

Nat. Acad. Sci. Letters, Vol. 16, No. 1, 1993

Experimental study of the system grossularite-spessartine at $P_{H_2O} = P_{\text{Total}} 1 \text{ kbar}$ and variable temperatures

(grossularite/spessartine/solid solution)

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Received 6-11-1992

ABSTRACT The system grossularite-spessartine has been studied at 1 kbar and 700, 750 and 800°C. Based on X-ray diffraction study and refractive index measurement it was observed that there is continuous solid solution relationship between the two end members; there is thus no basis for including grossularite and spessartine into two separate groups on the basis of the assumption that there may be immiscible relation between these two garnets.

Two different series of garnets are generally recognized¹, the pyralspite and ugrandite series. Continuous compositional variation is expected within the same series of garnets, but not between the members of two different series. Under favourable conditions, perfect miscibility between members of pyralspite and ugrandite series have also been advocated². Natural occurrence of garnets with composition intermediate between grossularite and spessartine have been reported by several authors^{3,4}. The system grossularite-spessartine was, therefore, investigated at 1 kbar and variable temperatures to see if there is complete miscibility between these two end members.

Synthesis of the two end members (e.g. grossularite-spessartine) and four intermediate ones in the same series at 550°C and 2 kb was made earlier^{5,6} and complete solid solution relationship was suggested.

On the basis of collected analyses of Mn and Al-rich garnets perfect miscibility between grossularite and spessartine under favourable conditions was suggested². Complete solid solution relationship between the two end members under P-T conditions similar to those of glaucophanitic metamorphism was also speculated⁷.

As a source of MnO, CaO and Al₂O₃, reagent grade MnCO₃, CaCO₃ and Al₂O₃ were used. As a source of silica, pure quartz (collected from Matheran, Maharashtra) was employed. CaCO₃ and MnCO₃ were dried in an oven overnight, whereas alumina was heated at 1100°C for several hours in a kanthal wire-wound furnace to drive away the presence of any possible H₂O present as diaspore. Crystals of quartz were crushed to very fine powder and then treated with hot conc. HCl. The material was then washed with distilled water and kept in an oven overnight so that it is free from moisture.

Appropriate chemicals were taken in an agate mortar in required proportions. The mixture was mixed thoroughly for 1 hour by using acetone. It was then taken in a platinum crucible and placed in a silicon carbide furnace. This was heated at 1000°C for 24 hours to obtain homogeneous sintered materials, which were then heated

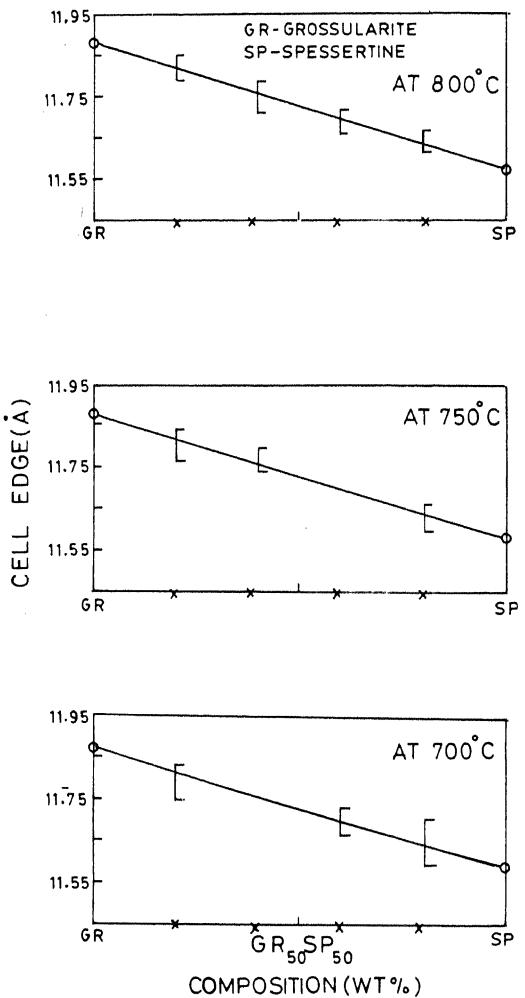
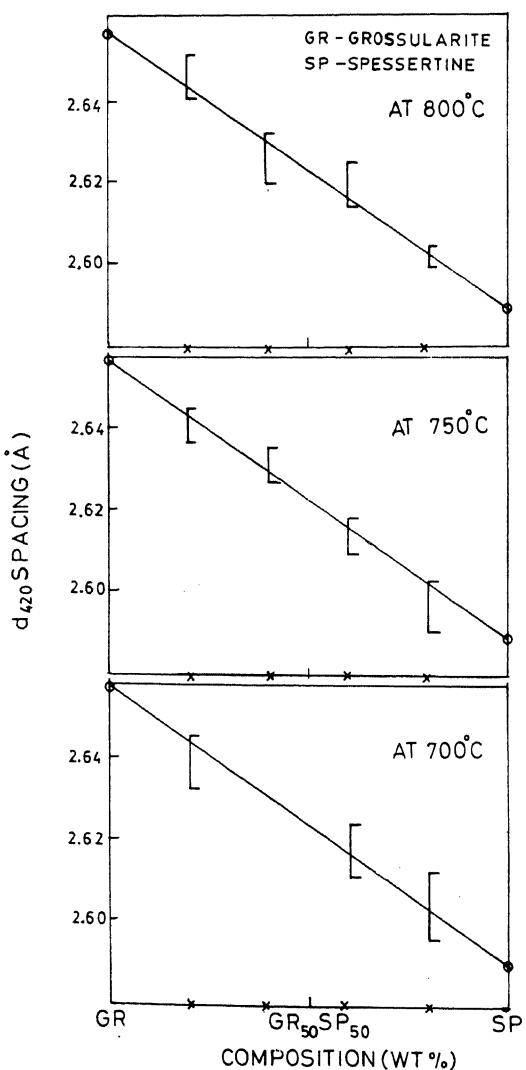


Fig. 1 - Variation in interplaner spacing of the grossularite-spessartine solid solution with respect to composition.

Fig. 2 - Variation in cell edge of the grossularite-spessartine solid solution with respect to composition.

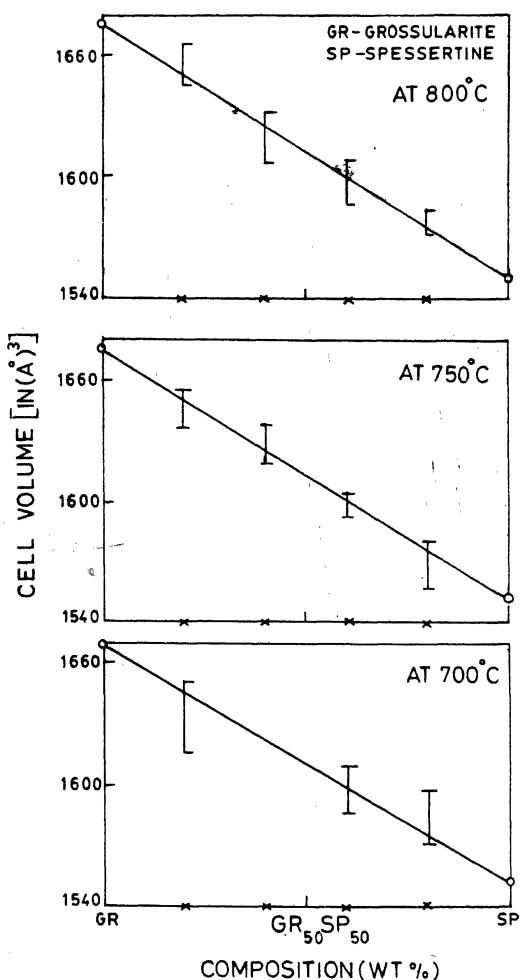


Fig. 3 - Variation in cell volume of the grossularite-spessartine solid solution with respect to composition.

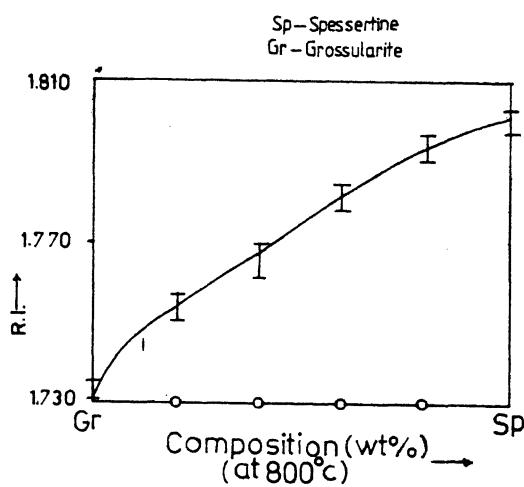


Fig. 4 - Variation in refractive indices of the grossularite-spessartine solid solution with respect to composition.

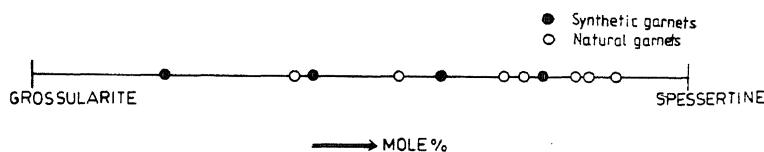


Fig. 5 - Plot of the compositions of natural and synthetic grossularite-spessartine garnets.

at 700°C under 1 kbar to obtain end member garnets. Four intermediate compositions ($Gr_{80}Sp_{20}$, $Gr_{60}Sp_{40}$, $Gr_{40}Sp_{60}$, $Gr_{20}Sp_{80}$) were prepared by mixing the two end members. Altogether eleven experimental runs have been made with these four compositions. X-ray diffraction and optical studies of the run products were made. Cell parameters of the garnets have been calculated. Compositions of the natural as well as synthetic garnets have been plotted. X-ray diffraction pattern suggested that there was no other phase except garnet.

Au and Ag capsules were used for experimental runs. They were sealed by means of a carbon arc spot welder. One end of the capsule was sealed first and its weight was noted. The capsule was again weighed after introducing some water within it with the help of a microsyringe. Powdered samples were placed within the capsule. Weight of the sample was noted. Then open end of the capsule was sealed. After the preparation of the capsule, it was again

weighed to check whether H_2O was lost or not during welding. The capsule was kept in the oven for an hour. The sealing was considered to be perfect if there was no loss of water.

Garnets were identified on the basis of their higher relief and isotropic nature. Pure grossularites were colourless, whereas spessartines were pale yellow to brownish yellow in colour. Refractive indices of the intermediate garnets were measured by liquid immersion method.

Results are summarised in Figs.(1-4), and Table 1. Figs.(1 & 2) are related to variation in interplanar spacings d_{420} and cell edge 'a' respectively, as a function of composition, whereas Fig. 3 shows changes in cell volume of the garnets. Fig. 4 refers to variation in the refractive indices of garnets with respect to the change in the composition of spessartine. Refractive index data are accurate to ± 0.0025 . These figures indicate continuous solid solution relationship between grossularite and spessartine. Figs. (1-3)

Table 1. Experimental results.

Run No.	Composition	Duration (in hours)	temp. (°C)	Interplaner spacing (Å)	Cell edge (Å)	Cell volume (Å) ³	R.I. ± 0.002
1.	$Gr_{80}Sp_{20}$	48	800	2.64-2.65	11.830-11.850	1655-1664	1.754
2.	$Gr_{40}Sp_{60}$	47	800	2.619-2.624	11.660-11.710	1585-1605	1.782
3.	$Gr_{20}Sp_{80}$	44	800	2.599-2.604	11.630-11.660	1573-1585	1.794
4.	$Gr_{60}Sp_{40}$	44	800	2.618-2.629	11.710-11.750	1605-1622	1.764
5.	$Gr_{60}Sp_{40}$	104	750	2.627-2.634	11.760-11.790	1626-1639	—
6.	$Gr_{40}Sp_{60}$	104	750	2.609-2.611	11.691-11.690	1598-1597	—
7.	$Gr_{20}Sp_{80}$	115	750	2.589-2.602	11.590-11.640	1557-1577	—
8.	$Gr_{80}Sp_{20}$	115	750	2.636-2.641	11.760-11.790	1626-1639	—
9.	$Gr_{40}Sp_{60}$	122.5	700	2.610-2.624	11.660-11.720	1585-1610	—
10.	$Gr_{80}Sp_{20}$	122.5	700	2.630-2.640	11.780-11.710	1635-1605	—
11	$Gr_{20}Sp_{80}$	109	700	2.597-2.624	11.650-11.720	1581-1610	—

demonstrate that the cell edge and interplaner spacings of the garnets decrease with increasing substitution of Ca^{2+} by Mn^{2+} . The values of cell edges for pure grossularite and spessartine were also determined in the present study. Uncertainty in measurement is shown by brackets.

In nature, intermediate grossularite-spessartine garnets are not unusual. In Fig.5, intermediate compositions between the two end members are plotted. In this plot, those garnets, containing very low amount of other garnet molecules were not taken into consideration. Their concentration was excluded and the bulk composition was recalculated to 100.

Present study demonstrates that as long as bulk rock composition is suitable, there is no physical restriction for the occurrence of intermediate garnets (with composition lying between the two end members). Such intermediate garnets are relatively more common in contact metamorphic rocks but are rare in regionally metamorphosed rocks⁸. Below 400°C spessartine breaks into quartz + Mn-chlorite + fluid⁹. It may be, therefore, possible that a homogeneous grossularite-spessartine solid solution may not be stable at lower temperature. In the present study, no Mn-chlorite or quartz was present to indicate that there was no quenching problem, and all the runs are related to equilibrium crystallization. The possibility of the presence of a miscibility gap between grossularite and spessartine under glaucophanitic metamorphic conditions have been earlier speculated⁷; however, no experimental verification was put forward.

Although not uncommon, intermediate grossularite spessartine garnets are rare; which may be due to lack of appropriate bulk chemistry¹⁰ rather than the absence of proper physical conditions. Manganese concentration occurs at the terminal stage of crystallization, before which most of the calcium enters in the structure of plagioclase, or other calcium-bearing phases. Moreover, geochemically (in terms of electronegativity and ionic size), Mn^{2+} is more close to Mg^{2+} and Fe^{2+} than Ca^{2+} . Hence if Fe^{2+} or Mg^{2+} is present in the bulk composition, during metamorphism complete substitution of Mg or Fe by Mn^{2+} occurs at the early stage of metamorphic crystallization resulting in non-availability of Mn. Careful study of Mn-bearing meta-sediments may throw more light in this problem. Present authors feel that breakdown of spessartine is an important factor for not finding garnets of intermediate composition.

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