Thermodynamic mixing properties and behavior of almandine–spessartine solid solutions

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Abstract

The heat capacity, C_p, of five solid-solution members of the almandine(Alm)–spessartine(Sps) binary, consisting of three synthetic polycrystalline and two natural single-crystal samples, was measured in the temperature range between 2 and 300 K using relaxation calorimetry and between 282 and 764 K using DSC methods. All garnets exhibit a λ-type heat-capacity anomaly at low temperatures resulting from a paramagnetic to antiferromagnetic phase transition. The temperature of the magnetic transition in Fe-rich garnets occurs between those of the two end-members (i.e. 9.2 K for almandine and 6.2 K for spessartine), but lies at lower values between 3.5 and 4.5 K for more Sps-rich compositions with $X_{Mn}^{grt} > 0.5$.

The calorimetric entropy at 298 K shows mechanical-mixture behavior for Sps-rich garnets and a slight possible negative deviation from such behavior for Alm-rich compositions. At the 2σ level all data are, however, consistent with ideal mixing behavior and the Margules entropy interaction parameter, $W_{S,FeMn}^{grt}$, is zero for the Alm–Sps binary. Thermodynamic analysis of published high P and T phase-equilibrium Fe–Mn exchange experiments between garnet and ilmenite shows that the excess Gibbs free energy of mixing, ΔG_{ex}, for Fe–Mn in garnet is positive and asymmetric towards spessartine. Margules enthalpy interaction parameters of $W_{H,FeMn}^{grt} = 4170 \pm 518$ J/cation·mol and $W_{H,MnFe} = 1221 \pm 588$ J/cation·mol are derived giving a maximum of $\Delta G_{ex} \approx 0.7$ kJ/cation·mol at $X_{Mn}^{grt} \approx 0.6$. ΔH_{ex} obtained using autocorrelation analysis of published IR spectra of Alm–Sps solid solutions is in reasonable agreement with that derived from phase-equilibrium and calorimetry data. Previous diffraction and spectroscopic results on Alm–Sps garnets and quantum mechanical calculations made on almandine are used to interpret the macroscopic thermodynamic behavior from a microscopic basis.

The relevance of the new garnet Fe–Mn mixing model for petrological calculations is demonstrated by incorporating it into the quaternary garnet mixing model of Berman (1990). Thus, better agreement for temperatures calculated using Fe–Mn garnet-ilmenite and Fe–Mg garnet-biotite geothermometry could be achieved. Temperatures calculated for Mn-poor and Mn-rich garnet-bearing assemblages, applying garnet-biotite thermometry, are in better agreement taking Fe–Mn mixing into account.

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1. INTRODUCTION

Many rock-forming garnets can be described by the four-component system almandine (Alm – $Fe_3Al_2Si_3O_{12}$)-pyrope (Py – $Mg_3Al_2Si_3O_{12}$)-grossular (Gr – $Ca_3Al_2Si_3O_{12}$)-spessartine (Sps – $Mn_3Al_2Si_3O_{12}$). Thus, extensive research has

been done over the years to investigate the thermodynamic behavior of this system (see review in Geiger, 1999). The thermodynamic properties ($\Delta H_f^o, C_p, S^o, V$) of the four end-member garnets, as based on calorimetric, phase- equilibrium and X-ray diffraction studies, are now known quite well. However, ΔH_f^0 for spessartine has not been determined directly via calorimetry. In spite of the increasing level of experimental sophistication over the years and the numerous published thermodynamic investigations on both binary and higher order solid-solution compositions, quantitative

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determinations of the enthalpy of mixing, ΔH_{mix} ($\equiv \Delta H_{ex}$), and the entropy of mixing, ΔS_{mix}, and thus the Gibbs free energy of mixing, ΔG_{mix}, are largely lacking.

Generally, ΔS_{mix} may be considered to consist of two contributions, that is $\Delta S_{mix} = \Delta S_{conf} + \Delta S_{ex}$, whereby ΔS_{conf} represents the ideal configurational entropy (i.e., $-R\Sigma X_i \ln X_i$ for a simple molecular solution) and ΔS_{ex} the excess entropy. The latter term may consist of vibrational ($\Delta S_{ex,vib}$) and non-lattice (e.g. magnetic, electronic) contributions ($\Delta S_{ex,mag}$, $\Delta S_{ex,el}$), all of which can be determined via calorimetry. That is, the sum of $\Delta S_{ex,vib} + \Delta S_{ex,mag} + \Delta S_{ex,el}$ gives the calorimetric excess entropy ($\Delta S_{ex,cal}$). An excess configurational entropy ($\Delta S_{ex,conf}$), e.g. due to short-range ordering, may also contribute to ΔS_{ex}. Such ordering effects have to be determined by diffraction and/or spectroscopic measurements (Bosenick et al., 1995, 1999).

Clearly, the problem of formulating quantitative thermodynamic mixing models for garnet centers on a lack of good and sufficient experimental data, especially direct measurements of ΔH_{mix} and $\Delta S_{ex,cal}$ on simple binaries as obtained through calorimetry. To date, only the $\Delta S_{ex,vib}$ behavior of pyrope–grossular garnets has been studied via calorimetric measurements (Haselton and Westrum, 1980; Bosenick et al., 1996; Dachs and Geiger, 2006). The data show substantial positive deviations from ideality for $\Delta S_{ex,vib}$ at 298 K, arising from positive excess heat capacities of mixing, $\Delta C_{p,ex}$, at lower temperatures. Between about 300 and 1000 K, on the other hand, $\Delta C_{p,ex} = 0$ and there is no further contribution to $\Delta S_{ex,vib}$ in this temperature range. These results underscore the critical need for low-temperature C_p measurements on other garnet compositions.

Several phase-equilibrium studies have investigated the thermodynamic behavior of almandine–spessartine ($(Fe_xMn_{1-x})_3Al_2Si_3O_{12}$) solid solutions. We restrict our short review to the more recent ones. Powncelby et al. (1987, 1991) studied Fe–Mn exchange between garnet and ilmenite at high pressures for binary Fe–Mn garnets in their first study and in their second work for garnets containing a grossular component. They proposed $W_{G,FeMn} = 1200 \pm 500$ J/cation·mol for the first study and $W_{G,FeMn} = 620 \pm 200$ J/cation·mol or 539 ± 218 J/cation·mol in their latter work, depending on how other garnet binaries were treated in their thermodynamic analysis. Ganguly et al. (1996) modeled the mixing properties of all six binaries in the system Alm–Py–Gr–Sps and accepted $W_{H,FeMn} = W_{H,MnFe} = 539$ J/cation·mol to describe ΔH_{ex}, thus assuming no excess entropy of mixing (i.e. $W_{S,i,j} = 0$). Feenstra and Engi (1998) also studied experimentally at high P and T the partitioning of Fe and Mn between garnet and ilmenite. They did not derive quantitative thermodynamic mixing properties, but did state that Mn–Fe mixing in garnet "deviate(s) more strongly from ideality than proposed till now". In terms of ΔV_{ex} behavior, almandine–spessartine garnets show very small positive deviations from ideality as described by $W_{V,FeMn} = 0.24 \pm 0.05$ cm³/mol (Geiger and Feenstra, 1997). Empirical pair potential simulations on garnet binary solid solutions were interpreted as indicating that elastic strain, mainly originating from differences in size between substituting cations, affects the magnitude of ΔV_{ex} and ΔH_{ex} (Bosenick et al., 2001). In the case of almandine–

spessartine garnets, where the volume differences between the two end-members is small, only slight positive ΔV_{ex} and ΔH_{ex} behavior is predicted.

In this paper, we present heat-capacity measurements between 2 and 764 K on both synthetic polycrystalline and natural single-crystal almandine–spessartine garnets using relaxation calorimetry and DSC methods. Our C_p measurements allow us to investigate $\Delta S_{ex,cal}$ behavior over a large temperature interval. Modeling the low temperature C_p data allows the contribution of a magnetic transition for all garnet compositions to their $\Delta S_{ex,cal}$ to be determined. This has not been done before, to the best of our knowledge, across a binary solid solution where both end-members posses paramagnetic cations and show low-temperature magnetic phase transitions. The macroscopic thermodynamic mixing behavior of almandine–spessartine garnets can also now be interpreted from a microscopic perspective using results obtained from quantum-mechanical simulations, and experimental diffraction and spectroscopic measurements.

2. SAMPLES AND EXPERIMENTAL METHODS

2.1. Samples

The garnets studied are three synthetic and two natural Alm–Sps intermediate solid solutions labelled, as based on their compositions, Alm75Sps25, Alm50Sps50, Alm25Sps75 and Alm71Sps26, Alm36Sps62. The polycrystalline synthetic samples were crystallized from glasses in a piston-cylinder device at 920–1000 °C and 20 kbar as described in Geiger and Feenstra (1997). The garnets were characterized by them using electron microprobe analysis, X-ray powder diffraction and ^{57}Fe Mössbauer spectroscopy. The measured compositions are $X_{Mn}^{grt} = 0.25$ for Alm75Sps25, $X_{Mn}^{grt} = 0.51$ for Alm50Sps50 and $X_{Mn}^{grt} = 0.79$ for Alm25Sps75, respectively, with an estimated error of 1–2 mol%. The amount of octahedral Fe^{3+} was determined to be less than 1–2% of the total Fe. The garnets were further studied by IR (Geiger, 1998), Raman (Kolesov and Geiger, 1998) and XAFS spectroscopy (Sani et al., 2004).

The two natural Alm–Sps garnet crystals were supplied by D.C. Smith (Lab. Minéralogie & Cosmochimie, Muséum National d'Histoire Naturelle, Paris). Their compositions, as determined by electron microprobe analysis and provided by him, are given by $X_{Fe}^{grt} = 0.71, X_{Mn}^{grt} = 0.26$, $X_{Mg}^{grt} = 0.03$ and $X_{Ca}^{grt} = 0.01$ for Alm71Sps26, and $X_{Fe}^{grt} = 0.36, X_{Mn}^{grt} = 0.62$ and $X_{Ca}^{grt} = 0.02$ for Alm36Sps62. Mössbauer spectroscopy done on these samples showed that only minor amounts < ~1% of total Fe in these natural materials is $^{[6]}Fe^{3+}$.

2.2. Low-temperature calorimetry

Low-temperature (i.e., 2–300 K) heat capacity was measured with the Physical Properties Measurement System (PPMS) constructed by Quantum Design® (Lashley et al., 2003; Dachs and Bertoldi, 2005). Heat capacity was