ESRF	**Experiment title:** **Low temperature thermal expansion of synthetic garnet solid solutions**	**Experiment number**: CH-936
Beamline: BM16	**Date of experiment**: from: 06/10/2000 to: 11/10/2000	**Date of report**: 05/09/01
Shifts: 15	**Local contact(s)**: Andy Fitch	*Received at ESRF:*

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Report:

The low-temperature thermal expansion of synthetic garnets along the join pyrope-grossular, $(Mg,Ca)_3Al_2Si_3O_{12}$, was measured by high resolution X-ray powder diffraction methods. Measurements were made between 5 and 298 K at intervals of 5-10 K. Five solid solutions, py75gr25, py60gr40, py50gr50, py40gr60, py25gr75 and the two end-members pyrope and grossular were analyzed. The goal is to investigate the low temperature structural behavior in garnet, because this is where excess heat capacities arise (Bosenick & Geiger, 1997). In addition, thermal expansion and lattice parameter saturation behavior are correlated to the lattice entropy and this needs to be studied in a quantitative way. It is also important to do measurements with a very high resolution, to be able to describe temperature behavior rigorously at very low temperature. In this way, it should be possible to check whether the Gruneisen relation ($C_p \propto \alpha$) is obeyed. Fig. 1 shows the variation in cell parameters for the different solid solutions as a function of temperature. Pyrope shows the highest temperature dependence, grossular the least, with the solid solutions in between the two end-members. Some of the solid solutions show unusual behavior at 90-100 K. This is shown in Fig. 2 for pyrope and py60gr40. Here, a discontinuity can be seen. It is larger than the measurement uncertainty (2 to 3 > σ), and this discontinuity can be seen in all the solid solutions with a pyrope mole percent greater than 40. The garnet composition py25gr75 and end-member grossular do not show any discontinuity. The reason for this discontinuity is being investigated further.

Little has been published on thermal expansion behavior of garnet, except for the work on end-member pyrope and grossular from room temperature to 1000 K (Skinner, 1956) and for pyrope-grossular solid solutions below room temperature from 300 K to 20 K (Bosenick & Geiger, 1997).

For complex materials there is no simple first-principle derivation of the temperature dependence of thermal expansion, so we preliminary rely on empirical modelling. Thermal expansion of pyrope and grossular were described by Skinner (1956) from room temperature to 1000 K and below room temperature to 20 K by Bosenick & Geiger (1997). The linear coefficients of thermal expansion for the two end-members and the various solid solutions, calculated in two different ways, are shown in Fig. 3. It can be seen that their behavior is similar in both cases as both increase with increasing pyrope content. Positive deviations from ideal mixing behavior were found for all solid solutions studied. Fig. 4 shows the excess molar volumes as a function of grossular mole fraction (temperatures of 5 and 298 K are only shown). Similar deviations were found also in previous works (Ganguly et al, 1993, and Bosenick & Geiger, 1997). The highest deviations are in the region

of high Ca content, in agreement with the former studies. No negative deviations (Haselton & Newton, 1980) were found in pyrope-rich garnets. Room temperature data of Bosenick & Geiger are shown for comparison.

Fig. 1

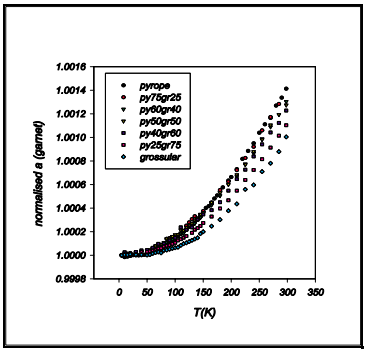

Fig. 2

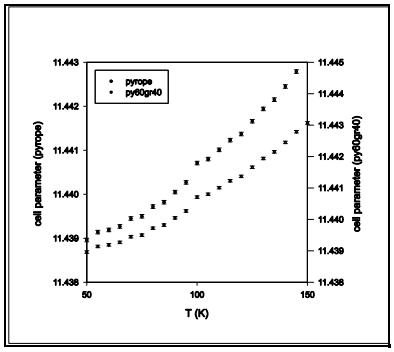

Fig. 3

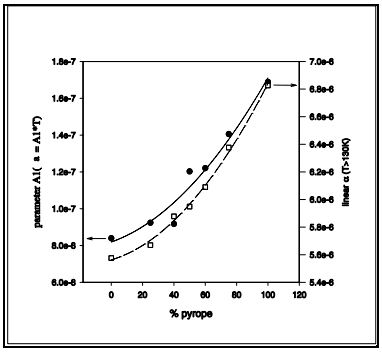

Fig. 4

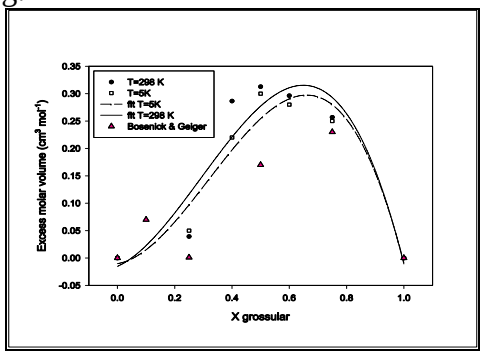

Fig. 1 – Normalized cell parameters (Å) of the end-members and of the various solid solutions
Fig. 2 – Cell parameters of pyrope and of solid solution py60gr40, showing the discontinuity at about 100 K
Fig. 3 – Linear thermal expansion coefficient (α) evaluated in two different ways
Fig. 4 – Excess molar volume of mixing as a function of grossular molar fraction

This study is the first presenting high resolution X-ray diffraction data at low temperatures on garnet (and perhaps any silicate) solid solutions. The data quality is outstanding, as demonstrated by the estimated standard deviations on the cell parameters (10^{-5} Å, about one order of magnitude lower than previous investigations). Our results can be summarized as follows:

1) A small discontinuity in thermal expansions is observed around 90-100 K in pyrope-rich solid solutions. This may indicate a previously unreported phase transition.

2) Non ideality in the volume of mixing is confirmed. Positive excess molar volumes are present in over the whole binary, with the largest values in grossular-rich garnets. There are no negative deviations from ideality and the mixing volume at all temperatures is similar.

3) The largest thermal expansion coefficients were found for pyrope and pyrope-rich compositions. This is to be related to the anharmonic behavior of Mg in garnets (Bosenick & Geiger, 1997).

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