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The infrared vibrational spectrum of andradite-grossular solid solutions: A quantum mechanical simulation

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(Article begins on next page)

1 **REVISION 2**

2 **The infrared vibrational spectrum of andradite-grossular solid**
3 **solutions. A quantum-mechanical simulation**

4
5 **MARCO DE LA PIERRE,^{1,*} YVES NOËL,² SAMI MUSTAPHA,³ ALESSIO MEYER,¹ PHILIPPE**
6 **D'ARCO,² AND ROBERTO DOVESI¹**

7
8 ¹*Dipartimento di Chimica, Università di Torino and NIS, Nanostructured Interfaces and Surfaces,*
9 *Centre of Excellence, Via P. Giuria 7, 10125 Torino, Italy*

10 ²*Institut des Sciences de la Terre de Paris (UMR 7193 UPMC-CNRS), UPMC, Sorbonne*
11 *Universités, Paris, France*

12 ³*Centre de Mathématiques de Jussieu (UMR 7193 UPMC-CNRS), UPMC, Sorbonne Universités,*
13 *Paris, France*

14
15 **ABSTRACT**

16 The IR vibrational spectra of andradite-grossular ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} - \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) solid solutions
17 were simulated at the *ab initio* level with the CRYSTAL09 code by using a large all-electron
18 Gaussian-type basis set and the B3LYP hybrid functional. All the 23 symmetry independent
19 configurations resulting from the substitution of 1 to 8 Fe atoms with Al atoms in the *16a*
20 octahedral site of the andradite primitive cell were considered. The IR active transverse optical
21 frequencies and their intensities were computed. Graphical representation of the spectra, animation
22 of the modes and isotopic substitution of the cations were used as additional interpretation tools.
23 The dominant high frequency modes, corresponding to Si-O stretching motions, show a simple
24 linear behavior of both frequencies and intensities with respect to the binary composition; this trend
25 is related to the linear behavior of the mean lattice parameter. Also the frequencies of the low
26 energy bands show, roughly speaking, a linear dependence on composition; however, the behavior
27 of the dominant intensities is more complicated and strongly connected to the Al and Fe atomic
28 fraction. When considering different possible structures at fixed composition, the spectral features
29 show a dependence upon short range cation ordering.

30
31 **Keywords** garnets, andradite, grossular, solid solutions, IR frequencies, IR intensities, ab initio
32 calculations, all electron gaussian basis sets, B3LYP, CRYSTAL code

* E-mail: marco.delapierre@unito.it

INTRODUCTION

33

34 Garnets ($X_3Y_2Si_3O_{12}$) are important rock-forming silicates, as major constituents of the Earth's
35 upper mantle and relevant phases of high-pressure metamorphic rocks in the Earth's crust (Deer et
36 al. 1992). From the technological point of view, they are largely used for a variety of industrial
37 applications, for example filtration media and abrasives, thanks to their recyclability and high
38 hardness (Olson 2001). The SiO_4 tetrahedra are the building blocks of the structure, interconnected
39 with YO_6 octahedra, whereas the X^{2+} cations fill the dodecahedral cavities. The highly symmetric
40 $Ia\bar{3}d$ space group contains 48 point-symmetry operations.

41 Natural garnets rarely exist as pure end members. They rather form solid solutions extending over a
42 broad chemical range involving up to 12 end members (Rickwood 1968). The most common cases
43 refer to substitutions of trivalent cations at Y sites or divalent cations at X sites. Simultaneous
44 substitutions at X and Y sites can also be observed. Intermediate compositions have been the object
45 of extensive studies, and a large set of experimental data is currently available, including structural
46 refinements (Merli et al. 1995), thermal expansion and elasticity (Isaak and Graham 1976; Isaak et
47 al. 1992; O'Neill et al. 1989), birefringence (Hofmeister et al. 1998; Akizuki 1984; Andrut and
48 Wildner 2001; Wildner and Andrut 2001) and Raman spectra (Kolesov and Geiger 1998).

49 Many investigations on silicon (McAloon and Hofmeister 1995; Hofmeister et al. 1996, 2004;
50 Geiger et al. 1989; Geiger 1998; Kolesov and Geiger 1998), aluminium (Chiriu et al. 2006) and
51 gallium (Papagelis et al. 2010) garnets dealt with the infrared (IR) response. In these studies the
52 effect of chemical substitution was investigated, and the dependence of the spectrum on the
53 composition (and cell volume) was interpreted on the basis of simple linear models, namely one-
54 and two- mode behaviors (Lucovsky et al. 1968; Chang and Mitra 1968; Fertel and Perry 1979),
55 which rely on the hypothesis of ideal mixing of the end members. However, several issues hinder a
56 full understanding of the experimental data: instrumental accuracy, correlation among model
57 parameters in the Kramers-Kronig analysis, proper symmetry analysis of the binary compounds,
58 hypothesis on mode decoupling, uncertainty on composition and structural distribution of cations.

59 In the context of solid solutions, computational techniques can be applied for a more detailed
60 analysis. Semi-classical models (Bosenick et al. 2000; Becker and Pollok 2002; van Westrenen et
61 al. 2003; Vinograd et al. 2004; Vinograd and Sluiter 2006; Vinograd et al. 2006) have been the
62 highest level of theory applicable to these problems for a long time. However, papers based on *ab*
63 *initio* DFT methods applied to pyrope-grossular (Sluiter et al. 2004; Freeman et al. 2006) and
64 pyrope-majorite (Yu et al. 2011) solid solutions have been published recently. In these studies the
65 computed energies were used within a Cluster Expansion Method (CEM) scheme (Connolly and
66 Williams 1983; Laks et al. 1992; Sluiter and Kawazoe 2003; Vinograd et al. 2004), the main goal
67 being the investigation of the thermodynamic properties of the solid solution.

68 Regarding garnets, quantum mechanical methods were successfully used to compute the vibrational
69 properties (frequencies and intensities), dielectric constants, IR reflectance spectra and magnetic
70 properties of pure garnet end members (Pascale et al. 2005; Zicovich-Wilson et al. 2008; Dovesi et
71 al. 2011; Meyer et al. 2010), including grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, indicated as Grs in the following)
72 and andradite ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, Adr). Structural and thermodynamical properties of the andradite-
73 uvarovite binary were also investigated with the same approach (Meyer et al. 2009).

74 In this paper we extend the analysis to the IR vibrational spectrum of andradite-grossular (Adr-Grs)
75 solid solutions. We investigate the dependence of the spectrum on the parameters characterizing the
76 Adr-Grs binaries: composition, structural parameters (in turn related to cations chemistry),
77 interactions among cations occupying the Y sites. The resulting representation of the evolution of
78 the IR spectrum, in going from one end member to the other, will provide clues for the critical
79 interpretation of the experimental findings. To our knowledge, this is the first *ab initio* study of the
80 infrared properties of a garnet solid solution.

81

82

MODELING APPROACH

83 **Computational details**

84 As in previous studies on end member garnets (Pascale et al. 2005; Zicovich-Wilson et al. 2008;

85 Dovesi et al. 2011; Meyer et al. 2010), the hybrid B3LYP spin-Hamiltonian (Becke 1993), all-
86 electron Gaussian type basis sets and the CRYSTAL09 code (Dovesi et al. 2009) were used.
87 B3LYP is widely and successfully used in molecular quantum chemistry (Koch and Holthausen
88 2000) as well as in solid state calculations, where it was shown to provide equilibrium geometries,
89 vibrational frequencies (Pascale et al. 2005; Zicovich-Wilson et al. 2008; Dovesi et al. 2011;
90 Zicovich-Wilson et al. 2004; Prencipe et al. 2004; Demichelis et al. 2011) and magnetic properties
91 such as the super-exchange coupling constants (Moreira et al. 2002; Moreira and Dovesi 2004;
92 Muñoz et al. 2004; Patterson 2008; Meyer et al. 2010) in good agreement with experimental data.
93 As regards the basis set, oxygen, silicon, calcium, aluminium and iron were described by
94 (8s)(411sp)(1d) (Pascale et al. 2005), (8s)(6311sp)(1d) (Pascale et al. 2005), (8s)(6511sp)(3d)
95 (Pascale et al. 2005), (8s)(611sp)(1d) (Zicovich-Wilson et al. 2008) and (8s)(64111sp)(411d)
96 (Pascale et al. 2005) contractions, respectively. For the discussion of the computational conditions
97 (tolerances for the truncation of the infinite Coulomb and exchange sums, SCF convergence
98 criteria, grid size for integration of the exchange-correlation density functional and number of
99 points in the reciprocal space) we refer to our previous studies on garnets (Pascale et al. 2005;
100 Zicovich-Wilson et al. 2008; Dovesi et al. 2011; Meyer et al. 2010), where the effect of the basis set
101 size on various properties was also investigated. Examples of input and output files can be retrieved
102 from the CRYSTAL web site (www.crystal.unito.it/supplement/index.html).
103 Structure optimizations were performed by using the analytical energy gradients with respect to
104 atomic coordinates and unit-cell parameters (Doll 2001; Doll et al. 2001; Civalleri et al. 2001), and
105 a Broyden-Fletcher-Goldfarb-Shanno scheme for Hessian updating (Broyden 1970; Fletcher 1970;
106 Goldfarb 1970; Shanno 1970). Convergence was checked on both the gradient components and the
107 nuclear displacements (TOLDEG and TOLDEX, see Dovesi et al. 2009, were set to $3.0 \cdot 10^{-5}$
108 Ha/Bohr and $1.2 \cdot 10^{-4}$ Bohr, respectively).
109 Point symmetry was used as extensively as possible. Symmetry lowering of intermediate Adr-Grs
110 configurations implies higher computational costs for the SCF cycle and a larger number of degrees

111 of freedom to be optimized, with a consequent increase of the number of optimization steps. For
 112 example, when symmetry drops from 48 (end members) to 2 point-symmetry operators (lowest
 113 symmetry mixed composition), the cost of a single SCF cycle increases from 50 to 800 seconds,
 114 and the number of optimization steps from 8 to 76 (timings refer to a DIRECT strategy, see Dovesi
 115 et al. 2009, and parallel running on a cluster of eight standard Intel Core2 CPUs).

116 The calculation of the transverse optical (TO) vibrational frequencies ν_0 at the Γ point was
 117 performed within the harmonic approximation. The mass-weighted Hessian matrix is constructed
 118 by numerical differentiation of the analytical gradients with respect to the atomic cartesian
 119 coordinates; one calculation would then require $(3N + 1)$ SCF+gradient calculations (241 for our
 120 unit cell, containing $N = 80$ atoms). However, symmetry reduces this number to between 9 (end
 121 members) and 133 (lowest symmetry cases). The calculation of the vibrational spectrum for a
 122 configuration with the lowest symmetry requires about one month on the 8-CPU node mentioned
 123 above.

124 Infrared intensities I_p were computed for each p^{th} mode by means of the mass-weighted effective
 125 mode Born charge \bar{Z}_p (Barrow 1962; Hess et al. 1986), evaluated through a Berry phase approach
 126 (Dall’Olio et al. 1997; Noël et al. 2002):

$$127 \quad I_p = \frac{\pi N_A}{3 c^2} \cdot d_p \cdot \left| \frac{\partial}{\partial Q_p} \bar{\mu} \right|^2 \quad (1)$$

$$128 \quad \left| \frac{\partial}{\partial Q_p} \bar{\mu} \right|^2 = |\bar{Z}_p|^2 = (Z_{p,x}^2 + Z_{p,y}^2 + Z_{p,z}^2) \quad (2)$$

129 where N_A is the Avogadro’s number, c is the speed of light, d_p is the degeneracy of the p^{th} mode, $\bar{\mu}$
 130 is the cell dipole moment, Q_p is the normal mode displacement coordinate, \bar{Z}_p is the Born charge
 131 vector in the basis of the normal modes. Further details on the calculation of vibrational frequencies
 132 can be found in Pascale et al. 2004; Zicovich-Wilson et al. 2004; Zicovich- Wilson et al. 2008.

133 A graphical representation of the infrared spectrum $S_L(\nu)$ for each configuration L was obtained as a

134 superposition of Lorentzian functions F , one for each mode:

$$135 \quad S_L(\nu) = \sum_p F(\nu; \nu_{0,p}, I_p, \gamma_p) \quad (3)$$

$$136 \quad F(\nu; \nu_{0,p}, I_p, \gamma_p) = \frac{I_p}{\pi} \left[\frac{\gamma_p/2}{(\nu - \nu_{0,p})^2 + (\gamma_p/2)^2} \right] \quad (4)$$

137 where γ_p is the damping factor of the p^{th} mode, which is related to the phonon lifetime. Being
 138 unable to compute this quantity, we used a constant value of 9 cm^{-1} , already adopted in Dovesi et al.
 139 2011 to simulate the reflectance spectra of six garnets. $S_L(\nu)$ curves were evaluated in the range
 140 $100\text{-}1000 \text{ cm}^{-1}$, in steps of 1 cm^{-1} .

141 When several configurations exist with a given composition x , the reported spectrum $\bar{S}_x(\nu, T)$ was
 142 obtained as a weighted average over all the corresponding spectra $S_L(\nu)$, by using the Boltzmann
 143 occupation probabilities P_L at temperature $T = 1300 \text{ K}$ and cell volume V as obtained upon structure
 144 optimization (for a given composition, V turns out to be constant to within 0.05% , see Table 1):

$$145 \quad \bar{S}_x(\nu, T) = \sum_L^{\text{fixed } x} P_L(V, T) \cdot S_L(\nu) \quad (5)$$

$$146 \quad P_L(V, T) = \left(\frac{M_L}{\sum_L^{\text{fixed } x} M_L \cdot e^{-\frac{E_L(V)}{k_B T}}} \right) e^{-\frac{E_L(V)}{k_B T}} \quad (6)$$

147 where $E_L(V)$ is the total energy of the L^{th} configuration, including the vibrational zero-point energy;
 148 M_L is the multiplicity of the L^{th} configuration (see Table 1 for M_L and P_L at 1300 K ; $E_L(V)$ reported
 149 in the Supplementary Material). Note that at 1300 K a single configuration provides more than 50%
 150 of the total weight for all but $x_{\text{Al}} = 0.5$ compositions. At 300 K this number increases to 80% (see
 151 Supplementary Material).

152 Graphical animation of the normal modes permits a visual reading of the corresponding
 153 eigenvectors. It is available for end member configurations at the CRYSTAL web site
 154 (www.crystal.unito.it/prtfreq/jmol.html), and permits a direct interpretation of the “nature” of the

155 mode (stretching, bending, rotation of the tetrahedra, translation of the X^{2+} cation, etc.) by simple
156 and intuitive means.

157

158 **Structural model**

159 The size of the reference cell has relevant effects on the description of the solid solution. In
160 particular, it affects the number of atomic distributions (configurations), the set of accessible
161 compositions, the order of the stars of neighbour pairs that can be populated independently. In order
162 to limit the computational cost (already quite high), the rhombohedral primitive cell of the end
163 members was taken as a reference in this study; it contains 8 trivalent Y cations (Y can be Fe and/or
164 Al) lying on a set of equivalent $16a$ octahedral sites. Figure 1 reports a schematic representation of
165 the octahedral sites in the structure of garnets: both the primitive and the cubic conventional cells
166 (80 and 160 atoms in total, respectively) are shown; the primitive cell Y sites contained in the
167 conventional cell are shaded and labelled from 1 to 8; translationally equivalent sites in the
168 conventional cell are labelled with primes.

169 Nine discrete compositions were considered, by varying the number of Al atoms substituting Fe
170 atoms in the Y sites from 0 to 8 (the atomic fraction x_{Al} of Al atoms then ranges from 0 to 1, in
171 steps of 0.125). Considering 2 chemical species distributed over the 8 sites, $2^8 = 256$ configurations
172 are possible. This set can be partitioned in classes of symmetry-equivalent configurations. A
173 symmetry analysis, carried out as described in Mustapha et al. 2012, shows that there are 23 such
174 classes. Among these, 2 correspond to the end members, Adr and Grs, the remaining 21 to
175 intermediate binaries. Pairs of Y cations can be populated independently up to the second
176 neighbours (i.e. up to a pair distance of 6.097 and 5.980 Å in Adr and Grs, respectively).

177 Table 1 summarizes the structural and symmetry information for the 23 symmetry independent
178 (classes of) configurations. Garnet end members show 48 symmetry operators (\leq in the Table);
179 upon substitution in the Y site, this number spans from 24 (the configuration at $x_{Al} = 0.5$ with the
180 highest symmetry) to 2 (the least symmetric configurations). As the symmetry reduces, the

181 multiplicity M of each configuration increases, as well as N_{df} , the number of degrees of freedom to
182 be considered in the structure optimization process.

183 The crystalline system ranges from cubic (end members) to triclinic (lowest symmetry), even if in
184 every case a quasi-cubic structure is easily identified, as reported in Table 1. Indeed, deviations
185 from the cubic metric are small and compare favorably to the experimental structures of “non-
186 cubic” garnets (McAloon and Hofmeister 1995). Figure 2 shows that the cubic root of the cell
187 volume \bar{a} (that coincides with the lattice parameter in the case of cubic systems) decreases linearly
188 from Adr to Grs, with a slope of -0.029 \AA per site substitution (in the primitive cell), very similar to
189 that obtained from experiments in McAloon and Hofmeister 1995 (-0.027 \AA per site substitution).

190

191

RESULTS AND DISCUSSION

192 **Vibrational properties: general features**

193 Frequencies and intensities of the IR vibrational modes were computed at the *ab initio* level for the
194 23 symmetry independent configurations. The most significant quantities are summarized in Table
195 2, in Figure 3 (providing the spectra of the seven independent configurations at $x_{Al} = 0.5$) and in
196 Figure 4, showing the weighted-average spectra for the various compositions from Adr to Grs, in
197 steps of 0.125.

198 As the symmetry reduces, the number of allowed IR active modes (N_{IR} in Table 2) increases and the
199 spectra become more complicated: there are 17 modes in the end members, 33 in the $x_{Al} = 0.5$
200 configuration with highest symmetry, and 129 in configurations with 2 symmetry operators only.
201 The additional allowed modes have intensities that are somehow proportional to the distortion from
202 the original cubic symmetry.

203 For convenience, the spectral range was divided in two regions, i.e. below (Lv) and above (Hv) 700
204 cm^{-1} (L and H stand for low and high frequency). Modes in the Hv region are related to stretching
205 motions of the SiO_4 tetrahedra, whereas Ca and Fe/Al cations provide important contributions to the
206 Lv modes (see the “type” column in Table 2). These attributions were obtained by combining

207 graphical animation of the modes with isotopic substitution (see Figure 5, which will be discussed
208 in the “IR wavenumbers” Section).

209 In the following, we will simplify the discussion by focusing on the dominant features of the
210 infrared spectra. The end members (see Figure 4) show four very intense bands with maxima at
211 277.8, 363.9, 792.4 and 866.9 cm^{-1} (Adr), and at 386.3, 432.7, 827.8 and 900.6 cm^{-1} (Grs). When
212 moving to binary systems, active modes (three-fold degenerate, F_{1u} symmetry) split, and many
213 others become active. As regards the high frequency Hv region, up to 15 and 8 modes appear in the
214 binaries (*L14* configuration) in the frequency ranges of the 792.4 and 866.9 cm^{-1} bands of Adr,
215 respectively (the end member shows only 2 and 1 modes). However, the convolution of such large
216 sets of modes in the binaries nearly coincides with the two bands of the end members. When
217 considering the low frequency Lv region, for lowly substituted binaries (1-2 atoms) the convolution
218 of the IR active modes still results in two well-defined spectral features. In highly substituted
219 binaries (3-5 atoms) the 290 ($x_{\text{Al}} = 3$) - 380 ($x_{\text{Al}} = 5$) cm^{-1} range shows a large number of modes of
220 similar intensity (24 in the case of *L14*), which makes the identification of bands more difficult and
221 the correspondence with the end members looser, whereas a well-defined feature is still found in the
222 370 ($x_{\text{Al}} = 3$) - 440 ($x_{\text{Al}} = 5$) cm^{-1} range (including up to 13 modes in *L14*). In the following, we
223 will call IR bands the four sets of features along the solid solution series described above, which
224 mimic the four intense structures in the end members spectra; they are labelled as Lv(1), Lv(2) and
225 Hv(3), Hv(4), respectively.

226 Each band is attributed the frequency of its most intense mode (“v” in Table 2). The integrated
227 intensity (“II” in the Table) of the four bands shows a very regular trend along the series from one
228 end member to the other, indicating that II is a significant quantity for our investigation. For each
229 band, II is the sum of the intensities I of all modes within the corresponding band range; note that,
230 given the high number of modes of similar intensity in highly substituted binaries (3-5 atoms), an
231 uncertainty in the order of a few hundreds km/mol should be considered for II values. For a more

232 detailed definition and description of IR bands and related quantities, see Supplementary Material.

233

234 **IR wavenumbers**

235 Figure 6(a) (and Table 2) shows that the frequencies of Hv(3) and Hv(4) bands (stretching modes of
236 the SiO₄ tetrahedra) vary linearly from one end member to the other. $\nu(3)$ increases from 792.4
237 (Adr) to 827.8 (Grs) cm⁻¹ ($\Delta\nu_{1-23} = 35.4$ cm⁻¹). The best fit straight line is $\nu(3) = (789.3 + 4.6 \cdot n_{Al})$
238 cm⁻¹, the maximum deviation from the linear behavior being 3.6 cm⁻¹ (in only 3 cases the deviation
239 is larger than 2.3 cm⁻¹, i.e. larger than half the difference between two contiguous compositions). As
240 regards $\nu(4)$, the two end members are at 866.9 (Adr) and 900.6 (Grs) cm⁻¹, respectively ($\Delta\nu_{1-23} =$
241 33.7 cm⁻¹). The slope is the same as for $\nu(3)$ (the fit function is $\nu(4) = (868 + 4.6 \cdot n_{Al})$ cm⁻¹); the
242 deviations are slightly larger than for $\nu(3)$, however they never exceed 5.0 cm⁻¹.

243 Given the anti-linear dependence of the cell parameter on the composition (Figure 2), the behaviors
244 of the wavenumbers of Hv bands show an anti-correlation with the cell parameter; a similar result
245 was found in the case of end member garnets both from *ab initio* calculations (Dovesi et al. 2011)
246 and experimental measurements (Hofmeister and Chopelas 1991). The reason is that, as the unit cell
247 becomes smaller, the interatomic distances between O atoms of the SiO₄ tetrahedra and the
248 neighboring atoms reduce; thus the potential (electronic and short range repulsion) perceived by the
249 SiO₄ tetrahedra becomes larger, resulting in higher frequencies. The behavior of the two bands is
250 ruled by this common factor (the reduction of the SiO₄ cage), as confirmed by the fact that the slope
251 of the two straight lines is the same.

252 The bars in Figure 6(a) represent the frequency differences between symmetry independent
253 configurations with the same composition, that are quite small for Hv bands: the difference with
254 respect to the average value (at fixed composition) exceeds 4 cm⁻¹ only in three cases, with a
255 maximum deviation of 8.4 cm⁻¹.

256 The situation is less simple for Lv(1) and Lv(2), because of the important contribution of the Y

257 cations, that are progressively substituted along the series, and whose motion couples to a large
258 extent. Isotopic substitution (see also Dovesi et al. 2011) permits to point out the participation of the
259 various chemical species to the vibrational modes. An extensive analysis was performed for the Lv
260 bands, by operating in three ways: the mass of Ca was increased by 20% (a); the Fe (b) or Al (c)
261 mass was reduced by 20%. In each case the spectrum was recalculated, and superposed to the
262 original one in order to identify the bands that are related to the motion of the three different
263 cations; these spectra are shown in Figure 5 for the nine compositions under study. As already
264 mentioned in the “Vibrational properties: general features” Section, information on the nature of the
265 two bands was summarized in the “type” column of Table 2, too.

266 The lowest band Lv(1) is dominated by Fe and Al motions in the case of Adr and Grs end members,
267 respectively (see top and bottom spectra in Figure 5); this simple attribution holds also in the case
268 of compositions close to the end members (see $x_{Al} = 0.125, 0.25, 0.75, 0.875$ spectra in Figure 5).
269 At intermediate compositions ($x_{Al} = 0.375 - 0.625$) a large number of modes appears in the Lv(1)
270 frequency range (up to 24 in the case of L14), which are related to the motion of both cations. In
271 general, modes associated to Al atoms lie at higher frequency (lighter mass) than those associated to
272 Fe; however, the two species appear to couple to a large extent, thus it was not possible to separate
273 the analysis for the two cations within the Lv(1) band.

274 The other low frequency band, Lv(2), corresponds to Ca motions in the case of pure Adr (top
275 spectrum in Figure 5). However, as far as Al atoms are inserted in the structure, the motion of this
276 relatively light atom couples with Ca. Indeed, a small component of the Lv(2) band appears to be
277 related to Al cations already in the case of $x_{Al} = 0.125$ (second spectrum in Figure 5); then, from x_{Al}
278 $= 0.25$ on, the whole band must be associated to mixed motions of both Ca and Al species (see
279 Figure 5).

280 Let us now analyze the behavior of the frequencies of Lv bands, by taking Figure 6(a) (and Table 2)
281 as a reference; again, a relatively simple behavior is detected. A linear fit provides $\nu(1) = (278 +$

282 $14.1 \cdot n_{\text{Al}} \text{ cm}^{-1}$ (correlation factor $R = 0.962$) and $\nu(2) = (373 + 8.0 \cdot n_{\text{Al}}) \text{ cm}^{-1}$ ($R = 0.963$),
283 respectively. The dispersion with respect to the fit is larger than in the case of Hv bands: in 10 and 6
284 out of 23 cases, respectively, the deviation is larger than half the difference between two contiguous
285 compositions (14.12 and 8.02 cm^{-1}), the largest ones being 16.4 and 9.7 cm^{-1} , respectively. The end
286 members frequencies are at 277.8 and 363.9 cm^{-1} (Adr), and at 386.3 and 432.7 cm^{-1} (Grs),
287 respectively. The step between the two end members $\Delta\nu_{1-23}$, that was as small as 35 cm^{-1} for the Hv
288 modes, is here much larger: 108.5 and 68.8 cm^{-1} , respectively.

289 As for the Si-O stretchings (Hv bands), the two Lv frequencies increase along the series; in this
290 case, this seems the combination of two effects: 1) the reduction of the cell volume; 2) the
291 substitution of a heavy atom (Fe) with a lighter one (Al). The latter issue justifies the higher slopes
292 of Lv bands with respect to Hv bands (the latter do not involve Y cations, thus are not affected by
293 its mass). Also the larger slope of Lv(1) with respect to Lv(2) may be explained in terms of the
294 different participation of cations to the vibrations (which was discussed above). In fact, Lv(2) is
295 essentially a Ca motion, which couples to a certain, but limited, extent with Al motion, when the
296 composition approaches the Grs end member; on the other hand, Lv(1) is a pure Y cation motion,
297 thus it is the most affected by the mass variation when spanning from Adr to Grs.

298

299 **IR intensities**

300 Figure 6(b) (see also Table 2) shows that the band intensity II of three out of four main bands varies
301 linearly with composition. The slope for II(3) is -1270 km/mol per site substitution; the maximum
302 deviation from the fit, 560 km/mol , and the maximum dispersion at fixed composition (see the two
303 horizontal bars in the Figure), 790 km/mol , are then smaller than the intensity difference between
304 two contiguous compositions. This suggests that the intensity of this band could be used as a marker
305 for the composition of the Adr-Grs solid solutions. For II(4) the slope is five times smaller (-260
306 km/mol per site substitution, with a maximum deviation from the fit equal to 830 km/mol).

307 The negative slope of both Hv curves is to be related to the reduction of the cell volume along the
308 series. The resulting shortening of the distances between O atoms of the SiO₄ tetrahedra and the
309 neighboring atoms constrains the motion of the tetrahedra, producing a reduction of the dipole
310 moment variation associated to the mode (i.e. of the Born charge vector modulus $|\vec{Z}_p|$, see Eqs. (1)
311 and (2) in the “Computational details” Section).

312 As regards the low frequency region, the two bands show a quite different behavior, that can be
313 related to the different participation of the Y cations (as discussed in the “IR wavenumbers”
314 Section). Intensity II(2) shows a large, positive, nearly linear behavior with respect to the
315 composition (the slope is +1380 km/mol per site substitution); the maximum dispersion at fixed
316 composition (see the two horizontal bars in Figure 6(b)) is always smaller than the intensity
317 difference between contiguous compositions. The growing intensity is possibly associated to the
318 important change in the atoms participating in the modes (see the “IR wavenumbers” Section and
319 Figure 5). Let us consider the case of the end members, whose Lv(2) bands are composed by only 1
320 (Adr) and 2 (Grs) modes (however, in the latter case one mode provides the 99 % of the total band
321 intensity); thus, in this case the band integrated intensity II(2) reduces to the intensity I of either the
322 unique or major component mode. Adr shows a pure Ca mode (top of Figure 5), the corresponding
323 intensity I being 8542 km/mol; Ca²⁺ is a bulky cation, with a radius of 1.12 Å (Shannon 1976)
324 against a cage size (estimated through the mean cation-oxygen distance within the unit cell) of
325 about 2.4 Å. In Grs, on the contrary, both Ca and Al contribute to the mode (bottom of Figure 5),
326 and I is as large as 20044 km/mol. Al³⁺ cations are much smaller than Ca²⁺ (0.54 Å radius, from
327 Shannon 1976, against a cage size of 1.94 Å); the smaller cation/cage size ratio is responsible for
328 larger cation motions, and thus for the larger dipole moment variations (and larger $|\vec{Z}_p|$ values, see
329 above).

330 The Lv(1) band shows a more complex behavior. Its intensity II(1) decreases from 16026 ($x_{Al} = 0$)
331 to about 7000 km/mol ($x_{Al} = 0.375$) on the Adr side, then it remains almost constant, showing a

332 plateau at about 8000-9000 km/mol on the Grs side. As already discussed, this band is mainly
333 related to the motion of Y cations. By looking at Figure 5, we notice that in the range $x_{Al} = 0 -$
334 0.375 , Lv(1) is dominated by Fe; the decreasing fraction of Fe in the unit cell implies a reduced
335 contribution to II(1). For compositions $x_{Al} \geq 0.5$, Al and Fe motions couple together in the Lv(1)
336 band. Thus, the decreasing contribution to II(1) coming from Fe cations is compensated by the
337 increasing contribution from Al; as a consequence, the total band intensity II(1) is almost constant
338 in this latter compositional range.

339 An overall analysis of intensities along the Adr-Grs binary is possible by considering the sum of
340 intensities $F = \sum_j II_j$ for the two spectral ranges, i.e. Lv and Hv, which is represented in Figure
341 6(c) (see also Table 2). The contribution at high ν shows a linear behavior, with a slope of -1530
342 km/mol per site substitution. This is not surprising, being the result of the superposition of the
343 trends observed for the Hv(3) and Hv(4) bands, which have already been discussed above. This
344 trend turns out to be dominant also for the F value integrated along the whole spectral range (with a
345 slope of -1390 km/mol per site substitution).

346 A rather peculiar trend is found in the case of the contribution at low ν , which is almost constant
347 with respect to the composition, the maximum variation being +1104 km/mol along the 23
348 configurations (+3%). This behavior is possibly related to a sort of compensation between two
349 opposite effects along the binary series: a) the decrease of the cell parameter, which likely implies a
350 reduction of the dipole moment variation (see discussion above for Hv(3) and Hv(4)), and b) the
351 role of the varying chemical composition in the Y sites, which somehow accounts for an increase of
352 the dipole moment of the modes. Concerning the latter point, one of the possible factors could be
353 the reduction of the Y cationic radius in the octahedral site ($r_{Fe} = 0.65 \text{ \AA}$, $r_{Al} = 0.54 \text{ \AA}$, from
354 Shannon 1976). Indeed, we observe that the ratio between the Y cation radius and the Y site size
355 (estimated again through the Y-O mean distance) reduces from 0.3173 (Fe, in Adr) to 0.2782 (Al in
356 Grs). Thus, the shortening of cell parameters turns out to be overcompensated by the reduced

357 dimension of the Y cation.

358

359 **Behavior at fixed composition**

360 In order to analyze the dependence of the IR spectra upon the structure at fixed composition, i.e.
361 upon the ordering of the Y cations, the $x_{Al} = 0.5$ case, with seven symmetry independent
362 configurations, was considered (see Table 2 and Figure 3).

363 As anticipated above (“Vibrational properties: general features” and “IR wavenumbers” Sections),
364 $Lv(2)$, $Hv(3)$ and $Hv(4)$ are essentially independent from the relative position of the Y cations: the
365 maximum variation of frequency ($\Delta\nu$) and intensity (ΔI) at fixed composition is 5 cm^{-1} and 10%,
366 respectively, and only minor differences (e.g. small shoulders and satellite peaks) can be observed
367 between the seven spectra.

368 The $Lv(1)$ band corresponds, on the contrary, to modes with large contributions from the Y cations
369 (“IR wavenumbers” Section). In this case $\Delta\nu$ can be as large as 24 cm^{-1} ($L10$ vs $L11$), and ΔI can
370 reach 20% ($L12$ vs $L14$). The differences in the $Lv(1)$ frequency range of the spectra become then
371 clearly visible (Figure 3).

372 Let us concentrate the analysis on a single, intense IR mode in the frequency range $320 - 370\text{ cm}^{-1}$
373 (see Figure 3, and also Table 3). $L9$ is our starting point: this configuration is cubic and
374 characterized by a very intense F_u mode at 347.2 cm^{-1} . In $L12$, trigonal, this triple degenerate mode
375 splits into a double degenerate (E_u) mode at 344.6 cm^{-1} and a singlet (A_u) at 324.2 cm^{-1} . The same
376 situation is found for $L11$, tetragonal, but in this case intensities are smaller. $L10$ is orthorhombic,
377 so that the single mode in $L9$ splits in three singlets at 361.1 , 365.9 and 327.4 cm^{-1} (with B_{1u} , B_{2u}
378 and B_{3u} symmetries, respectively). The last three configurations, $L13$, $L14$ and $L15$ display a larger
379 number of modes (the cell is monoclinic or triclinic), so that the link to the original mode is less
380 evident.

381 We can try to correlate the presence of the peak at about 350 cm^{-1} to the short range Y cation
382 ordering in the cell. To this aim, the first neighbors Y-Y couples were classified as shown in Table

383 3. Upon symmetry analysis of the end member cubic structure (Mustapha et al. 2012), these couples
384 split in two classes; for each class, the abundance of Fe-Fe, Al-Al and Fe-Al couples is given. The Δ
385 index (see the caption to the Table for the definition) summarizes the relative abundance of
386 heteroatomic and homoatomic couples. *L9* and *L12* are configurations where heteroatomic couples
387 are far more abundant than homoatomic couples (Δ_1, Δ_2 are equal to +1, +1 for *L9* and to +1, 0 for
388 *L12*). In the spectra, both configurations show very intense modes at about 350 cm^{-1} . *L11* displays a
389 positive Δ_1 but a negative Δ_2 ($\Delta_1 = +1, \Delta_2 = -0.33$); also in this case there is a mode at about 350 cm^{-1}
390 ¹, but the intensity is lower than for *L9* and *L12*. *L10* presents the largest abundance of homoatomic
391 couples ($\Delta_1 = -1, \Delta_2 = +0.33$); in this case there are no intense modes at about 350 cm^{-1} . For the
392 three remaining configurations both Δ_1 and Δ_2 are around zero, and then an intense peak at 350 cm^{-1}
393 cannot be identified. The presence of this peak can then be correlated to the occurrence of a
394 relatively large number of Fe-Al couples. This confirms that structural analysis of short range
395 ordering can be used to support the interpretation of spectroscopic features of binary systems.

396

397 **Comparison with experiments**

398 A detailed infrared reflectance study on a set of 14 natural garnets belonging to the Adr-Grs binary
399 was carried out in 1995 by McAloon and Hofmeister (McAloon and Hofmeister 1995). In this work
400 the authors presented a Kramers-Kronig analysis of the spectra, based on the hypothesis of quasi-
401 cubic symmetry of the whole series, i.e. 17 modes were searched for each sample; the subsequent
402 mode assignment was made on the assumption of complete decoupling of modes involving different
403 structural subunits. Then, the dependence of IR modes on the composition was classified into two
404 categories: a) one-mode behavior (Lucovsky et al. 1968), in which modes are found along the
405 whole series, showing a linear dependence of ν on the composition; intensity does not vary strongly
406 (thus it is not analyzed in detail in McAloon and Hofmeister 1995). Most of the modes (14 out of
407 17) were assigned to this class; b) two-mode behavior (Chang and Mitra 1968, Fertel and Perry

408 1979), according to which there are modes specific to each of the end members: the intensity
409 decreases when going to intermediate compositions, reaching zero when approaching the opposite
410 end member; ν still varies linearly with composition. According to McAloon and Hofmeister 1995,
411 only three modes have a two-mode behavior; they are in the low frequency region and associated to
412 the motion of either FeO_6 (244 and 297 cm^{-1} , Adr) or AlO_6 (425 cm^{-1} , Grs) octahedra. The two-
413 modes behavior was thus expected to be related to local modes (McAloon and Hofmeister 1995),
414 when the substituting atoms show largely different masses or force constants (Chang and Mitra
415 1968) and when end member bands do not overlap (Fertel and Perry 1979).

416 We compared the experimental reflectance spectra from McAloon and Hofmeister 1995 with our
417 calculated curves, and observed many similarities in the trends of the modes along the series. In
418 particular, our Lv(2), Hv(3) and Hv(4) bands can be interpreted according to the experimental one-
419 mode behavior. These bands have partial (Lv(2)) or no (the other two) dependence on the
420 substituting Y atoms, resulting in a smooth behavior of frequency on composition. In this respect,
421 the analysis we carried out in the “IR wavenumbers” and “IR intensities” Sections permits to
422 deepen the understanding of these trends, in particular with reference to the intensity, where we
423 discuss the influence of different factors, either structural (cell parameter) or compositional (effect
424 of substituting atoms on mixed modes).

425 It is worth also comparing the simulated and experimental slopes $d\nu/dx_{\text{Al}}$, as a correspondence can
426 be found between the frequencies of our Lv(2), Hv(3) and Hv(4) bands and the ones of modes
427 labelled I, D and B in McAloon and Hofmeister 1995, respectively. In our case, the values are 0.64,
428 0.36 and 0.37 $\text{cm}^{-1}/\text{mol}\%$ (converted in appropriate units from the “IR wavenumbers” Section), to
429 be compared with 0.67, 0.31 and 0.30 $\text{cm}^{-1}/\text{mol}\%$ from the experiment. The agreement is very
430 satisfactory; in particular, the difference in slope between Ca (Lv(2)) and SiO_4 (Hv(3) and Hv(4))
431 dominated modes is confirmed.

432 The case of low frequency, Y cation-specific modes is rather interesting. When comparing the so

433 called two-mode behavior in McAloon and Hofmeister 1995 with our Lv(1) band, we observe in
434 both cases a linear dependence of ν on composition. The significant issue is the different attribution
435 (here and in the experiment) of close-frequency Fe or Al dominated motions to either two separate
436 modes or to the same band. Indeed, both the experimental and the computational descriptions are
437 reasonable, focusing on different aspects of the spectra. Based on the hypotheses of quasi-cubic
438 symmetry and subunits decoupling, experimentalists attempt to perform a complete assignment of
439 all (actually “all 17”) modes of the binary. In this respect, simulation unveils aspects of complexity
440 that require to modify this basic assumption in two directions: a) the reduction of symmetry results
441 in a great number of non-degenerate, IR active modes at intermediate compositions (up to 129, ν_s
442 17 in the end members); b) isotopic substitution shows that different subunits couple together,
443 giving rise to mixed motions, especially in the case of Y cations.

444 As a consequence of this discussion, it is reasonable to complete the picture of the two-mode
445 behavior with the following remark. On the one hand, when moving towards one end member or
446 the other ($x_{Al} \leq 0.375$ for Adr, or $x_{Al} \geq 0.75$ for Grs), one mode becomes dominant in the Lv(1)
447 frequency range, being associated to motions of the most abundant Y species (either Fe or Al). On
448 the other hand, in the case of intermediate compositions, the same frequency range becomes
449 characterized by a large number of IR active modes (up to 24), that may show a different, and
450 somehow mixed, nature: Fe dominated, Al dominated, or Fe/Al coupled.

451

452

CONCLUSIONS

453 The infrared properties of nine compositions of the andradite-grossular solid solution were
454 computed at the *ab initio* level by using the hybrid B3LYP functional, an all-electron Gaussian-type
455 basis set and the CRYSTAL09 code. The calculations were performed for 23 independent
456 configurations, identified upon symmetry analysis within a primitive cell model.

457 Infrared bands in the range 700-1000 cm^{-1} (related to Si-O stretchings) show frequencies and
458 intensities anti-correlated and correlated with the Al content, respectively. This behavior is directly

459 related to the linear trend of the cell parameters, and is in agreement with the “one-mode” behavior
460 identified by experimentalists.

461 Of the two most intense bands identified at low frequencies, the one that spans from 360 (Adr) to
462 430 (Grs) cm^{-1} is mainly related to Ca motions. Both its frequency and intensity increase linearly
463 with increasing Al content, with a “one-mode” behavior.

464 The band ranging from 280 (Adr) to 390 (Grs) cm^{-1} corresponds to pure Y cation motions. While
465 the frequency is roughly linearly dependent on composition, the intensity shows a non-constant
466 trend, with a maximum at the Adr side, and a plateau towards the Grs side. This analysis permits a
467 better characterization of the so called “two-mode” behavior in Adr-Grs solid solution. Rather than
468 two single modes with well distinct intensities (Fe and Al specific), a broad band is identified, made
469 up of many modes, whose intensities strongly depend on symmetry and Fe/Al cation-coupling
470 properties.

471 At fixed binary composition, the Y-specific frequency range (280-390 cm^{-1}) shows a dependence of
472 the spectral features upon short range Y cation ordering. In particular, a peak near 350 cm^{-1} is
473 found, whose intensity depends on the relative abundance of first neighbors Fe-Al heteroatomic
474 couples over Fe-Fe or Al-Al homoatomic ones.

475 We have shown that *ab initio* calculations are a powerful tool that permits to analyze complex
476 systems such as solid solutions. Relationships among structure and properties are established, so
477 that experimental findings may be critically and robustly interpreted.

478

479

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482

483 **FIGURES**

484

485 **Figure 1** Schematic picture of the Adr (Grs) structure: cubic conventional cell and rhombohedral
486 primitive cell. Only the Y sites, containing Fe (Al) atoms, are reported. Labelled sites belong to the
487 conventional cell; among them, shaded sites, labelled from 1 to 8 without primes, belong to the
488 primitive cell. Primed sites are translated images of the corresponding ones in the primitive cell.

489

490 **Figure 2** Dependence of $\bar{a}=V^{1/3}$ (V is the volume of the conventional cell, in \AA^3) on x_{Al} , the
491 fraction of Al atoms in the Y sites per unit cell. For each composition, the dot is the average among
492 the corresponding configurations, and the two bars on each dot refer to the highest and lowest value
493 within the set of corresponding configurations. Note that only for $x_{\text{Al}} = 0.5$ they do not coincide in
494 the figure scale (see also the Volume column in Table 1). The regression line is shown as well.

495

496 **Figure 3** Calculated infrared spectra for the seven configurations corresponding to $x_{\text{Al}} = 0.5$ ($n_{\text{Al}} =$
497 4). L and \wp are the label of the configuration and the occupation probability at 1300 K and
498 optimized cell volume, respectively, according to Table 1. A Lorentzian function is associated to
499 each calculated frequency (ν); the peak area is the calculated intensity (I); the peak width is set to γ
500 $= 9 \text{ cm}^{-1}$ (see the “Computational details” Section).

501

502 **Figure 4** Calculated infrared spectra at 1300 K for nine compositions of the Adr-Grs solid
503 solutions, with x ranging from 0 (Adr) to 1 (Grs), in steps of 0.125 (number of Al atoms $n_{\text{Al}} = 0-8$).
504 Spectra are constructed as in Figure 3. In the case of compositions corresponding to more than one
505 symmetry independent configuration ($x = 0.25-0.75$), spectra are averaged with \wp (the occupation
506 probability of the L^{th} configuration at 1300 K and optimized cell volume) weights, as described in
507 the “Computational details” Section.

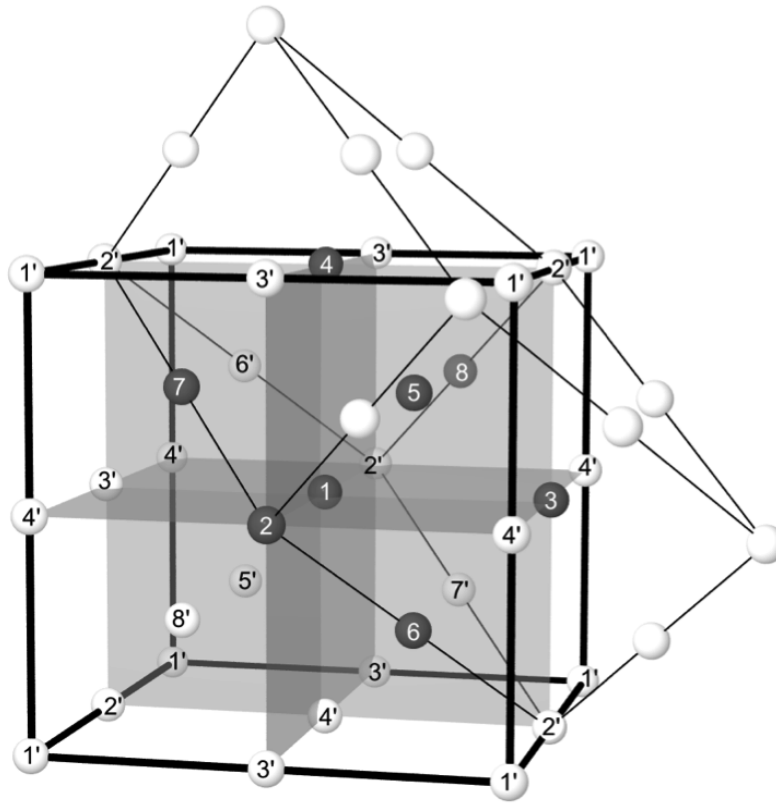
508

509 **Figure 5** Effect of cation isotopic substitution on the calculated spectra at 1300 K of nine
510 compositions of the Adr-Grs solid solutions, with x ranging from 0 (Adr) to 1 (Grs), in steps of
511 0.125 (number of Al atoms $n_{\text{Al}} = 1-8$). Only the low frequency range 200-600 cm^{-1} is plotted.
512 Isotopic spectra are obtained by increasing (Ca) or decreasing (Al and Fe) the masses of the
513 corresponding cations by 20%. Spectra are constructed as in Figure 4.

514

515 **Figure 6** Infrared properties as a function of x_{Al} , the fraction of Al atoms in the Y sites per unit cell
516 (see also Table 2): (a) wavenumbers ν , and (b) integrated intensities I of the four bands; (c) sum of
517 the infrared intensities $F = \sum_j I_j$. The frequency range is divided in two regions: below (Lv) and
518 above (Hv) 700 cm^{-1} . For each composition, the point and the error bars refer to the average value
519 and to the highest/lowest values, respectively, among the corresponding configurations. The
520 regression line is shown in all cases; note that, for the integrated intensities I of Lv(1) band, two
521 distinct lines are drawn, for the ranges $x_{\text{Al}} = 0 - 0.375$ and $x_{\text{Al}} = 0.375 - 1$, respectively.

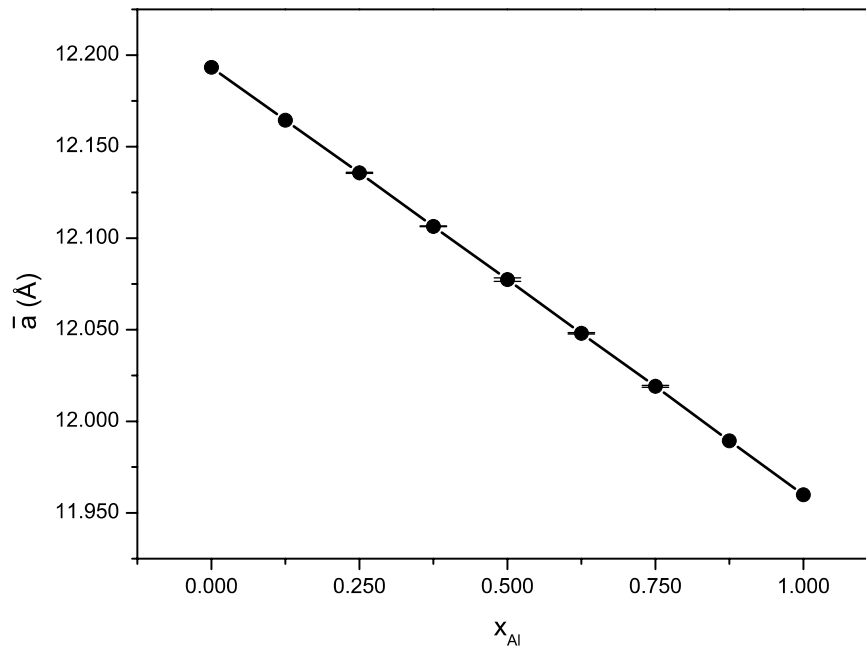
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Figure 1

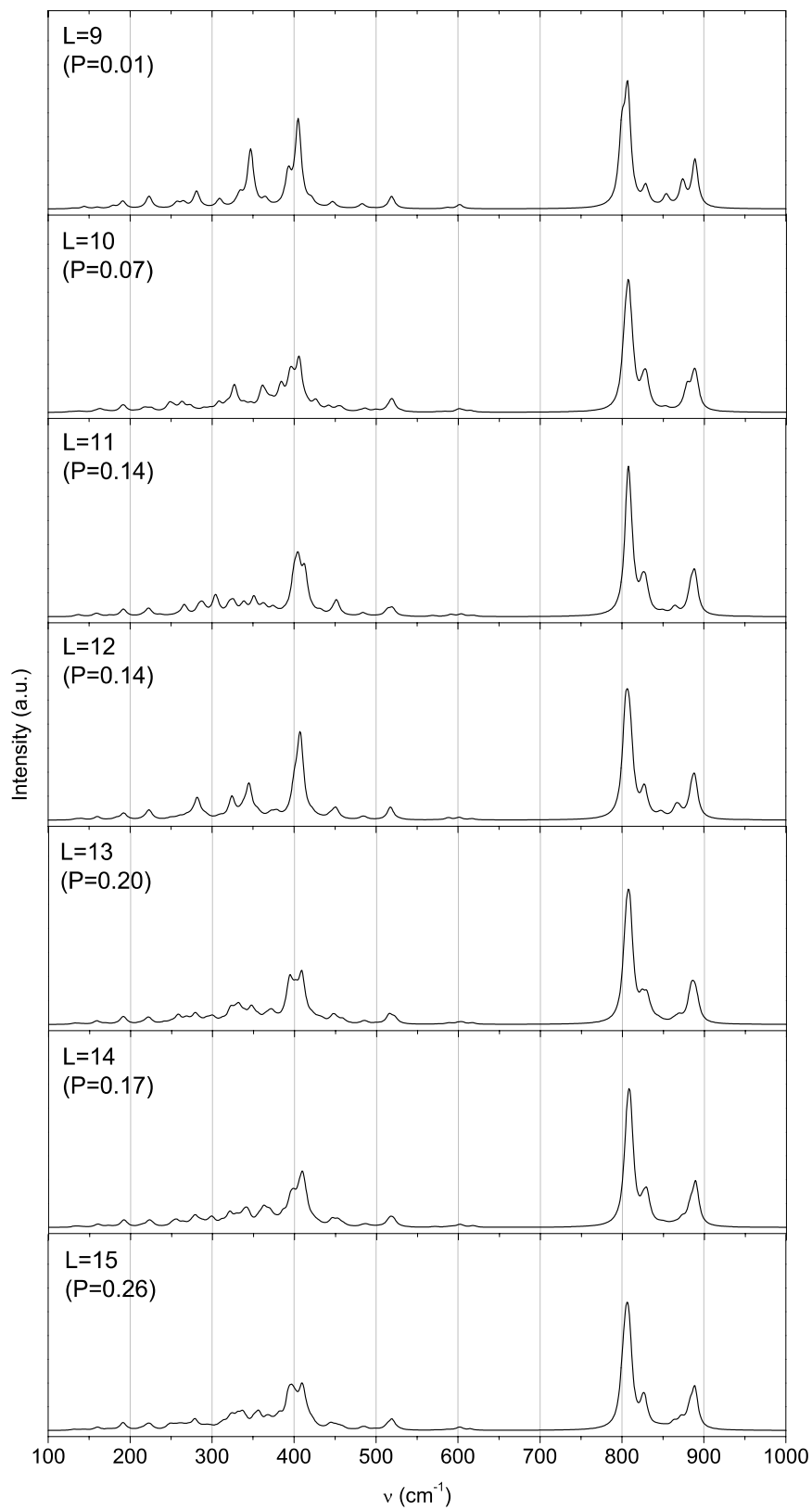


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Figure 2

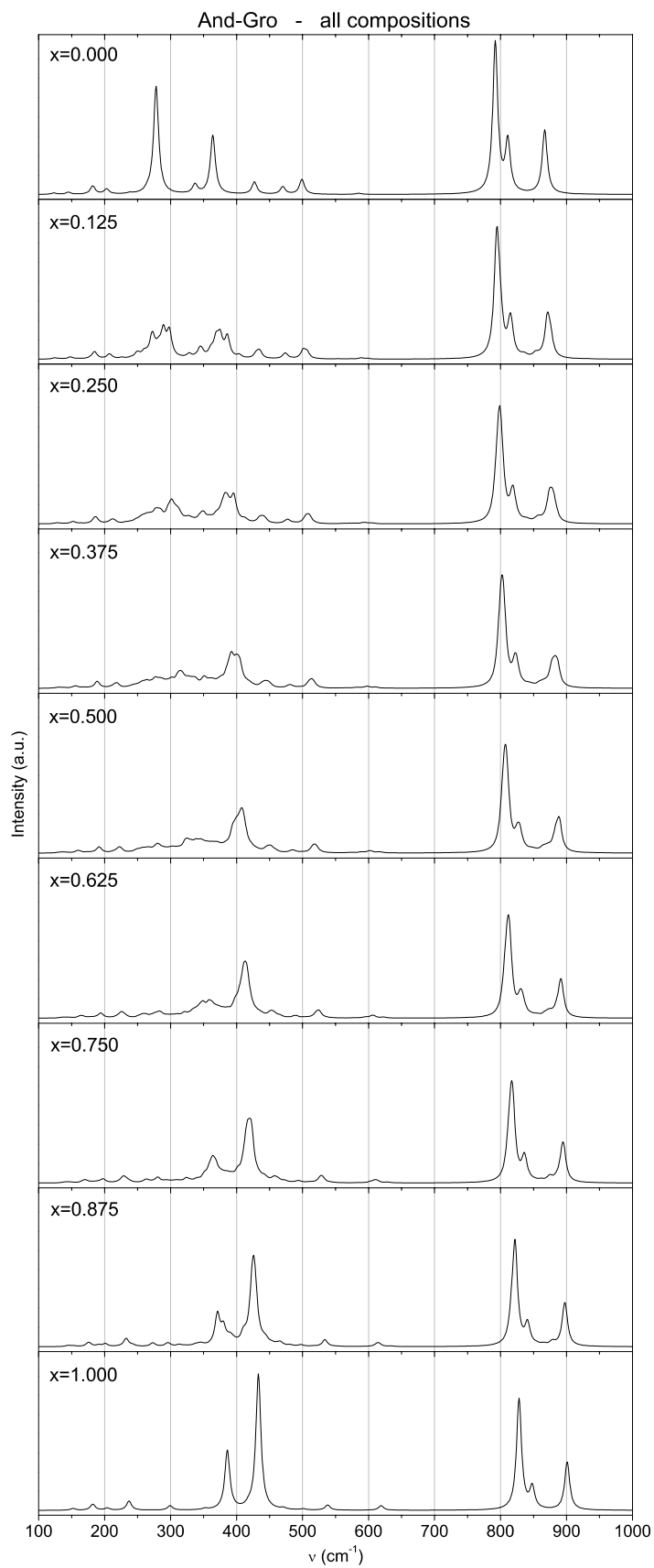
And-Gro - $x=0.500$ ($n_{Al}=4$)



527

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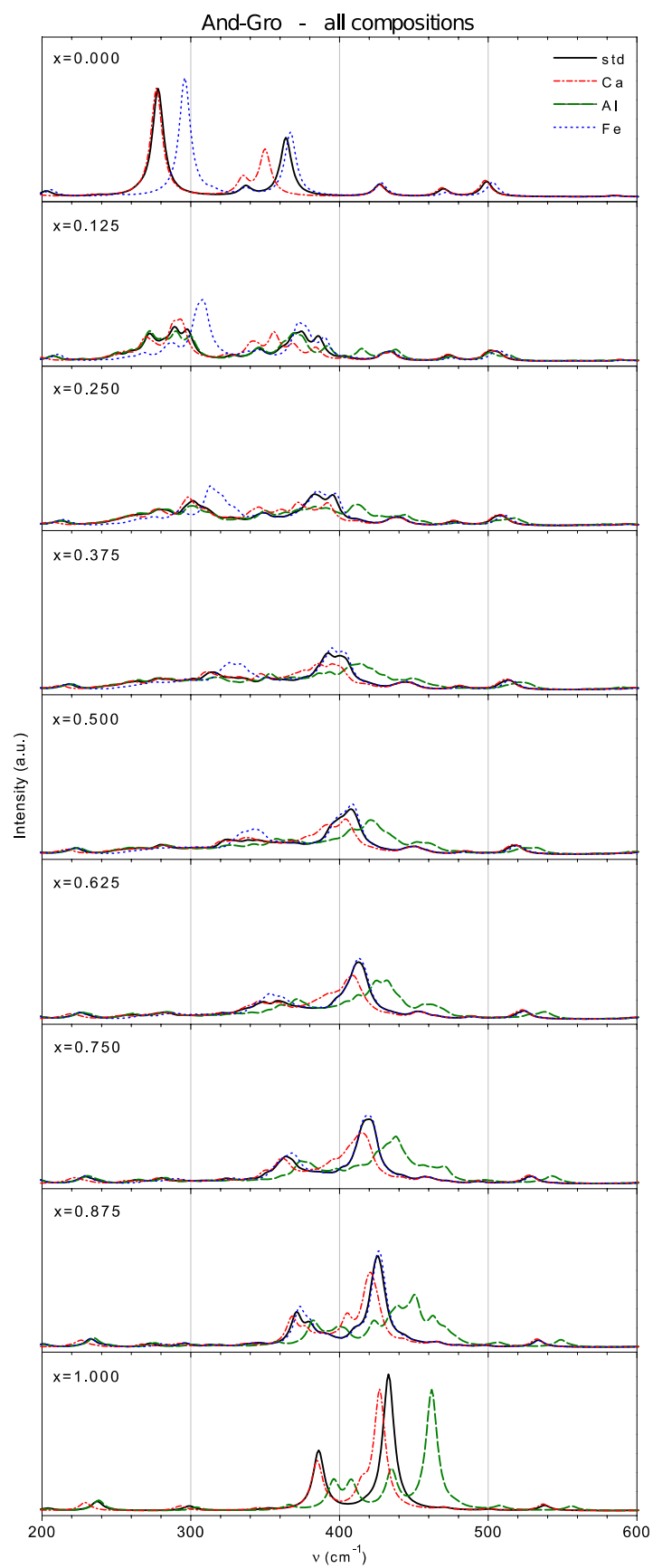
Figure 3



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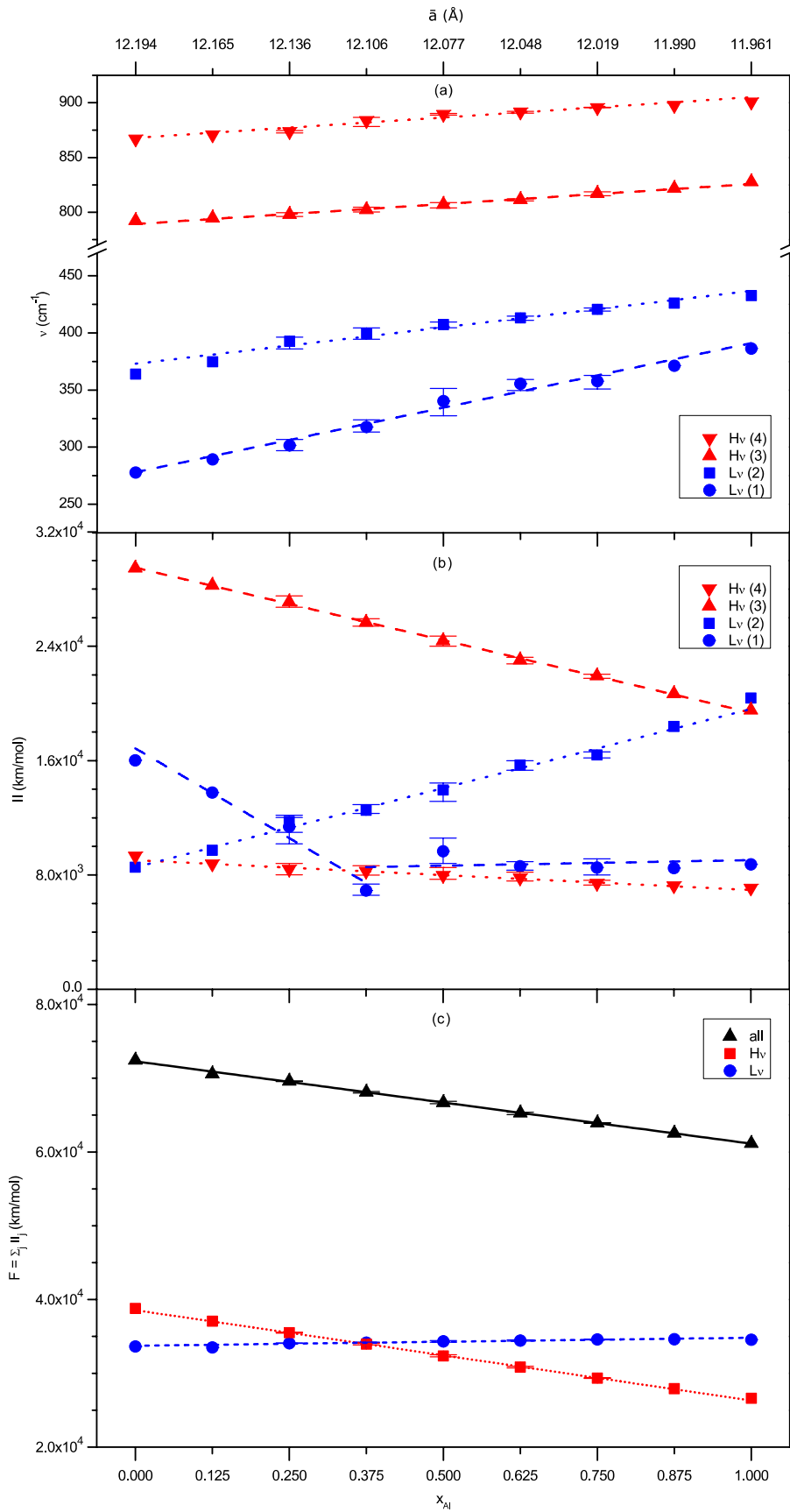
Figure 4



531

532

Figure 5



533

534

Figure 6

535 **TABLES**

n_{Al}	x_{Al}	L	M	S	N_{df}	CRY	D	a	b	c	α	β	γ	V	\mathcal{P}
0	0.000	1	1	48	4	CUB	none	12.193	12.193	12.193	90.000	90.000	90.000	1812.8	1.00
1	0.125	2	8	6	38	TRG	1	12.164	12.164	12.164	89.848	89.848	89.848	1800.0	1.00
2	0.250	3	4	12	19	TRG	1-5	12.136	12.136	12.136	89.706	89.706	89.706	1787.5	0.11
		4	12	4	56	MON	3-4	12.134	12.135	12.137	90.000	90.000	90.293	1787.2	0.37
		5	12	4	57	MON	1-6	12.135	12.138	12.135	89.962	89.673	89.962	1787.2	0.53
3	0.375	6	8	6	38	TRG	5-6-7	12.106	12.106	12.106	89.853	89.853	89.853	1774.3	0.09
		7	24	2	114	TRC	1-2-5	12.105	12.103	12.113	89.850	89.920	89.603	1774.5	0.37
		8	24	2	114	TRC	1-2-7	12.106	12.108	12.104	90.171	89.881	89.880	1774.4	0.54
4	0.500	9	2	24	9	CUB	5-6-7-8	12.077	12.077	12.077	90.000	90.000	90.000	1761.5	0.01
		10	6	8	28	ORT	1-3-5-8	12.086	12.075	12.075	89.383	90.000	90.000	1762.1	0.07
		11	6	8	27	TET	1-2-7-8	12.079	12.079	12.072	90.000	90.000	90.000	1761.3	0.14
		12	8	6	38	TRG	1-6-7-8	12.077	12.077	12.077	89.970	89.970	89.970	1761.5	0.14
		13	12	4	57	MON	1-2-5-7	12.075	12.079	12.079	89.965	89.699	89.699	1761.7	0.20
		14	12	4	57	MON	1-2-5-8	12.074	12.084	12.074	89.732	90.089	89.732	1761.6	0.17
5	0.625	15	24	2	114	TRC	1-2-3-5	12.080	12.073	12.080	89.704	89.982	89.658	1761.8	0.26
		16	8	6	38	TRG	1-2-3-4-8	12.048	12.048	12.048	90.174	90.174	90.174	1748.8	0.08
		17	24	2	114	TRC	3-4-6-7-8	12.048	12.048	12.050	90.137	90.158	90.400	1749.1	0.38
6	0.750	18	24	2	114	TRC	3-4-5-6-8	12.052	12.042	12.049	89.846	90.069	90.085	1748.7	0.54
		19	4	12	19	TRG	2-3-4-6-7-8	12.020	12.020	12.020	90.331	90.331	90.331	1736.5	0.12
		20	12	4	56	MON	1-2-5-6-7-8	12.018	12.018	12.021	90.000	90.000	89.675	1736.2	0.34
7	0.875	21	12	4	57	MON	2-3-4-5-7-8	12.021	12.021	12.015	90.025	90.025	90.267	1736.1	0.55
		22	8	6	38	TRG	2-3-4-5-6-7-8	11.989	11.989	11.989	90.159	90.159	90.159	1723.4	1.00
8	1.000	23	1	48	4	CUB	all	11.960	11.960	11.960	90.000	90.000	90.000	1710.7	1.00

536

537 **Table 1** Structural properties of the Adr-Grs solid solutions. n_{Al} and x_{Al} are the number and the
538 fraction of Al atoms in the Y sites, respectively; n_{Al} refers to the primitive cell (80 atoms). L labels
539 the symmetry independent configurations. M , S and N_{df} are the multiplicity of each configuration,
540 the number of symmetry operators and the number of geometry variables to be considered in the
541 structure optimization, respectively; CRY indicates the crystal system of the primitive cell,
542 attributed on the basis of the set of symmetry operators. Column **D** indicates the Al atoms of the
543 primitive cell according to the labels of Figure 1. The cell parameters a , b , c [Å], α , β , γ [deg] and
544 V [Å³] are given with reference to the quasi-cubic conventional cell (160 atoms), to facilitate the
545 comparison among configurations. \mathcal{P} is the occupation probability of the L^{th} configuration at 1300 K
546 and optimized cell volume.

n_{Al}	x_{Al}	L	N_{IR}			Lv(1)			Lv(2)			Hv(3)		Hv(4)		F			
			Lv	Hv	all	v(1)	II(1)	type(1)	v(2)	II(2)	type(2)	v(3)	II(3)	v(4)	II(4)	Lv	Hv	all	
0	0.000	1	14	3	17	277.8	16026	Fe	363.9	8542	Ca	792.4	29479	866.9	9323	33636	38802	72437	
1	0.125	2	70	16	86	289.2	13766	Fe	374.7	9733	Ca+Al	794.7	28264	870.7	8771	33518	37059	70577	
2	0.250	3	53	12	65	296.9	10169	Fe	385.9	12062	Ca+Al	798.0	27530	874.7	8016	34042	35546	69587	
			4	105	24	129	306.7	11947	Fe	395.8	12182	Ca+Al	796.2	26735	874.0	8811	34080	35557	69637
			5	105	24	129	301.0	12024	Fe	396.3	10983	Ca+Al	799.7	27042	872.5	8367	34100	35444	69544
3	0.375	6	70	16	86	315.7	6575	Fe	394.4	12924	Ca+Al	804.6	25416	886.6	8643	34125	34064	68188	
			7	105	24	129	323.9	7371	Fe	400.1	12304	Ca+Al	802.4	25925	886.1	7990	34224	33921	68145
			8	105	24	129	313.2	6790	Fe	404.4	12359	Ca+Al	800.3	25669	878.2	8164	34132	33864	67996
4	0.500	9	27	6	33	347.2	10074	Al+Fe	404.6	14430	Ca+Al	807.5	23999	888.6	8524	34202	32523	66724	
			10	80	18	98	327.4	9549	Al+Fe	406.2	14194	Ca+Al	807.6	24711	889.9	7725	34427	32436	66863
			11	53	12	65	351.3	9818	Al+Fe	405.0	13590	Ca+Al	807.0	24427	889.5	7768	34320	32229	66550
			12	70	16	86	344.6	8804	Al+Fe	407.5	14050	Ca+Al	808.1	24142	888.6	8166	34226	32338	66565
			13	105	24	129	331.8	9612	Al+Fe	409.1	13900	Ca+Al	804.0	24505	890.2	7763	34371	32283	66654
			14	105	24	129	343.0	10577	Al+Fe	409.6	13156	Ca+Al	808.7	24664	889.1	7699	34415	32374	66789
			15	105	24	129	336.6	9167	Al+Fe	409.2	14305	Ca+Al	807.5	24256	889.1	8142	34362	32403	66765
5	0.625	16	70	16	86	357.8	8564	Al+Fe	413.8	15756	Ca+Al	810.4	22773	890.5	8194	34418	30972	65390	
			17	105	24	129	359.1	8934	Al+Fe	414.8	15991	Ca+Al	812.1	23232	892.1	7594	34531	30834	65365
			18	105	24	129	349.5	8337	Al+Fe	411.0	15333	Ca+Al	812.2	23123	892.2	7586	34358	30722	65080
6	0.750	19	53	12	65	350.9	8431	Al	420.7	16384	Ca+Al	815.1	22040	895.4	7300	34622	29340	63962	
			20	105	24	129	359.4	9127	Al	419.3	16191	Ca+Al	817.4	21765	895.5	7632	34536	29402	63938
			21	105	24	129	362.8	7994	Al	421.9	16620	Ca+Al	818.6	21987	896.0	7322	34590	29316	63906
7	0.875	22	70	16	86	371.2	8487	Al	426.1	18395	Ca+Al	821.8	20688	897.6	7241	34619	27930	62549	
8	1.000	23	14	3	17	386.3	8741	Al	432.7	20383	Ca+Al	827.8	19535	900.6	7079	34553	26614	61167	

549 **Table 2** Infrared properties of the Adr-Grs solid solutions: overall features and IR bands. n_{Al} , x_{Al} and L as in Table 1. The frequency range is divided

550 in two regions: below (Lv) and above (Hv) 700 cm^{-1} . N_{IR} is the number of IR-active modes. For each band, ν [cm^{-1}] is the frequency of the most
551 intense mode belonging to the band and I is the integrated intensity [km/mol]. The participation of Ca and Fe/Al cations to the Lv bands is analyzed
552 on the basis of isotopic substitution (see Figure 5); the cations providing the largest contribution to Lv(1) and Lv(2) bands are reported in the “type”
553 column. $F = \sum_j I I_j$ is the sum of intensities [km/mol].

<i>L</i>	CRY	Low ν features			Y-Y(1)				Y-Y(2)			
		ν	I	Sym	$n_{\text{Fe-Fe},1}$	$n_{\text{Al-Al},1}$	$n_{\text{Fe-Al},1}$	Δ_1	$n_{\text{Fe-Fe},2}$	$n_{\text{Al-Al},2}$	$n_{\text{Fe-Al},2}$	Δ_2
9	CUB	347.2*	6763	F _u	0	0	8	+1.00	0	0	24	+1.00
10	ORT	361.1	2237	B _{1u}	4	4	0	-1.00	4	4	16	+0.33
		365.9	756	B _{2u}								
		327.4	2360	B _{3u}								
11	TET	351.3*	1975	E _u	0	0	8	+1.00	8	8	8	-0.33
		326.2	1268	A _u								
12	TRG	344.6*	3774	E _u	0	0	8	+1.00	6	6	12	0.00
		324.2	2302	A _u								
13	MON	--	--	--	2	2	4	0.00	6	6	12	0.00
14	MON	--	--	--	2	2	4	0.00	6	6	12	0.00
15	TRC	--	--	--	2	2	4	0.00	4	4	16	+0.33

555

556 **Table 3** Relationships between IR features in the low frequency region and ordering of Y cations
557 for the seven configurations corresponding to $x_{\text{Al}} = 0.5$ ($n_{\text{Al}} = 4$). *L* is the label of the configuration.
558 CRY indicates the crystal system of the primitive cell. ν , I and Sym are the frequency [cm^{-1}],
559 intensity [km/mol] and symmetry, respectively, of the most intense IR modes lying in the
560 interesting frequency range 320-370 cm^{-1} (see discussion in the “Behavior at fixed composition”
561 Section). In the case of *L*13, *L*14 and *L*15 it is not possible to unambiguously identify single intense
562 modes in this range. First neighbors Y cations lie at a distance of about 5.2 Å. According to
563 symmetry analysis, the first neighbors Y-Y couples are classified into two inequivalent classes
564 (columns “Y-Y(1)” and “Y-Y(2)”); $n_{\text{Fe-Fe}}$, $n_{\text{Al-Al}}$ and $n_{\text{Fe-Al}}$ are the numbers of couples of the three
565 different kinds. The total number of couples per unit cell, i.e. $N_{\text{Y-Y}} = n_{\text{Fe-Fe}} + n_{\text{Al-Al}} + n_{\text{Fe-Al}}$, is 8 and
566 24 for the two classes, respectively. $\Delta = [n_{\text{Fe-Al}} - (n_{\text{Fe-Fe}} + n_{\text{Al-Al}})]/N_{\text{Y-Y}}$ is an indicator of the relative
567 abundance of heteroatomic ($\Delta > 0$) or homoatomic ($\Delta < 0$) couples in each configuration. *Modes
568 near 350 cm^{-1} : see the “Behavior at fixed composition” Section.

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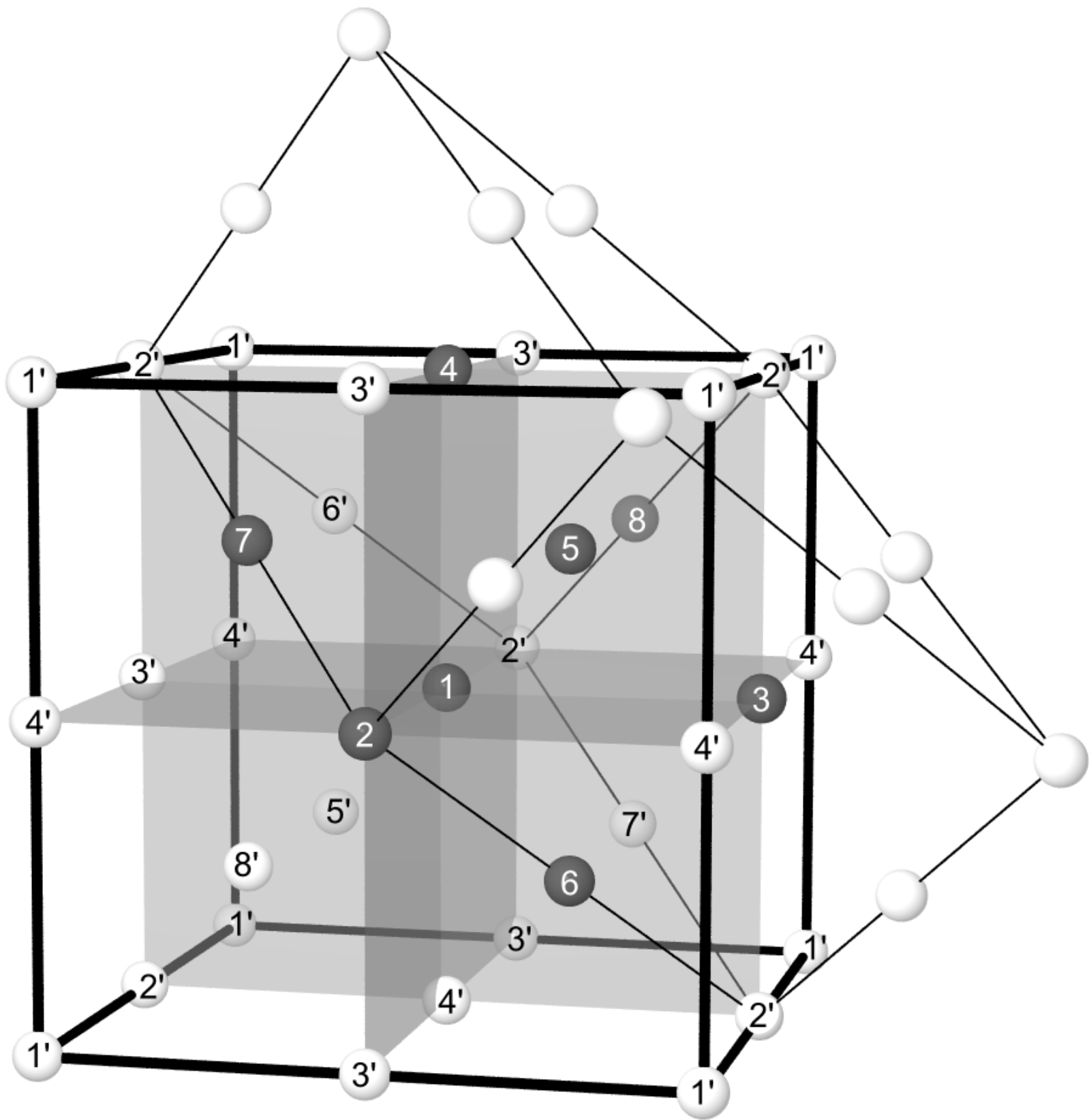
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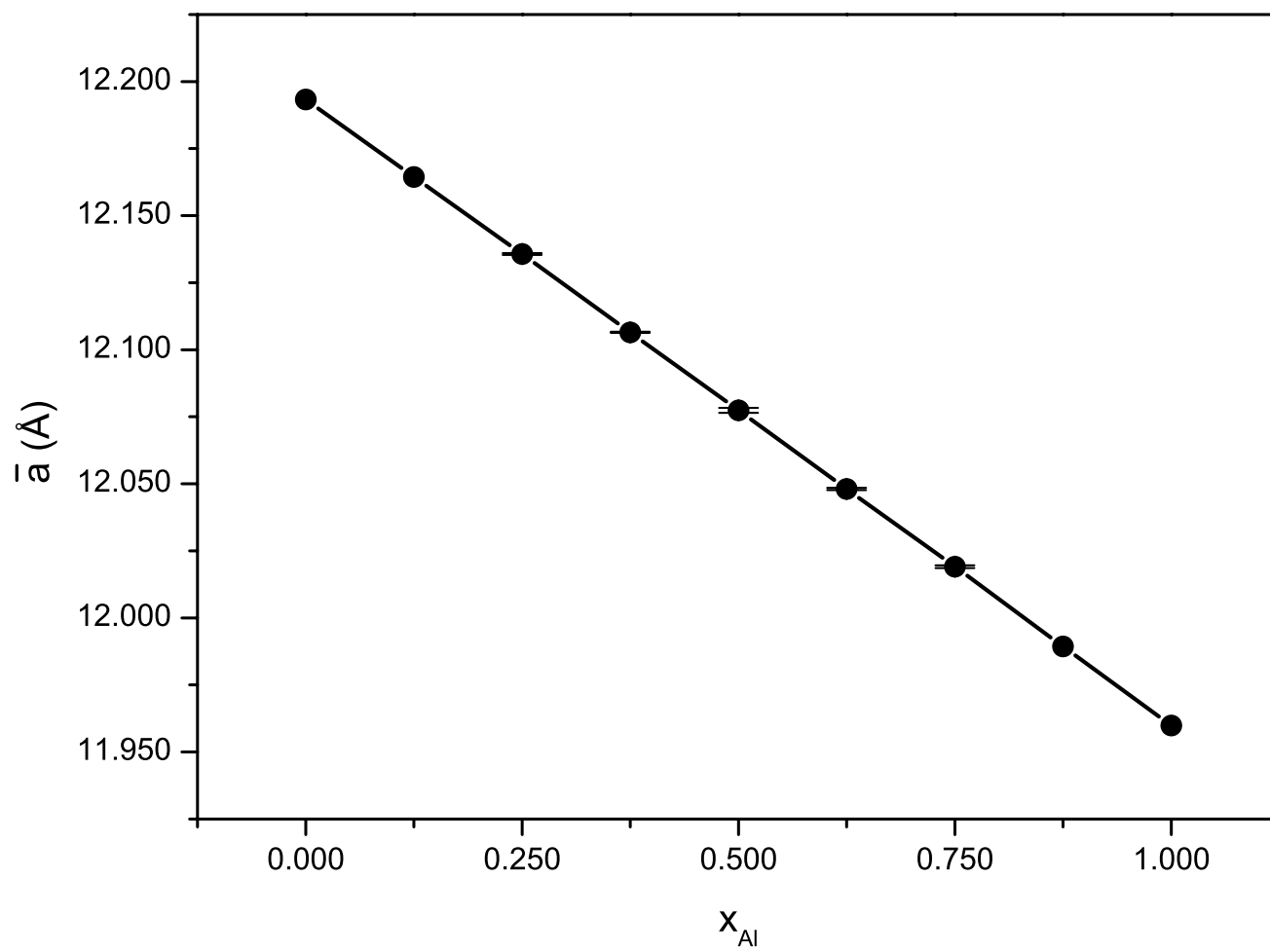
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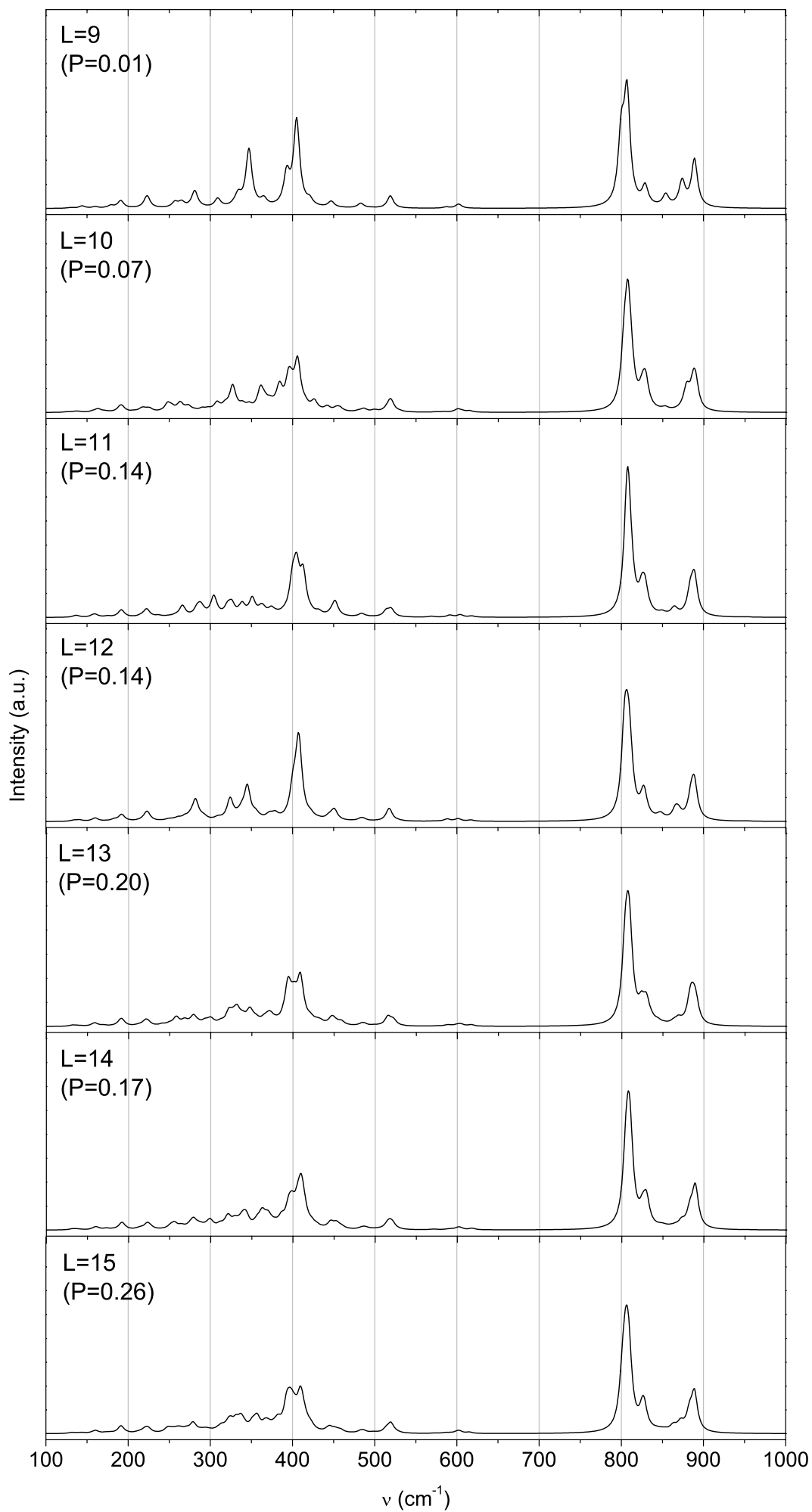
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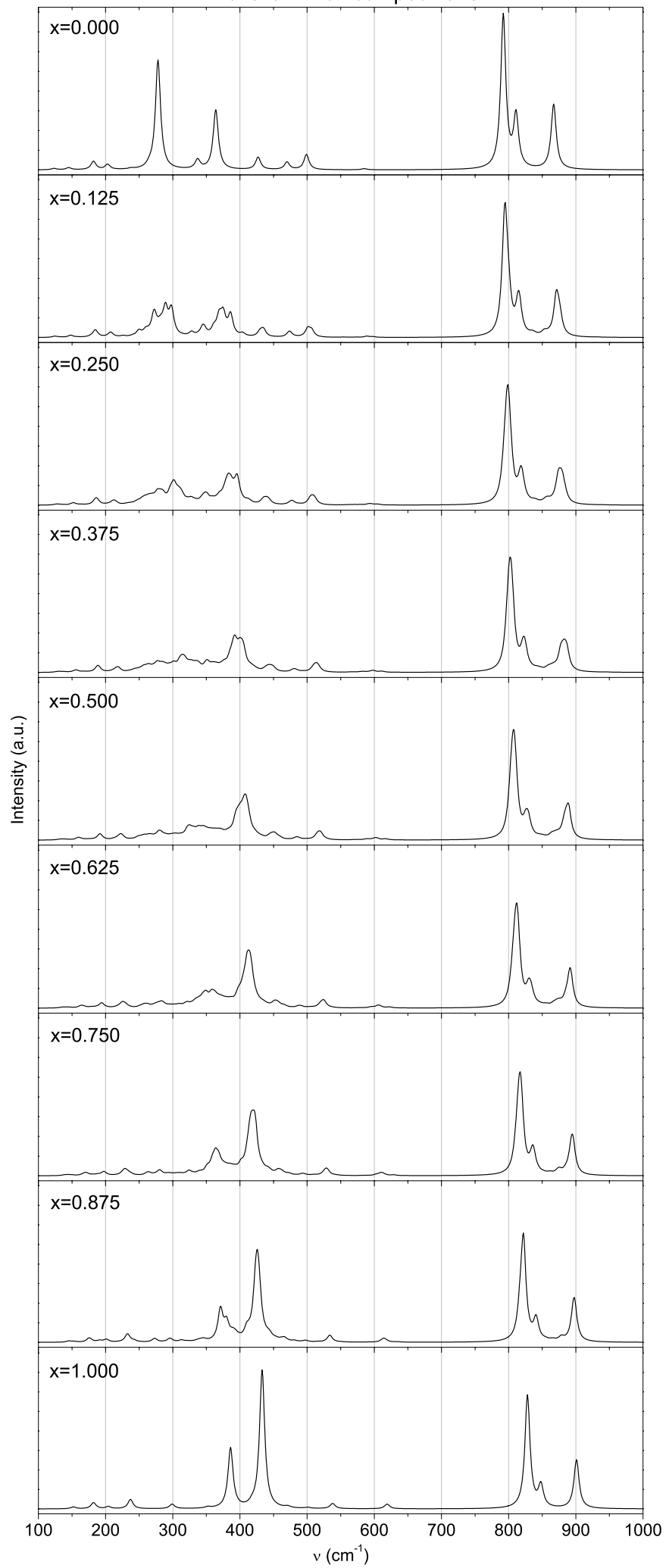




And-Gro - $x=0.500$ ($n_{Al}=4$)



And-Gro - all compositions



And-Gro - all compositions

