INDEX-OF-REFRACTION AND UNIT-CELL CONSTRAINTS ON CATION VALENCE AND PATTERN OF ORDER IN GARNET-GROUP MINERALS

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ABSTRACT

Uncertainty in the structural formula of garnet can result from incomplete or inaccurate analysis, lack of valence determination, and an uncertain distribution of elements among crystallographic sites. However, each specific composition and structural state of garnet have characteristic physical parameters that can be used to constrain the valence and pattern of order of ions. Each element in a particular site has a characteristic ionic contribution to the net index of refraction (n) and to the unit-cell dimension (a). The refractivity and size of an ion depend on its valence and its location in the crystal structure, and this dependence affects the values of n and a (nm). Each mechanism of substitution, such as Mg–Fe, then produces a vector (Δn–Δa) per atom through compositional space. After compositional analysis, the index of refraction and unit-cell dimension of garnet are calculated from a proposed structural formula. The structural formula is then varied to minimize the difference between calculated and measured physical parameters, thus constraining the valence and site occupancy of ions in garnet. This approach gives the ratio $^{2}\text{Fe}^{2+}$ / $^{3}\text{Fe}^{3+}$ and a quantitative measure of the light-element concentrations.

Keywords: garnet, index of refraction, unit-cell dimensions, optical mineralogy, valence determination, mineral composition.

INTRODUCTION

A revised model of light (Teertstra 2003) is generating new ideas concerning the relations between the index of refraction, composition and the crystal structure of minerals. Until recently, mineralogists have lacked an atomic theory of refraction, but a revised Gladstone–Dale relation applicable to ions in minerals (Teertstra 2005) provides the basis for further developments. In this model, each ion has a characteristic contribution to the net index of refraction, the unit-cell volume and the density. The model is extended in this paper to identify the valence of ions occupying particular sites in the crystal structure. As ions of particular valence occupy specific structural sites in garnet, a specific change of index of refraction (Δn) and unit-cell parameter (Δa) is attributed to each mechanism of substitution.

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BACKGROUND INFORMATION

An outstanding problem in the characterization of minerals (including garnet) is the difficulty of distinguishing between an inaccurate composition of an analytical standard and error in the analytical method (e.g., electron microprobe ZAF or other matrix corrections). An accurate analytical result is indicated by ion weight totals of 100, an electroneutral structure, and maximum site-occupancy in a calculated formula. The accuracy of analytical data is improved by cross-analysis of standards, especially for standards of similar matrix.

The accuracy of a composition is further improved by analyzing a series of garnet samples. If each electroneutral formula \(X_iY_jZ_kO_{l2}\) is normalized to 12 atoms of oxygen per formula unit, and the occupancy of the \(Z\) site is idealized by a calculation such as \(\text{Fe}^2+ = 3 - \text{Si}\), then the net error of analysis with respect to \(\Sigma X\) and \(\Sigma Y\). If the net errors of analysis are negligible, then the net error of analysis shifts to the \(\Sigma Z\). In an accurate set of analytical results, a plot of each element versus \(\Sigma X\) is devoid of correlations. For example, varying concentrations of Ca do not relate with an increase in \(\Sigma X\). If increasing Ca relates to increasing \(\Sigma X\), then the standard for Ca is high, and the weight fraction of Ca can be systematically reduced to correct the analytical results.

Nevertheless, the problem remains that a wet-chemical or electron-microprobe analysis accounts for only half the formula weight of garnet, as the analysis does not include the light elements from H to O. These methods of analysis are insensitive to structural state (e.g., crystal and glass are indistinguishable), and a calculated formula based on the stoichiometry of the crystal structure can remain ambiguous. However, the light elements from H to O are major contributors to the observed physical properties. Refracting (visible) and reflecting (X-ray) light encounters more atoms of oxygen than cations. These observations indicate the need for an additional structural constraint: that both the reference standards and the analyzed material must have the expected physical properties. Error is indicated if the measured values of \(n\) and \(a\) (nm) do not agree with the values calculated from the proposed structural formula. If close relations are documented between the composition of garnet and the \(n\) and \(a\) values expected for each mechanism of substitution, then these relations may be used to constrain the valence and site occupancy of the cations in garnet.

PHYSICAL PROPERTIES OF GARNET-GROUP MINERALS

The structural formula of garnet is \(X_iY_jZ_kO_{l2}\). The most common species are structurally simple, with divalent cations Mg, Fe, Mn and Ca in a distorted cubic \(X\) site, trivalent cations Al, Fe, Cr and V in an octahedral \(Y\) site, and tetravalent Si in a tetrahedral \(Z\) site. The \(X\), \(Y\) and \(Z\) sites lie on elements of symmetry in the structure, but oxygen occurs at a single general position. Each oxygen ion is coordinated by two \(X\)-, one \(Y\)- and one \(Z\)-cation, and of these, the three-field-strength cations are closest to O (Novak & Gibbs 1971). Data on the crystal structure and physical properties of samples analyzed in various studies are compared as follows: if a single-crystal structural analysis defines the state of order and the cell dimension \(a\), then another sample of identical composition and cell dimension has the same state of order.

Linear relations of \(\Delta n\) and \(\Delta a\) are established along the major exchange-mechanisms between end-member species (e.g., Moench & Meyrowitz 1964, Skinner 1956, Strens 1965, Deer et al. 1992, Henmi et al. 1995). Each common garnet \(X_iY_jZ_kO_{l2}\), with \(X = \text{Mg}, \text{Fe}, \text{Mn}\) or Ca, is linked to rarer species by the exchange vectors \(\text{Al}_i\text{Fe}^{3+}, \text{Al}_j\text{V}\) and \(\text{Al}_k\text{Cr}\) (Fig. 1). Over compositional space, each species has a characteristic \((n, a)\) coordinate (Table 1) resulting from the operation of specific exchange-vectors (Fig. 1). Points along the vector from pyrope to almandine are described by the linear equations \(n = n_{\text{pyrope}} + \text{Fe}^{2+}(\Delta n/\text{Fe}^{2+})\) and \(a = a_{\text{pyrope}} + \text{Fe}^{2+}(\Delta a/\text{Fe}^{2+})\), with \(\text{Fe}^{2+}\) read from the formula in atoms per formula unit (apfu). With established values of \(\Delta n\) and \(\Delta a\) for each mechanism of substitution (Table 2), any point in the compositional space of garnet can be reached by vector addition. This gives a new method to calculate \(n\) and \(a\) (nm) from the formula of garnet.

Note that certain vectors (e.g., \(\text{Mg}_i\text{Fe}\)) are most accurately resolved by \(\Delta n\), whereas other vectors (e.g., \(\text{Mg}_i\text{Ca}\)) are most accurately resolved by \(\Delta a\) (Fig. 1, Table 2). For example, the \(\text{Mg}_i\text{Fe}\) vector from end-member pyrope [with \(n = 1.714(1)\) and \(a = 1.1459(2)\) nm] to end-member almandine [with \(n = 1.830(1)\) and \(a = 1.1526(2)\) nm] has \(\Delta n = 0.03867\) and \(\Delta a = 0.002233\) nm per atom of \(\text{Fe}^{2+}\). With \(n\) determined using immersion liquids calibrated in steps of 0.001, the optical resolution of the \(\text{Mg}_i\text{Fe}\) vector is 0.026 \(\Delta a\). Conversely stated, an increase of 0.026 Fe

<table>
<thead>
<tr>
<th>Species</th>
<th>Symbol</th>
<th>Formula</th>
<th>(n)</th>
<th>(a) (nm)</th>
<th>(\Delta a)</th>
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<td>1.834</td>
<td>1.2070</td>
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<td>1.1604</td>
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apfu will increase the index of refraction \( n \) by 0.001. With \( a \) determined to 0.0002 nm, the XRD resolution is 0.090 Fe apfu. Conversely stated, an increase of 0.090 Fe apfu will increase \( a \) by 0.0002 nm. For comparison, if analysis of the garnet for Fe by electron microprobe gives results accurate to 1%, then the EMPA resolution of Fe in almandine is 0.030 apfu. Conversely stated, an EMPA analysis of Fe with an error greater than 0.026 apfu is noticeable by optical measurement of \( n \), whereas an error greater than 0.090 apfu is noticeable by refinement of \( a \) from the XRD data.

Although investigators in mineralogy may point out the difficulty of measuring index of refraction of strongly refracting minerals, problems of EMPA matrix corrections across broad ranges of composition, or the technical limits of X-ray diffraction, it is interesting to note that the elemental concentrations per formula unit are constrained to similar levels of accuracy by three independent methods of analysis.

Solid solution in natural garnet is complex, and end-member compositions are rare. Nevertheless, it is common to find a natural series in which a specific mechanism of substitution was dominant during crystallization. For example, (Ca,Mg)-poor almandine–spessartine is common in granitic pegmatites, allowing definition of a linear \( \Delta n \) and \( \Delta a \) per Fe,1,Mn apfu that extrapolates to the \((n, a)\) of the end members. The resulting determinative curves are accurate only for samples in the pure almandine–spessartine series. But considering two samples of (Fe,Mn,Ca) garnet at the
same Ca apfu, the $\Delta n$ and $\Delta a$ along the Fe$_{6.1}$Mn vector remains defined, despite the relocation from Ca = 0 across compositional space. After accounting for the effects of Fe$_{3.1}$Mn, reference to an end-member garnet now defines the $(\Delta n - \Delta a)$ residual vector (owing to Fe$_{6.1}$Ca pfu). Therefore, the $(n, a)$ metrics of end-members of complex solid-solutions can be determined by vector analysis, without the need for synthesis of end-members. By translation through compositional space, the well-characterized vectors are applied to any species (Fig. 2).

That the $(n, a)$ vectors translate across compositional space is also illustrated in Figure 1, in which four examples of Al$_{1.1}$Cr substitution have nearly identical values of $n$ and $a$ across compositional space. After accounting for the effects of Fe$_{3.1}$Mn, reference to an end-member garnet now defines the $(\Delta n - \Delta a)$ residual vector (owing to Fe$_{6.1}$Ca pfu). Therefore, the $(n, a)$ metrics of end-members of complex solid-solutions can be determined by vector analysis, without the need for synthesis of end-members. By translation through compositional space, the well-characterized vectors are applied to any species (Fig. 2).

Using the formula and $(n, a)$ metrics of end-member pyrope as the origin, the $(\Delta n, \Delta a)$ of a substitution mechanism such as Mg$_{1.1}$Fe becomes the change in physical metrics $(\Delta n^{3/2}Ca, \Delta a^{3/2}Ca)$ per X-site atom in the formula unit.

Based on composition alone, the structural formula of a mineral commonly remains ambiguous; garnet with VIAl and possible IVAl provides an example (Deer et al. 1992). These authors relied on site preferences and maximum site-occupancy to distribute cations among various sites in the structure and looked to a sensible maximum site-occupancy to distribute cations among various sites in the structure and looked to a sensible formula to substantiate the choices. The result is a reasonable range of valence states and possible states of cation order. Structural complexity occurs with substitution of Ti in (Fe,Ca)-rich species, as there is considerable disorder and uncertainty of valence, and deviation from cubic symmetry can occur. It is possible for Al or Fe$^{3+}$ to enter the Z site, and for Si to enter the Y site.

For Ti-rich garnet, there are few index-of-refraction measurements on compositionally and structurally well-characterized samples, and the mechanisms of substitution are poorly defined. There is considerable controversy concerning the valence and pattern of order of ions in (Fe,Ti)-rich garnet. However, the approximate $(n, a)$ coordinates of schorlomite, kimzeyite (Milton et al. 1961) and morimotoite (Henmi et al. 1995) indicate differences in the composition and mechanism(s) of substitution in these minerals. Once the values of $\Delta n$ and $\Delta a$ are determined for each mechanism of substitution, the valence and pattern of order of ions can be defined.

**ESTIMATING COMPOSITION FROM $(n, a)$ COORDINATES**

With measurement of $n$ and $a$, a likely species is named (Fig. 1). The compositions of samples along the limits of $(n, a)$ values are unambiguous (e.g., along the Prp–Alm line), as are synthetic ternary solid-solutions (e.g., in the Prp–Alm–Grs plane), but natural compositional space is more difficult to assess. Faced with a complex solid-solution, it has been considered inappropriate to go further and claim a quantitative measurement of composition. This is because the $(n, a)$ metrics of a single sample of a common garnet such as (Mg,Fe,Mn,Ca)$_3$Al$_2$Si$_3$O$_{12}$ might also be explained by substitution of Fe$^{3+}$, V for Cr for Al. However, such Y-site substitution would immediately restrict the possible proportions of X-site cations that are consistent with the values of $n$ and $a$, and furthermore the resulting composition may be identified as unlikely for equilibrium to occur with other minerals in the rock.

Such ambiguity of compositional determination from $(n, a)$ values applies mainly to individual samples. In a geological context, compositional trends among related samples are commonly due to a single exchange-vector that tightly constrains the compositional possibilities. Now the exact $(n, a)$ metrics of samples related by a specific vector such as Mg$_{1.1}$Fe cannot be explained by more unusual substitutions. With the action of an additional exchange-vector, the compositional definition can be exact.

Using the formula of pyrope as a reference point to consider possible substitutions, the index of refraction of a sample at a general point G in Figure 1 is calculated from a proposed structural formula by $n_G = n_{pyrope} + Ca(\Delta n^{3/2}Ca) + Mn(\Delta n^{3/2}Mn) + Fe^{3+}(\Delta n^{3/2}Fe^{3+}) + Y(\Delta n^{3/2}Y) + Fe^{2+}(\Delta n^{3/2}Fe^{2+}) + V(\Delta n^{3/2}V) + Cr(\Delta n^{3/2}Cr) + H(\Delta n^{3/2}H) + Na(\Delta n^{3/2}Na) + Al(\Delta n^{3/2}Al)$. The term $\Delta n^{3/2}Y$ refers to the combined change of $n$ of the yttrium–aluminum garnet (YAG) substitution $(\Delta Ca^{2+}Si)^{1/2}(\Delta Y^{2+}Al)^{1/2}$. Some values of $\Delta n$ are unknown, such as the proposed $\Delta n^{3/2}Al$, the $\Delta n^{1/2}Si$ of majorite, and the $\Delta n^{3/2}Mn^{2+}$ of henritermierite (Gaudefroy et al. 1969). The calculated cell-edge of G is $a_G = a_{pyrope} + Ca(\Delta a^{3/2}Ca) + Mn(\Delta a^{3/2}Mn)$.
The compositional analysis of garnet is invariably incomplete. However, the analysis can become complete with determination of the \((n, a)\) coordinate. For example, the calculated index of refraction of ferroan “hydrospessartine” can be expressed as the sum of the ionic contributions, \(n = n(\text{Mn}^{2+}) + n(\text{Fe}^{2+}) + n(\text{Al}^{3+}) + n(\text{Si}^{4+}) + n(\text{H}^{+}) + n(\text{O}^{2-})\) (Teertstra 2003, 2005). The problem is that different compositions can share the same \((n, a)\) coordinate. Nevertheless, the number of possible compositions is limited. Consider a sample at point G in Figure 1, with \(n = 1.760\) and \(a = 1.1640\) nm. Point G is outside the Prp–Alm–Sps triangle, and must contain Mg and Ca. The \((n, a)\) coordinates of G may be reached by a finite number of additive vectors. The two simplest compositions of G, determined by iterating the proportions of cations at the X site, are Mn-free \((\text{Mg}_{0.60}\text{Ca}_{0.23}\text{Fe}_{0.17}\text{Al}_{0.06})_2\text{Si}_{2.80}\text{O}_{12}\) and Fe-free \((\text{Mg}_{0.23}\text{Ca}_{0.32}\text{Al}_{0.45})_2\text{Si}_{2.80}\text{O}_{12}\). The Fe-free composition is an unlikely geochemical product. Specific concentrations of Mg and Ca are required if the \((n, a)\) coordinates of G are maintained by (Fe,Mn) solid solution.

The coordinates of G might also be reached by Y-site substitutions, with \(\text{Al}_{1.17}\text{Fe}^{3+}\), to give \(\text{Mg}_{2.05}\text{Ca}_{0.98}\text{Al}_{1.17}\text{Fe}^{3+}_{0.51}\text{Si}_{2.80}\text{O}_{12}\), with \(\text{Al}_{1.17}\text{V}\) to give \(\text{Mg}_{2.31}\text{Ca}_{0.69}\text{Al}_{1.17}\text{V}_{0.83}\text{Si}_{2.80}\text{O}_{12}\) or with \(\text{Al}_{1.17}\text{Cr}\) to give \(\text{Mg}_{1.95}\text{Ca}_{0.15}\text{Al}_{1.17}\text{Cr}_{0.83}\text{Si}_{2.80}\text{O}_{12}\). For each concentration of \(\text{Fe}^{3+}\), \(\text{V}\) or \(\text{Cr}\), note that specific proportions of cations are required at the X site to maintain the \((n, a)\) coordinates. Clearly, the composition is closely constrained if a set of samples exhibits a trend of \((n, a)\) coordinates. Any trend of \((n, a)\) coordinates is tightly constrained by a small number of exchange vectors that are expected to be realistic for garnet in rocks.

Any composition of garnet that is estimated from \((n, a)\) coordinates is also tightly constrained by a partial measurement of composition (which could be estimated from partition coefficients and a knowledge of the bulk composition of the rock). For an economic program of geological mapping or exploration, grains may be sorted by index of refraction, with a range of samples selected for X-ray diffraction, and with a fewer number of grains selected for partial to complete compositional analysis.

**Fe valence and pattern of order**

A significant problem is raised in estimating Fe valence and order. Suppose the electron-microprobe data for a garnet give the ion weight-fractions 0.0119 Mg, 0.1346 Ca, 0.2230 Fe (total), 0.0647 Al, 0.1726 Si and 0.3796 O (by stoichiometry, assuming divalent Fe), sum 0.9864. The calculated formula, \((\text{Fe}_{2.03}\text{Ca}_{1.70}\text{Mg}_{0.25})_{2.39}\text{Al}_{1.23}\text{Si}_{3.11}\text{O}_{12}\), has \(\Sigma X > 3\), \(\Sigma Y < 2\) and \(\Sigma Z > 3\). The \(X\)-cation proportions, normalized to 3, give \(a_{\text{calc}} = 1.166\) nm and \(a_{\text{calc}} = 1.78\). However, refinement of the X-ray-diffraction data gives \(a = 1.1784\) nm, and measurement of the index of refraction gives \(n = 1.833\). The measured \((n, a)\) values are consistent only with replacement of \(Y\)-site Al by a strongly refracting ion (Fig. 2). The formula is improved by assuming that a portion of the weight fraction of iron is trivalent, then recalculating O. This step increases the weight fraction of O. Iteration splits the weight fraction of total Fe into 0.1281 \(\text{Fe}^{2+}\) and 0.0949 \(\text{Fe}^{3+}\) and gives the formula \((\text{Ca}_{1.64}\text{Fe}_{0.12}\text{Mg}_{0.24})_{2.33}\text{Al}_{1.17}\text{Fe}^{3+}_{0.85}\text{Si}_{2.80}\text{O}_{12}\), with a match of calculated and measured \((n, a)\) values.

**Optical analysis of a garnet for H content**

Incorporation of H in garnet according to the \(\text{Si}_2\text{H}_4\) mechanism to give katoite strongly decreases \(n\) and expands the unit cell. Suppose EMPA analysis of spessartine gives the ion weight-fractions 0.2912 Mn, 0.0455 Fe, 0.1100 Al, 0.1603 Si and 0.3783 O (by stoichiometry, assuming divalent Fe), sum 0.9853. The formula \((\text{Mn}_{0.60}\text{Fe}_{0.41}\text{Al}_{0.27}\text{Si}_{2.86}\text{O}_{12}\) indicates \(\Sigma X > 3\), \(\Sigma Y > 2\) and \(\Sigma Z < 3\). Is there \(Y\)-site \(\text{VIFe}^{3+}\) and \(Z\)-site \(\text{Al}^3+\)? That would appear to correct the formula, but is inconsistent with the physical measurements of \(n = 1.797\) and \(a = 1.1682\) nm, which indicate the action of \(\text{Mn}_2\text{Fe}, \text{Mn}_2\text{Ca}, \text{Si}_1\text{H}_4\) (or all three). With Mn and Fe constrained by analysis, and Ca not detected, the low \(n\) and high \(a\) can only be explained by incorporation of H according to the substitution \(\text{Si}_2\text{H}_4\). Iterating the weight fraction H and recalculating the proportion of O give consistency with the measured \((n, a)\) metrics for the structural formula \((\text{Mn}_{2.05}\text{Fe}_{0.10})\text{Al}_{1.20}\text{Si}_{2.80}\text{O}_{12}\text{H}_{0.30}\) (note that H occupies a site near Si).

Although the values of \(\Delta n\) and \(\Delta a\) of each mechanism of substitution are specific to the garnet structure-type, the methods of analysis proposed here are applicable to any mineral. An example is provided by Palmer & Gunter (2000), in which the index of refraction of heulandite-group minerals is used to determine the H content.

**Conclusions**

The valence and pattern of order of ions in minerals are determined by partial compositional analysis, followed by an iteration to a formula that is constrained by maximum site-occupancy, electroneutrality, and a match of calculated and measured \((n, a)\) metrics. If the composition and physical parameters of an analytical standard are known, then the composition of the analyzed minerals must be within the range expected by measurement of \(n, a,\) or both. Confidence in the analytical standard is increased by analysis of numerous samples with the stoichiometry expected from a model.
of the crystal structure; if this is not the case, systematic error may be identified, and the composition of the standard can be corrected.

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