Crystal chemistry and light elements analysis of Ti-rich garnets

EMANUELA SCHINGARO1,*, MARIA LACALAMITA1, ERNESTO MESTO1, GENNARO VENTRUTI1, GIUSEPPE PEDRAZZI2, LUISA OTTOLINI3, AND FERNANDO SCORDARI1

1Dipartimento di Scienze della Terra e Geoambientali, Università degli Studi di Bari “Aldo Moro”, via E. Orabona 4, I-70125, Bari, Italy
2Dipartimento di Neuroscienze, Università di Parma, via Volturno 39, I-43100, Parma, Italy
3CNR-Istituto di Geoscienze e Georisorse, Unità di Pavia, via A. Ferrata 1, I-27100 Pavia, Italy

ABSTRACT

A suite of Ti-bearing garnets from magmatic, carbonatitic, and metamorphic rocks was studied by electron probe microanalysis (EPMA), X-ray powder diffraction (XRPD), single-crystal X-ray diffraction (SCXRD), Mössbauer spectroscopy, and secondary ion mass spectrometry (SIMS) to better characterize their crystal chemistry. The studied garnets show TiO2 varying in the range of 4.9(1) to 17.1(2) wt% and variable Fe3+/ΣFe content. SIMS analyses allowed quantification of light elements yielding H2O in the range 0.091(7)–0.46(4), F in the range 0.004(1)–0.040(4), and Li2O in the range 0.0038(2)–0.014(2) wt%. Mössbauer analysis provided spectra with different complexity, which could be fitted to several components variable from one (1Fe3+) to four (1Fe2+, 2Fe2+, YFe3+, ZFe3+). A good correlation was found between the Fe3+/ΣFe resulting from the Mössbauer analysis and that derived from the Flank method.

X-ray powder analysis revealed that the studied samples are a mixture of different garnet phases with very close cubic unit-cell parameters as recently found by other authors. Single-crystal X-ray refinement using anisotropic displacement parameters were performed in the Ia3d space group and converged to 1.65 ≤ R ≤ 2.09% and 2.35 ≤ wR ≤ 3.02%. Unit-cell parameters vary in the range 12.0641(1) ≤ a ≤ 12.1447(1) Å, reflecting different Ti contents and extent of substitutions at tetrahedral site.

The main substitution mechanisms affecting the studied garnets are: YR4+ + ZR3+ ↔ YSi + XCa2+, with YR4+ = Ti, Zr; YR3+ = Fe3+, Al3+, Cr3+; Y = Ti; Z = Fe2+, Mg2+, Mn2+. Major substitutions, such as 2YTi4++ ZFe2+ ↔ 2YFe3+ + ZSi, (SiO4)4– ↔ (O4H4)4–, F– ↔ OH–, and YR3+ + ZFe3+ ↔ Y′Fe3+ + Z′Si, with Y′R3+ = Ti, Zr; Z′R3+ = Fe3+, Al3+, Cr3+; 3R′3+ ↔ Na, Li also occur.

Keywords: Ti-bearing garnets, light elements, SCXRD, XRPD, EPMA, SIMS, Mössbauer spectroscopy, crystal chemistry

INTRODUCTION

Garnets are a supergroup of rock-forming minerals, with generalized chemical formula {X}2[{Y}3(Z)2]2 where dodecahedral {X}, octahedral {Y}, and tetrahedral (Z) are the three symmetry unique atomic sites and the anionic site (φ) represents O, OH, and F (Grew et al. 2013). Alternating Zφ tetrahedra and Yφ octahedra share corners to form a three-dimensional framework containing Xφ triangular, dodecahedra.

These minerals are widespread in the Earth’s crust, upper mantle and transition zone and occur in various rocks. In a recent revision of the nomenclature of garnets (Grew et al. 2013), 32 species of the garnet supergroup were approved, out of which 29 were further divided into five groups, on the basis of the symmetry and of the total charge of cations at the tetrahedral site: henrertermierite (tetragonal, Z charge = 8), bitikleite (cubic, Z charge = 9), schorlomite (cubic, Z charge = 10), garnet (cubic, Z charge = 12), berzellite (cubic, Z charge = 15). Ti-garnets may belong to the schorlomite or to the garnet group, depending on the composition and cation distribution (see below). In previous literature, Ti-garnets are referred to as Ti-bearing andradite, melanite, schorlomite, and morimotoite, and Chakhmouradian and McCammon (2005) reviewed the criteria historically used to distinguish between melanite and schorlomite. From a geological viewpoint, Ti-rich garnets are found in various silica undersaturated alkaline igneous rocks (Huggins et al. 1977a, 1977b; Dingwell and Brearley 1985; Gwalani et al. 2000; Saha et al. 2011) and are related to alkali metasomatism and magmatism of carbonatitic affinity (Platt and Mitchell 1979; Deer et al. 1982).

Depending on the species occupying the crystallographic sites, they may be used as tracers of magma evolution (Lupini et al. 1992; Gwalani et al. 2000; Brod et al. 2003), as indicators of fO2, fH2O, and other thermodynamic parameters active during the mineral crystallization. In addition, their crystal chemistry is recognized to affect the partitioning of trace elements between the garnets and the melt, and this information can be used to constrain petrogenetic processes in planetary interiors (Dwarzski et al. 2006).

However, the determination of the correct crystal chemistry of garnets is very complex because of the great number of sub-
stuting cations over the three independent crystallographic sites and, with particular regards to Ti-rich garnets, of the multiple oxidation states and coordination environments of transition elements such as Fe and Ti. This topic has been thoroughly reviewed by Grew et al. (2013), also in view of the relevant implications for classification and nomenclature of garnets.

Ti-garnets may also incorporate hydrogen, fluorine, and lithium in trace but measurable amounts. In particular, the OH-bearing garnets may be a reservoir of hydrogen in the Earth’s mantle and may also affect the evolution of the hydrosphere through its influence on mantle melting and isotopic fractionation (Bell et al. 2004).

Quantitative analysis of trace hydrogen is therefore necessary for a better understanding of its role in geological processes but, unfortunately, there is no routine method to obtain this information. For instance, the hydrogen content (conventionally quantified as H₂O, wt%) in schorlomites and Ti-andradites was often estimated from the summed integrated OH⁻ absorbance in the infrared spectra using a wavenumber-dependent calibration (Lager et al. 1989; Müntener and Hermann 1994; Locock et al. 1995; Amthauer and Rossman 1998; Katerinopoulou et al. 2009; Phichaijamjornwut et al. 2011). Actually, it has been demonstrated that the choice of a calibration method for garnets is not unambiguous since considerable discrepancies exist among the available calibrations (e.g., Maldener et al. 2003). The hydrogen content of titanian andradites from Sanbagawa metamorphic rocks (Central Japan), melilitic rocks of the Osečná complex (Bohemia), and schorlomites from Afrikanda (Kola Peninsula) silicocarbonatite was measured, respectively, by means of wet analysis, gravimetry, and combustion (Onuki et al. 1982; Ulyrch et al. 1994; Chakhmouradian and McCammon 2005). Küblerger et al. (1989) used the solid’s moisture analyzer to determine the water content in synthetic Ti-andradite.

Multiple mechanisms have been proposed to describe the hydrogen uptake in garnets. The hydrogarnet substitution (4H + 2SiO₄ → 2H₂O) to the tetrahedral site, was often invoked because only the Z but also the Y, X, and interstitial Ti-free, Li-rich garnets it was proposed that lithium occupies not only the Z but also the Y, X, and interstitial 96h sites (Cussen et al. 2006; Cempirek et al. 2010). These garnets have high-ionic conductivity (e.g., Wang and Lai 2012) or notable implications as a geobarometer (Yang et al. 2009).

In the present study, hydrogen, fluorine, and lithium were measured in a suite of Ti-garnets from various rock types by means of secondary ion mass spectrometry (SIMS). This technique was only previously used to derive an H₂O calibration curve employing, however, garnets with pyralspite composition, whose hydrogen abundance were determined by manometry and IR measurements (Koga et al. 2003).

The results of SIMS, electron microprobe analysis (EPMA), X-ray powder diffraction (XRPD), single-crystal X-ray diffraction (SCXRD), and Mössbauer spectroscopy have been integrated in the present study of Ti garnets of different origin and provenance to provide a comprehensive crystal chemical characterization of the studied samples.

### Materials and Methods

#### Samples

The analyzed samples are from different geologic environments: magmatic alkaline, carbonatitic, and metamorphic rocks. The details of samples origin and provenance are reported in Table 1. Most of the analyzed samples have been previously partially characterized and the relevant results published in the papers reported in the last column of Table 1. In the present work, for the first time a full crystal chemical characterization is accomplished for W6 and W16 samples. In addition, a re-examination of the crystal-chemical formulas of W12, NZALA, and ZER2 samples, previously studied by some of the authors, is here proposed on the basis of EPMA, SIMS, XRPD, and SCXRD measurements on new crystals. Non-routine chemical analysis (EPMA with the Flank method, SIMS see below) is reported for the first time on the whole suite of study samples as well as the results of XRPD measurements.

#### EPMA

Quantitative elemental analyses of the studied crystals (embedded in epoxy resin and polished) were performed with a JEOL JXA-8200 electron microprobe (Dipartimento di Scienze della Terra, University of Milano) operating at 15 kV acceleration voltage, 5 nA beam current, ~1 μm beam size, and 30 s counting time. All the elements were analysed in wavelength-dispersive spectrometry (WDS) mode and the adopted standards were: wollastonite (Si), anorthite (Al, Ca), olivine (Mg), fayalite (Fe), omphacite (Na), ilmenite (Ti), Cr pure (Cr), rhodonite (Mn), and zircon jasorite (Zr). A Phi-Rho-Z routine as implemented in the JEOL suite of programs was used for the matrix correction. Analytical measurements were affected by a relative uncertainty of 1% for major elements and 4% for minor elements. “Flank method” measurements for the determination of the Fe³⁺/ΣFe were carried out with the same electron microprobe as above, in WDS mode, employing a TAP crystal and a 300 μm slit. Feβ and Feα peaks were searched and measured for counting times of 300 s. The correction for self-absorption was applied (Höfer and Brey 2007) and natural synthetic garnet end-members with fixed Fe³⁺/ΣFe were used as standards (Malaspina et al. 2009). The accuracy of the Flank method has been defined by a maximum error of ±0.04 for Fe³⁺/ΣFe in samples with total Fe in the range 8–11wt% (Höfer and Brey 2007).

#### Table 1. Origin, provenance, and literature data of the analyzed samples

<table>
<thead>
<tr>
<th>Label</th>
<th>Provenance</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>W6</td>
<td>Ilavaara, Finland</td>
<td>Howie and Woolley (1968)</td>
</tr>
<tr>
<td>W16</td>
<td>Rusinga Island, Kenya</td>
<td>Howie and Woolley (1968)</td>
</tr>
<tr>
<td>W12</td>
<td>Magnet Cove, Arkansas</td>
<td>Howie and Woolley (1968); Pedrazzi et al. (2002)</td>
</tr>
<tr>
<td>NZALA</td>
<td>Atlas mountains, Morocco</td>
<td>Armbruster et al. (1998); Pedrazzi et al. (2002)</td>
</tr>
<tr>
<td>ZER2</td>
<td>Zermatt, Switzerland</td>
<td>Armbruster et al. (1998); Pedrazzi et al. (2002)</td>
</tr>
</tbody>
</table>
**RESULTS AND DISCUSSION**

**Chemical composition**

EPMA data calculated as average over 4–10 spots are reported in Table 2 together with SIMS data. Indeed, the within grain coefficient of variation (CV) is <10% for all the measured oxides with the exception of Na₂O, ZrO₂, Cr₂O₃, whereas as far as light elements are concerned, it is ~10% for H₂O, generally >50% for Li₂O and variable (4–44%) for the F content.

In particular, the studied Ti-garnets are characterized by variable degree of hydration. SIMS analyses provide H₂O concentration in the range 0.091(7)–0.46(4) wt% (Table 2) which is in agreement (see also Fig. 1) with the values measured for most of the Ti-garnets with andradite, andradite-grossular, andradite-uvarovite, or schorlomite component (Müntener and Hermann 1994; Locock et al. 1995; Amthauer and Rossman 1998; Chakhmouradian and McCammon 2005; Katerinopoulou et al. 2009; Pichchaikamjornwut et al. 2011). However, higher H₂O contents (from 1.25 to 2.90 wt%) were reported for other Ti-garnets (Onuki et al. 1982; Lager et al. 1989; Ulrych et al. 1994; Amthauer and Rossman 1998). Galuskin (2005) calculated, on the basis of charge balance, ~5 wt% H₂O in the “hydrochoromelite,” whereas up to 10 wt% H₂O was estimated from cell dimensions considerations in the “hydrandradite” (Armbruster 1995).

Very low amount of Li₂O (0.0038(2)–0.014(2) wt%) equivalent to 0.001–0.005 atoms per formula unit (apfu) was detected in the studied samples (Table 2). These values are similar to those (0–0.004 apfu) found in Ti-free garnets (Grew et al. 1990). Cempírek et al. (2010) measured 0.019–0.079 Li pfu in almandine from leucocratic granulite of Czech Republic. For

<table>
<thead>
<tr>
<th>Table 2. Chemical composition (wt%) of the studied garnets</th>
</tr>
</thead>
<tbody>
<tr>
<td>W6</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>Na₂O</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>MnO</td>
</tr>
<tr>
<td>FeO</td>
</tr>
<tr>
<td>Al₂O₃</td>
</tr>
<tr>
<td>ZrO₂</td>
</tr>
<tr>
<td>TiO₂</td>
</tr>
<tr>
<td>Cr₂O₃</td>
</tr>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>Total</td>
</tr>
<tr>
<td>H₂O</td>
</tr>
<tr>
<td>Li₂O</td>
</tr>
<tr>
<td>F</td>
</tr>
<tr>
<td>Fe⁺/Fe²⁺</td>
</tr>
<tr>
<td>Fe²⁺/Fe³⁺</td>
</tr>
</tbody>
</table>

a SIMS data.
b From Flank method.
c Calculated on the basis of the charge balance according to Grew et al. (2013) [see details in the text].
Regarding the fluorine concentration, in our samples it ranges from 0.004(1) to 0.040(4) wt% (Table 2), which corresponds to 0.001–0.010 apfu. Literature data indicate F content ranging from 0.004(1) to 0.040(4) wt% (Table 2), which corresponds to 0.001–0.010 apfu. Literature data on W12, NZALA and ZER2 samples (Pedrazzi et al. 2002) are also reported.

Table 3. Mössbauer parameters of W6 and W16 garnets as obtained by Lorentzian fitting and corrected according to Dyar et al. (2012)

<table>
<thead>
<tr>
<th>x'</th>
<th>Site</th>
<th>Species</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>F (mm/s)</th>
<th>A(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W6</td>
<td>0.93</td>
<td>Z</td>
<td>Fe⁴⁺</td>
<td>0.39(6)</td>
<td>0.64(1)</td>
<td>0.38(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z</td>
<td>Fe³⁺</td>
<td>0.20(1)</td>
<td>1.20(5)</td>
<td>0.32(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z</td>
<td>Fe²⁺</td>
<td>0.72(1)</td>
<td>1.77(2)</td>
<td>0.62(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z</td>
<td>Fe¹⁺</td>
<td>0.40(4)</td>
<td>0.61(1)</td>
<td>0.37(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z</td>
<td>Fe⁰⁺</td>
<td>1.3(7)</td>
<td>2.8(3)</td>
<td>0.52(6)</td>
</tr>
<tr>
<td>W16</td>
<td>1.40</td>
<td>Z</td>
<td>Fe⁴⁺</td>
<td>0.22(1)</td>
<td>1.28(6)</td>
<td>0.37(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z</td>
<td>Fe³⁺</td>
<td>0.72(1)</td>
<td>1.68(2)</td>
<td>0.46(6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z</td>
<td>Fe²⁺</td>
<td>0.39(5)</td>
<td>0.617(6)</td>
<td>0.326(5)</td>
</tr>
<tr>
<td>W12⁺</td>
<td>1.29</td>
<td>Z</td>
<td>Fe⁴⁺</td>
<td>0.22(1)</td>
<td>1.208(4)</td>
<td>0.40(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z</td>
<td>Fe³⁺</td>
<td>0.40(5)</td>
<td>0.597(3)</td>
<td>0.331(6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z</td>
<td>Fe²⁺</td>
<td>0.20(1)</td>
<td>1.253(3)</td>
<td>0.318(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z</td>
<td>Fe¹⁺</td>
<td>0.70(1)</td>
<td>1.66(1)</td>
<td>0.25(9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z</td>
<td>Fe⁰⁺</td>
<td>1.28(8)</td>
<td>2.91(2)</td>
<td>0.48(2)</td>
</tr>
<tr>
<td>ZER2⁺</td>
<td>1.16</td>
<td>Y</td>
<td>Fe⁴⁺</td>
<td>0.39(9)</td>
<td>1.582(3)</td>
<td>0.312(4)</td>
</tr>
</tbody>
</table>

Notes: x' = reduced χ² = χ²/degrees of freedom. Literature data on W12, NZALA and ZER2 samples (Pedrazzi et al. 2002) are also reported.

aData from Pedrazzi et al. (2002).

Iron speciation

The iron oxidation state was determined both via electron microprobe analysis [the Flank method (Höfer and Brey 2007)] and Mössbauer spectroscopy. Specifically, the Flank method was used on the same single crystals that underwent structure refinement, whereas Mössbauer analyses were carried out on powders of the W6 and W16 samples. The results are reported, respectively, in Tables 2 and 3. Mössbauer spectra of samples W6 and W16 are in Figures 2a and 2b, whereas comparison between Mössbauer and Flank method is in Figure 3. In Table 3 Mössbauer data on W12, NZALA, and ZER2 samples from previous work (Pedrazzi et al. 2002) are also reported for comparison. The fitting of the room-temperature Mössbauer spectra (Fig. 2) allowed to identify different iron species: Fe³⁺, Fe⁴⁺, Fe⁵⁺, Fe³⁺, and Fe⁴⁺. The assignment and the values of the hyperfine parameters (Table 3) are in agreement with the results of previous investigations on Ti-garnets (Ortalli et al. 1994; Pedrazzi et al. 1998, 2002; Scordari et al. 1999; Schingaro et al. 2004; Dyar et al. 1995; Chakhmouradian and McCammon 2005), but its interpretation is still uncertain and, recently, Chakhmouradian and
The qualitative analysis evidenced that no phase impurity occurs. However, splitting or asymmetry of the diffraction peaks was observed, suggesting the presence of different garnet phases with similar unit-cell parameters (Fig. 5). Indeed in all samples, at least two cubic garnet phases were detected. (Color online.)

**Structural features**

**XRPD results.** The X-ray powder diffraction analysis was performed on all the study samples (see the patterns in Fig. 4) with the exception of ZER2, whose amount was too scarce to be measured. The qualitative analysis evidenced that no phase impurity occurs. However, splitting or asymmetry of the diffraction peaks is observed, suggesting the presence in our powders of different garnet phases with similar unit-cell parameters (Fig. 5). Indeed in all samples, at least two cubic garnet phases (labelled phase I and II on the basis of the relative abundances) were clearly distinguished and their weight fractions and cell parameters were refined using GSASII; the results are shown in Table 4. In the case of W6 and W16 samples, a third phase seems to be present (Fig. 5), but the attempts to refine it were unsuccessful. These results are in agreement with recent findings relevant to the study of optical anomalies in garnets. In particular, these studies have shown that both Ti-bearing and Ti-free garnets can actually be a mixture of two or more cubic phases with slightly different cell parameters and composition (Antao 2013, 2014; Antao and Klincker 2013; Antao and Round 2014).

The consequent structural mismatch causes strain that results in low-to-strong degree of optical anisotropy (birefringence). In our case, the garnets appear not completely extinct upon observation under cross-polarized light, but did not show difference in chemical composition at least at the EPMA scale (see above). Similar results were reported for a Ti-andradite from Magnet Cove (Antao 2013). In brief, anomalous optical behavior is due to intergrowth of more than one cubic phase, that, if occurs at a fine scale, leads to homogeneous EPMA data, whereas at a large scale should be detected as a slight variation of chemical composition. To the best of our knowledge, it is the first time that a mixture of cubic phases has been detected for Ti-garnets with laboratory instrumentation. In addition, data in Table 4 show that the dominant phase of the mixture (phase I) has, in most cases, unit-cell parameters similar to those obtained from the relevant samples in SCXRD analysis (see below).

**SCXRD results.** The main results of SCXRD investigation, in particular about crystal data, data-collection parameters, and figures of merit on structure refinements, are also summarized in Table 4. Refined site positions, atomic occupancies, and anisotropic displacement parameters are listed in Table 5, whereas distances and distortional parameters are reported in Table 6. (CIF is available.)

All structure refinements converged to good values of the discrepancy factors: $1.65 \leq R_1 \leq 2.09\%$ and $2.35 \leq wR_2 \leq 3.02\%$.

The cell-edges variation of the analyzed crystals (Table 4) reflects different Ti contents (Table 2), a correlation already pointed out by Howie and Woolley (1968). In particular, a positive trend of the $a$ parameter vs. the TiO$_2$ content has been found (Fig. 6). However, by inspection of Figure 7 it is evident that the $a$-cell parameter increment depends on the increase of both the $<X-O>$ ($R^2 = 0.90$ in Fig. 7a) and $Z-O$ ($R^2 = 0.86$ in Fig. 7c), whereas the dependence from the Y-O variation seems to be negligible ($R^2 = 0.004$ in Fig. 7b). Since the X-site composition is almost constant in the study samples (see Table 7), the increase of $<X-O>$ is induced by the polyhedral edge-sharing (X/Z) occurring in the garnet structure.

From Table 6 it can be noticed that the $\Delta(X-O)$ and $\alpha$ values are in the range of variability for the known natural silicate garnets (Ungaretti et al. 1995; Yang et al. 2009). The tendency to the decrease of $\Delta(X-O)$ with increasing Fe$^{3+}$ content along the grossular-andradite join (Ungaretti et al. 1995) is also present in our samples, where it appears also related to the Fe$^{3+}$+Ti content.

**Figure 3.** Comparison between Fe$^{3+}$/ΣFe as determined by Mössbauer spectroscopy and Flank method. The 1:1 line is shown. The error bars for Fe$^{3+}$/ΣFe correspond, respectively, to $\sigma = 3\%$ for the Flank method (Malaspina et al. 2012) and $\sigma = 3\%$, the latter being the maximum error for Mössbauer data (Dyar et al. 2008).

**Figure 4.** XRD patterns of the W6, W12, W16, and NZALA samples. (Color online.)

---

1 Deposit item AM-16-25459, CIF. Deposit items are free to all readers and found on the MSA web site, via the specific issue’s Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/).
Octahedral and tetrahedral sites in garnets are variously distorted, as evident from the analysis of octahedral angle variance and tetrahedral angle variance (OAV and TAV, Table 6), which quantifies the deviation from the ideal value of 90° and 109.47°, respectively, of the relevant polyhedra (Table 6, Figs. 8 and 9). In particular, the tetrahedron is the most distorted polyhedron in garnets and the distortion increases with increasing the Z (Fe²⁺ + Al³⁺ + Fe³⁺ + Ti) content (Fig. 8). On the other hand, since each tetrahedron in the garnet structure shares edges with two dodecahedra, the shared O-O tetrahedral edges, S(Z), are always shorter than the unshared ones, U(Z) and, at the same time, the tetrahedron is elongated along the 4 axis (see tSZ, the distance between shared edges in Table 6) for a better screening of the repulsive interaction between the X and Z cations. The octahedron is most distorted in grossular and becomes more regular with the entrance of high charge cations or of trivalent cations different from Al³⁺ (Fig. 9). In addition, substitutions at Y affect the tSY parameter in that, starting from pure grossular, where the octahedron is flattened along the 3 axis, if a cation larger than Al occurs at Y the octahedron tends to elongate along the same axis, as also observed by other authors (Ungaretti et al. 1995).

The ZER2 sample has bond distances and distortion parameters very similar to that of pure andradite (Adamo et al. 2011). For instance, for this sample the <D-O> parameter (2.131 Å) is identical to that of the pure andradite (2.132 Å, Adamo et al. 2011) and is a consequence of its short Z-O distance (Table 6), indicating a low extent of substitution at the Z site. The increase in the Z-O distances in the other samples accounts for a greater extent of schorlomitic and hydrogarnet substitutions. These features entail the increase of the <D-O> parameters up to values close to that (2.186 Å) of kimzeyite of Schingaro et al. (2001), see Table 6.

Crystal chemical formulas

Grew et al. (2013) suggested a procedure to perform a cation distribution for Ti-garnets basing only on chemical data; the results obtained using their spreadsheet are reported in Table 7. In the same table we also reported the structural formulas of the study garnets, obtained using a multimethodic approach adopted in the present work. Specifically, they were calculated combining the EPMA-SIMS data with the Mössbauer results. The latter were considered representative of the single crystals. This assumption is generally sensible, on the basis of the Flank method analysis (see above). From the two sets of crystal chemical formulas, mean atomic numbers as well as bond distances using ionic radii from Shannon (1976) have been calculated. These values are shown in Table 8 where they are compared with those derived from the structure refinement.

Samples W12 and ZER2 contain the smallest number of Fe species (¹Fe⁺, ³Fe⁺ the former and only ⁵Fe⁺ the latter, see Table 3) and in particular ZER2 has the simplest composition among the whole suite here considered. Comparison to the formulas derived through the approach devised by Grew et al. (2013) indicates that charge balance tends to overestimate the
TABLE 4. Powder and single-crystal X-ray diffraction data of the studied garnets

<table>
<thead>
<tr>
<th>Sample</th>
<th>Site</th>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>U1</th>
<th>U2</th>
<th>U3</th>
</tr>
</thead>
<tbody>
<tr>
<td>W6</td>
<td>Ca</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>1.0000</td>
<td>0.0087</td>
<td>0.0063(2)</td>
<td>0.0099(1)</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>a/4</td>
<td>0</td>
<td>0</td>
<td>0.7304(8)</td>
<td>0.0049</td>
<td>0.0049(1)</td>
<td>0.0049(1)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.8787(1)</td>
<td>0.0056</td>
<td>0.0046(2)</td>
<td>0.0059(2)</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.3727(3)</td>
<td>0.0049</td>
<td>0.0038(4)</td>
<td>0.0038(4)</td>
</tr>
<tr>
<td>W12</td>
<td>Ca</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>1.0000</td>
<td>0.0078</td>
<td>0.0058(2)</td>
<td>0.0088(2)</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>a/4</td>
<td>0</td>
<td>0</td>
<td>0.7321(8)</td>
<td>0.0044</td>
<td>0.0044(2)</td>
<td>0.0044(2)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.9362(2)</td>
<td>0.0041</td>
<td>0.0038(3)</td>
<td>0.0043(3)</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.6451(4)</td>
<td>0.0052</td>
<td>0.0034(4)</td>
<td>0.0034(4)</td>
</tr>
<tr>
<td>W16</td>
<td>Ca</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>1.0000</td>
<td>0.0085</td>
<td>0.0059(1)</td>
<td>0.0099(1)</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>a/4</td>
<td>0</td>
<td>0</td>
<td>0.7291(8)</td>
<td>0.0045</td>
<td>0.0045(1)</td>
<td>0.0045(1)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.8597(2)</td>
<td>0.0052</td>
<td>0.0042(2)</td>
<td>0.0057(2)</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.1435(3)</td>
<td>0.0052</td>
<td>0.0042(2)</td>
<td>0.0057(2)</td>
</tr>
<tr>
<td>NZALA</td>
<td>Ca</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>1.0000</td>
<td>0.0083</td>
<td>0.0062(1)</td>
<td>0.0094(1)</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>a/4</td>
<td>0</td>
<td>0</td>
<td>0.7932(9)</td>
<td>0.0050</td>
<td>0.0050(1)</td>
<td>0.0050(1)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.9121(2)</td>
<td>0.0052</td>
<td>0.0045(2)</td>
<td>0.0055(2)</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.2071(3)</td>
<td>0.0052</td>
<td>0.0045(2)</td>
<td>0.0055(2)</td>
</tr>
<tr>
<td>ZER2</td>
<td>Ca</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>1.0000</td>
<td>0.0064</td>
<td>0.0046(2)</td>
<td>0.0074(1)</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>a/4</td>
<td>0</td>
<td>0</td>
<td>0.7921(9)</td>
<td>0.0046</td>
<td>0.0046(2)</td>
<td>0.0046(2)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.2081(3)</td>
<td>0.0052</td>
<td>0.0045(2)</td>
<td>0.0055(2)</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.0049</td>
<td>0.0052</td>
<td>0.0043(2)</td>
<td>0.0052(2)</td>
</tr>
</tbody>
</table>

TABLE 5. Crystallographic coordinates, site occupancies, equivalent/isotropic (Å²), and anisotropic displacement parameters (Å²) of the studied crystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Site</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U1</th>
<th>U2</th>
<th>U3</th>
</tr>
</thead>
<tbody>
<tr>
<td>W6</td>
<td>Ca</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>1.0000</td>
<td>0.0087</td>
<td>0.0063(2)</td>
<td>0.0099(1)</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>a/4</td>
<td>0</td>
<td>0</td>
<td>0.7304(8)</td>
<td>0.0049</td>
<td>0.0049(1)</td>
<td>0.0049(1)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.8787(1)</td>
<td>0.0054</td>
<td>0.0046(2)</td>
<td>0.0059(2)</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.3727(3)</td>
<td>0.0058</td>
<td>0.0046(2)</td>
<td>0.0059(2)</td>
</tr>
<tr>
<td>W12</td>
<td>Ca</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>1.0000</td>
<td>0.0078</td>
<td>0.0058(2)</td>
<td>0.0088(2)</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>a/4</td>
<td>0</td>
<td>0</td>
<td>0.7321(8)</td>
<td>0.0044</td>
<td>0.0044(2)</td>
<td>0.0044(2)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.9362(2)</td>
<td>0.0041</td>
<td>0.0038(3)</td>
<td>0.0043(3)</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.6451(4)</td>
<td>0.0052</td>
<td>0.0034(4)</td>
<td>0.0034(4)</td>
</tr>
<tr>
<td>W16</td>
<td>Ca</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>1.0000</td>
<td>0.0085</td>
<td>0.0059(1)</td>
<td>0.0099(1)</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>a/4</td>
<td>0</td>
<td>0</td>
<td>0.7291(8)</td>
<td>0.0045</td>
<td>0.0045(1)</td>
<td>0.0045(1)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.8597(2)</td>
<td>0.0052</td>
<td>0.0042(2)</td>
<td>0.0057(2)</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.1435(3)</td>
<td>0.0052</td>
<td>0.0042(2)</td>
<td>0.0057(2)</td>
</tr>
<tr>
<td>NZALA</td>
<td>Ca</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>1.0000</td>
<td>0.0083</td>
<td>0.0062(1)</td>
<td>0.0094(1)</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>a/4</td>
<td>0</td>
<td>0</td>
<td>0.7932(9)</td>
<td>0.0050</td>
<td>0.0050(1)</td>
<td>0.0050(1)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.9121(2)</td>
<td>0.0052</td>
<td>0.0045(2)</td>
<td>0.0055(2)</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.2071(3)</td>
<td>0.0052</td>
<td>0.0045(2)</td>
<td>0.0055(2)</td>
</tr>
<tr>
<td>ZER2</td>
<td>Ca</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>1.0000</td>
<td>0.0064</td>
<td>0.0046(2)</td>
<td>0.0074(1)</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>a/4</td>
<td>0</td>
<td>0</td>
<td>0.7921(9)</td>
<td>0.0046</td>
<td>0.0046(2)</td>
<td>0.0046(2)</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.2081(3)</td>
<td>0.0052</td>
<td>0.0045(2)</td>
<td>0.0055(2)</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>a/4</td>
<td>0</td>
<td>1/4</td>
<td>0.0049</td>
<td>0.0052</td>
<td>0.0043(2)</td>
<td>0.0052(2)</td>
</tr>
</tbody>
</table>

"Fe" specie. For example, for the ZER2 garnet, both the Flank method and Mössbauer analysis provide Fe²⁺/ΣFe = 100%, whereas from Grew et al. (2013) Fe³⁺/ΣFe = 86% is estimated (see Tables 2, 3, 7 and Fig. 3). Comparison to the crystallographic data (Table 8) shows that a better agreement is obtained with our multi-methodic approach for the Y site, that allows a better modeling of this site in terms of mean atomic number as well as bond distances. In particular good agreement is found between the Y-O distance derived from the X-ray refinement (Y-O_Crystal) and that calculated from the EPMA (Y-O_EPMA) with Δ = (Y-O_Crystal) − (Y-O_EPMA) = 0.008 Å (see Table 8). On the contrary, if the approach in Grew et al. (2013) is used, Δ increases to 0.021 Å. Note that the use of the directly measured iron speciation implies that the Y site hosts significant amount of Ti³⁺, as pre-
Table 6. Refined bond distances (Å) and distortional parameters of the studied samples, selected literature Ti-garnets and natural end-member garnets

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>X-O</td>
<td>2.371(1)</td>
<td>2.366(1)</td>
<td>2.371(1)</td>
<td>2.364(1)</td>
<td>2.362(1)</td>
<td>2.369(1)</td>
<td>2.365(1)</td>
<td>2.361(1)</td>
</tr>
<tr>
<td>X-O</td>
<td>2.495(1)</td>
<td>2.498(1)</td>
<td>2.471(1)</td>
<td>2.463(1)</td>
<td>2.434(1)</td>
<td>2.439(1)</td>
<td>2.439(1)</td>
<td>2.436(1)</td>
</tr>
<tr>
<td>Y-O</td>
<td>2.088(1)</td>
<td>2.088(1)</td>
<td>2.101(1)</td>
<td>2.012(1)</td>
<td>2.009(1)</td>
<td>2.013(1)</td>
<td>2.014(1)</td>
<td>1.999(1)</td>
</tr>
<tr>
<td>Z-O</td>
<td>1.684(1)</td>
<td>1.671(1)</td>
<td>1.681(1)</td>
<td>1.661(1)</td>
<td>1.661(1)</td>
<td>1.666(1)</td>
<td>1.669(1)</td>
<td>1.670(1)</td>
</tr>
<tr>
<td>tO−(Å)</td>
<td>2.145</td>
<td>2.139</td>
<td>2.145</td>
<td>2.136</td>
<td>2.131</td>
<td>2.140</td>
<td>2.137</td>
<td>2.135</td>
</tr>
<tr>
<td>Δ(X-O)</td>
<td>0.147</td>
<td>0.138</td>
<td>0.145</td>
<td>0.143</td>
<td>0.137</td>
<td>0.139</td>
<td>0.146</td>
<td>0.149</td>
</tr>
<tr>
<td>S(Y)</td>
<td>0.259</td>
<td>0.471</td>
<td>0.329</td>
<td>0.705</td>
<td>0.973</td>
<td>0.579</td>
<td>0.969</td>
<td>0.580</td>
</tr>
<tr>
<td>S(Z)</td>
<td>2.851</td>
<td>2.858</td>
<td>2.855</td>
<td>2.867</td>
<td>2.863</td>
<td>2.868</td>
<td>2.871</td>
<td>2.845</td>
</tr>
<tr>
<td>U(Y)</td>
<td>2.827</td>
<td>2.825</td>
<td>2.828</td>
<td>2.827</td>
<td>2.816</td>
<td>2.831</td>
<td>2.824</td>
<td>2.809</td>
</tr>
<tr>
<td>tSY</td>
<td>2.298</td>
<td>2.294</td>
<td>2.298</td>
<td>2.292</td>
<td>2.280</td>
<td>2.297</td>
<td>2.287</td>
<td>2.279</td>
</tr>
<tr>
<td>tSZ</td>
<td>2.338</td>
<td>2.347</td>
<td>2.343</td>
<td>2.357</td>
<td>2.357</td>
<td>2.356</td>
<td>2.363</td>
<td>2.338</td>
</tr>
<tr>
<td>ψ(°)</td>
<td>133.55</td>
<td>133.42</td>
<td>133.53</td>
<td>133.49</td>
<td>133.64</td>
<td>133.39</td>
<td>133.70</td>
<td>133.81</td>
</tr>
<tr>
<td>V(V)</td>
<td>2.42</td>
<td>2.368</td>
<td>2.408</td>
<td>2.324</td>
<td>2.31</td>
<td>2.348</td>
<td>2.312</td>
<td>2.358</td>
</tr>
<tr>
<td>TAV(°)</td>
<td>33.847</td>
<td>30.567</td>
<td>32.915</td>
<td>31.801</td>
<td>29.135</td>
<td>31.102</td>
<td>31.803</td>
<td>32.615</td>
</tr>
<tr>
<td>S(Z)</td>
<td>2.618</td>
<td>2.605</td>
<td>2.615</td>
<td>2.587</td>
<td>2.586</td>
<td>2.596</td>
<td>2.582</td>
<td>2.598</td>
</tr>
<tr>
<td>U(Z)</td>
<td>2.813</td>
<td>2.789</td>
<td>2.807</td>
<td>2.773</td>
<td>2.764</td>
<td>2.781</td>
<td>2.768</td>
<td>2.788</td>
</tr>
<tr>
<td>tUZ</td>
<td>2.118</td>
<td>2.094</td>
<td>2.112</td>
<td>2.085</td>
<td>2.073</td>
<td>2.089</td>
<td>2.081</td>
<td>2.097</td>
</tr>
<tr>
<td>tXZ</td>
<td>1.851</td>
<td>1.842</td>
<td>1.849</td>
<td>1.829</td>
<td>1.828</td>
<td>1.836</td>
<td>1.826</td>
<td>1.837</td>
</tr>
</tbody>
</table>

Notes: <D-O> = [(Z-O) + (Y-O) + (X1-O) + (X2-O)]/4 according to Antao (2013); Volume of X, Y, and Z sites calculated using the IVTON software (Balić-Žunić and Hermann 1994; 175, 274, 275, 276 crystals in Merli et al. 2005) this species is taken into account by Grew et al. (2013) in the Magnet Cove andradite from Antao (2013). In addition, circle with vertical line indicates the single crystal is not representative of the powder. Several cation distributions have been checked, until the best fit to the data from different techniques was obtained (see Tables 2 and 3). Although a general good agreement with X-ray data is observed for both formulas, the difference between Y-O_EPMA and Y-O_X-ref distances gives <0.01 Å in our case and ~0.02 Å considering only chemical data (see Table 8). Notice that the calculated and measured Fe3+/ΣFe values are very similar (see Tables 2 and 3). The difference between cell parameter from single crystal and powder is Δa ≈ -0.01–0.02 Å. The above evidences indicate that the single crystal is not representative of the powder. Schingaro et al. (2013) was adopted. For sample NZALA, which contains negligible Fe2+, our distribution and the one from Grew et al. (2013) are almost identical. Notice that the calculated and measured Fe3+/ΣFe values are very similar (see Tables 2 and 3). Although a general good agreement with X-ray data is observed for both formulas, the difference between Y-O_EPMA and Y-O_X-ref distances gives <0.01 Å in our case and ~0.02 Å considering only chemical data (see Table 8). For sample W6, Mössbauer and charge balance derived Fe3+/ΣFe coincide, whereas a discrepancy is observed with respect to the value determined via the Flank method (see Tables 2 and 3 and Fig. 3). The difference between cell parameter from single crystal and powder is Δa ≈ 0.01–0.02 Å. The above evidences indicate that the single crystal is not representative of the powder. Several cation distributions have been checked, until the best fit to the data from different techniques was obtained by considering Fe3+/ΣFe from Flank method and the iron site population from Mössbauer. Sample W6 has ferrous iron only at tetrahedral site. As in previous sample, inspection of Table 4 evidences that the single crystal has cell parameter shorter than those found in the powder.
(Δa = 0.01–0.02 Å). Accordingly, for the study single crystal a lower degree of tetrahedral substitution is expected with respect to the analysed powders. The best fit to all the experimental data is obtained varying the $^{5}$Fe$^{2+}$ component within one standard deviation.

The main substitution mechanisms affecting the studied garnets are:

1. $^{1}$R$^{4+}$ + $^{1}$R$^{3+}$ ↔ $^{2}$Si + $^{1}$Y$^{3+}$ (schorlomite substitution);
2. $^{1}$Y$^{3+}$ + $^{1}$R$^{4+}$ ↔ $^{2}$R$^{3+}$ (morio site substitution);
3. $^{1}$R$^{3+}$ ↔ $^{1}$Y$^{2+}$ (andradite substitution);

where $^{2}$R$^{3+}$ = Fe$^{2+}$, Mg$^{2+}$, Mn$^{2+}$; $^{1}$R$^{4+}$ = Ti; $^{1}$Y$^{3+}$ = Fe$^{3+}$, Al$^{3+}$, Cr$^{3+}$; $^{2}$R$^{3+}$ = Fe$^{3+}$, Al$^{3+}$.

Minor substitutions, such as:

- (a) $^{2}$Ti$^{4+}$ + $^{2}$Fe$^{2+}$ ↔ $^{2}$Fe$^{3+}$ + $^{2}$Si;
- (b) (SiO$_4$)$^{4-}$ ↔ (O$_4$H$_4$)$^{4-}$;
- (c) F$^{-}$ ↔ OH$^{-}$;
- (d) $^{4}$R$^{4+}$ + $^{4}$R$^{3+}$ ↔ $^{4}$R$^{5+}$ + $^{4}$Ca$^{2+}$;

with $^{1}$R$^{4+}$ = Ti, Zr; $^{1}$Y$^{3+}$ = Fe$^{3+}$, Al, Cr$^{3+}$; $^{2}$R$^{3+}$ = Na, Li also occur. On the whole, light elements, although occurring in detectable amounts, do not play a significant crystal chemical role. No systematic trend was here evidenced from the analysis of Ti and water content in relation to the garnets host rocks (see also Fig. 1).

For a better crystal-chemical comparison, in Table 7, in addition to the structural formulas derived for the samples under study, also formulas taken from the literature are reported, selected to include natural end-member garnets (grossular, Novak and Gibbs 1971; andradite, Adamo et al. 2011) as well as Z-substituted Ti garnets for which cation partition was provided on the basis of evidences from multiple methods-combination of chemical and/or X-ray diffraction and/or spectroscopic data (Müntener and Hermann 1994, Ulrych et al. 1994, Locock et al. 1995, Scordari et al. 1999, Schingaro et al. 2001; Chakhmouradian and McCammon 2005; Katerinopoulou et al. 2009; Antao 2013, 2014). It can be seen that the chemical complexity of Ti-garnets is such that every sample has to be considered on a one to one basis. In some cases, to get the best agreement, with X-ray data, Ti has to be distributed over octahedral and tetrahedral site (sample W6 and W16, this work; Scordari et al. 1999; Katerinopoulou et al. 2009). Evidence of the occurrence of Ti at Z site have been reported by Malitesta et al. (1995) and Armbruster et al. (1998) for garnets with similar composition, as well as in Si-poor natural garnets, like elbrusite and bitikleite (Galuskina et al. 2010a, 2010b). The Ti valence state is a controversial topic in the Ti-garnets literature and has been thoroughly reviewed by Grew et al. (2013). In particular, in natural Ti-garnets, Malitesta et al. (1995) found significant Ti$^{3+}$ using X-ray photoelectron spectroscopy (XPS), whereas Waychunas (1987) and Locock et al. (1995) detected low or negligible Ti$^{3+}$ via X-ray absorption near edge structure (XANES) spectroscopy. This discrepancy may be due to a greater contribution of the mineral surface in the case of XPS (Grew et al. 2013) as well as to the problems in the interpretation of XPS signals related to the adopted method of background removing (Guascito et al. 2014). In the present work, the Ti speciation has not been determined by direct measurements, but it was constrained indirectly through the quantification of the water content, the determination of the iron oxidation state and the balance of the substitution mechanisms in garnets.

The two approaches discussed above and used to calculate the crystal-chemical formulas lead to a different classification of the study samples as shown in the plot of Figure 10. In particular, when the only chemical data are used, the samples fall in the schorlomite field together with the Afrikanda schorlomite (Chakhmouradian and McCammon 2005) and the morimotoite (Antao 2014). On the contrary, when the multimethodic approach is used, the study garnets plot in the andradite field very close to most of the considered literature garnets (Müntener and Hermann...
1994; Ulyrych et al. 1994; Locock et al. 1995; Amthauer and Rossman 1998; Katerinopoulou et al. 2009; Phichaikamjornwut et al. 2011; Antao 2013). Notice that kimzeyite sample investigated by Schingaro et al. (2001) should be classified as belonging to the garnet group rather than to schorlomite group. Generally speaking, the approach to the garnet crystal chemical formula proposed by Grew et al. (2013) is effective and constitutes a good starting point in absence of other information, but then the obtained formula needs to be refined by comparison at least to X-ray data and possibly also to element specific techniques selected depending on the peculiar composition of the sample. Major chemical variability is, indeed, observed for the Y site, which is why a totally chemical approach is here found to have problems with the modeling cation distribution at the Y site.

**TABLE 7.** Structural formulas in atoms per formula unit (apfu) of the studied samples, selected literature Ti-garnets and natural end-member garnets

<table>
<thead>
<tr>
<th>Sample</th>
<th>X site</th>
<th>Y site</th>
<th>Z site</th>
</tr>
</thead>
<tbody>
<tr>
<td>W6</td>
<td>(Ca\textsubscript{4.20}Mg\textsubscript{0.80}Na\textsubscript{0.30}Al\textsubscript{0.20})\textsubscript{Σ=4.12}</td>
<td>(Mg\textsubscript{0.99}Fe\textsubscript{0.01}Al\textsubscript{0.13}Ti\textsubscript{0.60}Zr\textsubscript{0.12})\textsubscript{Σ=2.12}</td>
<td>(Si\textsubscript{2.30}Al\textsubscript{0.81}Fe\textsubscript{3.00})\textsubscript{Σ=3.00}</td>
</tr>
<tr>
<td>W12</td>
<td>(Ca\textsubscript{4.20}Fe\textsubscript{0.80}Fe\textsubscript{0.01}Na\textsubscript{0.30})\textsubscript{Σ=4.12}</td>
<td>(Mg\textsubscript{0.99}Fe\textsubscript{0.01}Al\textsubscript{0.13}Ti\textsubscript{0.60}Zr\textsubscript{0.12})\textsubscript{Σ=2.12}</td>
<td>(Si\textsubscript{2.30}Al\textsubscript{0.81}Fe\textsubscript{3.00})\textsubscript{Σ=3.00}</td>
</tr>
<tr>
<td>W16</td>
<td>(Ca\textsubscript{4.20}Fe\textsubscript{0.80}Fe\textsubscript{0.01}Na\textsubscript{0.30})\textsubscript{Σ=4.12}</td>
<td>(Mg\textsubscript{0.99}Fe\textsubscript{0.01}Al\textsubscript{0.13}Ti\textsubscript{0.60}Zr\textsubscript{0.12})\textsubscript{Σ=2.12}</td>
<td>(Si\textsubscript{2.30}Al\textsubscript{0.81}Fe\textsubscript{3.00})\textsubscript{Σ=3.00}</td>
</tr>
<tr>
<td>NZALA</td>
<td>(Ca\textsubscript{4.20}Fe\textsubscript{0.80}Fe\textsubscript{0.01}Na\textsubscript{0.30})\textsubscript{Σ=4.12}</td>
<td>(Mg\textsubscript{0.99}Fe\textsubscript{0.01}Al\textsubscript{0.13}Ti\textsubscript{0.60}Zr\textsubscript{0.12})\textsubscript{Σ=2.12}</td>
<td>(Si\textsubscript{2.30}Al\textsubscript{0.81}Fe\textsubscript{3.00})\textsubscript{Σ=3.00}</td>
</tr>
<tr>
<td>ZER2</td>
<td>Ca\textsubscript{1.990}Mg\textsubscript{0.015}Mn\textsubscript{0.003}Fe\textsubscript{2.90}</td>
<td>(Mg\textsubscript{0.99}Fe\textsubscript{0.01}Al\textsubscript{0.13}Ti\textsubscript{0.60}Zr\textsubscript{0.12})\textsubscript{Σ=2.12}</td>
<td>(Si\textsubscript{2.30}Al\textsubscript{0.81}Fe\textsubscript{3.00})\textsubscript{Σ=3.00}</td>
</tr>
</tbody>
</table>

**FIGURE 7.** Plot of a cell parameter vs. <X-O> (a), Y-O (b), and Z-O (c) distances of Ti-garnets. Symbols as in Figure 6.

**IMPLICATIONS**

Garnet is a widespread mineral stable in wide range of temperature (from <300 to 2000 °C) and pressure (from ambient pressure to 25 GPa). The renewed interest in the garnet species is testified by a recent issue of *Elements* [vol. 9(6), December 2013] devoted to the garnet supergroup of minerals. The relative structural formulas in atoms per formula unit (apfu) of the studied samples, selected literature Ti-garnets and natural end-member garnets.
evance of elemental substitutions in determining the properties of garnets has been highlighted in Grew et al. (2013), Geiger (2013), and Antao (2013). In particular, Grew et al. (2013) evidence that recently (2009–2010) 10 new garnet species with unusual constituents were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association and the 32 approved species also encompass three ungrouped species but new species are expected due to the extreme compositional variations in natural garnets. Geiger (2013), other than reviewing synthetic non-silicate garnets and the relevant technological employment, stresses the significance of studying substitutional solid solutions in natural garnets. Cation substitutions involve strain fields resulting in structural heterogeneities from the scale of the unit cell to the nanoscale. Structural and chemical bonding properties of garnets are believed to control element partitioning (Wood et al. 2013) and thermodynamic behavior of the garnet solid solutions. For a complete characterization of these phases, both techniques sensitive to long-range ordering (such as X-ray diffraction) and to short range ordering (spectroscopic techniques) are needed. This is the approach adopted in the present work. Regarding natural Ti-garnets, their relevance from a petrological point of view has been mentioned in the introduction section. However, it is generally recognized that determination of cation site population is really complicated for such compositions. In turn, cation exchange mechanisms produce polyhedral distortions, which have been reported here, but unravelling the contribution of each of the multiple substitutions requires further work. In this study, the detailed characterization of substitution mechanisms by single-crystal X-ray diffraction is associated to the observation of structural heterogeneities from the scale of the unit cell to the nanoscale. Structural and chemical bonding properties of garnets are believed to control element partitioning (Wood et al. 2013) and thermodynamic behavior of the garnet solid solutions. For a complete characterization of these phases, both techniques sensitive to long-range ordering (such as X-ray diffraction) and to short range ordering (spectroscopic techniques) are needed. This is the approach adopted in the present work. Regarding natural Ti-garnets, their relevance from a petrological point of view has been mentioned in the introduction section. However, it is generally recognized that determination of cation site population is really complicated for such compositions. In turn, cation exchange mechanisms produce polyhedral distortions, which have been reported here, but unravelling the contribution of each of the multiple substitutions requires further work. In this study, the detailed characterization of substitution mechanisms by single-crystal X-ray diffraction is associated to the observation of structural heterogeneities from the scale of the unit cell to the nanoscale. Structural and chemical bonding properties of garnets are believed to control element partitioning (Wood et al. 2013) and thermodynamic behavior of the garnet solid solutions. For a complete characterization of these phases, both techniques sensitive to long-range ordering (such as X-ray diffraction) and to short range ordering (spectroscopic techniques) are needed. This is the approach adopted in the present work. Regarding natural Ti-garnets, their relevance from a petrological point of view has been mentioned in the introduction section. However, it is generally recognized that determination of cation site population is really complicated for such compositions. In turn, cation exchange mechanisms produce polyhedral distortions, which have been reported here, but unravelling the contribution of each of the multiple substitutions requires further work. In this study, the detailed characterization of substitution mechanisms by single-crystal X-ray diffraction is associated to the observation of structural heterogeneities from the scale of the unit cell to the nanoscale. Structural and chemical bonding properties of garnets are believed to control element partitioning (Wood et al. 2013) and thermodynamic behavior of the garnet solid solutions. For a complete characterization of these phases, both techniques sensitive to long-range ordering (such as X-ray diffraction) and to short range ordering (spectroscopic techniques) are needed. This is the approach adopted in the present work. Regarding natural Ti-garnets, their relevance from a petrological point of view has been mentioned in the introduction section. However, it is generally recognized that determination of cation site population is really complicated for such compositions. In turn, cation exchange mechanisms produce polyhedral distortions, which have been reported here, but unravelling the contribution of each of the multiple substitutions requires further work. In this study, the detailed characterization of substitution mechanisms by single-crystal X-ray diffraction is associated to the observation.
of occurrence of multiple cubic phases from laboratory XRPD data. Even if, in our case, the samples appeared homogeneous at the EPMA scale it is here suggested that compositional differences at the nanoscale may occur, as found by other authors (Antao 2013). These findings, in turn, may have implication for the studied samples whose formulas have been calculated according to CITH3110 samples from Amthauer and Rossman (1998).

**ACKNOWLEDGMENTS**

The authors are grateful to Stefano Poli (University of Milano) for the facilities at the Electron Microprobe Laboratory and Nadia Malaspina for the assistance during the “Flank method” analyses at the Dipartimento di Scienze della Terra, University of Milano. Thomas Armbruster is gratefully thanked for providing NZALA and ZER2 garnet samples. Thanks are due to the Associate Editor, Gatta Giacomo Diego, and to Redhammer Günther Josef and a anonymous Referee that contributed to significantly improve the manuscript.

The XRPD laboratory at the Dipartimento di Scienze della Terra and Geoenvironmental University of Bari “Aldo Moro,” was funded by Potenziamento Strutturale PONa3.00369 “Laboratorio per lo Sviluppo Integrato delle Scienze e delle Tecniche dei Materiali Avanzati e per dispositivi innovativi (SISTEMA).” This work was also supported by the COPIN-MIUR.

**REFERENCES CITED**


Armbruster, T. (1995) Structure refinement of hydrous andradite, Ca$_3$Fe$_{1.54}$Mn$_{0.20}$Al$_{12/3}$SiO$_{32/3}$O$_{12}$, from the Wessels mine, Kalahari manganese field, South Africa. European Journal of Mineralogy, 7, 1221–1225.


Bruker (2003b) SAINT (ver. 7.60A). Bruker AXS Inc., Madison, Wisconsin, USA.

SCHINGARO ET AL.: CRYSTAL CHEMISTRY OF Ti-RICH GARNETS


(1977b) Titanium-containing silicate garnets. II. The crystal chemistry of melilites and schorlomite. American Mineralogist, 62, 646–655.


(1998) RECOIL, Mössbauer Spectral Analysis Software for Windows (version 1.0). Department of Physics, University of Ottawa, Canada.


