Raman modes in Pbca enstatite (Mg2Si2O6): an assignment by quantum mechanical calculation to interpret experimental results

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Raman modes in *Pbca* enstatite ($Mg_2Si_2O_6$): an assignment by quantum mechanical investigation and possible implications on the determination of intracrystalline ordering

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Abstract

Raman spectra of orthoenstatite have been computed from first principles, employing the hybrid Hamiltonian WC1LYP (Wu & Cohen 2006). The calculated data show excellent agreement with the experimental data from literature with an absolute average difference of ~5 cm^{-1}. The quantum mechanical simulation allowed the assignment of Raman features to specific vibrational modes. The modes were described by the decomposition of the building units. This allowed to quantitatively assess the contributions of internal (tetrahedral stretching) and external (tetrahedra chains and M1 and M2 cations) vibrations. Moreover isotopic substitution of Fe for Mg in the M1 and M2 sites, of Si^{30} and O^{18} for the Si and O sites was done in order to point out the relative contributions of the cations in the different sites to each mode.

The description of the Raman modes enabled to relate the major experimental peaks to specific structural deformations , providing a link to relate specific structural features to the changes with pressure, temperature and composition of the mode frequencies. Namely, the contribution of the most intense peaks from mass and structural changes for the Fe-Mg substitution in orthopyroxenes was assessed.

The results may provide new clues to identify peaks most suitable for the investigation of the intracrystalline ordering between Fe and Mg in the M1 and M2 sites, and of Al in the tetrahedral and octahedral sites, as well as in suggesting the peaks most suitable to constrain crystal structural features, like tetrahedral bond distances, at the micron size of the Raman probe.

Introduction

Enstatite is a major constituent of natural pyroxenes. In most occurrences enstatite is found in solid solution with minor ferrosilite ($Fe_2Si_2O_6$) in the mineral orthopyroxene (s.g *Pbca*), which is a rock forming phase in mafic and ultramafic assemblages of the Earth crust and upper mantle. Moreover, enstatite is present in planetary bodies and meteorites, where a specific class of undifferentiated chondrites takes its name (enstatite chondrites). It is also one of the few silicate minerals that has been observed in crystalline form outside our Solar System, around evolved stars and planetary nebulae (Demichelis et al. 2010). Also, the enstatite phases are important constituents of steatite ceramics (Reynard et al. 2008).

Enstatite displays a complex polymorphism. Although the orthorhombic phase is the most common, monoclinic $P2_1/c$ clinoenstatite is also found at room temperature. At non ambient conditions clinoenstatite transforms in the high pressure and high temperature HP*C2/c* and HT*C2/c* phases, sharing the same space group, but with quite different structure (Angel et al. 1992), whereas orthoenstatite tranforms in the *Pbcn* protoenstatite at high temperature and low pressure (Yang & Ghose 1995) and in a HP*P2_1/c* phase at high pressure (Zhang et al 2013, 2014). Phase transitions between the enstatite phases exert a considerable importance in modelling the thermodynamic and geophysical behaviour of the upper mantle; relations between different polymorphs, their structure, and their vibrational properties have been therefore widely investigated, at room conditions and at high pressure and temperature.

Extensive spectroscopic studies were done on enstatite; among spectroscopic methods, microRaman has a special interest, since it analyses at a micrometer scale the polymorphic varieties of enstatite, often mixed together, providing an effective tool for their identification (Ulmer and Stalder 1999).

Previous Raman studies have shown the differences between the spectra of clino, ortho and protoenstatite (Ulmer e Stalder, 1999, Reynard et al. 2008); compositional changes in orthopyroxenes were related to Raman spectra, to provide a tool to determine the orthopyroxene composition (Huang et al 2000, Wang et al 2001, Stalder et al 2009). The high temperature and high pressure phase transitions were also investigated by Raman (Ross and Reynard 1999, Zhang et al 2013, 2014), and detailed spectra at non ambient conditions were collected to describe the high pressure and high temperature mode behaviour (Lin 2003, 2004; Zucker 2009). Moreover, a number of studies used Raman spectroscopy to identify the enstatite phases in rocks and meteorites (among others Wang et al 2004).

The Raman spectra of clino and orthoenstatite were also simulated by numerical modelling. A pioneering study was done by Choudhury et al 1998, who calculated the Raman peak positions of orthoenstatite by means of molecular dynamics, comparing with carefully determined experimental spectra in parallel and cross polarization. However, due to the limitation in molecular dynamics, the difference between calculated and experimental positions is quite large (up to 100 cm^{-1}). A more precise fit to the experimental results was determined by the DFT quantum mechanical investigation: Raman peak positions of ortho and clinoenstatite were calculated by a quantum mechanical density functional approach by Yu & Wentzcovitch (2009) as a by-product in a paper aimed to determine the energetics and stabilities of the different polymorphs. Although their calculations are in closer agreement with experimental data, peak intensities were not computed. In fact, the high number of allowed Raman peaks (120 in orthoenstatite) makes peak assignment a challenging task, due to overlapping peaks. The calculation of the intensities is therefore needed to provide for several overlapping peak a correct assignment, i.e. to link a given experimental peak to a calculated one. Most recently, within the Wurm project (Caracas and Bobociu 2011), DFT modelling was done systematically over a series of mineral families; intensities and peak positions were calculated and reported for ortho and clino enstatite, however the results were not object of any further study.

Here we discuss the results of new simulation of Raman spectra of orthoenstatite from first principles, by means of CRYSTAL14 (Dovesi et al., 2014), employing the hybrid Hamiltonian WC1LYP (Wu & Cohen 2006), which is particularly suitable to calculate vibrational frequencies, as demonstrated by other calculations performed on $C2/c$ pyroxenes, like jadeite, diopside and spodumene (Prencipe 2013, Prencipe et al 2012, Stangarone et al 2014) and in the -1 plagioclase albite (Aliatis et al. 2015). Full Raman spectra are simulated, and the peak assignment is discussed in comparison with computational and experimental literature; the contribution of the different atoms to each vibration mode is assessed performing a building unit decomposition of the vibrational modes and by means of isotopic substitutions. Last, the specific changes of the crystal structure with Fe-Mg substitution, temperature and pressure have been related to the orthoenstatite Raman modes, to enlighten major structural features affecting the changes in Raman peak positions.

The results, compared with the available literature data, will provide the basis to model details in Raman peak changes for composition and cation ordering in natural samples.

Computational details

To simulate the Raman spectra of orthoenstatite from first principles, the below algorithm must be followed. The first step consists in solving the ground-state wave functions, then in the

calculation of the corresponding energies at the static limit, i.e. not taking into accounts the zero point and thermal energies (Prencipe et al. 2011). The complete analytical calculation of the Raman intensities is performed after the optimization of the crystal structure. All calculations are performed with the CRYSTAL code, which employs localized Gaussian-type basis sets and hybrid Hamiltonian.

The contracted basis sets used are 8-511d1G for Mg, 88-31G* for Si and 8-411d11G for O. The chosen Hamiltonian (WC1LYP) is a hybrid HF/DFT one, based on the generalized gradient approximation (GGA) exchange functional WC, proposed by Wu and Cohen (2006), mixed with 16% of the exact non-local Hartree-Fock exchange, and employing the LYP correlation functional proposed by Lee et al. (1988). Such percentage of exact Hartree-Fock exchange is essential for the correct reproduction of the elastic and vibrational properties, as demonstrated in previous works that employ these hybrid functionals (Zicovich-Wilson et al. 2004; Demichelis et al. 2009; Ungureanu et al. 2010, 2012; De La Pierre et al. 2011; Prencipe 2012; Prencipe et al. 2014; Scanavino et al. 2012). The Coulomb and Hartree-Fock exchange is controlled in CRYSTAL with the parameter TOLINTEG, set on 8 8 8 8 18, thus it evaluates the level of accuracy in the exchange.

Geometry optimization is conducted by analytical gradient methods, optimizing cell parameters and fractional coordinates. The operation is considered done when the two parameters TOLDEG and TOLDEX (convergence tolerances on gradient and on displacement) are smaller than 0.00001 and 0.00004, respectively.

The equilibrium lattice parameters optimized by CRYSTAL. are here reported in the Table 1, and compared with the experimental data (Yang & Ghose 1995).

Vibrational wavenumbers and normal modes were calculated within the limit of the harmonic approximation, by diagonalizing a mass weighted Hessian matrix, whose elements are the second derivatives of the full potential of the crystal with respect to mass weighted atomic displacements. The first derivatives of the energy with respect to the atomic positions are calculated analytically (Doll et al. 2001), whereas second derivatives are calculated numerically by setting to 0.003 Å the nuclear displacements with respect to the equilibrium positions. The threshold for the convergence of the total energy, in the self-consistent field cycles, is set to 10^{-9} hartree. Relative Raman intensities were computed using a fully analytical approach. It combines analytical gradients (Doll at al. 2001) with solutions of first-order and second-order coupled perturbed Hartree–Fock/Kohn–Sham equations (Ferrero et al. 2008) for the linear and quadratic orbital responses to electric fields in the different Cartesian directions. For the linear response, there are three directions to consider; for the quadratic response, there are six pairs corresponding to the six independent components of the polarizability tensor. The thresholds for convergence of the coupled perturbed

equations were set to the default values. The diagonalization of the Hessian matrix was performed at six independent k vectors in the reciprocal space (Monkhorst net) by setting to 2 the shrinking factor (IS parameter).

The results are shown in Figs. 2 and 3, comparing the experimental and calculated spectra to the unpolarised spectra; the calculated polarized spectra are also reported. In Tables 1 and 2 the experimental data of orthoenstatite were compared with our calculated ones. The comparison was done using both the peak positions and their intensities.

Results

Mode analysis

The orthoenstatite Raman spectrum is one of the most complex in pyroxenes, being the result of as much as 120 Raman active modes; it can be best described in comparison with other enstatite polymorphs and their structure.

Pyroxenes are chain silicates, with tetrahedral chains along the c axis, and two metal sites in between, M1 and M2. The M1 site is a slightly distorted octahedral site, whereas the M2 is a distorted polyhedron, with cations in six and eightfold coordination. In enstatite Mg fills both the M1 and the M2 sites, and Mg enters in six-fold coordination in the M2 site. In $C2/c$ pyroxenes the M2 polyhedron is eightfold, and hosts cations with higher ionic radius, like Ca and Na. The different coordination requirements promote a change in the tetrahedral chains arrangement. In $C2/c$ pyroxenes the chains are symmetry equivalent, whereas in monoclinic $P2_1/c$ they are not: in the $P2_1/c$ symmetry the chain distortion is different in two of the four tetrahedral chains in the unit cell of the former $C2/c$ pyroxene.

The orthorhombic enstatite occurs by twinning at the unit cell scale along a* of the $P2_1/c$ cell. The unit cell doubles its size, to a $Pbca$ s.g.; like in the $P2_1/c$, in the $Pbca$ enstatite we have two symmetry independent chains.

Factor group analysis shows that 30 Raman active and 30 IR active peaks are present in $C2/c$ pyroxenes; most of the Raman active modes can be experimentally identified in $C2/c$ pyroxenes, in polarized light experiments (Etchepare, 1972, Prencipe et al 2012). In the $P2_1/c$ symmetry we have 60 Raman and 60 IR active modes, of which 30 can be observed in parallel polarization symmetry (A_g) and 30 in crossed polarization (B_g). The unit cell, doubled in $Pbca$ orthoenstatite, doubles also the number of the modes, to 120 Raman and 120 IR active modes. According to the polarization selection rules for Raman scattering, in orthoenstatite we have in parallel polarization 30 A_g Raman active modes and in crossed polarizations 90 B_g modes. The B_g

modes are further divided in three groups 30 each, according to the direction of polarization, named B_{1g}, B_{2g} and B_{3g}. The A_g modes are the most intense and useful for the purpose of mineral identification and spectroscopic analysis: unpolarised spectrum consists almost completely of A_g modes (figure 2). The B_g are generally weaker and can be identified by the analysis of spectra in cross polarization configuration (Choudhury et al. 1998, Chopelas 1999). However the high number of modes hinders a careful experimental analysis: in their investigation on polarized spectra of orthoenstatite, Choudhury et al. 1998 managed to measure and identify successfully all the A_g and some of the B_{1g} and B_{3g} modes, but none of the B_{2g}.

It is very complex to ascribe a given experimental peak to a specific mode, due to overlap in close peaks. Also the simple description of the modes in terms of structural vibrations is difficult: the pyroxene structure has little crystallographic constrains, due to its low symmetry, and allows significant polyhedral deformation.

In previous papers (Chowbury et al 1998, Huang et al 2000, Wang et al 2001) three different kind of deformation were identified: 1) vibration of cations in M1 and M2 polyhedron, occurring with varying contribution from the tetrahedral chains; 2) bending of the tetrahedral chains, involving both or one of the two symmetry equivalent chains; 3) stretching into the SiO_4 tetrahedron, with very minor contribution from the M1 and M2 cations. They were identified to specific group of frequencies, i.e. group 1 to frequencies between 200 and 400 cm^{-1}, group 2 between 400 and 800 cm^{-1}, and tetrahedral stretching to higher frequencies. However, although the above assignment can provide a preliminary information, peaks assignment is a more complex task: previous quantum mechanical investigation on the $C2/c$ pyroxenes showed that a combination of the above mechanisms may occur at the same time in a given mode (Prencipe et al 2012, Prencipe 2014). As it is described in the following paragraphs, it has little meaning to say that a mode is due e.g. to M1-O bending, as long as it will likely have a significant contribution in bending and stretching from the tetrahedral chain. Instead, the description of a given mode should enlighten the prevailing mechanism, and account for the different contributions.

To unravel the different contributions of the atomic vibrations we have performed a building units decomposition of the vibration modes. The vibrational modes are decomposed in terms of internal and external motions of some units defined by input. The latter correspond to rotations and translations of the units behaving as rigid blocks, while the former to the relative motions of the constitutive atoms. In pyroxenes, internal contributions come from the bending or stretching of the tetrahedral units, while the external contribution comes from the vibration the tetrahedral chain without an internal deformation; also, the vibrations of the M2 and M1 atoms fall in the range of the external contribution.

The contribution of a given atom to the overall vibration was also assessed by means of isotopic substitution of Fe atomic mass for Mg mass in the M2 and M1 sites, separately and together, and of ^{18}O and ^{30}Si isotopes for the oxygen and silicon respectively. These calculations are activated by the keyword ISOTOPES, which allows the modification of the atomic mass of a specific atom defined by input. With ISOTOPES calculations, the isotopic mass of one atom symmetry related to others is modified, though the symmetry of the electronic wave function is not modified, as the mass of the atoms is not present in the single particle electronic Hamiltonian. Moreover, if a frequency calculation was performed with standard atomic masses, new frequencies values with different atomic masses for selected atoms can be computed from the Hessian already computed. This has the advantage to separate the contributions due to the changing mass within the vibrating atoms, with those from the interatomic force constants. It must be noted that when the isotopic mass of one atom symmetry related to others is modified, the symmetry of the electronic wave function is not modified, as the mass of the atoms is not present in the single particle electronic Hamiltonian. The choice of the much heavier Fe mass, instead of a Mg isotope, was done in order to assess the mass contribution for the Fe-Mg substitution in the Raman spectra of enstatite-ferrosilite orthopyroxenes.

The contributions of the building units, and of the isotopic shift for substitution from enstatite can be found for each vibrational mode in Table 3.

In the following discussion general trends are discussed, in order to identify prevailing vibrational behaviour in a given range.

Building unit decomposition

As expected from the results in calculated clinopyroxenes $C2/c$ s.g., we find that also for orthopyroxene most modes are a combination of internal and external contributions (Fig. 3, Table 3). Internal contributions are most at higher wavenumber, where they account almost completely for the description of the Raman mode intensities, and decrease with decreasing frequencies. This is quite similar for A_g and B_g vibrations. The external contribution is complementary, but it must be further divided in a contribution from the tetrahedral vibrations and another for the vibration of Mg in the M1 and M2 sites.

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The internal contribution (Fig. 3) identifies five ranges: 1) below 200 cm^{-1} where the internal contribution is less than 10%, 2) between 200 and 350 cm^{-1} where it is below 20%, 3) between 350 and 470 cm^{-1} where it increases in an almost linear fashion between 20 to 80%, 4) between 500 and 750, where it is between 75 and 90%, and 5) for higher energy where it is more than 80%. Purely internal contribution is never found.

 In Fig 4 the percentage of tetrahedral contributions, summing up internal and external contributions, is shown with wavenumber; the remaining contribution is due to the vibration of Mg in the M2 and M1 sites.

The contribution from tetrahedral vibration is almost complete for frequencies above 700 cm^{-1}. A contribution of Mg in M1 and M2 atoms is present at the lower wavenumbers, mostly between 200 and 400 cm^{-1}, but tetrahedral internal and external contributions generally prevail. In detail the contribution for the M2 and M1 makes possible to define further ranges: below 200 cm^{-1} the tetrahedral contribution never goes below 80%, between 200 and 350 we have several peaks where the tetrahedral contribution decreases below 50%, for higher wavenumbers the minimum contribution is higher than 70%, and almost 95% for peaks close between 600 and 700 cm^{-1}.

M1 and M2 isotopic substitution

The isotopic substitution of Fe in the M1 and M2 sites induces a downshifting of peak positions for modes below 760 cm^{-1} (Figure 6).

In the substitution of Fe for Mg in the M1 site the downshifting is maximum at 250 cm^{-1}; between 250 to 400 cm^{-1} the frequency decreases between 20 and 40 cm^{-1}. The downshifting is less between 400 and 500 cm-1, but it stabilizes to about 10 cm^{-1} up to 760 cm^{-1}. The same substitution for the M2 site shows a similar trend, but with the maximum shift observed in few modes at lower energy, at about 200 cm^{-1}.

The complete Fe isotopic substitution in M2 and M1 sites decreases the frequency by 40 to 60 cm^{-1} between 200 to 400 cm^{-1}. The maximum downshift increases up to 200 cm^{-1} and decreases from 400 to 760 cm^{-1}, showing a pronounced linear trend.

Si and O isotopic substitution

The isotopic substitution was calculated for each of two Si atoms of the A and B chains separately, and for each of the six symmetry independent oxygen; eight separate calculations were

performed, but in the analysis of Figures 7 and 8 the contributions for Si and O atoms equivalent in the *C2/c* symmetry were shown together. This was done because the corresponding atoms have very similar structural environment also in *Pbca* enstatite, albeit with slightly different bond distances. The contribution of the corresponding atoms in the A and B chains is shown in Fig. 8.

Oxygen isotopic substitution downshifts the frequency for most modes, whereas the Si isotopic substitution affects significantly the calculated frequency only at higher frequencies (above 600 cm^{-1}). In fact oxygen are involved also in vibration mostly due to the M1/M2-O stretching and bending, even if the internal tetrahedral contributions are little significant. However, only in few modes the isotopic substitution changes the frequency by more than 5 cm^{-1}. This occurs for the O1A and B and the O2A and B in some peaks between 400 and 600 cm^{-1} and above 900 cm^{-1}, and for the O3A and B, which show high deviation only between 600 and 900 cm^{-1}; at frequencies in excess of 900 cm^{-1} the contribution for the O1 and O2 atoms is maximal, whereas that of the O3 becomes not significant. At the highest frequencies the contribution for the O2 oxygen is most significant.

Discussion

Mode assignment

Combining the results of isotopic analysis and building units decomposition, we outlined the prevailing mechanism of vibrations for each frequency range. Detailed analysis for each range can be found in table 3 where we analyse the more intense and diagnostic peaks, reported by Lin, (2003), comparing them with our calculated data. Moreover, the motion has been described by means of graphic interface software (Moldraw), which performs the graphical animation of each phonon frequencies calculated, by analysing their eigenvectors.

The area of the spectrum, defined as range 1 (R1), from 79 cm^{-1}, first mode, to 150 cm^{-1}, shows stiff lattice movements, without an internal deformation of tetrahedra, thus it has been defined as external lattice vibrations. The mode with the highest intensity in this group is found at 79 cm^{-1}, where tetrahedra oscillate stiffly along the b axis and where the contribution of chain A prevails; here both Mg cations are dragged by tetrahedra, but at a greater extent for the Mg in the M2 site. This mode has often been overlooked as most Raman spectra have been measured from 100 cm^{-1}, but it is diagnostic for the identification of the orthopyroxene phase (Reynard et al 2008). The motion for the mode at 127 cm^{-1} is rather similar to the one at 79 cm^{-1}, but here the B chain is predominant. Modes at 81 cm^{-1} and 108 cm^{-1} are respectively of B$_{2g}$ and B$_{3g}$ symmetry, as reported in Lin (2003) spectra. They are again stiff lattice oscillations, where chains vibrates, above and

below a and b axes, respectively, along the (001) orientation. At higher wavenumbers the vibration of Mg in the M2 sites becomes most significant.

In the second range (R2) we have recognized two subranges:

a) from 150 to 300 cm^{-1}, where Mg (M2) contributions are predominant against that of other cations. The peak with higher Mg2 contribution is at 248 cm^{-1}. In this range both chains are involved in the vibration, but the motion can be different for the two chains. For example at 206 cm^{-1} (A$_g$), the A chain performs a Si-O3-Si bending, whereas the B chain swings rigidly above and below the c axis, onto the (001) plane. On the other hand it has been observed that at 161 cm^{-1}, 236 cm^{-1} and 277 cm^{-1}, the chains vibrate with the same tilting motion along the a axis, but with a different percentage of the two;

b) in the second subrange, from 300 to 350 cm^{-1}, the contribution of Mg in the M1 site increases consistently, reaching its maximum at about 325 cm^{-1} (A$_g$). In the mode at 325 cm^{-1} the B chain is almost stationary and the A chain vibrates for the bending of the O2 atom with Mg in the M2 site. There is also a contribution of the internal deformations of the tetrahedra, due to the bending of cations with oxygen, as we can see in the Table 3. The most intense peak, in unpolarised spectra, is the one at 343 cm^{-1} where the motion is characterized by the tilting of both tetrahedra in the two chains and is mainly due to O1 and O2 tilting (Figure 8). Both cations vibrate, but the isotopic contribution from the M2-O vibration is higher.

The range between 350-600 cm^{-1} (R3) is characterized by an equal percentage of both rigid movements of the lattice and internal strains of the tetrahedra. The contribution from the internal tetrahedral vibration increases steeply, and in some peaks isotopic contribution from the oxygen may be significant. In this range a lower, but significant contribution from the M1 and less from the M2 is still present. Also here the range can be further divided into two sub-ranges: a first one (R3a) between 350 and 470 cm^{-1}, characterized by low intensity doublets and triplets, and a second one (R3b), where the vibration of both cations starts to decrease gradually and the contribution to the overall vibration is given by the internal bending of the tetrahedra. In the R3a subrange both chains vibrate, but with different movements and the vibration of Mg in the M1 site gives the higher contribution. The triplet consisting of three A$_g$ modes at 387 cm^{-1}, 406 cm^{-1} and 426 cm^{-1} is noteworthy. The motion of the chains for the first mode is a prevailing stretching of O1 inside the A tetrahedron; for the second mode both chains vibrate, O1 oxygen swinging along the a axis in the B chain and the tetrahedra tilting above and below the b axis. For the last mode of the triplet, at 426 cm^{-1}, the vibration occurs in both chains, but more in the A chain, where the motion of tetrahedra is mainly due to the O1 oxygen. In general, in the R3 range, oxygen isotopic substitution shows that most of the contribution to the vibration comes for the O1 and O2 atoms, i.e. those having shorter

bonds with the M1 and M2 cations, respectively. In the second subrange (R3b) few significant experimental peaks are present, but the one at 594 cm^{-1}, a O2-Si-O1 bending by the A chain combined by the vibration of the O2 together with the two Mg in M1 and M2.

A fourth range (R4) in the spectrum appears between 600 and 760 cm^{-1}, where the most intense peaks are those at 660 and 680 cm^{-1}. This range was defined as bending zone (Huang et al 2000), where the contribution to the overall vibration consists of internal strains of the tetrahedra, with the characteristic bending of O3-Si-O3. The peak at 660 and 680 cm^{-1} show differential contributions from the A and B chains respectively.

In a fifth range (R5) the M2 and M1 cations contribution is less than 1%. The modes in this final part of the spectrum are characterized by internal strains of the tetrahedra, and by a marked alternation of the two chains within the vibration. This range can be further divided in two subgroups: R5a) modes with a higher contribution from the O3 oxygen, the most intense being the A_g mode at 866 cm^{-1} and the doublet, not very intense, consisting of two A_g modes at 924 cm^{-1} and 933 cm^{-1}, b) modes where the higher contribution is a stretching within the tetrahedron, of Si with the O1 and O2 atoms. In this last sub-range we find the final triplet at frequencies higher than 1000 cm^{-1}, which can be described as symmetric and asymmetric stretching within the tetrahedra.

The above observations can be easily related in terms of bond distances and crystal chemical requirements (Table 4). The average bond distances are shorter in the M1 and M2 polyhedra rather than in the Si centred tetrahedra: this accounts for the lower energy of the modes with higher contribution from the M1 and M2 sites. In the fifth range, where peaks are above 760 cm^{-1}, the bond distances within the tetrahedron explain the prevailing contribution for the O3, especially between 760 and 933 cm^{-1}. In the high intensity A_g doublet at 1012 cm^{-1} and 1027 cm^{-1} the higher frequency is explained as the contribution of O2 is significant, and the Si-O2 distances are shorter.

In terms of crystal chemistry (Cameron et al 1979, Mantovani et al 2014, Gori et al 2015) the O3 oxygens are overbonded, as they are bridging between tetrahedra and receive their charge contribution from the two Si atoms and the M2 atoms, whereas the O2 and, less, the O1 is underbonded. Tetrahedral bond distances change consequently, and a change in the reduced mass for O1 and O2 promotes a higher shift in the higher energy modes. Moreover only the O1 and O2 atoms are bonded to the M1 cations, which explains the contribution at 350-500 cm^{-1} of the O1 and O2 oxygen, but not of the O3. For the O3, the contribution from the modes involving the M2 and M1 atoms is quite small. The contribution from the O3 atoms becomes significant in the lower energy modes from stretching, between 750 and 900 cm^{-1}, and, being the O3 the tetrahedral chain bridging atoms, in modes related to chain bending, in the 600-700 cm^{-1} range.

Fe-Mg substitution and orthopyroxene composition by Raman spectroscopy

Natural orthopyroxenes are a solid solution between $Mg_2Si_2O_6$ and $Fe_2Si_2O_6$. In the partial substitution of Fe^{2+} for Mg^{2+}, Fe^{2+} has a higher mass and a larger ionic size than Mg, but the same charge. The space group does not change for the solid solution, but Mg and Fe do not enter randomly in the two M1 and M2 sites: Fe enters preferentially in the more distorted M2 polyhedron, and Mg in the M1 site (Domeneghetti et al 1985). The intracrystalline distribution coefficient $K_D=$ FeM2*MgM1/FeM1*MgM2 is temperature dependent (Tarantino et al 2002a, b, Wang et al 2005), and varies in volcanic and metamorphic orthopyroxenes between 0.2 to 0.02. It is an important marker for the cooling history in meteoritics, volcanics and slowly cooled terranes (Tribaudino and Talarico 1991, Domeneghetti et al 1995, Stimpfl et al 2005).

In figure 10, we report the Raman shift vs composition of several peaks along the $Mg_2Si_2O_6$ - $Fe_2Si_2O_6$ series. The expectation is that the increased mass of Fe decreases the energy of the modes, at least those where a significant contribution from the M1 and M2 cation exists. This is observed for the peaks up to 800 cm^{-1}, but the experimentally measured peak frequencies decrease with Fe content more than calculated by simple isotopic substitution of Fe with the lighter Mg. The difference is explained by changing structure. The higher ionic radius of Fe promotes longer bond lengths and lower coulombic contribution to the oxygen bonding (Table 4) in the lower frequency modes, where the contribution for the cations in the M1 and M2 sites is significant, thus giving a further contribution to decrease the energy of the same modes when Fe exchanges for Mg. It looks that the contribution from mass, which can be modelled by our isotopic substitutions, and that for the changing structure are comparable (Figure 9).

The above considerations do not hold for modes higher than 800 cm^{-1}, which are ascribed to tetrahedra internal vibrations. Actually, the peaks at 866 and 933 cm^{-1} do show an increase in frequencies with Fe content, whereas the peak at 1010 cm^{-1} shows higher frequencies in Mg richer orthopyroxenes. Again, changes in tetrahedral bond distances along the $Mg_2Si_2O_6$-$Fe_2Si_2O_6$ series must be taken into account. In Mg orthopyroxene the two O1 and O2 atoms are closely bound to Si, whereas the O3 bridging oxygen distances with Si are longer. As Fe increases, the bond distances in the tetrahedron become closer together: the distance of Si with the O3 decreases, and that with the O1 and O2 increase (Table ; Mantovani et al 2013). To note, on average the tetrahedral size does not change. As shown by isotopic substitution in Figure 7 the modes at 866 and 933 cm^{-1} are most affected by the O3 atomic vibrations, and, decreasing the Si-O3 bond distance with increasing Fe, it is not surprising that the mode frequency increases also. On the contrary, the mode at 1010 cm^{-1},

dominated by the O2 vibrations, decreases its frequency coherently with increasing Si-O bond distance in Fe richer pyroxenes.

Isotopic analysis predicts also that Fe-Mg ordering can have a significant effect on Raman peak positions. In natural intermediate orthopyroxenes Fe is almost completely confined in the M2 site, and Mg in the M1 site (Tribaudino and Talarico 1991); Fe occupies at a larger extent the M1 site only in Fe richer orthopyroxenes. In the isotopic modelling of the partitioning between M1 and M2, the configuration with Mg fully occupying the M1 site is an ordered model close to the experimental observation, whereas that with Fe in M1 and Mg in M2, is an antiordered one. In most cases the difference between the ordered and antiordered models is very small, but in the relatively strong mode at 302 cm^{-1} a marked difference between ordered and antiordered configuration is found; this mode could be a candidate to reveal differences in the Fe-Mg ordering, as the substitution of Fe in M1 downshifts the peak much more than that of Fe in M2. The few experimental available data for the peak at 302 cm^{-1} indicate a trend which can be better fitted in the ordered model (Fig. 10).

Raman modes and structure: relations with HP/HT Raman behaviour

The above discussion shows that changing mass and bond distances provide a clue to interpret and, potentially, predict the mode behaviour in response to changing composition, once the mode assignment has been done correctly. Furthermore, such approach can be extended conveniently to the analysis of the behaviour of high pressure/high temperature Raman modes in comparison with HP/HT structural data. In enstatite this can be best done, as a number of in situ high quality single crystal XRD data are available, and with changing pressure and temperature only bond distances are modified. Here, as an example, we will examine the high temperature/pressure behaviour of the doublet at 660/685 cm^{-1}, which is intense and well resolved, and therefore most useful for diagnostic purposes (Huang et al 2000, Wang et al 2004, Tribaudino et al. 2012)

The doublet at 660/685 cm^{-1} has been described as a bending of the tetrahedral chains (Huang et al. 2000) for each peak. However, according to our calculations on the isotopic substitution (fig. 6) also a contribution from the M1 and M2 atoms is present. The split of the doublet occurs as only one of the two symmetry independent tetrahedral chains is in turn involved in the mode vibrations: the mode at 660 cm^{-1} involves a vibration of the B chain, whereas that at 685 cm^{-1} of the A chain. In *C2/c* pyroxenes a single mode at 670 cm^{-1} is present, and the transition from C centred to P pyroxenes is marked by the peak split at 660-680 cm^{-1} of the formerly unique

peak at 665 cm^{-1} (Tribaudino et al 2012, Mantovani et al 2015). The higher energy of the vibration from the A chain can be explained considering that the tetrahedral distances are shorter in the SiA tetrahedron, on average (1.629 vs 1.640 Å) and with the bridging O3 oxygen, which most contributes to the mode vibration (1.653 vs 1.675 Å). Moreover the shorter distance between M1 and the tetrahedral chain, i.e. the M1-O2 distance, is less between M1 and the A tetrahedral chain than between M1 and the B chain (2.001 vs 2.053 Å). This distance, which is the shortest between M1/M2 cations and a tetrahedral oxygen, is supposed to significantly affect the tetrahedral chain vibration.

In Figure 11 we have plotted the peak position of the peaks at 660/685 cm^{-1} *vs* the bond distance of the shorter M1-O2 distance in the M1 polyhedron and *vs* the average T-O distance. The peak positions were also plotted *vs* the O3-O3-O3 kinking angle, a parameter which is expected to vary with intratetrahedral chain rotation, i.e. chain bending. Each point corresponds to a given P-T condition. The Raman peak positions were interpolated from the trend by Lin 2003 and Zucker et al 2009 to the P-T conditions of the *in situ* single crystal measurements (Periotto et al 2009, Yang et al. 1999). A single linear trend with pressure and temperature could be clearly observed between the two modes and the M1-O distances; the same could be observed, but with higher scattering of the data points, from the average tetrahedral bond distance (Fig.). The higher scattering likely comes from the higher relative experimental uncertainty in structural determination, in turn due to lower changes in bond distances with pressure and temperature in the tetrahedron. On the contrary the O3-O3-O3 chain kinking shows separate trends for the A and B chains. It appears therefore that the mode changes are determined mostly by bonding with the M1 cation and by internal intratetrahedral stretching, rather than by the chain rotation. It is therefore expectable that these modes, quite strong and well measureable, will be very sensitive to any structural substitution in the M1 site.

Implications

We have shown that quantum mechanical calculations predicting reliable Raman intensities, combined with a careful description of the modes, and taking advantage of isotopic substitution, enable to assess the contribution of bond distances and mass to a given vibration. There are modes most sensitive to specific structural substitutions, whose frequency is well related to the structural changes with pressure, temperature and composition.

Atomic mass and bond distances are related to the composition and a first obvious implication is to provide a clue for the most significant modes to address a specific cation

substitution, within structural sites. For instance we have found that in the peak at 920 cm^{-1} even relatively minor changes in the tetrahedral bond distances, like those for the T-O3

between enstatite and ferrosilite promote significant changes in Raman peak positions. This again relates to atomic composition, for instance Al-Si content, and makes Raman spectroscopy a probe for a site specific compositional determination, i.e. a probe for intracrystalline ordering.

As an example, the entrance of Al in the tetrahedral sites will affect mostly the tetrahedral stretching modes at higher wavenumber, reducing their frequency as Al increases the tetrahedral bond distances (Okamura et al 1974, Tribaudino 1996). Instead, the entrance of Al in the M1 site will affect the modes involved with M1 vibrations: we can predict that an increasing amount of Al in the M1 site, which has shorter bonding, higher charge and lower mass, can shift the vibrations more affected by the M1 site to higher energy. As a result the intracrystalline disorder of Al between the tetrahedral and octahedral sites could be potentially investigated. Although Raman data on natural Al-rich orthopyroxenes are lacking, the presence of tetrahedral Al is expected to be experimentally significant. In $C2/c$ pyroxenes the highest energy peak at 1010 cm^{-1} in diopside decreases to 953 cm^{-1} in the Ca-Tschermak pyroxene ($CaAl_2SiO_6$), where half of the tetrahedral sites are centered by Al (Sharma et al 1983).

Another example of potential application is Fe-Mg intracrystalline ordering: we have shown that the mode at 302 cm^{-1} is a potential probe for Fe-Mg intracrystalline ordering. In a mode like that at 302 cm^{-1} we do not expect linear changes with Fe content, as the mode is more sensitive to the site occupancy in either M1 and M2 sites. At the author knowledge, no experimental investigation was performed to verify the effect of Fe-Mg cation ordering on Raman active modes. However in their infrared study on the mixing properties of the enstatite-ferrosilite solid solution, Tarantino et al. 2012a found one phonon line dominated by the bending of the tetrahedral chains, which is sensitive to changes in the degree of cation order.

An experimental calibration should be performed to assess the effect of intracrystalline disorder on Raman peak positions, which goes beyond the scopes of this work. However, we have shown that careful assignment of the Raman peaks can be extremely useful to fully exploit the potential of Raman spectroscopy in the analysis of orthopyroxenes. Even if a calibration of the Raman peak position with ferrosilite content could be done without an understanding of the meaning of the Raman modes (Huang et al 2000, Wang et al 2001), an understanding of the structural meaning of the modes opens a new field in the understanding and prediction of structural changes in Raman spectra. We believe that our approach can be fruitfully done also in other minerals and mineral families, providing a basis and a key for future experimental Raman investigations and applications to mineral sciences.

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