

Mechanism of reductive decomposition of $\text{Fe}_x\text{Mg}_{3-x}\text{Al}_2\text{Si}_3\text{O}_{12}$ garnets: The crucial role of iron content

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The thermal decomposition of garnets belonging to pyrope-almandine solid-solution generally occurs between 750 °C and 1200 °C. The character of decomposition products depends on the chemical composition of garnet and actual experimental conditions, i.e. temperature and duration of heating, heating and cooling rates, pressure and type of atmosphere. This study reports on the effect of iron content in the structure of garnet on the variation of decomposition temperature and mechanisms in reducing atmosphere.

Thermally-induced reductive decomposition of natural iron-bearing garnets of the almandine-pyrope series, with the following crystallochemical formula $^{\text{VIII}}(\text{Fe}^{2+}_x, \text{Mg}_{3-x})^{\text{VI}}(\text{Al}, \text{Fe}^{3+})_2\text{Si}_3\text{O}_{12}$ ($0.54 \leq x \leq 2.85$; except pyrope exhibiting significant amount of Fe^{3+} in octahedral sites) were studied at temperatures up to 1200 °C (heating rate of 10 °C/min) under atmosphere of forming gas (10 % of H_2 in N_2). The observed decomposition temperature, determined from differential scanning calorimetry and thermogravimetry, is greater than 1000 °C in all cases and showed almost linear dependence on the iron content in dodecahedral sites of the studied garnets. An exception is decomposition of pyrope garnet represented by two weak endothermal effects instead of one strong endothermal effect as in the case of other garnets (Figure 1, left). The initial garnet samples and its decomposition products were characterized in detail by means of X-ray powder diffraction and Mössbauer spectroscopy (Figure 1, right).

All garnets decompose into metallic iron (particles below 4 μm) and Fe-spinel; the other identified decomposition products were cristobalite, fayalite, cordierite, enstatite, anorthite and pigeonite depending on chemical composition of actual garnet (all phases are usually well crystallized). Anorthite and pigeonite are present only if there is Ca in the dodecahedral site of the garnet structure.

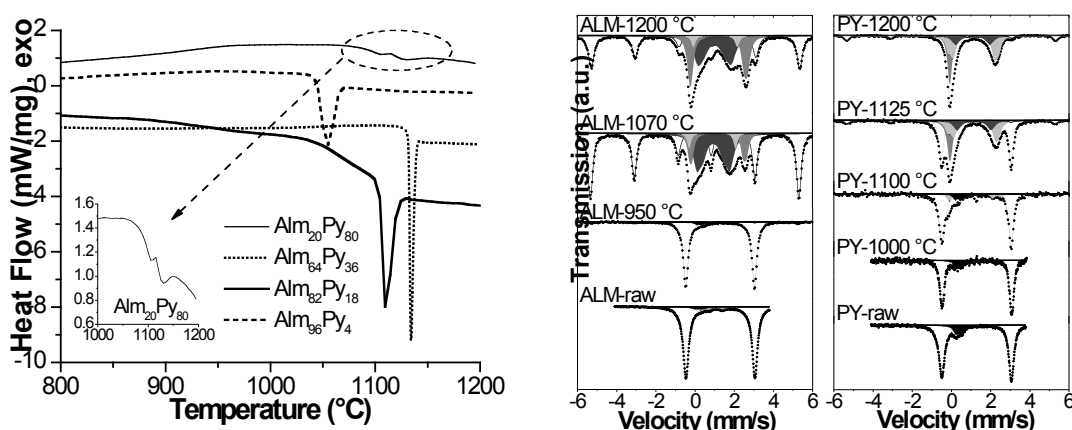


Figure 1. Left - differential scanning calorimetry of natural almandine-pyrope garnets; right - Mössbauer spectra of thermally-treated almandine (ALM) and pyrope (PY) samples (modified from Aparicio et al., *High-temperature decomposition of almandine and pyrope in reducing atmosphere*, AIP conference proceedings, 2010, 1258, 47-54).