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Thermodynamic Consistencies and Anomalies among End-Member Silicate Garnets

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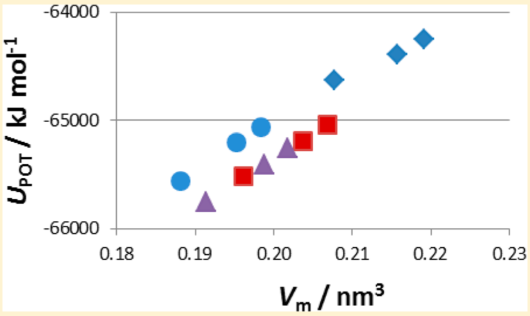
ABSTRACT: Materials with the garnet crystal structure include silicate minerals of importance both in geology, on account of their use in geothermobarometry, and industrially as abrasives. As a consequence of the former, there is considerable published thermodynamic information concerning them. We here examine this thermodynamic information for end-member silicate garnets (some of which are synthetic since not all occur in nature) for consistencies and anomalies, using thermodynamic relations between thermodynamic properties that we have established over recent years. The principal properties of interest are formula volume, heat capacity, entropy, formation enthalpy (from which the Gibbs energy may be obtained), and isothermal compressibility. A significant observation is that the ambient-temperature heat capacities of the silicate garnets are rather similar, whereas their ambient-temperature entropies are roughly proportional to their formula volumes. Evaluation of their Debye temperatures implies that their vibrational contributions to heat capacity are fully excited at ambient temperatures. The relatively small isothermal compressibilities of these garnets is related to the rigidity of their constituent silicate tetrahedra. We here establish additive single-ion values for each of the thermodynamic properties, which may be applied in estimating corresponding values for related materials.



■ INTRODUCTION

Silicate garnets are among the commonest metamorphic minerals[1,2] and are of significant interest in respect of their use in geothermobarometry, that is, the quantitative study of the temperature and pressure regimes at which a metamorphic or igneous rock reached chemical equilibrium. This application relies on the relatively slow diffusion through the dense and hard structure of the garnets thus resisting alteration. The common availability, denseness, and hardness of silicate garnets also result in their use as industrial abrasives.

As a consequence of the use of silicate garnets in geothermobarometry, there is considerable interest in examining their thermodynamic properties and those of their extensive mutual solid solutions. We have recently examined the thermodynamic properties of the lanthanoid (or lanthanide) garnets,[3] which are of particular concern in technological applications and for the systematics of their distributions as chemical tracers. In the current Paper we apply the same methods to investigate the silicate garnets with their wider and less systematic ranges of properties.

The methods that we apply are based upon correlations, principally those that we have termed "Volume-Based Thermodynamics" (VBT), that we have observed between formula volumes of ionic solids and their standard thermophysical properties (such as heat capacity, compressibility, entropy, enthalpy—and so Gibbs energy). These correlations rely on the fact that the energetics of ionic solids are essentially controlled by long-range charge (Coulombic) interactions opposed by short-range repulsions, with only small contributions from other interactions. In fact, roughly 85% of the interaction energy can be ascribed to Coulombic interactions.[4]

The mineral silicate garnets[5] have cubic structures, space group $Ia\bar{3}d$ (No. 230), with general formula $A_3B_5(SiO_4)_3 \equiv A_3B_5Si_3O_{12}$.[6] They are classified as *nesosilicates*,[1] (Greek *nêsos* = island) that is, materials that contain independent, distorted SiO_4 tetrahedra, sharing their corners with distorted BO_6 octahedra (typically, $B \equiv$ Al, Fe, Cr), thus forming a three-dimensional network. The divalent A cations (typically $A \equiv$ Ca, Fe, Mg, and Mn) occupy the dodecahedral interstices where they are surrounded by eight oxygens at the corners of a distorted cube. The oxygen anions are each coordinated by two A, one B, and one Si cation. The cation coordinates are all symmetry-determined, with only the oxygen coordinates variable.

Two groups of silicate garnets have earlier been identified, based on their extensive mutual solid solubilities,[7] namely, the *pyralspite* group (name based on the names of the three principal members—*pyrope*: $Mg_3Al_2Si_3O_{12}$; *al*mandine: $Fe_3Al_2Si_3O_{12}$; *s*pessartine: $Mn_3Al_2Si_3O_{12}$) and the *ugrandite* group (*u*varovite: $Ca_3Cr_2Si_3O_{12}$; *g*rossular: $Ca_3Al_2Si_3O_{12}$; *and*radite: $Ca_3Fe_2Si_3O_{12}$). This subclassification is, however, no longer recommended.[5,8]

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Table 1. Standard Thermodynamic Data for Silicate Garnets[10,11]

minerals, reference	formula	$\Delta_f H^{\circ}$[a]	S°[b]	$\Delta_f G^{\circ}$[c]	V[d]	V_m[e]	C_p°[f]	C_p/S[g]	β[h] [12,13]
		kJ mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}	cm^3 mol^{-1}	nm^3	J K^{-1} mol^{-1}		$10^3 \times$ GPa^{-1}
pyrope, 10	$Mg_3Al_2Si_3O_{12}$	−6290.8	266	−6370.2	113.3	0.1881	325.5	1.22	5.9
14		−6284.3	266			0.1881	325.3	1.22	
11		−6284.2	266	−5933.6	113.2	0.1879	325.0	1.22	
majorite, 15	$Mg_3(MgSi)Si_3O_{12}$		266		113.5	0.1885	318	1.19	
almandine, 10	$Fe_3Al_2Si_3O_{12}$	−6261.3	343	−5363.4	115.3	0.1914	332.5	0.97	5.6
16		−5269.3	337			0.1914	337.4	1.00	
11		−5263.7	340	−4939.8	115.1	0.1911	342.6	1.01	
spessartine, 10	$Mn_3Al_2Si_3O_{12}$	−5686.9	332	−5785.8	118.1	0.1962	331.0	1.00	5.5
17		−5693.6	335	−5364.3		0.1962	342.1	1.02	
11		−5646.3	367	−5326.3	117.9	0.1958	340.2	0.93	
grossular	$Ca_3Al_2Si_3O_{12}$	−6632.8	260	−6710.3	125.1	0.2078	327.1	1.26	6.0
18		−6627.0	259			0.2078	331.6	1.28	
11		−6644.1	255	−6280.9	125.4	0.2082	329.0	1.29	
hydrogrossular, 19 (katoite)	$Ca_3Al_2H_{12}O_{12}$	−5551.5	422	−5021.2		0.2464	462.4	1.10	17.9
uvarovite, 10	$Ca_3Cr_2Si_3O_{12}$	−6034.6	287	−6120.1	130.0	0.2158	331.1	1.15	7.0
20			321			0.2158	356.1	1.11	
andradite, 10	$Ca_3Fe_2Si_3O_{12}$	−5758.9	316	−5853.2	132.0	0.2192	339.5	1.07	6.8
11		−5768.1	318	−5424.3	132.0	0.2193	351.7	1.11	
knorringite, 10	$Mg_3Cr_2Si_3O_{12}$	−5576.1	305	−5667.1	117.6	0.1953	331.1	1.08	6.5
calderite, 10	$Mn_3Fe_2Si_3O_{12}$	−4719.8	415	−4843.4	124.6	0.2069	346.8	0.84	6.5
skiagite, 10	$Fe_3Fe_2Si_3O_{12}$	−4276.2	370	−4386.5	121.6	0.2018	325.8	0.88	6.6
khoharite, 10	$Mg_3Fe_2Si_3O_{12}$	−5299.5	344	−5402.2	119.4	0.1983	340.9	0.99	6.1
MnCr garnet, 10	$Mn_3Cr_2Si_3O_{12}$	−5007.1	368	−5116.7	122.7	0.2037	342.9	0.93	
FeCr garnet, 10	$Fe_3Cr_2Si_3O_{12}$	−4555.3	358	−4662.0	119.7	0.1988	334.4	0.93	
goldmanite	$Ca_3V_2Si_3O_{12}$					0.2203[12]			7.2
blythite	$Mn_3Mn_2Si_3O_{12}$					0.2105[12]			6.7

[a] Formation enthalpy. [b] Absolute entropy. [c] Formation Gibbs energy. [d] Molar formula volume. [e] Formula volume. [f] Isobaric heat capacity. [g] Ratio of heat capacity to entropy. [h] Compressibility.

RESULTS AND DISCUSSION

Thermodynamic Properties. Table 1 lists recent data for the silicate garnets, collected from the various referenced sources. A noticeable feature of the Table is the departures of the ratio C_p/S from unity, whereas ambient heat capacities and entropies of ionic solids are generally closely equal.[9] This behavior is further considered in connection with Figure 3, below.

Thermodynamic Correlations. Figure 1 demonstrates that there is a general tendency of the heat capacities of the garnets to increase with formula volume. This agrees with our earlier observation[21] that heat capacity is roughly proportional to formula volume, noting that the expanded scales of the current plot emphasize the deviations from strict proportionality. The garnets with the largest cations (Ca^{2+}) are seen to have the smallest heat capacities relative to their volumes.

In Figure 2, ambient entropies are plotted versus formula volume, and again, the Ca^{2+}-based garnets have the smallest entropies relative to their volumes. Conversely, silicate garnets with Fe^{2+} in the *A* positions have entropies that are relatively large due to an electronic heat-capacity contribution (C_{el}, Schottky anomaly) superimposed on a larger magnetic heat-capacity effect (C_{mag}) at ∼17 K.[16] The entropies of the Mn^{2+} silicate garnets are consistent with their neighbors following recent calculations by Geiger and colleagues,[17] which have reduced the magnetic contribution by about 15% relative to the maximum possible magnetic entropy of $3R \ln 6$.

It becomes easier to understand the complex relations between these thermodynamic properties in a plot of heat capacity versus entropy[9] (Figure 3), which shows that the heat capacities of the garnets are roughly constant among the varying compositions, while the entropies cover a considerable range. The heat capacities may be estimated using an extended Neumann−Kopp rule[24] by summing the contribution from each of the five cations of 25 J K^{-1} mol^{-1} together with a

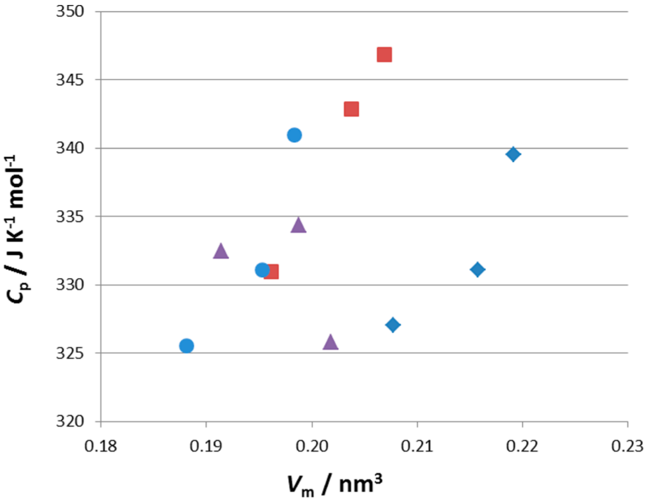

Figure 1. Ambient heat capacity vs formula volume. Cations in *A* position: blue ◆ = Ca^{2+} (volume[22] 0.0201 nm^3); red ■ = Mn^{2+} (volume 0.0087 nm^3); purple ▲ = Fe^{2+} (volume[22] 0.0067 nm^3); blue ● = Mg^{2+} (volume[22] 0.0049 nm^3). The ion volume for Mn^{2+} has been estimated by comparison with an earlier volume data set.[23] The anomalous datum for the hydroxy-garnet katoite (V_m = 0.2464 nm^3, S = 421.7 J K^{-1} mol^{-1}) was omitted from the upper right-hand corner.

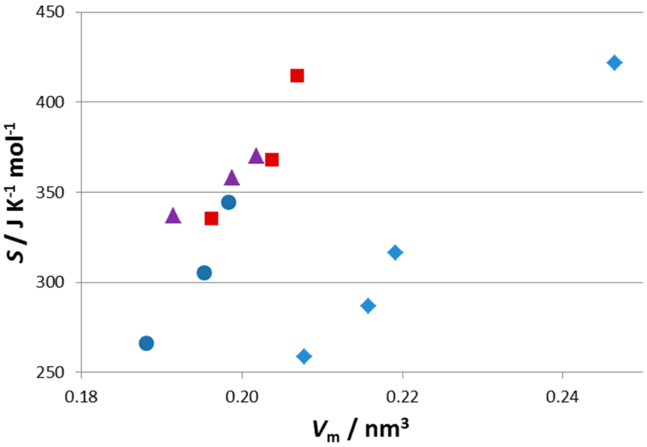

Figure 2. Ambient absolute entropy vs formula volume. The isolated blue ◆ in the upper right-hand corner corresponds to the hydroxy-garnet katoite.[19] Cations in *A* position: blue ◆ = Ca^{2+} (volume[22] 0.0201 nm^3); red ■ = Mn^{2+} (volume 0.0087 nm^3); purple ▲ = Fe^{2+} (volume[22] 0.0067 nm^3); blue ● = Mg^{2+} (volume[22] 0.0049 nm^3). The ion volume for Mn^{2+} was estimated by comparison with an earlier volume data set.[23]

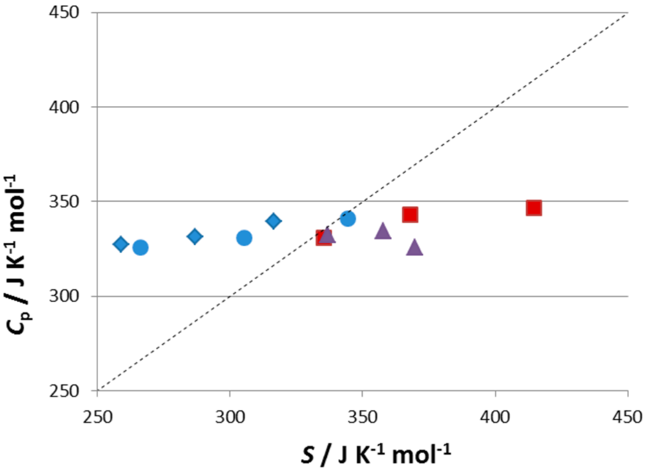

Figure 3. Ambient heat capacity vs ambient absolute entropy. Cations in *A* position: blue ◆ = Ca^{2+}; red ■ = Mn^{2+}; purple ▲ = Fe^{2+}; blue ● = Mg^{2+}. The diagonal line represents equality of heat capacity and entropy values. The anomalous datum for the hydroxy-garnet katoite (C_p = 462.4 J K^{-1} mol^{-1}, S = 421.7 J K^{-1} mol^{-1}) in the upper right-hand corner was omitted.

contribution from each of the three SiO_4^{4-} anions of 13.8 × 5 J K^{-1} mol^{-1}, making an estimated total of 332 J K^{-1} mol^{-1}. The average of the entries in Table 1 (omitting the hydroxy-garnet katoite) is 335 J K^{-1} mol^{-1} (a difference of less than 1%). This constancy of C_p with increasing values of S corresponds to decreasing values of the Debye temperatures as the entropy rises, from roughly Θ_D = 300 to 230 K.[9] The implication of this graphic, that Debye temperatures for the silicate garnets are consistently near or below ambient temperatures and roughly constant, is that their vibrational modes are fully excited at ambient temperatures. This results primarily from the rigidity of the silicate tetrahedra, which in turn relates to the hardness of the silicate garnets.

The plot in Figure 4 shows that the compressibilities of the silicate garnets are rather similar, again consistent with the rather rigid structures of the silicate anions, which tend to rotate slightly with altering pressure[2,25] rather than compress.

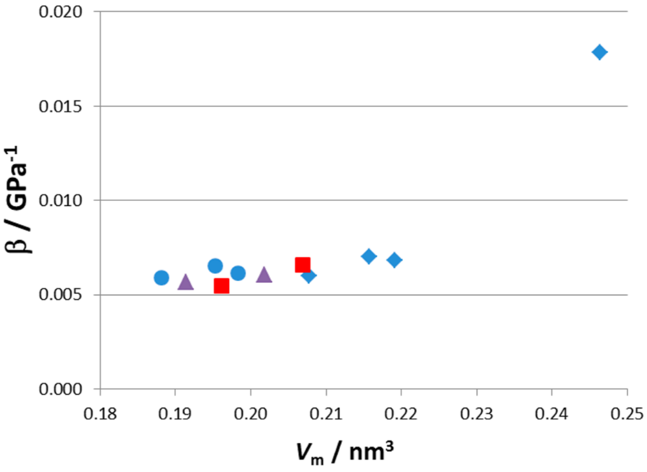

Figure 4. Isothermal compressibility β/GPa^{-1} of silicate garnets plotted against formula volume. The isolated blue ◆ corresponds to the hydroxy-garnet katoite.[19] Cations in *A* position: blue ◆ = Ca^{2+} (volume[22] 0.0201 nm^3); red ■ = Mn^{2+} (volume 0.0087 nm^3); purple ▲ = Fe^{2+} (volume[22] 0.0067 nm^3); blue ● = Mg^{2+} (volume[22] 0.0049 nm^3).

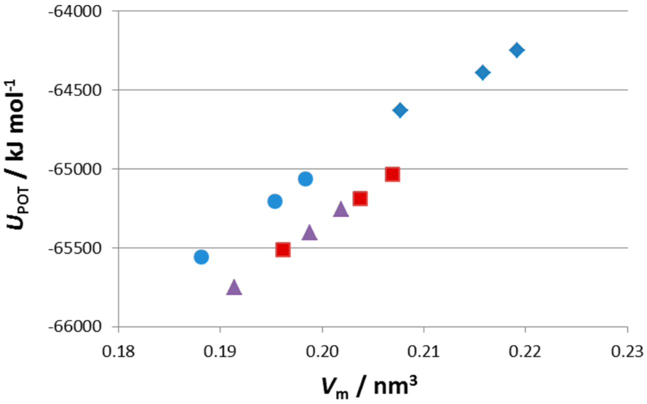

Figure 5. Plot of lattice energy U_{POT}(BHFC) against formula volume. Cations in *A* position: blue ◆ = Ca^{2+} (volume[22] 0.0201 nm^3); red ■ = Mn^{2+} (volume 0.0087 nm^3); purple ▲ = Fe^{2+} (volume[22] 0.0067 nm^3); blue ● = Mg^{2+} (volume[22] 0.0049 nm^3).

The hydroxy-garnet, katoite, is considerably more compressible, consistent with its expanded volume.

Figure 5 is a plot of lattice energy U_{POT} (calculated in a Born–Haber–Fajans thermochemical cycle, BHFC, using published formation enthalpies) against formula volume. It is striking that the Mn- and Fe-containing garnets are more stable (have more negative lattice energies) than Ca- and Mg-containing silicate garnets. The Mg^{2+} ions are rather too small for their dodecahedral sites, which may reduce the coulomb interaction, whereas the Ca^{2+} ions may slightly destabilize the crystal structure by their larger size. The U_{POT}(BHFC) data are listed in Table 2 together with values of U_{POT}(limiting equation) obtained from a generalization[26] of the Kapustinskii equation. The tabulated values are within 1% of one another (2% for pyrope).

Additive Single-Ion Enthalpies. Using previously established single-ion enthalpies[27] together with a value for the grouped ion $(SiO_4^{4-})_3 = Si_3O_{12}^{12-}$ derived from the established formation enthalpies for the silicate garnets, ion sums may be used to obtain formation enthalpies of silicate garnets to good accuracy, as may be seen in Table 2. It is interesting to note that

Table 2. Mineral Silicate Garnet Lattice Energies U_{POT} and Formation Enthalpies Δ_fH Both from Experiment[10] and as a Sum of Single-Ion Values, as Summed from the Values Listed in the Final Two Columns.[27] The Value for the Ion $Si_3O_{12}^{12-}$ is the Mean Value

garnet mineral	chemical formula	U_{POT} (BHFC)	U_{POT} (limit. eqn)[26]	Δ_fH/kJ mol^{-1}	% diff.		Δ_fH single-ion values[27]	
		kJ mol^{-1}		expt.	ion sum		kJ mol^{-1}	
katoite	$Ca_3Al_2H_{12}O_{12}$		−61 158	−5551.5	−5067.7	−8.7	$Si_3O_{12}^{12-}$	−4241
pyrope	$Mg_3Al_2Si_3O_{12}$	−78 485	−66 921	−6284.3	−6287.7	0.1		
almandine	$Fe_3Al_2Si_3O_{12}$	−78 027	−66 531	−5269.3	−5266.2	−0.1	OH^-	−228.6
spessartine	$Mn_3Al_2Si_3O_{12}$	−77 391	−65 988	−5693.6	−5649.3	−0.8		
grossular	$Ca_3Al_2Si_3O_{12}$	−75 926	−64 739	−6627.0	−6565.5	−0.9	Mg^{2+}	−374.1
uvarovite	$Ca_3Cr_2Si_3O_{12}$	−71 726	−63 925	−6034.6	−5812.1	−3.7	Ca^{2+}	−466.7
andradite	$Ca_3Fe_2Si_3O_{12}$	−74 971	−63 595	−5758.9	−5766.7	0.1	Sr^{2+}	−558.7
knorringite	$Mg_3Cr_2Si_3O_{12}$	−74 585	−66 085	−5576.1	−5534.3	−0.7	Ba^{2+}	−570
calderite	$Mn_3Fe_2Si_3O_{12}$	−77 505	−64 829	−4719.8	−4850.5	2.8	Mn^{2+}	−161.3
skiagite	$Fe_3Fe_2Si_3O_{12}$	−76 032	−65 364	−4276.2	−4467.4	4.5	Fe^{2+}	−33.6
khoharite	$Mg_3Fe_2Si_3O_{12}$	−77 108	−65 747	−5299.5	−5488.9	3.6		
goldmanite	$Ca_3V_2Si_3O_{12}$		−68 380				Al^{3+}	−462.2
blythite	$Mn_3Mn_2Si_3O_{12}$		−69 433				Cr^{3+}	−85.5
Mn Cr garnet	$Mn_3Cr_2Si_3O_{12}$	−76 423	−65 163	−5007.1	−4895.9	−2.2	Fe^{3+}	−62.8
Fe Cr garnet	$Fe_3Cr_2Si_3O_{12}$	−77 053	−65 700	−4555.3	−4512.8	−0.9		

the value of −4241 kJ mol^{-1} for the 15-atom $Si_3O_{12}^{12-}$ agrees well with the value of −4104 kJ mol^{-1} earlier established[27] for the 15-atom species $Si_4O_{11}^{6-}$.

■ CONCLUSION

It is observed that there is a rough correlation for the silicate garnets between their formula unit volumes and their standard thermodynamic properties, namely, heat capacity, entropy, and lattice energy, with these properties most discrepant for the Ca^{2+}-containing materials, which have the largest cations. Surprisingly, the Mg^{2+}-containing materials (with the smallest cations) have less negative lattice energies together with the larger Ca^{2+}-containing materials. It is suggested that this arises from their smaller and larger sizes, respectively, relative to the available volume in the cation *A* site. In general, the heat capacities C_p and the compressibilities β are independent of formula unit volume, consistent with full excitation of the vibrational modes at ambient temperatures.

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Notes

The authors declare no competing financial interest.

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