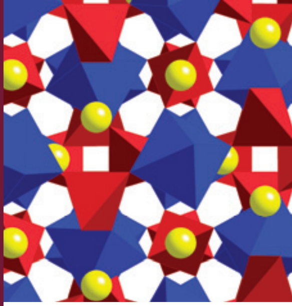

Garnet: A Key Phase in Nature, the Laboratory, and Technology

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Silicate garnet is a key rock-forming mineral, and various synthetic nonsilicate garnets find important use in a number of technological areas. Garnet's crystal structure provides the basis upon which many microscopic–macroscopic property relationships may be understood. Most rock-forming garnets are substitutional solid solutions and, thus, mineral scientists are focusing their efforts on investigating local structural properties, lattice strain, and thermodynamic mixing properties. Nonsilicate compositions are used, or have potential use, in various scientific and industrial areas because of their magnetic, optical, lasing, and ion-conducting properties. Research on garnet is multidisciplinary and involves scientists in the materials and mineral sciences, physical and inorganic chemistry, and solid-state physics.

Keywords: garnet, crystal chemistry, thermodynamics, solid solutions, structure–property relationships, strain, lasers, magnetic materials, ion conductors

INTRODUCTION

Garnet is a key rock-forming mineral. It also finds important use in a number of advanced technologies. The silicate garnets are very widespread in geological occurrence; they are stable over a great range of pressure and temperature conditions and geochemical environments. They are found, for example, in low-pressure metamorphic contact aureoles, and they also occur as compositionally complex solid solutions in Earth's transition zone. Over the years much mineralogical, petrological, geochemical, and geophysical research has been directed toward both natural garnets and their synthetic analogues. In addition, a large variety of nonsilicate garnets have been synthesized, and extensive studies on their chemical and physical properties have been undertaken by a diversity of scientists interested in the solid state. This article presents important past studies and describes several current research thrusts on the structure, crystal chemistry, thermodynamics, and physical properties of garnet, and it hopefully conveys the excitement associated with each of them.

THE COMMON SILICATE GARNETS: STRUCTURE AND CRYSTAL CHEMISTRY

The crystallographer and mineralogist Georg Menzer solved the crystal structure of grossular garnet, $Ca_3Al_2Si_3O_{12}$, and reported his initial results to the German Mineralogical Society in 1925. His work must be considered of benchmark importance, not only for mineralogy but also for all solid-state sciences, as it appears that this was the first crystal-structure determination of a silicate. Menzer solved the structure using an insightful combination of X-ray diffraction measurements (from X-ray powder results recorded on film in a 5.8 cm diameter camera!) and known atomic radii. He expanded this study, as reported in an extensive paper (Menzer 1928), by describing the structures of the six common garnets—grossular, andradite ($Ca_3Fe_2Si_3O_{12}$), uvarovite ($Ca_3Cr_2Si_3O_{12}$), almandine ($Fe_3Al_2Si_3O_{12}$), spessartine ($Mn_3Al_2Si_3O_{12}$), and pyrope ($Mg_3Al_2Si_3O_{12}$)—and he showed that all end-members are isostructural with one another.

Starting in the mid 1950s and continuing to the present, many refinements based on diffraction results from a large variety of synthetic and natural silicate garnets, as well as nonsilicate types, have been made. The garnet crystal structure has been described in great detail, but new discoveries are still being made (e.g. see Li oxide garnets below). The "standard" garnet structure has cubic symmetry, space group $Ia\bar{3}d$. Several competing forms are used to represent its general crystal-chemical formula. In mineralogy one often reads $\{X_3\}[Y_2](Z_3)O_{12}$ or sometimes $\mathbf{E}_3\mathbf{G}_2[\mathbf{TX}_4,\mathbf{X}_4]_3$, and in the materials science and physics literature one often finds $A_3B_2C_3O_{12}$. The structure consists of ZO_4 tetrahedra and YO_6 octahedra that share corners, giving rise to a three-dimensional framework (Fig. 1a). The X cations are coordinated by 8 oxygen atoms in the form of a triangular dodecahedron (i.e. distorted cube). Because of its high symmetry, the basic garnet crystal structure can be described using solely the unit cell parameter, a_o, and the x, y, and z atomic coordinates of the anion. Local structural relationships among the three coordination polyhedra are shown in Fig. 1b–f. Following in the spirit of Menzer's 1928 work, Novak and Gibbs (1971) presented a quantitative crystal-chemical analysis of silicate garnet, $\{X_3\}[Y_2](Si_3)O_{12}$, based on X-ray refinements of crystals of 9 different compositions. They presented a "stability" field as a function of the ionic radii of the X and Y cations, which can be constructed by the high symmetry of garnet and the structural relations shown in Figure 1. This "stability" field describes and predicts well silicate garnets of natural and synthetic origin.

The Effect of Pressure and Temperature on the Garnet Structure

A relatively recent thrust in terms of studies of the solid state, and a field in which mineral scientists played a central developmental role, involves investigating the

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response of crystals to high pressure and temperature, and, here, garnet is no exception. Such studies are necessary, for example, in order to understand the geophysical and geochemical nature of Earth's deep interior. The effect of pressure on synthetic pyrope and natural grossular was first investigated by Hazen and Finger (1978), who measured the compression of single crystals to 6 gigapascals (GPa) in a diamond anvil cell using X-ray techniques. Zhang et al. (1998) extended the upper pressure range to 33 GPa in their study of synthetic pyrope. It turns out that the common silicate garnets are, compared to most other silicates, relatively incompressible, with bulk modulus values between 155 and 190 GPa. This property is mostly related to the large number of shared polyhedral edges, which act to buttress and stiffen the structure (Fig. 1). It also accounts for garnet's high density and optical refractive indices. It appears that the main compression mechanism is related to changes in polyhedral rotation as given by the Si–O–Y angle. Bond shortening also occurs, with the large dodecahedron (XO_8) being the most compressible polyhedron.

The first high-temperature single-crystal diffraction study of garnet (i.e. pyrope to 750 °C and grossular to 675 °C) was published by Meagher (1975). Detailed temperature-dependent properties from 100 K to 500–550 K were investigated in a series of studies on different synthetic end-member garnets by Armbruster, Geiger, and coworkers (see Geiger 2008 and 2013 for references). Normally, a diffraction experiment gives a static structural description of a crystal, but careful analysis can give dynamic information on the cations and anions. The studies showed that the SiO_4 tetrahedron and the Al/FeO_6 octahedron in garnet can be considered, in terms of the diffraction experiment, as rigid vibrating bodies. The XO_8 dodecahedron, however, is not rigid, and it was argued that the X cations are thermally disordered in an anisotropic manner. This question has long been a matter of dispute, and other workers have proposed, instead, static positional disorder for the X cations, especially for Mg in pyrope (Geiger 2013). Determining the exact behavior is necessary for understanding both the microscopic lattice-dynamic and macroscopic thermodynamic properties of garnet.

OTHER NATURAL GARNETS: CHEMISTRIES, STRUCTURES, AND DEFECTS

Garnets of many different compositions have been found in nature, with at least 25 essential elements identified (Fig. 2). To date, 32 natural species have been described as belonging to the garnet supergroup (Grew et al. 2013), and new ones are continually being found. The compositional range is remarkable, as are the resulting chemical and physical properties. What are some of the compositions and their structures?

The so-called hydrogarnets form a class of garnet where the central tetrahedrally coordinated Z cation is missing. It is replaced locally by four H^+ atoms in OH^- groups, giving the general formula $X_3Y_2(\square_3)H_{12}O_{12}$. Various end-member hydrogarnets have been synthesized in the lab (e.g. Ito and Frondel 1967), but none has been found in nature. Notably, at relatively low temperatures, as shown in the lab, there is complete solid solution between grossular and katoite, $Ca_3Al_2H_{12}O_{12}$. Such solid solution garnets have geologic relevance and are found, for example, in low-temperature rodingite assemblages. They also have importance for certain cements (Damidot et al. 2011).

Many silicate garnets contain "water," as work starting in the 1970s showed (Wilkins and Sabine 1973). Indeed, many nominally anhydrous rock-forming silicates (e.g. garnet, olivine, pyroxene, feldspar, etc.) often contain very small concentrations of structural OH. At first, this result was considered just a mineralogical curiosity with little geologic relevance. However, this research area has expanded to include various global-scale geological questions (Keppler and Smyth 2006). The role of trace OH in garnet, as well as in pyroxene and olivine, is critical in affecting rheological rock properties (weakening) and, furthermore,

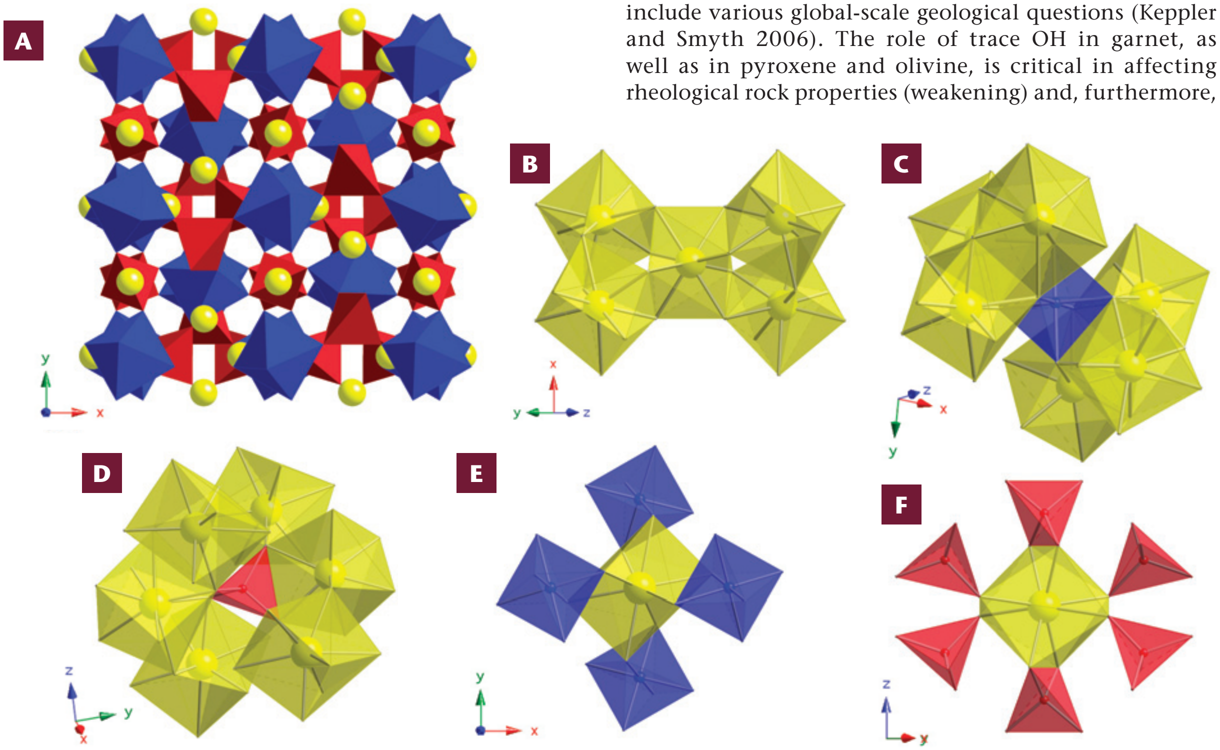


Figure 1 (**A**) Polyhedral model of garnet and unit cell directions. The tetrahedra and octahedra share corners, building a three-dimensional framework. The X cations (yellow spheres) are located in small cavities of triangular dodecahedral coordination. Various local coordination polyhedra relationships are shown in (B) to (F). (**B**) Edge-sharing relationship between neighboring dodecahedra (yellow). (**C**) A central octahedron (blue) and six edge-shared dodecahedra. (**D**) A central tetrahedron (red) and two edge-shared and four corner-shared dodecahedra. (**E**) A central dodecahedron and four edge-shared octahedra. (**F**) A central dodecahedron and two edge-shared and four corner-shared tetrahedra.

in determining the reservoir of H_2O that is partially held in the deep Earth (Bell and Rossman 1992). Interestingly, in spite of the amount of research that has been done on these garnets (cf. the more water-rich grossular–katoite compositions), it is still not exactly clear in most cases how and where in the garnet structure the minor OH groups are incorporated. Various defect-type substitutional mechanisms must be operating.

High-pressure and high-temperature investigations in the 1960s showed that, with increasing depths in Earth's upper mantle, pyroxene becomes unstable and should be "taken up" via solid solution into garnet (e.g. Ringwood and Major 1966). In terms of pure enstatite, $Mg_2Si_2O_6$, for example, this leads to an aluminum-free garnet with Si and Mg in octahedral coordination and with the formula $\{Mg_3\}[MgSi]_2(Si_3)O_{12}$. The discovery of a more compositionally complex garnet in a shocked meteorite led to the name majorite for this phase. Ringwood, a pioneer in the area of high-pressure work and mantle petrology, suggested, quite importantly, that at certain depths Earth's mantle consists in large part of a majorite-containing garnet solid solution.

Finally, in terms of chemistry, there are a number of seldom-occurring nonsilicate garnets. Five examples are:
schäferite $\{Ca_2Na\}[Mg_2](V^{5+}{}_3)O_{12}$,
berzeliite $\{Ca_2Na\}[Mg_2](As^{5+}{}_3)O_{12}$,
yafsoanite $\{Ca_3\}[Te^{6+}{}_2](Zn_3)O_{12}$,
elbrusite $\{Ca_3\}[U^{6+}{}_{0.5}Zr_{1.5}](Fe^{3+}{}_3)O_{12}$,
and cryolithionite $\{Na_3\}[Al_2](Li_3)F_{12}$, the last of which has F as the anion (see Grew et al. 2013 for a full listing).

In terms of crystallography and structure, as known for many years from their optical anisotropy, some common silicate garnets are noncubic (e.g. Shtukenberg et al. 2001). Here, grossular and andradite (i.e. grandites) as well as uvarovite play the most prominent, but not exclusive, role. Crystals can show sector-like features or complex, very fine oscillatory zonation (see Fig. 4a in Baxter et al. 2013 this issue). Detailed X-ray work on nonisotropic garnets indicates small deviations from metric cubic behavior in symmetries such as orthorhombic, monoclinic, and even as low as triclinic. The reason(s) for the reduction in symmetry is (are) not clear in all cases, but partial long-range cation ordering, mostly at the Y site, and/or structural strain might be the cause.

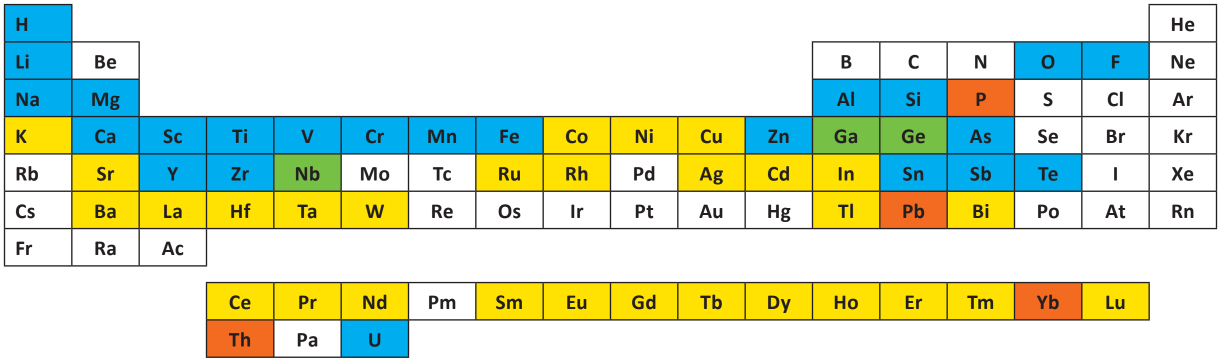
GARNET STABILITY

The different pressure–temperature stability fields of the silicate garnet end-members are remarkable (e.g. Deer et al. 1997; Baxter et al. 2013). Aluminosilicate spessartine with Mn^{2+} can be synthesized at 1 atmosphere (atm) at elevated temperatures, while pyrope with Mg^{2+} is not stable below 1.5 GPa. The calcium garnets andradite and uvarovite are also stable at 1 atm. Almandine and grossular have not been synthesized at 1 atm and may be thermodynamically stable only at greater pressures, although experimental work shows that garnet often nucleates with difficulty in the laboratory. Majorite is stable only above roughly 15 GPa. In nature, silicate garnet first crystallizes in metamorphic rocks at about 400 °C and is stable up to the highest temperatures in the crust and mantle, above 1500 °C.

GARNET SOLID SOLUTIONS

Most rock-forming garnets are multicomponent substitutional solid solutions. Different cations can be exchanged for one another at the X and Y sites (there is less exchange of cations at the Z site, but some garnets, such as those of the schorlomite group, show exchange here; Grew et al. 2013). Winchell and Winchell (1927), in an early study describing the solid solution behavior of garnet, classified two species and six subspecies, namely the pyralspites (**pyr**ope-**al**mandine-**sp**essartine, with cation mixing at the X site) and ugrandites (**u**varovite-**gr**ossular-**and**radite, with cation mixing at the Y site). At that time, it was thought that solid solution between the two species was restricted, while within a species it was much greater. This classification is standard in mineralogy textbooks, but its use is limited and even potentially misleading, because extensive solid solution between the two "species" and various "subspecies" does occur (Geiger 2008; Grew et al. 2013). What are some of the key, current research problems related to garnet solid solutions?

Aluminosilicate garnet, $\{X_3\}[Al_2](Si_3)O_{12}$, because of its high symmetry and single crystallographic X site, offers an excellent system to study solid solution and thermodynamic behavior in silicates (Geiger 2001, 2008). Various divalent cations can be located at the X site (Mg, Fe^{2+}, Mn^{2+}, and Ca). Solid solution in other silicates occurs at two or more sites and/or in lower symmetries, making it more difficult to interpret experimental results. Any crystalline solid solution must have local structural heterogeneities and strain fields resulting from the exchange of atoms with different sizes, whereby strain can occur from the scale of the unit cell to the nanoscale. Investigating these heterogeneities and strain fields is a challenging but vital research problem, because, for example, structural and chemical bonding properties control the nature of intra- and interelement partitioning behavior for major, minor, and trace elements (Wood et al. 2013 this issue) and the *P*–*T* stability of garnet. In terms of the local properties of solid solutions, the standard diffraction experiment has limitations as it gives long-range structural information,



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🟦 Reported as an essential element in a natural garnet.
🟩 Reported as an essential element in a natural garnet (unapproved species).
🟧 Reported as a significant but non essential element in a natural garnet.
🟨 Reported in a synthetic garnet only.

FIGURE 2 Periodic table showing elements occurring in garnet, either as an essential constituent or in significant amounts (Grew et al. 2013; Grew pers. comm.).

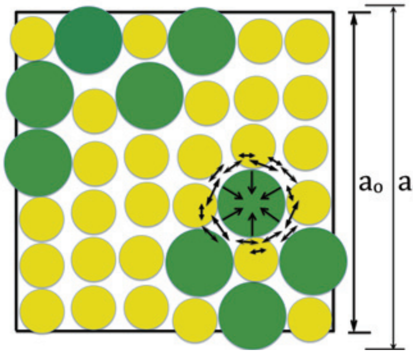
such as diffraction-averaged bond lengths and angles, as measured over thousands of unit cells. It follows, furthermore, that diffraction can determine long-range cation ordering (which must occur in symmetries lower than $Ia\bar{3}d$), but not short-range ordering (SRO) in solid solutions. To obtain local structural and chemical information, say from the atomic scale to the nanoscale (1 to 100 nanometers), spectroscopic measurements are required.

Nuclear magnetic resonance (NMR) spectroscopy is an element-specific measurement technique and thus is an excellent probe of local structure. It is powerful, especially when applying the magic-angle spinning (MAS) technique, because it can be used to determine quantitatively local states of atomic order–disorder (e.g. short-range order), for example. ^{29}Si MAS NMR measurements have been made to study the distribution of Mg and Ca over the dodecahedral sites (Fig. 1) in synthetic pyrope–grossular $\{Mg_{3-x}Ca_x\}Al_2Si_3O_{12}$ garnets (Bosenick et al. 1995). The experiment is possible because ^{29}Si's nuclear quantum states and their energy splittings, which are what is measured in the experiment, in an SiO_4 group are sensitive towards the various local Ca and Mg configurations in immediately surrounding dodecahedral sites (two of which are edge shared and four corner shared; Fig. 1d). Up to 15 different local Ca–Mg configurations are possible, whose probabilities depend on the bulk composition of the garnet, and their associated resonances can be recorded and assigned in a ^{29}Si NMR spectrum. Furthermore, the intensity of a given resonance gives the concentration of the associated configuration. An analysis indicates that certain cation configurations are slightly preferred over what a random statistical distribution of Ca and Mg would give. That is, there is probably clustering or SRO of Mg and Ca in synthetic garnets crystallized above 1000 °C (Fig. 3a). If SRO can be observed in garnets equilibrated at such high temperatures, it is important to ask what the degree of order could be at 400 to 700 °C, where many natural garnets crystallize.

Consider the effect of substitutional solid solution on garnet stability. Much research has been done over the past 50 or so years to determine the thermodynamic properties of garnet solid solutions, but a full and quantitative understanding is not at hand. An exception is again binary $\{Mg_{3-x}Ca_x\}Al_2Si_3O_{12}$ garnets, which have received much study, making their macroscopic thermodynamic behavior known fairly well. Take the function enthalpy, H, defined as $H = U + pV$, where U is the internal energy, p is pressure, and V is volume. The lower H is, the more stable is the crystal ($G = H - TS$, where G is the Gibbs energy and S the entropy). For solutions, including solid ones, the thermodynamic mixing functions come into play, and it is a necessary condition for ideal behavior that $\Delta H^{xs} = 0$. This means that for an ideal garnet solid solution, for example, its enthalpy value is given by a linear combination of the H values of its garnet end-members in proportion to their concentration. However, most silicate solid solutions are not thermodynamically ideal (Geiger 2001). This is clearly the case for pyrope–grossular garnets (Newton et al. 1977; Dachs and Geiger 2006), where ΔH^{xs} (Fig. 3b), ΔS^{xs}, and ΔV^{xs} are nonideal.

It has long been thought that nonideal, positive ΔH^{xs} behavior, which is energetically destabilizing, results from microscopic lattice strain (Geiger 2001). An experimental investigation demonstrating this was made using X-ray powder diffraction measurements at the European Synchrotron Radiation Facility (Fig. 3C) on a series of binary $\{Mg_xCa_{1-x}\}_3Al_2Si_3O_{12}$ garnets (Dapiaggi et al. 2005). Such a large-scale international radiation facility offers high-resolution and intense X-ray beams, and measurements can be made at very low temperatures (e.g. 5 K) and on small milligram-sized samples. This allows a quantitative determination of minor variations in powder reflection line widths, which, in turn, give information on elastic strain. The results show that strain is smallest for end-member grossular and pyrope, which have no local structural heterogeneity caused by cation mixing. Intermediate compositions, on the other hand, show reflection broadening, reflecting their local structural heterogeneity. This produces elastic strain that is asymmetric in nature across the $\{Mg_{3-x}Ca_x\}Al_2Si_3O_{12}$ join (Fig. 3B). The simplest crystal-chemical interpretation is that it is easier to incorporate the smaller Mg cation (0.89 Å) in a larger-volume grossular-rich host than the larger Ca (1.12 Å) cation in a smaller-volume pyrope-rich garnet (Fig. 3a). The actual physical situation is more complicated and involves the distortion of strongly

A



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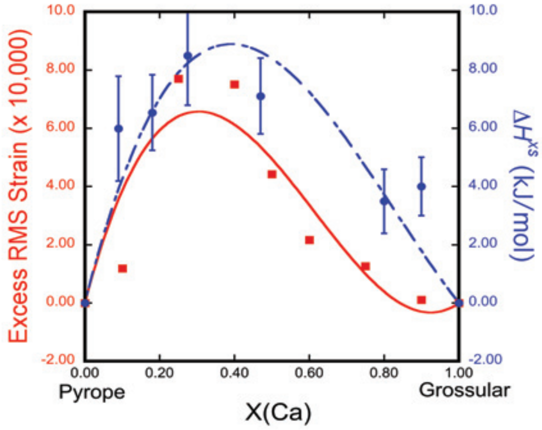

Figure 3 (**A**) Schematic, two-dimensional lattice showing Ca (green) and Mg (yellow) atoms. Note the local compression and shearing associated with the large Ca cation. (**B**) Excess enthalpy of mixing, ΔH^{xs}, obtained via solution calorimetry (blue line; Newton et al. 1977) and excess root-mean-squared strain measured from synchrotron diffraction measurements (red line; Dapiaggi et al. 2005) for pyrope–grossular garnets. The curves are calculated using a two-parameter asymmetric mixing model. (**C**) The European Synchrotron Radiation Facility in Grenoble, France, is a modern X-ray light source supported and shared by 20 countries (www.esrf.eu/about).

bonded edge-shared SiO_4 and AlO_6 groups (see Bosenick et al. 2000 and Fig. 1e, f). Because ΔH^{xs} behavior mimics that of microstrain, the latter controls the macroscopic thermodynamic behavior. This is an important finding in terms of understanding substitutional solid solution behavior.

SYNTHETIC NONSILICATE GARNETS AND TECHNOLOGICAL USES

A great number of garnets have been synthesized in the laboratory, and their compositional range is very large (Fig. 2). Geller (1967) reviewed a number of compositions. Certain nonsilicate types have found important use in technological areas, and others may follow in the future. The more notable garnets and their applications are discussed here.

Yttrium Iron Garnet (YIG)

The Nobel Prize–winning physicist Louis Néel published an important paper introducing the theory of ferrimagnetism in crystals (Néel 1948). His research explained the nature of the magnetic moment of the well-known spinel ferrites (e.g. magnetite). In a ferrimagnetic compound, unlike a ferromagnet, the total magnetic moment derives from the difference in the magnetic moments between two or more sublattices. In addition, each sublattice can have a different magnetic temperature behavior. Néel's findings spawned a burst of activity that led to the synthesis of a plethora of magnetic garnets. The prototype, yttrium iron garnet [acronym YIG, $\{Y_3\}[Fe^{3+}{}_2](Fe^{3+}{}_3)O_{12}$], was discovered in 1956. Since then a large number of different end-member-composition magnetic garnets, as well as solid solutions, have been synthesized. Because of the different magnetic elements that can be incorporated in garnet and the presence of three crystallographic sites/sublattices (Fig. 1), the possible types of magnetic interactions are large and rich in complexity. Thousands of papers have been published on these garnets and on their magnetic and optical behavior. The noted physicist Charles Kittel wrote, "What the fruit fly is for genetics, the garnets are for magnetics" (Winkler 1981). The latter author wrote the standard treatise *Magnetic Garnets*, in which many results are discussed. Crystals up to several centimeters across and roughly 600 g in weight have been grown using high-temperature fluxed melts, as first developed at Bell Telephone Laboratories. Other magnetic phases are often not stable at high temperatures and the synthesis of large crystals is simply not possible. Here, garnet is, once again, rather special.

In the early years (1960s and 1970s) of computer development, there was great interest and much work done to test if magnetic garnets could be used as "bubble" (domain) memory for storing data. This technology was never realized, but magnetic garnets have found application in a number of other electronic devices. They are used as magneto-optical isolators because of their Faraday effect (i.e. rotation of the polarization plane of light in a magnetic field) and in microwave technology as magnetic resonance filters, tuned oscillators, and band-reject and band-pass filters. Even YIG thin films, often grown on gadolinium gallium garnet substrates, have been produced for use in integrated optical devices.

Yttrium Aluminum Garnet (YAG) and Gadolinium Gallium Garnet (GGG)

Following the discovery of maser and laser action in the late 1950s, the latter using Cr^{3+}-doped crystalline Al_2O_3, intense effort was undertaken worldwide to synthesize a large variety of crystals to study their possible lasing properties. Research done at Bell Laboratories in the early 1960s demonstrated that by doping yttrium aluminum garnet, $\{Y_3\}[Al_2](Al_3)O_{12}$, and gadolinium gallium garnet, $\{Gd_3\}[Ga_2](Ga_3)O_{12}$, with Nd^{3+}, a good lasing medium could be created (Geusic et al. 1964). Analogous to YIG, the acronyms YAG and GGG, respectively, thus came into use. Research showed that trivalent Nd, at roughly the 1% atomic level, can replace Y^{3+} at the X site in YAG or Gd^{3+} in GGG, and it fluoresces at wavelengths optimal for lasers. Later work showed that a variety of rare earth and other elements (e.g. Er^{3+}, Ho^{3+}, Tm^{3+}, Yb^{3+}, Cr^{3+}) can be incorporated into YAG and GGG (Fig. 4). The concentration of the lasing elements should not be too high, otherwise they interact and the fluorescence lifetime decreases significantly. Each laser-active element is associated with its characteristic emitted wavelength, allowing for a wide range of technical, industrial, and medical applications. This property, along with garnet's hardness, stability, and good thermal conductivity, makes it an ideal phase for use in pumped solid-state lasers. YAG and GGG can be grown by high-temperature crystal-growth techniques, such as the Czochralski and Verneuil methods (Roy 1992).

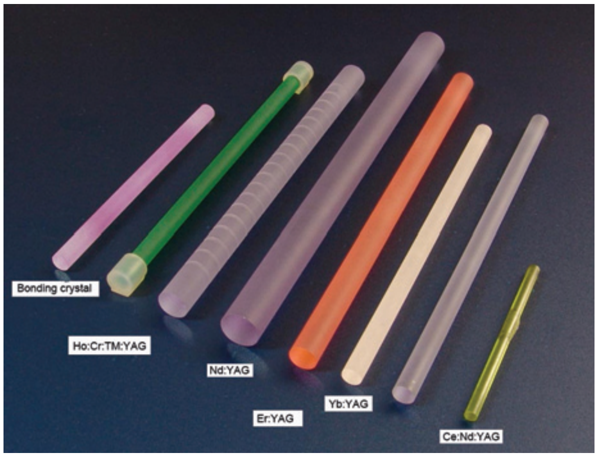

Figure 4 YAG rods doped with various elements (courtesy of WTS Photonics Co., Ltd)

There are a number of applications and uses for Nd:YAG lasers with a wavelength of 1064 nm, and just a few are mentioned here. At several microwatts power, they are used in pointers. At higher powers, precisely focused beams are used in medicine to destroy lesions and to weld tissue together, and at slightly higher power, they are employed in laser surgery. Nd:YAG lasers find widespread application in (micro)engraving, including diamond. A well-known use for lasers of roughly 5 kW power is the welding, cutting, and boring of metals, as in the automobile and steel industries. Dense, highly transparent, ceramic Nd:YAG lasers with powers of roughly 25 kW have been developed for use in confinement fusion research and for possible military applications.

Lithium Oxide Garnets

Synthetic Li oxide garnets have been known for a number of years, but a special new class is receiving much current attention (Cussen 2010), for example, from major automobile companies, due to their fast-ion behavior. Certain compositions may have the necessary high ionic conductivities to be considered for use as electrolytes and also possibly as active materials in rechargeable solid-state batteries. Garnet has physical properties well suited for use in batteries, because it is stable at high temperatures and resistant to attack by molten Li and to corrosion by moisture. Its high cubic symmetry permits isotropic diffusion of Li cations.

Li oxide garnet is characterized by tetrahedral coordination of lithium (Z site). There are compositions with "standard" stoichiometry, for example, $\{Nd_3\}[W_2](Li_3)O_{12}$. However, a number of new Li oxide garnets have recently been synthesized. End-member compositions can have nominally from 4 to 7 Li cations and up to 12 cations in the formula unit, while solid solutions show non-integer cation contents. Examples are $Li_4Nd_3TeSbO_{12}$; $Li_5Ln_3Sb_2O_{12}$, where Ln = La, Pr, Nd, Sm, and Eu; $Li_6ALa_2Nb_2O_{12}$, where A = Ca, Sr, and Ba; $Li_7La_3Zr_2O_{12}$; and $Li_{6.4}Sr_{1.4}La_{1.6}Sb_2O_{12}$. Rather confusingly, their formulas are presented in nonstandard form. The large alkaline earth and lanthanide cations are located at the X site and the highly charged Te^{6+}, Nb^{5+}, Sb^{5+}, and Zr^{4+} cations at the Y site. The important point is that those phases with more than three Li cations, the so-called "Li-stuffed garnets" (Cussen 2010), have Li located at one or even two additional crystallographic sites not found in the "standard" cubic structure. The "extra" lithium cations are located between faces of opposing LiO_4 tetrahedra. Li oxide garnets of standard stoichiometric composition are poor ion conductors, because the distances between tetrahedral sites are relatively large and they are fully occupied by Li. Favorable jump mechanisms are not present. In the case of the Li-stuffed garnets, all structural sites with Li are only partially occupied and the distances between them are short. This apparently leads to their high ion conductivities.

Cubic garnet of nominal composition $Li_7La_3Zr_2O_{12}$, but doped with Al (Geiger et al. 2011), has some of the highest measured ion conductivities, comparable to or even greater than those of other well-known, fast Li-ion conductors such as Li_3N, Li-β-Al_2O_3, and LIPON (Li phosphorus oxynitride). X-ray diffraction work on this garnet phase shows that some Li atoms are delocalized, and $^{6/7}Li$ NMR spectra at room temperature show just a single Li resonance, indicating fast-ion diffusion (Geiger et al. 2011). Doping $Li_7La_3Zr_2O_{12}$ with small amounts of Al (or other similar cations) stabilizes the cubic phase, which is a better ion conductor than pure $Li_7La_3Zr_2O_{12}$; the latter has tetragonal symmetry and an ordered Li arrangement at ambient conditions. This new research field on Li oxide garnets is developing quickly, and interesting findings are expected in the future.

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REFERENCES

Baxter EF, Caddick MJ, Ague JJ (2013) Garnet: Common mineral, uncommonly useful. Elements 9: 415-419

Bell DR, Rossman GR (1992) Water in Earth's mantle: The role of nominally anhydrous minerals. Science 255: 1391-1397

Bosenick A, Geiger CA, Schaller T, Sebald A (1995) A ^{29}Si MAS NMR and IR spectroscopic investigation of synthetic pyrope-grossular garnet solid solutions. American Mineralogist 80: 691-704

Bosenick A, Dove MT, Geiger CA (2000) Simulation studies on the pyrope-grossular solid solution. Physics and Chemistry of Minerals 27: 398-418

Cussen EJ (2010) Structure and ionic conductivity in lithium garnets. Journal of Materials Chemistry 20: 5167-5173

Dachs E, Geiger CA (2006) Heat capacities and entropies of mixing of pyrope-grossular ($Mg_3Al_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$) garnet solid solutions: A low-temperature calorimetric and a thermodynamic investigation. American Mineralogist 91: 894-906

Damidot D, Lothenbach B, Herfort D, Glasser FP (2011) Thermodynamics and cement science. Cement and Concrete Research 41: 679-695

Dapiaggi M, Geiger CA, Artioli G (2005) Microscopic strain in synthetic pyrope-grossular solid solutions determined by synchrotron X-ray diffraction at 5 K: The relationship to enthalpy of mixing behavior. American Mineralogist 90: 506-509

Deer WA, Howie RA, Zussman J (1997) Rock-Forming Minerals, Volume 1A, Orthosilicates. The Geological Society, London

Geiger CA (ed) (2001) Solid Solutions in Silicate and Oxide Systems. European Mineralogical Union Notes in Mineralogy 3, Eötvös University Press, Budapest, 465 pp

Geiger CA (2008) Silicate garnet: A micro to macroscopic (re)view. American Mineralogist 93: 360-372

Geiger CA (2013) Static disorders of atoms and experimental determination of Debye temperature in pyrope: Low- and high-temperature single-crystal X-ray diffraction study—Discussion. American Mineralogist 98: 780-782

Geiger CA and 9 coauthors (2011) Crystal chemistry and stability of "$Li_7La_3Zr_2O_{12}$" garnet: A fast lithium-ion conductor. Inorganic Chemistry 50: 1089-1097

Geller S (1967) Crystal chemistry of the garnets. Zeitschrift für Kristallographie 125: 1-47

Geusic JE, Marcos HM, Van Uitert LG (1964) Laser oscillations in Nd-doped yttrium aluminum, yttrium gallium and gadolinium garnets. Applied Physics Letters 4: 182-184

Grew ES, Locock AJ, Mills SJ, Galuskina IO, Galuskin EV, Hålenius U (2013) Nomenclature of the garnet supergroup. American Mineralogist 98: 785-811

Hazen RM, Finger LW (1978) Crystal structures and compressibilities of pyrope and grossular to 60 kbar. American Mineralogist 63: 297-303

Ito J, Frondel C (1967) New synthetic hydrogarnets. American Mineralogist 52: 1105-1109

Keppler H, Smyth JR (eds) (2006) Water in Nominally Anhydrous Minerals. Reviews in Mineralogy & Geochemistry 62, 478 pp

Meagher EP (1975) The crystal structures of pyrope and grossularite at elevated temperatures. American Mineralogist 60: 218-228

Menzer G (1928) Die Kristallstruktur der Granate. Zeitschrift für Kristallographie 69: 300-396

Néel L (1948) Propriétés magnétiques des ferrites: Ferrimagnétisme et antiferromagnétisme. Annales de Physique (Paris) 3: 137-198

Newton RC, Charlu TV, Kleppa OJ (1977) Thermochemistry of high pressure garnets and clinopyroxenes in the system CaO-MgO-Al_2O_3-SiO_2. Geochimica et Cosmochimica Acta 41: 369-377

Novak GA, Gibbs GV (1971) The crystal chemistry of the silicate garnets. American Mineralogist 56: 791-825

Ringwood AE, Major A (1966) High-pressure transformations in pyroxenes. Earth and Planetary Science Letters 1: 351-357

Roy BN (1992) Crystal Growth from Melts. John Wiley & Sons, New York, 322 pp

Shtukenberg AG, Punin YuO, Frank-Kamenetskaya OV, Kovalev OG, Sokolov PB (2001) On the origin of anomalous birefringence in grandite garnets. Mineralogical Magazine 65: 445-459

Wilkins RWT, Sabine W (1973) Water content of some nominally anhydrous silicates. American Mineralogist 58: 508-516

Winchell NH, Winchell AN (1927) Elements of Optical Mineralogy, 2nd Edition, Part II. Wiley, New York

Winkler G (1981) Magnetic Garnets. Vieweg tracts in pure and applied physics 5. Vieweg and Sohn, Braunschweig

Wood BJ, Kiseeva ES, Matzen AK (2013) Garnet in the Earth's mantle. Elements 9: 421-426

Zhang L, Ahsbahs H, Kutoglu A (1998) Hydrostatic compression and crystal structure of pyrope to 33 GPa. Physics and Chemistry of Minerals 25: 301-307