\text{Al}_2(\text{SiO}_4)_3$	—	+	1100	11.60
$(\text{Mn}_{2.1}\text{Sr}_{0.9})\text{Al}_2(\text{SiO}_4)_3$	—	+	1150	11.75
Substitutions in the six-coordinated sites				
$\text{Mn}_3(\text{Ti}_{0.5}\text{Al}_{1.5})[(\text{Si, Al})\text{O}_4]_3$	+	+	1050	11.75
$\text{Mn}_3\text{TiFe}_2\text{SiO}_{12}$	+	+	1100	11.90
$\text{Mn}_3\text{ZrFe}_2\text{SiO}_{12}$	+	+	1100	11.95
$\text{Mn}_3(\text{ZrAl})[(\text{Al, Si})\text{O}_4]_3$	—	+	1150	11.80
$\text{Mn}_3(\text{YtAl})(\text{SiO}_4)_3$	—*	+	1150	11.75
$\text{Mn}_3(\text{ScAl})(\text{SiO}_4)_3$	—*	+	1150	11.70

* Two garnet phases are formed with a c. 11.64 and 12.01 Å.

† Time, 10 hours; for all other syntheses the time was 5 hours.

TABLE II. Absorption maxima of synthetic garnets, cm^{-1}

$\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$	—	450	475	560	—	630	—	720	—	800	865	890	—	950	—	1095
$\text{Cd}_2\text{Al}_2(\text{SiO}_4)_3$	415	465	475	545	—	615	—	—	—	770	850	870	—	950	—	1080
$(\text{MnCd}_2)\text{Al}_2(\text{SiO}_4)_3$	—	445	470	555	—	625	—	710	—	785	830	—	940	960	—	1120
$(\text{Mn}_2\text{Be})\text{Al}_2(\text{SiO}_4)_3$	435	460	—	540	570	620	665	720	—	765	—	890	—	970	1040	1080
$(\text{Mn}_{2-8}\text{Mg}_{0-2})\text{Al}_2(\text{SiO}_4)_3$	—	465	476	535	—	620	—	720	—	—	800	—	—	960	—	1100
$(\text{Mn}_{1-5}\text{Ca}_{1-3})\text{Al}_2(\text{SiO}_4)_3$	—	450	—	—	—	610	—	725	—	—	850	870	930	—	—	1100
$(\text{Mn}_{2-1}\text{Sr}_{0-9})\text{Al}_2(\text{SiO}_4)_3$	410	—	470	540	570	625	—	740	767	780	—	870	—	960	1030	1080
$(\text{Mn}_{2-8}\text{Pb}_{0-1})\text{Al}_2(\text{SiO}_4)_3$	—	460	—	540	580	630	—	720	—	800	865	890	—	960	—	1100
$(\text{Mn}_2\text{Cu})\text{Al}_2(\text{SiO}_4)_3$	410	445	475	565	—	630	—	710	—	790	860	890	—	960	—	1100
$(\text{Mn}_{2-5}\text{Co}_{0-3})\text{Al}_2(\text{SiO}_4)_3$	410	435	470	565	—	630	—	720	—	770	800	870	890	950	—	1090
$(\text{Mn}_{2-4}\text{Ni}_{0-1})\text{Al}_2(\text{SiO}_4)_3$	410	—	470	565	—	630	—	—	—	790	800	890	—	950	—	1100
$(\text{Mn}_{1-2}\text{Fe}_{1-9})\text{Al}_2(\text{SiO}_4)_3$	410	440	465	560	—	620	—	730	—	790	830	880	900	960	—	1100
$(\text{Mn}_2\text{Yt})\text{Al}_2(\text{Al, Si})\text{O}_{4\frac{1}{2}}$	—	430	480	560	—	620	—	720	—	800	—	890	—	960	—	1100
$(\text{Mn}_3\text{Sc})\text{Al}_2(\text{Al, Si})\text{O}_{4\frac{1}{2}}$	410	430	465	530	—	630	—	720	—	800	—	860	—	970	—	1100
$\text{Mn}_3(\text{YtAl})(\text{SiO}_4)_3$	—	—	—	—	—	—	665	—	760	820	—	890	—	960	—	1080
$\text{Mn}_3(\text{ScAl})(\text{SiO}_4)_3$	415	440	475	565	—	630	—	720	—	775	—	860	890	960	—	1100
$\text{Mn}_3(\text{ZrAl})(\text{Al, Si})\text{O}_{4\frac{1}{2}}$	415	435	450	500	565	620	665	710	740	—	870	890	—	960	—	1130
$\text{Mn}_3(\text{Ti}_{0-5}\text{Al}_{1-3})(\text{Si, Al})\text{O}_{4\frac{1}{2}}$	—	430	470	—	—	620	—	710	—	760	830	890	—	960	—	1080
$\text{Mn}_3\text{TiFe}_2\text{SiO}_{12}$	420	—	470	—	—	625	—	720	—	760	850	890	—	965	—	1100
$\text{Mn}_3\text{ZrFe}_2\text{SiO}_{12}$	415	440	460	510	—	630	—	715	745	760	880	890	—	970	—	1100

being attributed by Moencke (1962) to the AlO_6 octahedra. Only the low absorption maxima ($410\text{--}75\text{ cm}^{-1}$) may be due to the metal-oxygen vibrations of the bivalent cation in eightfold coordination. All these spectra are very similar to that of spessartine, except those of Mn-Be and Mn-Sr garnets, which show shifts and broadening of some absorption bands apparently due to the very different radii of these ions.

Discussion. The results of those experiments aimed at the substitution in the eightfold coordination positions showed a positive effect of the inert atmosphere. All unsuccessful runs carried out in open-air conditions produced spinel, $R^{\text{II}}R_2^{\text{III}}\text{O}_4$. The tendency of such elements as Ni, Zn, Co to form an alumina spinel is well known; these elements, however, may also easily form a spinel $Me\text{Mn}_2\text{O}_4$, using the trivalent manganese, which is present in the starting material as Mn_2O_3 (as found by X-rays). It might be supposed that the formation of spinel in this case will be enhanced by factors favourable to the stabilization of Mn^{3+} ; in particular, the higher P_{O_2} in the open-air experiments will raise the dissociation temperature of Mn_2O_3 , and the formation of spinel may bind the trivalent manganese before the temperature of garnet formation is attained.

The Ba^{2+} ion is probably too large to enter the spessartine lattice, and only a little lead could be introduced. The ready formation of gahnite is well known, but it was surprising to find that a zinc-bearing spessartine could not be obtained though the radii of Mn^{2+} (0.79 \AA) and Zn^{2+} (0.78) are very close, whereas Cd^{2+} , with a much larger radius (0.96) readily forms a garnet. This anomaly may possibly be connected with the fact that both Zn^{2+} and Cd^{2+} have the electron configuration d^{10} , while Mn^{2+} does not; the lower electron density on the trivalent element, which in the garnets is bonded to the strongly electronegative SiO_4^{4-} , may effect a contraction of the effective ionic radii of Zn^{2+} and Cd^{2+} , due to their d -electrons being involved; and this contraction could reverse the expected stabilities of Zn and Cd garnets.

Attempts at substitution of aluminium, which is six-coordinated in spessartine, by Cr^{3+} or Fe^{3+} were unsuccessful. Yttrium and scandium could be substituted for part of the Al in argon, but in air two phases were formed, with a approx. 11.64 and 12.01 \AA , probably near spessartine and the silica-free yttrogarnet or its scandium analogue. Yoder and Keith (1951) have made a detailed study of the system spessartine-yttrogarnet.

Garnets containing Ti^{4+} or Zr^{4+} were successfully synthesized, and in these Al could be replaced by Fe^{3+} . Taken in conjunction with the failure to replace six-coordinate Al by Fe^{3+} , this suggests that the Ti^{4+} or Zr^{4+} may be in the six-coordinate positions and the Al or Fe^{3+} replaces four-coordinated Si^{4+} . In agreement with Ito and Frondel (1967) and with Howie and Woolley (1968) we found an increase in cell dimensions with increasing Ti.

REFERENCES

- GELLER (S.), 1960. *Journ. Appl. Phys.* **31**, 30S-37S, Suppl.
 — 1967. *Zeits. Krist.* **125**, 1.
 GENTILE (A. L.) and ROY (R.), 1960. *Amer. Min.* **50**, 260.

- HOWIE (R. A.) and WOOLLEY (A. R.), 1968. *Min. Mag.* **36**, 775.
ITO (J.) and FRONDEL (C.), 1967. *Amer. Min.* **52**, 773.
MOENCKE (H.), 1962. *Mineralspektren* (Akademie-Verlag, Berlin).
SIEBERT (H.), 1966. *Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie*. Berlin (Springer Verlag).
STRENS (R. G. J.), 1965. *Min. Mag.* **35**, 547.
YODER (H. S.) and KEITH (M. K.), 1951. *Amer. Min.* **36**, 519.

[Manuscript received 29 April 1969; revised 29 May 1969]