



# Spectral reflectance (0.35–2.5 μm) properties of garnets: Implications for remote sensing detection and characterization



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## ABSTRACT

The utility of spectral reflectance for identification of the main end-member garnets: almandine ( $\text{Fe}^{2+}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), andradite ( $\text{Ca}_3\text{Fe}^{3+}_2\text{Si}_3\text{O}_{12}$ ), grossular ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), pyrope ( $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), spessartine ( $\text{Mn}^{2+}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), and uvarovite ( $\text{Ca}_3\text{Cr}^{3+}_2\text{Si}_3\text{O}_{12}$ ) was studied using a suite of 60 garnet samples. Compositional and structural data for the samples, along with previous studies, were used to elucidate the mechanisms that control their spectral reflectance properties. Various cation substitutions result in different spectral properties that can be determined to the presence of various optically-active cations and help differentiate between garnet types. It was found that different wavelength regions are sensitive to different compositional and structural properties of garnets. Crystal-field absorptions involving  $\text{Fe}^{2+}$  and/or  $\text{Fe}^{3+}$  are responsible for the majority of spectral features in the garnet minerals examined here. There can also be spectral features associated with other cations and mechanisms, such as  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ – $\text{Ti}^{4+}$  intervalence charge transfers. The visible wavelength region is useful for identifying the presence of various cations, in particular, Fe (and its oxidation state),  $\text{Ti}^{4+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Cr}^{3+}$ . In the case of andradite, spessartine and uvarovite, the visible region absorption bands are characteristic of these garnets in the sense that they are associated with the major cation that distinguishes each:  $^{6}\text{Fe}^{3+}$  for andradite,  $^{8}\text{Mn}^{2+}$  for spessartine, and  $^{6}\text{Cr}^{3+}$  for uvarovite. For grossular, the presence of small amounts of  $\text{Fe}^{3+}$  leads to absorption bands near 0.370 and 0.435 μm. These bands are also seen in pyrope–almandine spectra, which also commonly have additional absorption bands, due to the presence of  $\text{Fe}^{2+}$ . The common presence of  $\text{Fe}^{2+}$  in the dodecahedral site of natural garnets gives rise to three  $\text{Fe}^{2+}$  spin-allowed absorption bands in the 1.3, 1.7, and 2.3 μm regions, providing a strong spectral fingerprint for all  $\text{Fe}^{2+}$ -bearing garnets studied here. Garnets containing  $\text{Mn}^{2+}$  have additional visible (~0.41 μm) spectral features due to  $^{8}\text{Mn}^{2+}$ . Garnets containing  $\text{Cr}^{3+}$ , exhibits two strong absorption bands near ~0.7 μm due to spin-forbidden  $^{6}\text{Cr}^{3+}$  transitions, as well as  $^{6}\text{Cr}^{3+}$  spin-allowed features near 0.4–0.41 μm and 0.56–0.62 μm, and  $^{6}\text{Cr}^{3+}$  spin-allowed transitions between 0.41 and 0.68 μm. Common silicate garnet spectra, in summary, are distinct from many other rock-forming silicates and can be spectrally distinct from one garnet species to another. Iron dominates the spectral properties of garnets, and the crystallographic site and oxidation state of the iron both affect garnet reflectance spectra.

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## 1. Introduction

Garnets are a widely distributed group of rock-forming minerals, and are important petrogenetic indicators. The presence of garnets is commonly indicative of high-pressure formation con-

ditions (Juhin et al., 2010), though some garnets, especially calcic varieties, also form at lower pressures e.g., in skarn deposits (e.g., Meinert, 1992). Their crystal chemistry can provide information concerning the composition and petrogenetic conditions of their source region (e.g., Ghent, 1976; Holdaway, 2001). In addition to high pressure environments, garnets may also form during the crystallization of magma in some pegmatites and aluminous felsic intrusive rocks, by regional or contact metamorphism, and in hydrothermal systems (Galoisy, 2013). The crystal structure of garnets allows for a wide range of chemical substitutions, some of which

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are unknown in nature but are important industrial materials (e.g., Nd-doped yttrium–aluminum garnet). Garnet compositional variations are also used in diamond exploration to determine whether kimberlites are likely to be diamond-bearing or barren (Nixon and Hornung, 1968). Because garnets are stable at higher pressures than plagioclase, garnets are the dominant repository of aluminum during deep subduction of the Earth's crust and are expected to occur at moderate depth in other planetary interiors. Detecting the presence of garnet minerals can therefore be used to identify areas where deep-seated (lower crust or mantle) materials may be exposed on planetary surfaces. For example, garnets are assumed or modeled to be present in the lunar mantle (Ridley et al., 1973; Neal 2001; Elardo et al., 2011, and references therein) and could be present on the lunar surface in erupted deep-seated materials or exhumed by, and exposed in, the largest impact basins, such as South Pole-Aitken. Almandine-rich garnet was reported in mare basalt 12021 (Traill et al., 1970) but Hazen et al. (2015) concluded that this garnet was terrestrial contamination. Garnets are also, rarely, found in meteorites, but their origin as primary constituents of the interiors of large parent bodies or due to shock is not yet resolved (e.g., Kimura et al., 2013). Modeling of infrared spectra of Mercury allows for the presence of garnets (Sprague et al., 2009).

To date, there has been no systematic study of the ultraviolet-visible-near infrared (UVVNIR; 0.35–2.5  $\mu\text{m}$ ) reflectance spectral properties of garnets, yet reflectance spectra are widely used to interpret Earth and planetary remote sensing data. In this study, we link the crystal chemistry of garnet minerals with their reflectance spectral properties and assess the extent to which garnet can be identified and characterized by remote spectroscopic techniques. The emphasis of this study is on the spectroscopic detection of garnet and the qualitative discrimination of major garnet types and major cations.

## 2. Garnet structure and composition

Structurally, garnets consist of isolated  $\text{SiO}_4$  tetrahedra interconnected by ions of various divalent and trivalent metals (Novak and Gibbs, 1971), and the type of garnet that is formed is determined by the isomorphic substitution of those ions (Grew et al., 2013). The garnet structure is commonly generalized as  $\text{X}_3\text{Y}_2(\text{Z}_3)\Phi_{12}$ , space group  $la3d$  (e.g., Meagher, 1982; Geiger, 2008). Sites X, Y and Z host cations, site  $\Phi$  hosts anions. The co-ordinations of the cation sites with respect to the  $\Phi$  anion sites are X = distorted 8-coordinated dodecahedral geometry, Y = octahedral and Z = tetrahedral (Allen and Buseck, 1988; Smyth and Bish, 1988). In all garnets studied here, we assume that the  $\Phi$  sites consist entirely of  $\text{O}^{2-}$  anions. Some minor substitution of  $\text{F}^-$  can also enter the  $\Phi$  sites (Flohr and Ross, 1990; Smyth et al., 1990), however, none of our samples appear, or are expected, to contain significant F, and the presence of F is not expected to produce spectral features in the wavelength range investigated here. Hydrogarnets, a related class of minerals in which an  $\text{Si}^{4+}$  vacancy in the Z site is compensated by the incorporation of  $\text{H}^+$  forming hydroxyl groups, are not considered in this study.

The site preferences of the elements analyzed in the present study are as follows (the bold-faced cations being the most common ones in the most abundant naturally-occurring garnets):

- X = distorted 8-fold coordination (dodecahedral) with point symmetry, preferentially occupied by divalent cations { $\text{Na}^+$ ,  **$\text{Mg}^{2+}$** ,  **$\text{Ca}^{2+}$** ,  **$\text{Mn}^{2+}$** ,  **$\text{Fe}^{2+}$** }
- Y = octahedral with point symmetry (2 2 2), preferentially occupied by trivalent cations { $\text{Mg}^{2+}$ ,  **$\text{Al}^{3+}$** ,  $\text{Ti}^{4+}$ ;  $\text{V}^{3+}$ ;  **$\text{Cr}^{3+}$** ;  $\text{Mn}^{3+}$ ;  $\text{Fe}^{2+}$ ;  **$\text{Fe}^{3+}$** }
- Z = tetrahedral site with point symmetry preferentially occupied by tetravalent cations { $\text{Al}^{3+}$ ;  **$\text{Si}^{4+}$** ;  $\text{Fe}^{3+}$ }

Several cations under investigation here (e.g.,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ ) may enter multiple sites in the garnet structure to provide charge balance. While  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ , among others, can enter the tetrahedral Z site, all the garnets under consideration here are dominated by  $\text{Si}^{4+}$  in the Z site. Naturally-occurring garnets are complex solid solutions that can incorporate a variety of elements. The subdivisions of the garnet group are based on ideal end member compositions which are primarily determined by the physical limits of cation substitution in the octahedral and dodecahedral sites (e.g., Meagher 1982).

We have studied the utility of reflectance spectroscopy for garnet identification in the most common rock-forming garnet minerals: almandine ( $\text{Fe}^{2+}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), andradite ( $\text{Ca}_3\text{Fe}^{3+}_2\text{Si}_3\text{O}_{12}$ ), grossular ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), pyrope ( $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), spessartine ( $\text{Mn}^{2+}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), and uvarovite ( $\text{Ca}_3\text{Cr}^{3+}_2\text{Si}_3\text{O}_{12}$ ). Complete solid solution exists between pyrope, almandine, and spessartine due to the ease of substitution between  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  in the X site (Meagher, 1982), therefore, natural garnets rarely approach end-member compositions. Due to various types of substitutions, crystal field transition absorptions by transition series metals with unpaired d-electrons are possible. Magnetically coupled spin-forbidden crystal field transitions in metals with fully occupied unpaired electrons, such as  $\text{Fe}^{3+}$  are also possible (Sherman and Waite, 1985), as are intervalence charge transfers, such as  $\text{Fe}^{2+}-\text{Ti}^{4+}$  and  $\text{Fe}^{2+}-\text{Fe}^{3+}$ . The various cation substitutions and availability of multiple crystallographically unique sites may result in unique spectral properties that can be used to determine the presence of various optically-active cations, and different cation site occupancies, whose spectral properties may vary among different garnet species.

## 3. Previous spectroscopic studies of garnets

A number of investigators have studied garnet absorption spectra in the past and developed a number of spectral-compositional relationships for limited numbers of samples. In particular, absorption features in the visible spectral region have been the subject of numerous interpretations, and these are summarized in Appendix A.

Garnets have the potential to exhibit complex UVVNIR spectra for a number of reasons: (1) they have three sites available to host various cations; (2) a number of transition series elements can be present in garnets; and (3) these cations can potentially exhibit absorption bands due to multiple mechanisms: spin-forbidden transitions, spin-allowed transitions, and intervalence charge transfers.

Color changes in garnets as a function of composition have been noted by a number of investigators (Galoisy, 2013, and references therein), suggesting that cation substitutions may cause changes or distortions in the geometry of sites occupied by various cations. Changes in site dimensions is supported by a number of structural studies (e.g., Novak and Gibbs, 1971; Wildner and Andrut, 2001; Juhin et al., 2008) and X-ray diffractometry, visible, infrared and Raman spectroscopic studies (e.g., Clark, 1957; Bailey, 1960; Bancroft et al., 1967; Huffman 1970; Moore et al., 1971; Manning 1967a,b; Wickersheim and Lefever 1962; Wildner and Andrut, 2001). These changes are due to coupled cation substitutions that take place to maintain charge balance, cations being forced into less preferred sites by other cations, and changes in site dimensions as cations of different size substitute for one another in a single site (e.g., Dowty, 1971; Hunt et al., 1971). An expanded review of garnet spectral studies and band assignments are summarized in Appendix B.

Spectral features in common silicate garnets include intravalence transitions, metal–metal intervalence charge-transfer transitions, and metal–oxygen intervalence charge-transfer transitions. Dodecahedral ferrous iron typically produces three features due

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