Periodico di Mineralogia (2011), 80, 1 (Special Issue), 135-144 DOI: 10.2451/2011PM0011

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on *Environment*, *Archeometry* and *Cultural Heritage*

Special Issue in memory of Sergio Lucchesi

High temperature structure and thermal expansion of $Co_3Al_2Si_3O_{12}$ garnet

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Abstract

Synchrotron radiation powder diffraction patterns were taken on synthetic $Co_3Al_2Si_3O_{12}$ garnet at BM8-GILDA (ESRF), at T = 298, 423, 573, 723 and 873 K. The cell parameters and atomic positions were refined by Rietveld analysis; the volume thermal expansion coefficient is $\alpha_V = 28.5(9)\ x10^{-6}\ K^{-1}$.

The results on synthetic $Co_3Al_2Si_3O_{12}$ garnet were compared with the high temperature structure data of $X_3Al_2Si_3O_{12}$ garnets with X = Mg, Ca, Mn and Fe taken from literature. The thermal expansion of the unit cell is very similar in $X_3Al_2Si_3O_{12}$ garnets, whereas the thermal expansion of the longest bonds in the distorted cubic cage surrounding the X cation decreases with increasing cation size. Contrarily to the compression behaviour, the thermal expansion in $X_3Al_2Si_3O_{12}$ garnets does not change significantly as a function of composition.

Key words: garnet; thermal expansion; Cobalt; synchrotron radiation; powder diffraction; crystal structure.

Introduction

Natural garnets are silicates with general formula $X_3Y_2T_3O_{12}$ and cubic $Ia\bar{3}d$ symmetry. Their structure can be described by the building of three different polyhedra: a tetrahedron, an octahedron, and a distorted eight-fold coordinated cage, hosting respectively the T, Y and X cations. Whereas the T site is filled almost completely by Si, there is a considerable variability among the cations which can be hosted in the X and Y cages, but the symmetry is retained in the end members, allowing direct comparison in their physical properties. Garnets therefore provide a good test on how the physical properties are changed by chemical substitutions within a given structure.

Silicate garnets with the Y site completely or almost completely filled by Al are most common in nature; in the X site the natural end members host Ca, Fe^{2+}, Mn and Mg, respectively in the minerals grossular, almandine, spessartine and pyrope. The physical and thermodynamic properties of the end members and their solid solutions were widely studied, focussing on features such as the deviation from the ideal behaviour in solid solutions (Merli et al., 1995; Ungaretti et al., 1995; Geiger, 1999; 2000; Rodehorst et al., 2002), local positional and dynamic disorder within the cubic distorted cage (Pavese et al., 1995; Geiger et al., 1992; Armbruster et al., 1992; Armbruster and Geiger, 1993; Pilati et al., 1996; Geiger and Armbruster, 1997; Quartieri et al., 1997), and thermal expansion and compressional behaviour (for thermal expansion: Skinner, 1956; Meagher, 1975; Thieblot et al., 1998; Isaak et al., 1992; Ottonello et al., 1996; for the compressional behaviour, among others: Levien et al., 1989; Leger et al., 1990; Zhang et al., 1999; Milman et al., 2001; for investigations at high pressure and temperature: Pavese et al., 2001; Fan et al., 2009). This last point has an interest as garnets are major constituents in the upper mantle and an understanding of their thermoelastic properties is relevant in geophysical modelling. The thermal expansion and compressional behaviour were studied mostly by X-ray diffraction, to obtain the changes in volume and the structural evolution with T and P or both.

Beyond garnets having composition occurring in nature, also the end member with Co at the X site was synthesized (Ohashi et al., 1981; 1995, $Co_3Al_2Si_3O_{12}$, Co-garnet). Its interest resides in testing models over garnet crystal chemistry, and in ceramic science to understand the mechanism with which the colour in silicates occurs (Taran et al., 2002; 2007).

In this paper the results of a high temperature study on Co-garnet are reported. Cell parameters and atomic structure were determined by Rietveld refinement of X-ray diffraction patterns collected in a third generation synchrotron source. The results on volume and polyhedral expansion are compared with the high pressure data on Co-garnet (Taran et al., 2007) and the high temperature behaviour of Ca, Mg, Fe and Mn end members.

Experimental

Sample characterisation and Rietveld refinements

Powder diffraction patterns were taken on Co-garnet, synthetized at T = 1173K and 5 GPa in a high pressure belt type apparatus (Ohashi et al., 1995), and characterized by subsequent spectroscopic and microprobe analysis (details of the sample characterization can be found in Taran et al., 2007). This work sample comes from the same synthesis of the crystals studied by X-ray single crystal diffraction by Ohashi et al. (1995), and subsequently by Dubrovinsky et al. (2006). Powder diffraction patterns were taken at T = 298, 423, 573, 723 and 873 K, exploiting synchrotron radiation at the ESRF - BM8 GILDA beamline, and a hot air blower heating system.

The collection was done using an angle-dispersive set-up based on an imaging plate (IP) camera and a fixed wavelength $\lambda = 0.55133$ Å, with one minute exposure at each temperature. Details on the apparatus are reported in Meneghini et al. (2001). Sample powders were enclosed in glass capillaries (inner diameter = 0.5 mm) which were mounted horizontally on a goniometer head placed 300 mm from the IP. The capillaries were kept rotating during the acquisition in order to improve the grain statistics. The sample-to-image plate distance and the instrumental line shape were calibrated by refining the diffraction patterns of reference c-Si powders (NIST). The 2D diffraction patterns collected on the IP were digitised and integrated to standard one dimension diffraction patterns (Intensity vs. 2θ). Maximum 2θ was 45° in all samples.

The diffraction patterns were quantitatively analysed with the Rietveld structure refinement approach as implemented in the GSAS (Larson and Von Dreele, 2004) package. The profile function of Finger et al. (1994), which models peak asymmetry arising from axial divergence and describes well the low-angle tails of the peaks, was used. In all refinements both Lorentzian (Lx, Ly) and Gaussian contributions were allowed to vary, although the Gaussian contribution was negligible. The background was modelled by a polynomial Chebyshev function using 12 coefficients and the zero shift was refined to a value of ≈ 0.01(2)°. In agreement with single crystal room temperature data a $Ia\bar{3}d$ space group was assigned.

A refinement of the site occupancies did not show a significant deviation from the stoichiometry, either at room or the highest temperature. Therefore the X, Y and T sites were always assumed to be fully occupied by Co, Al and Si respectively. During the first stages of refinement a soft constrain was added to the tetrahedral bond lengths, which was subsequently removed. The refinements started with coordinates and isotropic displacement parameters taken from the single crystal room temperature refinement by Ohashi et al. (1995); the oxygen atomic coordinates were refined in the late stages of the Rietveld analysis. Owing to the strong correlations with the profile parameters, the refined isotropic parameters are not reported.

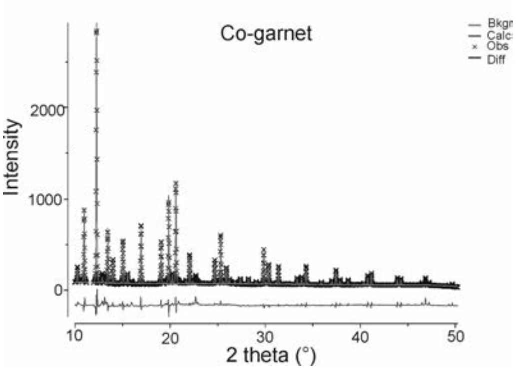

Figure 1. Measured and calculated intensities in the diffraction pattern taken at 298K.

In Figure 1 the fit between observed and calculated patterns at T = 298 K is reported. Cell parameters, atomic co-ordinates and bond lengths are reported in Table 1.

Results and discussion

Thermal expansion of $Co_3Al_2Si_3O_{12}$

The evolution with temperature of the bond lengths and of the cell parameter in Co-garnet is shown in Figure 2. The parameters were fitted assuming that the thermal expansion coefficient does not change with temperature. This means that, being the thermal expansion of a given parameter (*par*) $\alpha_{par} = 1/par_0\ (\partial par/\partial T)_P$, the data were fitted according to the integrated equation:

$$\ln(par/par_0) = \alpha(T-T_0) \qquad (1)$$

which is very close to a linear fit with temperature (Tribaudino et al., 2010).

Moreover, due to the relatively large uncertainty in the refined bond distances, the

Table 1. Cell edge, bond distances and O atom coordinates in Co-garnet between 298 and 873 K.

T (K)	298	423	573	723	873
a (Å)	11.4593(1)	11.4744(1)	11.4922(1)	11.5039(1)	11.5245(1)
Si-O	1.637(6)	1.640(6)	1.642(5)	1.642(5)	1.643(5)
Al-O	1.889(6)	1.893(6)	1.892(6)	1.891(5)	1.892(6)
Co-O2	2.205(5)	2.205(5)	2.209(5)	2.211(4)	2.225(5)
Co-O4	2.333(5)	2.335(5)	2.343(4)	2.351(4)	2.356(4)
x_O	0.0332(4)	0.0330(4)	0.0331(4)	0.0331(4)	0.0339(4)
y_O	0.0511(4)	0.0512(4)	0.0508(4)	0.0503(3)	0.0502(4)
z_O	0.6532(5)	0.6533(5)	0.6531(5)	0.6530(5)	0.6525(5)

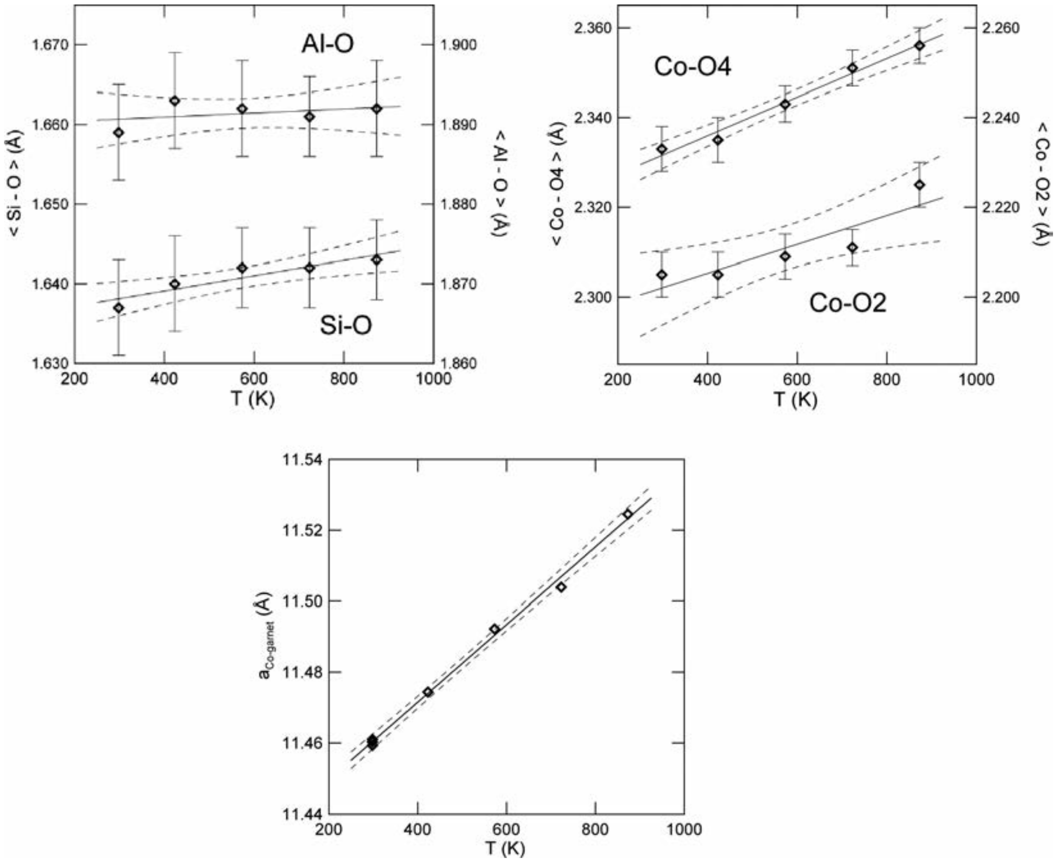

Figure 2. Bond lengths and *a* cell parameter vs temperature in $Co_3Al_2Si_3O_{12}$ garnet; 95% confidence lines are dashed. For the *a* parameter also the experimental datum at room temperature by Ohashi et al. (1995) and Dubrovinsky et al. (2006) are reported.

interpretation of the observed trends was done after the calculation of a 95% confidence interval, shown in the plots.

In garnets, tetrahedral and octahedral site cations have respectively 4 and 6 equivalent bond lengths with the surrounding oxygen, whereas in the distorted cubic cage, the X cation has respectively 4 shorter and 4 longer bonds. Although all oxygen atoms are symmetry equivalent, those making the shorter and longer bonds with the X cation are named O2 and O4 respectively. From the fits in Figure 2 a positive thermal expansion is observed for all polyhedra, lower in Al-O, slightly higher in Si-O and Co-O2, and significantly higher for the Co-O4 bond. However, as shown by confidence intervals the trends in Si-O, Al-O and Co-O2 are poorly defined, and the interpretation has to be that within error their difference is not significant. On the other side, the Co-O4 bond expansion is well constrained with temperature. This pattern is in agreement with previous observations on the thermal expansion in garnets (e.g. Rodehorst et al., 2002).

In a comparison with the high pressure structure of Co-garnet (Taran et al., 2007) an inverse behaviour is observed between compression and thermal expansion, in that a higher compression is observed in the Co-O4 bond, as a counterpart of the highest thermal expansion of the same bond. It is worthwhile to note, however, the step in the compression of the Co-O4 bond at $P \geq 5$ GPa, indicating the presence of a isosymmetric phase transition, was not found at high temperature.

Comparison with $X_3Al_2Si_3O_{12}$ garnets

In this work the thermal expansion data of the Co-garnet were first provided. It is of interest to compare the present results with those on the thermal expansion of other $X_3Al_2Si_3O_{12}$ garnets.

In any comparison among data sets the main problem is to have consistent data; these are seldom available as datasets are collected with different aims, in turn affecting the accuracy in calibration and the experimental temperature range (Fei, 1995).

The main sources of inconsistency in a high temperature investigation are:

1) the uncertainties in wavelength and zero positions which are inherent in any experimental setup. This affects the absolute value of the cell parameter and in turn of bond lengths, which may appear different in a comparison among different papers, but not the slope with temperature;

2) an incorrect calibration of the real to nominal temperature of the single crystal/powder to that of the heater. This may affect the slope, as generally the difference between real and nominal temperature increases with temperature. The differences may be significant close to the upper limits of the heater system: for instance deviations up to 20-30 K were observed at the upper limits of the air blower heater in an investigation on plagioclase thermal expansion (Tribaudino et al., 2010). As thermal expansion in the absence of phase transitions should not decrease at higher temperature, a decrease in thermal expansion at higher temperature can be an indication that a systematic error in the temperature calibration is present;

3) an uncertainty between the datasets can occur even in the absence of experimental errors, simply because data measured in a different range of temperature are compared. The thermal expansion changes with temperature, approaching zero at 0 K and increasing at higher temperature; beyond room temperature the increase is lower, but still present and significant (e.g. Tribaudino et al., 2008). The effect of the low temperature saturation, i.e. the reduced change in structural parameters with temperature below room temperature, can be modelled by physical models of thermal expansion as described for instance in Tribaudino et al. (2008); for such modelling data sets of high quality and measured as close as possible to 0 K must be available (Isaak et al., 1992; Thieblot et al., 1998). In $X_3Al_2Si_3O_{12}$ garnets such datasets are not available, and the results are generally discussed and compared assuming that thermal expansion does not change (e.g. in Rodehorst et al., 2002). A comparison between different datasets is then sensible if they are collected in the same temperature range, mostly if data at T below room temperature are compared. In garnets several data were collected below room temperature (Geiger et al., 1992; Armbruster et al., 1992; Rodehorst et al., 2002) and the problem may be significant. As an example, in Rodehorst et al. (2002), the thermal expansion for the Ca-O4 longest bond in grossular is $11.3(1.2)\text{x}10^{-6}\ K^{-1}$, when calculated over the whole experimental range (between 103 and 498 K), whereas the same parameter is $15.2(2.4)\ \text{x}10^{-6}\ K^{-1}$, when calculated using only data at T higher than room temperature.

It is not surprising that very few attempts were done to compare the thermal expansion of garnets, and when done, as in Rodehorst et al. (2002), the error was not estimated. The large variation in the thermal expansion of the

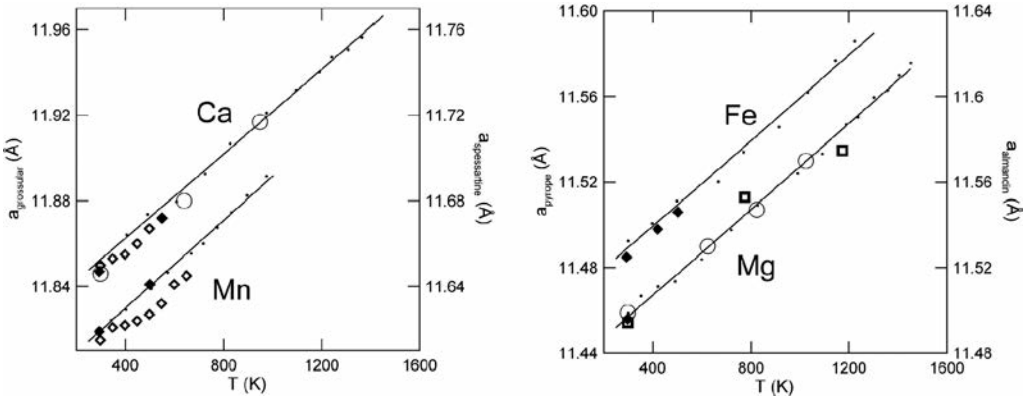

Figure 3. Cell parameter *a* vs temperature in $X_3Al_2Si_3O_{12}$ garnets with X = Ca, Mn (left) and X = Fe, Mg (right). Dots are from Thieblot et al. (1998) for Fe, Mg and Ca, from Skinner (1956) for Mn end members; full diamonds from Armbruster and Geiger (1993) for andradite, from Armbruster et al. (1992) for pyrope, from Geiger and Armbruster (1997) for grossular and spessartine; open diamonds from Rodehorst et al. (2002) for grossular and spessatine; open squares for pyrope from Pavese et al. (1995); open circles for pyrope and grossular from Meagher (1975). The fits were calculated using only data from Thieblot et al. (1998) and Skinner (1956).

different polyhedra measured from literature values, reported in Rodehorst et al. (2002), exemplifies very well how the above sources of error affect a comparative investigation.

Therefore we re-examined the bond length thermal expansion of $X_3Al_2Si_3O_{12}$ garnets; the consistency between datasets was checked by the thermal expansion of the a cell edge in papers giving structural data at high temperature against a reference thermal expansion (Figure 3). As a reference for grossular, pyrope and almandine the thermal expansion measured by Thieblot et al. (1998) and for spessartine by Skinner (1956) was used. The internal consistency of the chosen references was checked against the good match with literature data on grossular, pyrope and almandine by Skinner (1956) and grossular by Isaak et al. (1992).

The thermal expansion was calculated according to the equation 1, using only data at $T \geq 298$, where

Table 2. Volume, bond length and *a* cell parameter thermal expansion coefficients ($x10^{-6} K^{-1}$) as calculated from the single crystal data from the data plotted in Figure 2.

	Co	Mg	Ca	Mn	Fe
α_V	28.6(8)	26.9(1.4)	26.7(1.0)	19.4(2.1)	26.4(2)
α_V*	-	26.8(6)	26.0(3)	26.5(5)	25.9(10)
α_a	9.5(3)	9.0(5)	8.9(3)	6.7(1.0)**	8.8(1)
$\alpha_{Si\text{-}O}$	5.8(1.4)	1.4(1.4)	4.0(2.2)	0.1(2.0)	3.8(1.3)
$\alpha_{Al\text{-}O}$	3.9(2.7)	8.4(7)	8.4(1.9)	5.6(1.5)	6.9(1.0)
$\alpha_{Co\text{-}O2}$	7.1(1.5)	7.9(1.4)	8.0(1.4)	6.2(1.5)	8.6(3.0)
$\alpha_{Co\text{-}O4}$	18.3(1.4)	18.8(4)	10.8(1.3)	15.6(2.4)	16.2(7)

* reference volume thermal expansion coefficients from Thieblot et al. (1998) and Skinner (1956, for spessartine).
**8.5(2) in Skinner (1956).

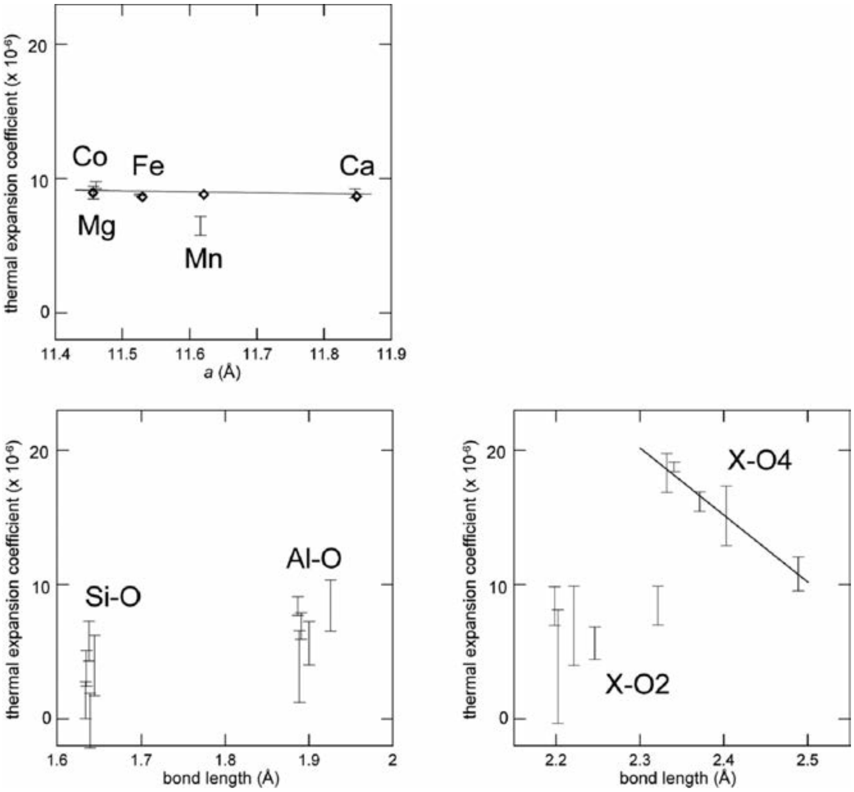

Figure 4. Thermal expansion coefficients (1/K) vs the relevant parameter for $X_3Al_2Si_3O_{12}$ garnets. The error bars refer to single crystal investigations aimed at structure investigation, diamonds in the *a* vs thermal expansion plot to studies aimed to determine thermal expansion (Skinner, 1956 for spessartine, and Thieblot et al., 1998 for the others).

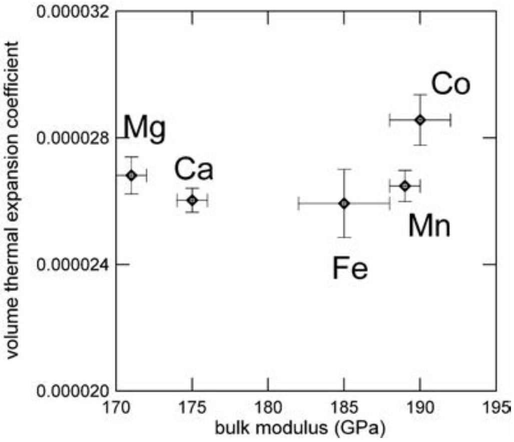

Figure 5. Bulk modulus vs volume thermal expansion (1/K) in $X_3Al_2Si_3O_{12}$ garnets. Thermal expansion is from Skinner (1956) in spessartine, from this work for Co-garnet and Thieblot et al. (1998) for the other end members. The bulk modulus was taken from Taran et al. (2007) for Co-garnet and Zhang et al. (1999) for all the others. The comparison between the different bulk modulus is consistent as the first derivative of the bulk modulus (K') is close to 4 in all the end members.

the linear approximation is a closer approach to the real case; the results are shown in Table 2.

The single crystal data show reasonable agreement, albeit with larger error, with the reference thermal expansion (Table 2) in all garnets, but in spessartine. In spessartine the data by Rodehorst et al. (2002) are significantly below the reference (Figure 3) and their reliability is therefore questionable. They also show larger error (Table 2). Another outlier is the datum by Pavese et al. (1995) on pyrope at T = 1173 K, which plots about a hundred degrees below the reference, which was discarded. For this result an overestimation of the real temperature is likely, being at the above limits of the air blower system used by Pavese et al. (1995).

In Figure 4 and Table 2 the thermal expansion coefficients for the a cell parameter in $X_3Al_2Si_3O_{12}$ garnets are reported. The coefficients do not change with the size of the unit cell, confirming that cation substitution in the X polyhedron does not affect the volume thermal expansion. By this respect there is a significant difference between thermal expansion and compression: as shown in Figure 5 the thermal expansion along the a axis in $X_3Al_2Si_3O_{12}$ garnets does not change with composition, while the bulk modulus does significantly. There is a difference between garnets with the cation in the X site as Ca or Mg, i.e. a non-transition element and those with a transition element like Fe, Mn or Co, that have significatly higher bulk modulus. This agrees with previous observations on carbonates (Zhang and Reeder, 1999) and pyroxenes (Nestola et al., 2005).

As concerns individual bond lengths (Figure 4) a general observation is that the bond length thermal expansion is lowest for Si-O, slightly higher for Al-O and X-O2, and most significant for X-O4. The difference between the end members is small, and non significant, apart for X-O4: the thermal expansion of the X-O4 shows a linear decrease with the bond length, i.e, with the size of the X-cation. The results confirms the preliminary observation by Rodehorst et al. (2002), that X-O4 bond expansion decreases with the cation size.

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Submitted, October 2010 - Accepted, January 2011