

Tetrahedrally-coordinated Co²⁺ in oxides and silicates:

effect of local environment on optical properties (Thursday, March 13th, 2014)

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ABSTRACT

The Co²⁺ ion in fourfold coordination provides *d-d* electronic transitions with the strongest optical density among oxides and silicates. For this reason, it is widely used in pigments and dyes to get blue shades detectable down to a very low cobalt concentration. Such a low detection limit turns the Co²⁺ ion into a suitable probe to disclose the local ligand environment in a wide range of materials by means of optical spectroscopy. Even if extensively studied in organometallic complexes, an in-depth investigation of optical properties of Co²⁺ in tetrahedral coordination into oxidic structures is limited to some case-study in minerals and synthetic analogues (spinel, zincite, gahnite, willemite, calcium cobalt selenite). The present study represents an attempt to outline crystal structural (long-range metal–oxygen distances, O–T–O bond angles and distortion parameters by XRD) and optical parameters ($10Dq$, Racah *B* and *C*, band splitting by EAS) in 13 samples of oxides and silicates providing a wide set of different local fourfold coordination around Co²⁺ added as a dopant. Subtle variations of crystal field strength and interelectronic repulsion can be appreciated in gahnite, Ca-Sr-hardystonite, Ca-Sr-Ba-åkermanite, willemite, Ba₂MgSi₂O₇ melilite-related (where Co²⁺ substitutes Mg²⁺ or Zn²⁺ by 0.25-0.3 apfu) as well as in gehlenite and fresnoite (where Co²⁺ substitutes Al³⁺ and Ti⁴⁺, respectively, by 0.2 apfu due to charge mismatch). Results are compared

27 with literature data about hibonite, spinel *s.s.*, staurolite, yttrium garnets and zincite. Spectral
28 interpretation is not straightforward owing to the occurrence of different Co^{2+} bands: spin-allowed
29 and spin-forbidden electronic transitions, two- or three-fold split due to both lowering of point
30 symmetry at the tetrahedron and spin-orbit coupling plus presumably vibronic transitions. Optical
31 spectra vary significantly even for apparently small changes in the long-range CoO_4 arrangement as
32 measured by XRD. The expected relationship between $10Dq$ and the mean Co–O distance is
33 fulfilled, but the accommodation into small AlO_4 sites in gehlenite (YAG and hibonite) implies a
34 significant structural relaxation around the Co^{2+} ion. The 3-fold splitting of the spin-allowed ${}^4\text{T}_1(\text{F})$
35 and ${}^4\text{T}_1(\text{P})$ bands can be related to the angular distortion of the CoO_4 tetrahedra. Overall, changes of
36 spectral features of tetrahedrally-coordinated Co^{2+} can be attributed to different local arrangement
37 of ligands with an effect correlated to the second nearest neighbors by the Bond Valence theory.
38 This was disclosed contrasting $10Dq$ with the ratio of the observed and ideal Bond Valence Sum for
39 the polyhedra sharing oxygen with the Co-centered tetrahedron.

40 **Keywords:** Co^{2+} ion, crystal structure, site distortion, optical properties, tetrahedral coordination.

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INTRODUCTION

43 The tetrahedral coordination of Co^{2+} (d^7) is disfavored relative to the octahedral one by the ligand
44 stabilization energies to a lesser extent than for the most of d^n configurations of the other transition
45 metal ions.

46 The Co^{2+} ion in fourfold coordination induces $d-d$ electronic transitions with the strongest optical
47 density among oxides and silicates: e.g., the ${}^4\text{T}_1(4\text{P})$ oscillator strength is approximately 800 times
48 stronger than that of Co^{2+} in octahedral coordination (Marfunin 1979). For this reason, cobalt is
49 largely used in pigments and dyes, as its intense bands in the visible spectrum absorb most of the
50 red-to-orange wavelengths, thus resulting in blue shades (Eppler 1993; Llusar et al. 2001;
51 Cavalcante et al. 2009; Leite et al. 2009; Ozel et al. 2010; Dondi et al. 2011).

52 Co^{2+} in fourfold coordination is detectable down to a very low cobalt concentration, approximately
53 1 ppm (Marfunin 1979; Lever 1984). Such a low detection limit turns the Co^{2+} ion into a suitable
54 probe to disclose the local ligand environment in a wide range of materials by means of optical
55 spectroscopy in crystalline phases (Solntsev et al. 2004; Taran et al. 2009; deMiranda Pinto et al.
56 2011; Ardit et al. 2012a and 2012b; D'Ippolito et al. 2012; Bosi et al. 2012), glasses and melts
57 (Nelson and White 1986; Keppler 1992; Keppler and Bagdassarov 1999). Incorporation of Co^{2+} ion
58 replacing Al^{3+} into the framework of zeotype aluminophosphates has been well documented. The
59 coexistence of cobalt extra-framework species at exchange cation site makes the spectroscopic
60 assignment not unambiguous (Verberckmoes et al. 1998). For this reason the zeotype structure will
61 not be considered in the present work.

62 Although extensively studied in organometallic complexes for a long time (Lever 1984 and
63 references therein), in-depth investigations of optical properties of Co^{2+} in tetrahedral coordination
64 into oxidic structures are limited to some single-crystal case-study in minerals and synthetic
65 analogues: zincite (Weakliem 1962; Koidl 1977), gahnite (Ferguson et al. 1969), willemite
66 (Brunold et al. 1996), calcium cobalt selenite (Wildner 1996) and spinel (Bosi et al. 2012).

67 The present study represents a first attempt to relate crystal structural features (as obtained by X-ray
68 diffraction, XRD) with optical properties (as determined by electronic absorption spectroscopy,
69 EAS) in powder samples over a wide range of oxides and silicates.

70 Optical properties encompass crystal field strength as given by $10Dq$, the electronic repulsion
71 quantified by the Racah B parameter, and band splitting Δ experimentally determined on spinel,
72 melilite-type and melilite-related, willemite, and fresnoite structures. This approach is strengthened
73 by including other crystal structures for which proper XRD and EAS data were taken from the
74 literature (hibonite, garnet, zincite, staurolite and further spinels) and by this covering most oxidic
75 structures able to accommodate Co^{2+} in fourfold coordination. In combination, these materials
76 provide a wide set of different local fourfold coordination environments around Co^{2+} added as a

77 dopant, that is a fundamental prerequisite for attempts to derive a tool able to relate optical spectral
78 features with local structural arrangements.

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EXPERIMENTAL

81 **Samples selection**

82 Thirteen samples pertaining to five different structures (spinel, melilite-type and -related, willemite,
83 and fresnoite) were selected in order to cover a wide range of point symmetry, metal–oxygen
84 distances, O–T–O bond angles and distortion parameters for tetrahedra where cobalt ion is
85 accommodated. Crystal-chemical formula, space group, tetrahedron point symmetry and cobalt
86 doping fraction are listed for each phase in Table 1. Additional structures were taken into account
87 when suitable EAS data of Co-doped samples were available together with crystal structure details:
88 i.e., hibonite (Leite et al. 2009; Nagashima et al. 2010), lanthanum magnesium hexaaluminate
89 (Kahn et al 1981; Yumashev et al. 2002), zincite (Pappalardo et al. 1961; Santos et al. 2008),
90 staurolite (Bringhurst and Griffen 1986; Taran et al. 2009), $MgAl_2O_4$ (Bosi et al. 2012) and
91 $ZnGa_2O_4$ spinels (Hornstra and Keulen 1972; Duan et al. 2006; Wendschuh-Josties et al. 1995),
92 yttrium aluminum and yttrium gallium garnets (Pappalardo et al. 1961; Euler and Bruce 1965;
93 Wood and Remeika 1967). Their crystal structural and optical features, as taken or elaborated from
94 literature data, are listed in Tables 4 and 6.

95 **Samples preparation**

96 Twenty-eight polycrystalline samples (13 undoped and 13 doped with Co plus two cobalt end-terms
97 used as spectroscopic references) were synthesized by solid state reaction. Stoichiometric quantities
98 of reagent-grade precursors (Al_2O_3 , $BaCO_3$, $CaCO_3$, Co_3O_4 , MgO , $SrCO_3$, SiO_2 , TiO_2 , ZnO) were
99 mixed in ethanol in an agate mortar and pelletized by using a piston cylinder pressing up to ~80
100 MPa. Calcination was carried out in sealed alumina crucibles in static air into an electric kiln
101 (Nabertherm) with the firing schedules reported in Table 1. Calcined samples underwent
102 pulverization in an agate mortar until passing a 50 μm sieve.

103 **XRD data collection and structural refinements**

104 Data collection was performed at room temperature on a Bruker D8 Advance diffractometer
105 equipped with a Si(Li) solid-state detector set to discriminate $\text{CuK}\alpha_{1,2}$ radiation, and operating in the
106 $5\text{--}130^\circ$ 2θ as maximum angular range, 0.02° 2θ step-size, and 10 s per step counting time.
107 Structural refinements, based on the Rietveld algorithm, were accomplished using the GSAS-
108 EXPGUI software package (Larson and Von Dreele 2004; Toby 2001). The presence of impurity
109 phases was accounted for by carrying out multiphase refinements in which only the scale factors
110 and the cell parameters were varied for the minor phases. The starting atomic models were taken
111 from single-crystal refinement of åkermanite by Hagiya et al. (1993), gahnite by O'Neill and
112 Dollase (1994), willemite by McMurdie et al. (1986), fresnoite by Moore and Louisnathan (1969),
113 and $\text{Ba}_2\text{MgSi}_2\text{O}_7$ melilite-related by Aitasalo et al. (2006). Experimental profiles, modeled by a
114 pseudo-Voigt function, included the θ -independent Gaussian (GW parameter), and the two $(\cos\theta)^{-1}$ -
115 and $(\tan\theta)$ -dependent Lorentzian (LX and LY parameters, respectively) broadening coefficients plus
116 an asymmetry contribution. Refinement variables also included: 18 shifted Chebyshev polynomial
117 coefficients to reproduce the background, cell parameters, final atomic coordinates, and isotropic
118 thermal parameters. Phase composition, agreement factors and refinement details are deposited in
119 Table I (undoped samples) and Table II (Co-doped samples).

120 **Electronic absorption spectroscopy**

121 Optical measurements were performed by diffuse reflectance (Perkin Elmer λ 19 spectrophotometer,
122 400–4000 nm range, 0.1 nm step size, BaSO_4 integrating sphere, white reference material: BaSO_4
123 pellet). Reflectance (R_∞) was converted to absorbance (K/S) by the Kubelka-Munk equation
124 (Marfunin 1979): $\text{K/S} = (1 - R_\infty)^2 / (2R_\infty)$. Absorbance bands were deconvoluted by a Gaussian
125 function (PFM, OriginLab) starting from peak maxima by automatic fitting to convergence, in order
126 to obtain the band energy (centroid). Its experimental error, including background correction and
127 reproducibility, is within 1%. Both the crystal field strength $10Dq$ and Racah parameters were
128 calculated for the 3 holes electronic configuration of Co^{2+} ion (d^7) by fitting the spin-allowed

129 transitions in the d^3 Tanabe-Sugano diagram (Fig. 1) that is used, according to the d^{10-N} rule, in the
 130 case of ions in fourfold coordination (Tanabe and Sugano 1954; Andrut et al. 2004). For sake of
 131 simplicity, band assignments are expressed with reference to cubic symmetry (T_d) although the
 132 point symmetry of Co^{2+} ions is actually lower in many cases. As the ${}^4T_2({}^4F)$ transition (ν_1), which
 133 would have directly given the $10Dq$ value, occurs partially outside of the investigated range, the
 134 energies of the ${}^4T_1({}^4F)$ transition (ν_2) and the ${}^4T_1({}^4P)$ transition (ν_3) were used to calculate the
 135 crystal field strength (Lever 1984; Wildner et al. 2004):

$$136 \quad \text{Crystal field strength } 10Dq = \{9(\nu_2 + \nu_3) - [85(\nu_2 - \nu_3)^2 - 4(\nu_2 + \nu_3)^2]^{1/2}\} / 340 \quad (1)$$

$$137 \quad \text{Racah } B \text{ parameter} = (\nu_2 + \nu_3 - 30 Dq) / 15 \quad (2)$$

$$138 \quad \text{Racah } C \text{ parameter} = 4.2B \quad (3)$$

139 These spin-allowed transitions are split three-fold due to the effect of both Co^{2+} spin-orbit coupling
 140 and point symmetry (Fig. 2). Their energy was calculated in two different ways: as the mean value
 141 of split sub-bands as well as by the baricenter method (Burns 1993); given that their difference is
 142 always within 1% and in most cases below 0.5%, the average of the two methods was taken as
 143 value for the band energies. The band splitting, Λ , due to the extremely complex features of the ν_3
 144 transition that prevent an adequately accurate resolution of the three sub-bands, was estimated for
 145 the ν_2 transition only. The value of Λ was fitted to the energy of sub-bands (Torres et al. 2007): ν_{21}
 146 = $\nu_{2(\text{expected})} - 1.5\Lambda$; $\nu_{22} = \nu_{2(\text{expected})} + \Lambda$; $\nu_{23} = \nu_{2(\text{expected})} + 2.5\Lambda$. The expected energies of spin-
 147 allowed transitions were calculated by: $\nu_{2(\text{expected})} = 0.5 (30Dq + 15B - b)$ and $b = [(10Dq - 9B)^2 +$
 148 $144B^2]^{1/2}$. The Λ values obtained by this way are linearly correlated with those achievable by the
 149 method followed by Bosi et al. (2012).

150 RESULTS

151 Overview of crystal structures: inspection of the tetrahedral environments

152 Unit-cell parameters, mean metal–oxygen bond distances, bond angles, and tetrahedral distortion
 153 indices are listed in Tables 2 and 3 for undoped and Co-doped samples, respectively. Crystal
 154 structure details of additional phases taken from the literature are summarized in Table 4.

155 This set of samples offers, on the whole, a wide range of local environments for cobalt. Such a
156 diversity is emphasized, as in Figure 3, by contrasting the mean T–O distance with the Tetrahedral
157 Quadratic Elongation (TQE), and the mean O–T–O angle with the Bond Angle Variance (BAV) as
158 defined by Robinson et al. (1971).

159 The Co^{2+} ion is accommodated in a perfect tetrahedron (point symmetry T_d) in the case of spinels
160 (TQE = 1, BAV = 0, mean O–T–O=109.47°) or a nearly regular tetrahedron in zincite,
161 hexaaluminates and staurolite (TQE < 1.002, BAV < 5). Among these structures with a high
162 tetrahedral point symmetry, the main difference is the T–O distance. A large variation of the local
163 environment at the tetrahedral site is exhibited by melilites, particularly Ca-Sr-Ba åkermanite and
164 Ca-Sr-hardystonite, as well as by monoclinic melilite-related $\text{Ba}_2\text{MgSi}_2\text{O}_7$ and willemite structures,
165 while yttrium garnets exhibit TQE = 1 but significantly high BAV.

166 As reported in the literature (e.g. Taran et al. 2009; Ardit et al. 2012a and 2012b; D'Ippolito et al.
167 2012; Bosi et al. 2012) as well as listed in Tables 2 and 3, the effect of a relatively low doping of
168 Co^{2+} ions at tetrahedral sites (with a Co^{2+} concentration that ranges between 0.2 and 0.3 atoms per
169 formula unit apfu) produces limited changes in unit-cell parameters and volume, average T–O
170 distances, O–T–O bond angles and distortion parameters (i.e. TQE and BAV). The slight variation
171 induced by such a doping can be well appreciated in Figure 4: both undoped and Co-doped samples
172 have the same relative mean metal-oxygen bond length variation, with values that fluctuate around
173 the experimental error.

174 Albeit negligible, the above mentioned variations can be simply explained in terms of ionic radii
175 (Shannon 1976). In fact, the ionic radius of fourfold coordinated Co^{2+} (0.58 Å) is very close to that
176 of Mg^{2+} (0.57 Å) and Zn^{2+} (0.60 Å) in the same coordination; the replacement of magnesium or zinc
177 for cobalt in a concentration equal to 0.25-0.30 apfu gives rise to an estimated variation of about
178 1%. Although the concentration of dopant was limited to 0.20 apfu for samples with a charge
179 mismatch of 1 or 2 electrons, the variation due to the Co^{2+} substitution for Al^{3+} (i.r. = 0.39 Å) and
180 Ti^{4+} (i.r. = 0.51 Å) increases to about 5%.

181 As a matter of fact, the choice of using a limited concentration of cobalt as dopant guarantees the
182 preservation of the long-range structure around the doped tetrahedral site and, at the same time,
183 makes each investigated sample strongly active to the electronic absorption spectroscopy.

184 **Optical properties**

185 Optical spectra are dominated by intense bands, due to the electronic transitions of high-spin Co^{2+}
186 (d^7) in tetrahedral or pseudotetrahedral fields, occurring in three regions of absorption around 4000,
187 7000 and 16,000 cm^{-1} , respectively. Within this overall picture, spectra vary conspicuously from
188 sample to sample despite the fact that the Co^{2+} occupancy of fourfold coordinated sites is essentially
189 the same (Fig. 5). These optical bands have different origins:

- 190 • *Electric dipole transitions* that are partially Laporte-forbidden (due to the absence of a centre of
191 symmetry in the tetrahedron) and spin-allowed. They occur as very intense bands in the 5600–
192 8200 cm^{-1} and 15,600–17,600 cm^{-1} ranges which are attributable to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ (${}^4\text{F}$) and ${}^4\text{A}_2$
193 $\rightarrow {}^4\text{T}_1$ (${}^4\text{P}$) transitions, respectively. These transitions are three-fold split due to the strong spin-
194 orbit coupling stemming from the d^7 electronic configuration of Co^{2+} (Weakliem 1962; Ferguson
195 et al. 1969; Koidl 1977) and the low point symmetry in several cases (Brunold et al. 1996;
196 Wildner 1996). The two-electrons ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ (${}^4\text{F}$) transition is electric dipole forbidden and
197 consequently has a low intensity (Taran et al. 2009). It occurs as a single weak sub-band around
198 4000 cm^{-1} , but for its large three-fold splitting the other sub-bands fall outside of the investigated
199 wavelength range. For this reason it was not possible to determine the crystal field strength by
200 the mean energy of the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ triplet.
- 201 • Although both Laporte- and spin-forbidden, *magnetic quadrupole transitions* give rise to low
202 intensity bands originating from several ${}^2\text{G}$, ${}^2\text{P}$ and ${}^2\text{H}$ terms. Their partial overlapping with the
203 strong ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ (${}^4\text{P}$) sub-bands in the 18,000–20,000 cm^{-1} range brings about an appreciable
204 spin-orbit mixing of states between quartet and doublet states (Weakliem 1962; Ferguson et al.
205 1969; Wildner 1996; Brunold et al. 1996).

206 • Presumable *vibronic effects* are invoked to explain the occurrence of bands that are not
207 attributable to the above-mentioned transitions (Ferguson et al. 1969; Koidl 1977). They are
208 usually found as sidebands of spin-allowed transitions, thus causing a remarkable complexity in
209 spectral features in the 5000–8000 and 15,000–17,000 cm^{-1} ranges (Fig. 2).

210 • *Cobalt* \leftrightarrow *oxygen charge transfer* gives rise to an increase of absorbance in the ultraviolet
211 (Lenglet and Lefez 1996), occurring around 30,000 cm^{-1} for melilites and willemite or around
212 25,000 cm^{-1} for gahnite and fresnoite.

213 Doublet states, like ${}^2\text{E}$ and ${}^2\text{T}_1$ (${}^2\text{G}$), have nearly the same hole configuration of the ground state ${}^4\text{A}_1$
214 (t_2e^2). Their occurrence at wavenumbers close to the ${}^4\text{T}_1$ (${}^4\text{P}$) quartet, which has a hole configuration
215 t_2^3 , induces a considerable spin-orbit mixing of states, with the quartet character ranging
216 approximately from 15% to 60% depending on crystal field strength (Weakliem 1962) but entailing
217 also vibronic sidebands (Ferguson et al. 1969). This circumstance promotes a noteworthy gain in
218 intensity of spin-forbidden bands, that may be twice the expected absorbance or even more
219 (Weakliem 1962; Brunold et al. 1996), by stealing the energy from spin-allowed sub-bands
220 (Wildner 1996).

221 Spectral deconvolution provided satisfactory results when using several Gaussian bands to account
222 for all the spin-allowed, spin-forbidden and “vibronic” transitions (Fig. 2 and Table 5). In such
223 complex spectra, the interpretation is robust for some intense and well-defined bands, as the high-
224 energy and low-energy sub-bands of ${}^4\text{T}_1$ triplets. In contrast, the deconvolution of minor bands or
225 more structured spectral areas leads to a rather uncertain interpretation; as a matter of fact, the mid-
226 energy sub-band of the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ (${}^4\text{P}$) triplet is often to a large extent superimposed with the low-
227 energy sub-band and, in these cases, its energy may only be estimated. For this reason, band
228 splitting was calculated only for the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ (${}^4\text{F}$) transition.

229 Spin-allowed transitions are three-fold split due to the strong spin-orbit coupling characterizing d^7
230 ions, like Co^{2+} (Marfunin 1979; Lever 1984; Burns 1993). Such a band splitting is as wide as 960
231 cm^{-1} for the ${}^4\text{T}_1$ (${}^4\text{F}$) transition in gahnite (with a T_d point symmetry of cobalt site) but it turns to be

232 from 1370 to 1850 cm^{-1} for the other samples where the point symmetry is lowered. Therefore, the
233 band splitting parameter Λ , as measured by EAS, contains information which is the convolution
234 product of both spin-orbit coupling and point symmetry, and it is not possible to isolate the two
235 terms in spectra from powder samples.

236 Optical properties of Co^{2+} in the structures under investigation (Table 5) fluctuate over a rather
237 wide range for crystal field strength ($3777 \leq 10Dq \leq 4288 \text{ cm}^{-1}$) and band splitting ($-18 \leq \Lambda \leq -140$
238 cm^{-1}). The variation of interelectronic repulsion ($738 \leq \text{Racah } B \leq 772 \text{ cm}^{-1}$) matches the literature
239 data well (Lever 1984; Burns 1993; Wildner 1996; Taran et al. 2009; Bosi et al. 2012). $10Dq$
240 exhibits an inverse relationship with the Racah B parameter, to a certain extent predictable as, for
241 shorter Co–O bond distances, a stronger crystal field strength is expected (*i.e.*, a higher $10Dq$)
242 together with an enhanced interelectronic repulsion (overlapping of electronic clouds of metal and
243 ligands) leading to an increased degree of covalency (*i.e.*, a lower Racah B).

244

245

DISCUSSION

246 Long-range vs. short-range metal-oxygen distances

247 The long-range XRD averaged T–O distances exhibit an inverse relationship with the crystal field
248 strength (Fig. 6), as expected by the Crystal Field Theory (Burns 1993). However, the crystal
249 structures where Co^{2+} replaces Al^{3+} at the tetrahedral site present a $10Dq$ much lower than that
250 predictable on the basis of the overall trend, as defined by samples from SB3M to *ygg*. This is
251 particularly true for samples C2A and *yag*, but to a certain extent also for the hexaaluminates (*hib*
252 and *lma*).

253 Another exception is represented by fresnoite: the average Ti–O distance for the TiO_{4+1} pyramidal
254 site is too short (1.910 Å) to satisfy the above-mentioned general trend. It can be hypothesized that
255 there exists an oxygen vacancy due to a charge mismatch in the Co^{2+} -centred site with respect to the
256 Ti^{4+} -centred tetragonal pyramid, which leaves the cobalt ion in an effective fourfold coordination

257 (Farges 1996; Schneider et al. 1998). A planar square coordination (T–O distance 1.959 Å) would
 258 result in a reasonable fit to match the overall T–O vs. $10Dq$ trend.

259 Looking in detail at Figure 6, subtle differences exist between the Mg and Zn terms, the former
 260 displaying slightly weaker $10Dq$ values than the latter for the same T–O distance. This is in
 261 apparent discrepancy with the Crystal Field Theory, as Co^{2+} would be expected to assume shorter
 262 bond lengths when replacing the smaller Mg^{2+} (hence undergoing a higher $10Dq$) than in the case of
 263 the larger Zn^{2+} ion. Such an observation is strengthened by considering Ca and Sr åkermanite and
 264 hardystonite (S2M vs. S2Z, CSM vs. CSZ and C2M vs. C2Z) that exhibit a crystal field strength not
 265 coherent with the mean T–O distance. This behavior can be explained by the different character of
 266 bonding between the MgO_4 and ZnO_4 tetrahedra, and the opposite effect played by Co^{2+} on it, *i.e.*
 267 decreasing the degree of covalency in Zn terms (Ozel et al. 2010, Ardit et al. 2012a) and increasing
 268 the same in Mg ones (Ardit et al. 2012b and 2012c; Bosi et al. 2012).

269 **Local Co–O distances**

270 The local Co–O distance can be calculated by optical spectroscopy data on the basis of the linear
 271 dependence of the crystal field strength on the fifth power of the mean metal–oxygen distance, as
 272 defined by the Crystal Field Theory (Marfunin 1979; Burns 1993; Langer 2001):

$$273 \quad 10Dq = 5/3 \cdot Q \cdot \langle r \rangle^4 \cdot \langle \text{Co–O} \rangle^{-5} \quad (4)$$

274 here both the effective charge on ligands, Q , and the average radius of d orbitals, $\langle r \rangle$, can be
 275 assumed as constant for the same metal ion in the same ligand environment, thus the equation (4)
 276 can be simplified as: $10Dq = \text{constant} \cdot \langle \text{Co–O} \rangle^{-5}$. The value of this constant was calculated for two
 277 different cobalt end-terms (116,235 for the CoAl_2O_4 spinel and 115,692 for the $\text{Ca}_2\text{CoSi}_2\text{O}_7$
 278 melilite) and averaged to get the local mean Co–O distance for each sample by:

$$279 \quad \langle \text{Co–O} \rangle_{\text{local}} = (115,964 / 10Dq)^{1/5} \quad (5)$$

280 for comparison the value for calcium cobalt selenite is 117,275 (Wildner 1996).

281 The average metal-oxygen distance at the tetrahedron, $\langle T-O \rangle$, as measured by XRD, can be seen as
 282 the additive contribution of two local bond distances weighed for the fractions of cobalt (x) and that
 283 of the other ion hosted at the same coordination site, i.e. $A \cdot (1-x)$:

$$284 \quad \langle T-O \rangle = x \cdot \langle Co-O \rangle_{local} + (1-x) \cdot \langle A-O \rangle_{local} \quad (6)$$

285 by which the local A–O distance can be estimated:

$$286 \quad \langle A-O \rangle_{local} = (\langle T-O \rangle - x \langle Co-O \rangle_{local}) \cdot (1-x)^{-1}. \quad (7)$$

287 The results obtained by this way are plotted in Figure 7 with the straight line $\langle Mg-O \rangle_{local} : \langle Co-O \rangle_{local}$
 288 = 1:1. The points plotting at the left of the line indicate a Co-centered tetrahedron greater than the
 289 one occupied by other ions in the same structure. It implies a structural relaxation to accommodate
 290 Co^{2+} ions replacing smaller cations. This is appreciable by comparing zinc terms (where Co^{2+} is
 291 hosted with an effective ionic radius comparable to that of Zn^{2+}) with magnesium terms (where
 292 Mg^{2+} ion appears to be systematically smaller than Co^{2+}). Such a difference turns to be conspicuous
 293 in the Al terms, where cobalt maintains values of $\langle Co-O \rangle_{local}$ much longer than the local Al–O
 294 distances. Such a structural relaxation, implied by these short-range to long-range differences, was
 295 already found in spinels and melilites (Hålenius et al. 2011; Ardit et al. 2012a and 2012b; Bosi et al.
 296 2012). This is confirmed here, with the first evidence being the very strong relaxation needed for
 297 AlO_4 tetrahedra in order to gehlenite data (confirmed by *hib*, *lma* and *yag* samples).

298 The three samples where cobalt replaces titanium, iron or gallium exhibit different behaviors, which
 299 are explainable by the different ionic radii in tetrahedral coordination. A limited structural
 300 relaxation is observed in both staurolite and fresnoite: the former plots at the right of the 1:1 line of
 301 Figure 7, since Co^{2+} is smaller than Fe^{2+} (0.58 against 0.63 Å, respectively) while the latter falls at
 302 the left due to the smaller size of Ti^{4+} ion (0.51 Å) in fivefold coordination. A strong structural
 303 relaxation, analog to that displayed by Al terms, is needed to accommodate cobalt in place of Ga^{3+}
 304 ion (0.47 Å) in *ygg*.

305 Overall, Co^{2+} acts as a hard ion, keeping its ionic radius even when hosted in structures with a very
 306 different local environment in terms of tetrahedron size and point symmetry. The changes observed

307 to the $\langle\text{Co-O}\rangle_{\text{local}}$, ranging from 1.93 to 1.98 Å, are limited when compared to the host frameworks,
308 where the $\langle\text{M-O}\rangle_{\text{local}}$ spans from 1.70 to 1.98 Å.

309 **Band splitting**

310 The more distorted the local arrangement around Co^{2+} ions is, the greater appears the ${}^4\text{T}_1({}^4\text{F})$ band
311 splitting Λ . A rather good direct correlation is observed with the bond angle variance for Λ over -80
312 cm^{-1} , including melilite, willemite and garnet samples (Fig. 8). However, this relationship holds
313 only for the larger angular distortion of CoO_4 tetrahedra: as a matter of fact, Λ values vary widely
314 between zero and -70 cm^{-1} for $\text{BAV} < 20$.

315 This empirical relationship is potentially a useful tool to assess the degree of distortion experienced
316 by fourfold coordinated Co^{2+} ions by means of EAS measurements, as it can be appreciated in the
317 inset of Figure 8. However, some caution is needed in the attribution of sub-bands of the three-fold
318 split ${}^4\text{T}_1({}^4\text{F})$ transition in complex optical spectra from powders. In particular, the high-energy sub-
319 band always peaks in between $16,800$ and $17,700 \text{ cm}^{-1}$ and must not be confused with the intense
320 band around $18,500 \text{ cm}^{-1}$ —apparently completing the ${}^4\text{T}_1$ triplet— that is originated from the
321 ${}^2\text{A}_1({}^2\text{G})$ transition strengthened by mixing of states and vibronic effects (Ferguson et al. 1969;
322 Brunold et al. 1996).

323 This general behavior has important repercussions on color: the fact that $\langle\text{Co-O}\rangle_{\text{local}}$ distances are
324 substantially retained in various structures means that the optical bands will remain more or less at
325 the same wavelengths, even in minerals with different tetrahedra. In particular, the band responsible
326 for the deep blue color, ${}^4\text{T}_1({}^4\text{P})$, has a steep onset between $15,800$ and $16,400 \text{ cm}^{-1}$ (only exception
327 being the peculiar case of fresnoite) and a splitting of sub-bands from 710 to 1490 cm^{-1} . However,
328 the main effect on color is due to the different structure in the $17,000$ - $19,000 \text{ cm}^{-1}$ region where a
329 very complicated interplay may occur between spin-allowed and spin-forbidden bands, entailing
330 mixing of states and vibronic effects.

331 **Effect of second nearest neighbors**

332 In a recent work (Dondi et al. 2013) evidences were shown that second nearest neighbors around
333 tetrahedra doped with cobalt can highly influence the local environment of those tetrahedra.
334 Since the conventional distortion parameters provide a measure of a deviation from regularity
335 (Quadratic Elongation as well as Bond Angle Variance) or return the effective coordination number
336 (ECoN) exclusively for a determined polyhedron (i.e. tetrahedron, octahedron, cube,
337 dodecahedron), they are useless to assess the lattice strain due to the second nearest neighbors
338 coordinating the Co-doped tetrahedron, for which a specific approach is proposed here. Based on
339 the bond-valence method (Brown 2002), the bond-valence sum of polyhedra which share the
340 oxygens coordinating the Co-doped tetrahedron for each selected sample was calculated. In order to
341 compare all the structural types here considered (i.e. spinel, willemite, fresnoite, melilite, and
342 melilite-related structures), the observed bond-valence sum ($BV_{sum_{obs}}$) was normalized for bond-
343 valence given by the sum of the formal valence of each polyhedron ($BV_{sum_{calc}}$). This
344 $BV_{sum_{obs}}/BV_{sum_{calc}}$ ratio correlates well with the crystal field strength $10Dq$ (Fig. 9).
345 In more detail, cations located in second nearest neighbors polyhedra of Co tetrahedra in structures
346 with $BV_{sum_{obs}}/BV_{sum_{calc}} < 1$ are relatively underbonded because the observed bond-lengths are
347 longer than the ideal values adopted by the bond-valence method (Brown 2002). Hence, the
348 oxygens shared between the Co-doped tetrahedron and polyhedra linked to it are closer to the
349 tetrahedral cation and promote short Co–O_{local} bond distances (i.e. for the crystal field theory, high
350 $10Dq$ values).
351 Vice versa, long Co–O_{local} bond distances (i.e. low $10Dq$ values) result from structures which
352 exhibit a $BV_{sum_{obs}}/BV_{sum_{calc}}$ ratio larger than 1. For these structures the observed bond-lengths in
353 polyhedra coordinating the Co-doped tetrahedron are shorter than the ideal ones, meaning that the
354 oxygens shared between the Co-doped tetrahedron and polyhedra linked to it are pulled at relatively
355 larger distances away from the tetrahedral cation.

356

357 In conclusion, even small variations in the local Co–O distance can be evaluated by EAS. However,
358 the optical band shift and splitting, associated to different local environments around Co^{2+} , occur
359 with complex changes of spectral features. Such effects, particularly complicated in the visible
360 range, affect the color and still represent a challenge for modelling.

361 The changes observed in optical spectra are mostly related, beyond Co–O bond length, to point
362 symmetry and angular distortion of tetrahedra. EAS proved to be able to discriminate between
363 nearly regular to highly distorted local tetrahedral arrangements around the Co^{2+} ion.

364 Co^{2+} acts as a hard ion, inducing a relaxation of the local environment that is increasing from Zn to
365 Mg terms and is particularly strong in the case of Al tetrahedra.

366 The crystal field strength scales inversely with the $\text{BV}_{\text{sum}_{\text{obs}}}/\text{BV}_{\text{sum}_{\text{calc}}}$ ratio. This relationship
367 offers a new approach to design materials with the desired $10Dq$ value of Co^{2+} in tetrahedral
368 coordination.

369

370

IMPLICATIONS

371 The peculiar feature of Co^{2+} transition metal ions to be hosted as a hard sphere in the tetrahedral
372 sites of a wide range of oxides and silicates provides a unique tool to explore the properties of solid
373 solutions in cobalt-bearing minerals and their synthetic analogues. The inverse relationship of
374 crystal field strength with the $\text{BV}_{\text{sum}_{\text{obs}}}/\text{BV}_{\text{sum}_{\text{calc}}}$ ratio, reported for the first time in this study,
375 paves the way for a new approach to design materials with the desired $10Dq$ value of Co^{2+} in
376 tetrahedral coordination. The above relationship is a step forward towards a deterministic modeling
377 of solid solutions and color based on the interplay between crystal structure and optical properties.
378 This issue has implications in development of crystalline materials with controlled optical response
379 for many kinds of technological applications.

380

381

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387

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592

593

FIGURE CAPTIONS

594 **FIGURE 1.** Example of DRS spectrum fitting with the Tanabe-Sugano diagram for d^3 ions (sample
595 S2Z).

596

597 **FIGURE 2.** Example of deconvolution of DRS spectra (sample S2Z): a) ${}^4T_1({}^4F)$ spectral area (5000–
598 10,000 cm^{-1}); b) ${}^4T_1({}^4P)$ spectral area (14,000–21,000 cm^{-1}).

599

600 **FIGURE 3.** Local environment of Co^{2+}O_4 tetrahedra as obtained by long-range XRD data: a) average
601 T–O distance versus Tetrahedral Quadratic Elongation; b) mean O–T–O angle versus Bond Angle
602 Variance.

603

604 **FIGURE 4.** Long-range T–O distance in Co-doped and undoped samples normalized for the absolute
605 value determined in the sample C2M.

606

607 **FIGURE 5.** EAS spectra of Co^{2+} -bearing silicates and oxides.

608

609 **FIGURE 6.** Average T–O distance by XRD as a function of crystal field strength.

610

611 **FIGURE 7.** A–O vs Co–O local distances.

612

613 **FIGURE 8.** ${}^4T_1({}^4F)$ band splitting versus Co^{2+}O_4 tetrahedra Bond Angle Variance.

614

615 **FIGURE 9.** Observed/calculated polyhedral Bond Valence sum ratio around Co^{2+} tetrahedra as a
616 function of the crystal field strength.

617

618

619

TABLES

620

621 **TABLE 1.** Crystal structures taken into consideration with their formula, cobalt doping, tetrahedron point symmetry and synthesis conditions.

code	synthetic analogue	mineral formula	Co (apfu)	space group	point symmetry	synthesis conditions
GAH	gahnite	ZnAl ₂ O ₄	0.25	<i>Fd-3m</i>	T _d	1300 °C (24 h)
C2Z	Ca-hardystonite	Ca ₂ ZnSi ₂ O ₇	0.25	<i>P-42₁m</i>	S ₄	1200 °C (24 h)
CSZ	CaSr-hardystonite	(Ca,Sr)ZnSi ₂ O ₇	0.30	<i>P-42₁m</i>	S ₄	1200 °C (24 h)
S2Z	Sr-hardystonite	Sr ₂ ZnSi ₂ O ₇	0.30	<i>P-42₁m</i>	S ₄	1200 °C (24 h)
C2A	Ca-gehlenite	Ca ₂ Al(Al,Si)O ₇	0.20	<i>P-42₁m</i>	S ₄	1200 °C (24 h)
C2M	Ca-åkermanite	Ca ₂ MgSi ₂ O ₇	0.30	<i>P-42₁m</i>	S ₄	1200 °C (24 h)
CSM	CaSr-åkermanite	(Ca,Sr)MgSi ₂ O ₇	0.30	<i>P-42₁m</i>	S ₄	1200 °C (24 h)
S2M	Sr-åkermanite	Sr ₂ MgSi ₂ O ₇	0.30	<i>P-42₁m</i>	S ₄	1200 °C (24 h)
SBM	SrBa-åkermanite	(Sr,Ba)MgSi ₂ O ₇	0.30	<i>P-42₁m</i>	S ₄	1200 °C (24 h)
SB3M	Sr ^{1/4} Ba ^{3/4} -åkermanite	(Sr _{0.5} Ba _{1.5})MgSi ₂ O ₇	0.30	<i>P-42₁m</i>	S ₄	1200 °C (24 h)
B2M	Ba-åkermanite	Ba ₂ MgSi ₂ O ₇	–	<i>P-42₁m</i>	S ₄	–
B2Mm	melilite-related	Ba ₂ MgSi ₂ O ₇	0.30	<i>C2/c</i>	C ₂	1200 °C (24 h)
WLL	willemite	Zn ₂ SiO ₄	0.30	<i>R-3</i>	C ₁	1300 °C (3 h)
FRE	fresnoite	Ba ₂ TiSi ₂ O ₈	0.20	<i>P4bm</i>	C ₄	1100 °C (24 h)

622

623

624 **TABLE 2.** Crystal structure data of undoped samples: unit-cell parameters, metal-oxygen bond distances and tetrahedral distortion indices.

<i>UNDOPED</i>	GAH	C2Z	CSZ	S2Z	C2A	C2M	CSM	S2M	SBM	SB3M	B2M	B2Mm	WLL	FRE
Unit-cell parameters														
<i>a</i> (Å)	8.0851(1)	7.8273(1)	7.9298(2)	8.0007(1)	7.6875(2)	7.8338(3)	7.9256(1)	8.0095(1)	8.1111(1)	8.1549(1)	8.2036(4)	8.4171(3)	13.9378(1)	8.5353(6)
<i>b</i> (Å)	–	–	–	–	–	–	–	–	–	–	–	10.7194(4)	–	–
<i>c</i> (Å)	–	5.0159(1)	5.0984(1)	5.1722(1)	5.0665(1)	5.0088(2)	5.0820(1)	5.1643(1)	5.2811(1)	5.3421(1)	5.4058(4)	8.4501(3)	9.3087(1)	5.2064(7)
β / γ (°)	–	–	–	–	–	–	–	–	–	–	–	110.77(1)	120.00(0)	–
<i>V</i> (Å ³)	528.52(1)	307.31(1)	320.60(2)	331.08(1)	299.41(1)	307.38(3)	319.23(1)	331.30(1)	347.44(1)	355.26(1)	363.81(2)	712.89(6)	1566.05(2)	379.29(9)
Mean metal-oxygen bond distances (Å)														
$\langle X-O \rangle$	–	2.579(4)	2.632(4)	2.669(4)	2.485(5)	2.579(4)	2.586(3)	2.672(4)	2.736(6)	2.766(7)	2.793(4)	2.820(12)	–	2.950(3)
$\langle Al-O \rangle$	1.912(1)	–	–	–	–	–	–	–	–	–	–	–	–	–
$\langle Tl-O \rangle$	1.953(1)	1.920(1)	1.937(1)	1.959(3)	1.748(1)	1.915(1)	1.925(2)	1.941(3)	1.954(1)	1.958(2)	1.966(4)	1.966(3)	1.941(13)	1.922(4)
$\langle Zn-O \rangle$	–	–	–	–	–	–	–	–	–	–	–	–	1.977(13)	–
$\langle Si-O \rangle$	–	1.615(1)	1.610(1)	1.610(2)	1.681(2)	1.615(2)	1.618(2)	1.617(4)	1.621(1)	1.626(2)	1.635(4)	1.629(5)	1.626(13)	1.628(4)
$\langle O-Tl-O \rangle$ (°)	109.47(0)	109.50(4)	109.54(2)	109.59(3)	109.48(3)	109.49(5)	109.52(8)	109.58(14)	109.66(7)	109.67(9)	109.70(14)	109.55(57)	109.33(59)	106.16(20)
Tetrahedral (<i>Tl</i>) distortion indices														
λ_{Tl}	1.0000	1.0025	1.0065	1.0115	1.0012	1.0019	1.0051	1.0110	1.0182	1.0204	1.0232	1.0210	1.0062	–
σ_{Tl}^2	0.00	9.66	24.78	42.98	4.68	7.25	19.44	41.00	66.61	74.49	84.11	86.58	20.08	–
ECoN	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	3.96	–
Reference	[1]	[2]	This Work	[3]	This Work	This Work	This Work	[4]	[4]	[4]	[5]	[4]	[6]	[7]
<i>Notes:</i> quadratic elongation (λ) and bond angle variance (σ) of <i>Tl</i> tetrahedra were computed according to Robinson et al. (1971); the effective coordination number (ECoN) of <i>Tl</i> tetrahedra was obtained by means of VESTA visualizer (Momma and Izumi, 2011).														
<i>References:</i> [1] Ardit et al. (2012b); [2] Ardit et al. (2012a); [3] Ardit et al. (2010); [4] Ardit et al. (2012c); [5] Shimizu et al. (1995); [6] Ozel et al. (2010); [7] Bindi et al. (2006).														

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627 **TABLE 3.** Crystal structure data of Co-doped samples: unit-cell parameters, metal-oxygen bond distances and tetrahedral distortion indices.

Co-DOPED	GAH	C2Z	CSZ	S2Z	C2A	C2M	CSM	S2M	SBM	SB3M	B2M	B2Mm	WLL	FRE
Unit-cell parameters														
<i>a</i> (Å)	8.0901(1)	7.8285(1)	7.9377(2)	8.0084(1)	7.6992(4)	7.8325(3)	7.9291(2)	8.0161(1)	8.1070(1)	8.1532(1)	8.1938(5)	8.4248(4)	13.9448(1)	8.5377(1)
<i>b</i> (Å)	–	–	–	–	–	–	–	–	–	–	–	10.7206(5)	–	–
<i>c</i> (Å)	–	5.0167(1)	5.0997(1)	5.1709(1)	5.0615(3)	5.0124(2)	5.0837(1)	5.1648(1)	5.2666(1)	5.3273(1)	5.3853(5)	8.4552(4)	9.3190(1)	5.2237(1)
β / γ (°)	–	–	–	–	–	–	–	–	–	–	–	110.93(1)	120.00(0)	–
<i>V</i> (Å ³)	529.50(2)	307.45(1)	321.32(2)	331.64(1)	300.03(3)	307.51(3)	319.62(2)	331.88(1)	346.14(1)	354.13(2)	361.56(3)	713.28(6)	1569.37(3)	380.77(2)
Mean metal-oxygen bond distances (Å)														
$\langle X-O \rangle$	–	2.577(6)	2.633(4)	2.674(2)	2.497(5)	2.580(4)	2.624(4)	2.673(4)	2.732(6)	2.758(7)	2.763(5)	2.820(14)	–	2.961(6)
$\langle Al-O \rangle$	1.914(1)	–	–	–	–	–	–	–	–	–	–	–	–	–
$\langle Tl-O \rangle$	1.952(13)	1.924(1)	1.943(1)	1.950(1)	1.750(1)	1.915(1)	1.929(2)	1.942(1)	1.952(2)	1.960(2)	1.965(4)	1.967(2)	1.959(14)	1.910(8)
$\langle Zn-O \rangle$	–	–	–	–	–	–	–	–	–	–	–	–	1.972(14)	–
$\langle Si-O \rangle$	–	1.615(1)	1.611(1)	1.611(1)	1.676(2)	1.616(2)	1.618(1)	1.617(2)	1.620(2)	1.626(2)	1.634(5)	1.628(4)	1.619(13)	1.617(2)
$\langle O-Tl-O \rangle$ (°)	109.47(0)	109.49(4)	109.54(2)	109.60(1)	109.49(3)	109.49(5)	109.52(8)	109.60(6)	109.67(11)	109.70(11)	109.70(14)	109.65(60)	109.32(59)	106.23(30)
Tetrahedral (<i>Tl</i>) distortion indices														
λ_{Tl}	1.0000	1.0023	1.0064	1.0123	1.0015	1.0013	1.0052	1.0124	1.0194	1.0224	1.0228	1.0240	1.0058	–
σ_{Tl}^2	0.00	8.73	24.31	45.70	5.94	5.17	19.95	46.12	70.89	81.26	82.81	99.01	24.73	–
ECoN	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	3.97	–
Reference	[1]	[2]	This Work	This Work	This Work	[8]	[8]	[8]	[8]	[8]	[8]	This Work	[6]	This Work

Notes: as Table 2. References: [1] Ardit et al. (2012b); [2] Ardit et al. (2012a)); [6] Ozel et al. (2010); [8] Dondi et al. (2013).

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630 **TABLE 4.** Crystal structure data of samples from the literature¹: unit-cell parameters, metal-oxygen bond distances and tetrahedral distortion indices.

<i>LITERATURE</i>	<i>hib</i>	<i>lma</i>	<i>spi</i>	<i>yag</i>	<i>ygg</i>	<i>zng</i>	<i>sta</i>	<i>zno</i>				
formula	CaAl ₁₂ O ₁₉	CaAl ₁₂ O ₁₉ Co = 0.30	LaMgAl ₁₁ O ₁₉	MgAl ₂ O ₄ Co = 0.07	MgAl ₂ O ₄ Co = 0.25	Y ₃ Al ₅ O ₁₂	Y ₃ Ga ₅ O ₁₂	ZnGa ₂ O ₄ Co = 0.10	ZnGa ₂ O ₄ Co = 0.10	Fe ₂ (M) ₂ Al ₁₈ Si ₈ O ₄₆ (OH) ₂ Co = 0.55	ZnO	ZnO Co = 0.20
Space group	<i>P6₃/mmc</i>	<i>P6₃/mmc</i>	<i>P6₃/mmc</i>	<i>Fd-3m</i>	<i>Fd-3m</i>	<i>Ia-3d</i>	<i>Ia-3d</i>	<i>Fd-3m</i>	<i>Fd-3m</i>	<i>C2/m</i>	<i>P6₃mc</i>	<i>P6₃mc</i>
Unit-cell parameters												
<i>a</i> (Å)	5.5909(1)	5.575(3)	5.588	8.0851(3)	8.0875(4)	12.0062(5)	12.273(1)	8.3342(3)	8.336	7.782(2)	3.2497(1)	3.2556(1)
<i>b</i> (Å)	–	–	–	–	–	–	–	–	–	16.608(3)	–	–
<i>c</i> (Å)	21.9893(4)	21.97(1)	22.00	–	–	–	–	–	–	5.648(2)	5.2034(2)	5.2024(8)
<i>β</i> / <i>γ</i> (°)	120.00(0)	120.00(0)	120.00(0)	–	–	–	–	–	–	90.04(3)	120.00(0)	120.00(0)
<i>V</i> (Å ³)	595.26	591.36	594.93	528.51	528.98	1730.7(2)	1848.7(4)	578.88	579.26	729.97	47.59	47.75
Selected tetrahedral <i>T1</i> parameters and distortion indices												
Point symmetry	C _{3v}	C _{3v}	C _{3v}	T _d	T _d	S ₄	S ₄	T _d	T _d	C _s	C _{3v}	C _{3v}
⟨ <i>T1</i> –O⟩ (Å)	1.845	–	1.847	1.9198(6)	1.9250(6)	1.754(4)	1.847(7)	1.976	1.978	1.968(3)	1.978	1.980
⟨O– <i>T1</i> –O⟩ (°)	109.45	–	109.45	109.47(0)	109.47(0)	109.58	109.63	109.47(0)	109.47(0)	109.43(10)	109.45	109.46
<i>λ</i> _{<i>T1</i>}	1.0007	–	1.0007	1.0000	1.0000	1.0116	1.0162	1.0000	1.0000	1.0016	1.0007	1.0005
<i>σ</i> ² _{<i>T1</i>}	3.15	–	3.01	0.00	0.00	47.28	66.07	0.00	0.00	4.64	2.91	1.89
ECoN	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	3.89	4.00	4.00
Reference	[1]	[2]	[3]	[4]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[10]

Notes: quadratic elongation (*λ*) and bond angle variance (*σ*) of *T1* tetrahedra were computed according to Robinson et al. (1971); the effective coordination number (ECoN) of *T1* tetrahedra was obtained by means of VESTA visualizer (Momma and Izumi, 2011).

Reference: [1] Nagashima et al. (2010); [2] Leite et al. (2009); [3] Kahn et al. (1981); [4] Bosi et al. (2012); [5] Nakatsuka et al. (1999); [6] Nakatsuka et al. (1995); [7] Wendschuh-Josties et al. (1995); [8] Reinen and Schmitz-DuMont (1961); [9] Bringhurst and Griffen (1986); [10] Santos et al. (2008).

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633 **TABLE 5.** Optical properties of Co-doped samples: energy of spin-allowed bands (**bold**) and spin-forbidden bands (*italic*); crystal field strength $10Dq$,
 634 interelectronic repulsion Racah B parameter and ${}^4T_1({}^4F)$ band splitting Λ . All the reported values are expressed in cm^{-1} .

	GAH	C2Z	CSZ	S2Z	C2A	C2M	CSM	S2M	SBM	SB3M	B2Mm	WLL	FRE
${}^4T_1({}^4F)$	6720	6530	6290	6110	6540	6660	6370	6120	5780	5670	5980	6120	6040
${}^4T_1({}^4F)$	7320	7270	7160	6730	7420	7450	7260	6720	6490	6360	6540	6870	6700
${}^4T_1({}^4F)$	7680	8210	7960	7740	8180	8030	7830	7680	7520	7520	7690	7750	7410
${}^2E({}^2G)$					<i>15100</i>							<i>15280</i>	
${}^4T_1({}^4P)^*$	16051	16200	16020	15880	16400	16170	16030	15950	15800	15690	15850	15880	15665
${}^4T_1({}^4P)$	16860	16960	16710	16280									15670
${}^4T_1({}^4P)$	17540	17480	17060	16970	17520	16880	17070	16980	16780	16690	17210	17000	17070
${}^2A_1({}^2G)^{**}$	<i>18380</i>	<i>18420</i>	<i>18490</i>	<i>18560</i>	<i>18630</i>	<i>18520</i>	<i>18510</i>	<i>18550</i>	<i>18640</i>	<i>18660</i>	<i>18370</i>	<i>18450</i>	<i>18540</i>
${}^2T_2({}^2G)$	<i>18910</i>	<i>19660</i>	<i>19370</i>	<i>19240</i>		<i>19540</i>	<i>19150</i>	<i>19080</i>	<i>19170</i>	<i>19260</i>	<i>19200</i>		<i>19870</i>
${}^2T_1({}^2P)$	<i>21020</i>	<i>20820</i>	<i>21080</i>	<i>21420</i>		<i>20500</i>	<i>20100</i>	<i>19540</i>	<i>20170</i>	<i>20680</i>		<i>20590</i>	
${}^2T_1({}^2H)$		<i>22170</i>	<i>22070</i>	<i>22140</i>				<i>21790</i>	<i>21910</i>	<i>21950</i>			
${}^2E({}^2H)$	<i>24720</i>	<i>24100</i>	<i>24200</i>	<i>24110</i>		<i>24530</i>	<i>24270</i>	<i>24170</i>	<i>23860</i>	<i>22880</i>			
$10Dq$	4178(9)	4261(8)	4127(2)	3982(14)	4269(4)	4274(8)	4125(12)	3967(13)	3817(12)	3777(17)	3913(21)	4001(5)	3878(2)
Racah B	766(1)	762(3)	754(2)	757(1)	768(1)	738(1)	753(2)	762(2)	764(2)	761(3)	772(4)	757(1)	756(11)
Λ	-16(4)	-97(9)	-67(8)	-115(10)	-60(6)	-38(3)	-30(3)	-109(9)	-112(10)	-134(11)	-140(8)	-87(7)	-66(5)

Notes: * plus ${}^2T_1({}^2G)$; ** plus vibronic effects.

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637 **TABLE 6.** Optical properties of Co-doped samples from the literature: energy of spin-allowed bands (**bold**) and spin-forbidden bands (*italic*); crystal
 638 field strength $10Dq$, interelectronic repulsion Racah B parameter and ${}^4T_1({}^4F)$ band splitting Λ . All the reported values are expressed in cm^{-1} .

	<i>hib</i>	<i>lma</i>	<i>spi</i>	<i>yag</i>	<i>ygg</i>	<i>zng</i>	<i>sta</i>	<i>zno</i>
${}^4T_1({}^4F)$	6680	6710	6600	6510	7380	6090	6200	6196
${}^4T_1({}^4F)$	7690	7770	7420	7270	7810	6920	7100	6798
${}^4T_1({}^4F)$	8130	8320	8110	8140	8760	7720	7900	7189
${}^2E({}^2G)$				14670	15030	14670		15408
${}^4T_1({}^4P)^*$	16050	15980	15850	15530	16060	15150	15700	16268
${}^4T_1({}^4P)$	16900	16740	16690	16380	16760	15820	16700	16666
${}^4T_1({}^4P)$	17560	17650	17390	16920	17410	16790	17200	17652
${}^2A_1({}^2G)^{**}$	18240	18540	18380	17640	18340	18030	18800	
${}^2T_2({}^2G)$		19110			19090	17980	17980	
${}^2T_1({}^2P)$	20990					23270	23270	20243
${}^2T_1({}^2H)$		21740				20780	20780	
${}^2E({}^2H)$								
$10Dq$	4324(21)	4391(19)	4274(5)	4251(4)	4696(10)	4000(2)	4083(3)	3861(8)
Racah B	753(2)	746(5)	745(1)	721(2)	712(2)	723(3)	753(3)	803(6)
Λ	-2(2)	-16(3)	-53(4)	-84(8)	-118(11)	-69(6)	-65(5)	-21(2)
Reference	[1]	[2]	[3]	[4]	[4, 5]	[6]	[7]	[4]

Notes: * plus ${}^2T_1({}^2G)$; ** plus vibronic effects.
 Reference: [1] Leite et al. (2009); [2] Yumashev et al. (2002); [3] Bosi et al. (2012); [4] Wood and Remeika (1967); [5] Pappalardo et al. (1961); [6] Duan et al. (2006); [7] Taran et al. (2009).

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DEPOSITED TABLES

642 **TABLE I.** Phase composition, agreement factors and refinement details of undoped samples.

<i>UNDOPED</i>	<i>GAH</i>	<i>C2Z</i>	<i>CSZ</i>	<i>S2Z</i>	<i>C2A</i>	<i>C2M</i>	<i>CSM</i>	<i>S2M</i>	<i>SBM</i>	<i>SB3M</i>	<i>B2M</i>	<i>B2Mm</i>	<i>WLL</i>	<i>FRE</i>
Quantitative phase analysis (apfu)														
Main phase	100.00	100.00	100.00	95.05(1)	100.00	88.90(6)	100.00	94.70(1)	94.70(2)	95.40(1)	100.00	95.34(1)	100.00	100.00
Others														
SrSiO ₃	–	–	–	4.95(7)	–	–	–	5.30(8)	–	–	–	–	–	–
CaMgSi ₂ O ₆	–	–	–	–	–	11.10(22)	–	–	–	–	–	–	–	–
Sr ₂ SiO ₄	–	–	–	–	–	–	–	–	5.30(21)	4.60(22)	–	–	–	–
BaSiO ₃	–	–	–	–	–	–	–	–	–	–	–	4.66(10)	–	–
Ba ₂ MgSi ₂ O ₇	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Agreement factors and refinement details														
χ^2	1.714	1.849	1.568	1.279	1.290	1.853	1.261	1.367	1.306	1.225	–	1.301	5.664	–
R_{wp}	0.1352	0.1150	0.1331	0.1130	0.1597	0.1508	0.1272	0.1146	0.1477	0.1552	–	0.1546	0.0812	–
R_p	0.0843	0.0846	0.0994	0.0793	0.1165	0.1109	0.0936	0.0806	0.1007	0.1066	–	0.1128	0.0520	–
No. of data	8333	8333	8333	8333	7999	6250	8000	6800	8333	8333	–	8000	6000	–
R(<i>F</i>)	0.0268	0.0377	0.0280	0.0216	0.0481	0.0478	0.0309	0.0249	0.0291	0.0284	–	0.0267	0.0378	–
R(<i>F</i> ²)	0.0300	0.0625	0.0481	0.0352	0.0789	0.0780	0.0497	0.0431	0.0484	0.0473	–	0.0494	0.0422	–
No. of reflections	68	363	378	394	342	364	355	284	416	423	–	1165	1184	–
Reference	[1]	[2]	This Work	[3]	This Work	This Work	This Work	[4]	[4]	[4]	[5]	[4]	[6]	[7]
Reference: [1] Ardit et al. (2012b); [2] Ardit et al. (2012a); [3] Ardit et al. (2010); [4] Ardit et al. (2012c); [5] Shimizu et al. (1995); [6] Ozel et al. (2010); [7] Bindi et al. (2006).														

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645 **TABLE II.** Phase composition, agreement factors and refinement details of Co-doped samples.

Co-DOPED	GAH	C2Z	CSZ	S2Z	C2A	C2M	CSM	S2M	SBM	SB3M	B2M	B2Mm	WLL	FRE
Quantitative phase analysis (apfu)														
Main phase	100.00	100.00	100.00	92.26(2)	100.00	92.52(4)	100.00	97.19(1)	88.24(3)	91.59(2)	–	97.40(1)	100.00	96.86(1)
Others														
SrSiO ₃	–	–	–	7.74(9)	–	–	–	2.81(1)	–	–	–	–	–	–
CaMgSi ₂ O ₆	–	–	–	–	–	7.48(5)	–	–	–	–	–	–	–	–
Sr ₂ SiO ₄	–	–	–	–	–	–	–	–	11.76(3)	8.41(3)	–	–	–	–
BaSiO ₃	–	–	–	–	–	–	–	–	–	–	–	2.60(21)	–	–
Ba ₂ MgSi ₂ O ₇	–	–	–	–	–	–	–	–	–	–	–	–	–	3.14(20)
Agreement factors and refinement details														
χ^2	1.467	1.678	1.434	1.247	1.646	1.524	1.485	1.438	2.227	2.080	–	1.496	2.038	6.818
R_{wp}	0.0951	0.1085	0.1294	0.1153	0.1698	0.1278	0.1375	0.1185	0.1118	0.1140	–	0.1663	0.0592	0.0656
R_p	0.0673	0.0824	0.0971	0.0832	0.1303	0.0965	0.1006	0.0857	0.0777	0.0761	–	0.1249	0.0455	0.0467
No. of data	8333	8333	8333	8333	7999	8333	8000	6800	6250	6250	–	8000	6000	8310
R(<i>F</i>)	0.0292	0.0506	0.0330	0.0230	0.0516	0.0543	0.0446	0.0307	0.0306	0.0265	–	0.0349	0.0636	0.0234
R(<i>F</i> ²)	0.0326	0.0736	0.0547	0.0359	0.0856	0.0889	0.0737	0.0574	0.0509	0.0449	–	0.0663	0.0679	0.0401
No. of reflections	68	363	378	393	342	364	356	284	415	422	–	1167	1186	399
Reference	[1]	[2]	This Work	This Work	This Work	[8]	[8]	[8]	[8]	[8]	[8]	This Work	[6]	This Work
Reference: [1] Ardit et al. (2012b); [2] Ardit et al. (2012a); [6] Ozel et al. (2010); [8] Dondi et al. (2013).														

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