Revision 1

Empirical electronic polarizabilities of ions for the prediction and interpretation of refractive indices.

I. oxides and oxysalts.

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Abstract

An extensive set of refractive indices determined at λ = 589.3 nm (n_D) from ~2600 measurements on 1200 minerals, 675 synthetic compounds, ~200 F-containing compounds, 65 Cl-containing compounds, 500 non-hydrogen-bonded hydroxyl-containing compounds, and approximately 175 moderately-strong hydrogen-bonded hydroxyl-containing compounds and 35 minerals with very strong H-bonded hydroxides was used to obtain mean total polarizabilities. These data, using the Anderson-Eggleton relationship $\alpha_T = \frac{(n_D^2-1)V_m}{4\pi+\left(\frac{4\pi}{3}-c\right)(n_D^2-1)}$ where α_T = the total polarizability of a mineral or compound, n_D = the refractive index at λ = 589.3 nm, V_m = molar volume in Å^3, and c = 2.26, in conjunction with the polarizability additivity rule and a least-squares procedure, were used to obtain 270 electronic polarizabilities for 76 cations in various coordinations, H_2O, 5 H_xO_y species [$(H_3O)^+$, $(H_5O_2)^+$, $(H_3O_2)^-$, $(H_4O_4)^{4-}$, $(H_7O_4)^-$], NH_4^+ and 4 anions (F^-, Cl^-, OH^-, O^{2-}).

Anion polarizabilities are a function of anion volume, V_{an}, according to $\alpha_- = \alpha_-^o \cdot 10^{-N_o/V_{an}^{1.20}}$ where α_- = anion polarizability, α_-^o = free-ion polarizability, and V_{an} = anion molar volume. Cation polarizabilities depend on cation coordination according to a light-scattering (LS) model with the polarizability given by $\alpha(CN) = (a_1 + a_2 CN e^{-a_3 CN})^{-1}$ where CN = number of nearest neighbor ions (cation-anion interactions), and a_1, a_2, and a_3 are refinable parameters. This expression allowed fitting polarizability values for Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Y^{3+}, (Lu^{3+}-La^{3+}), Zr^{4+}, and Th^{4+}. Compounds with (1) structures containing lone-pair and uranyl ions (2) sterically-strained (SS) structures (e.g., $Na_{4.4}Ca_{3.8}Si_6O_{18}$ (combeite), Δ = 6% and $Ca_3Mg_2Si_2O_8$ (merwinite), Δ = 4%), (3) corner-shared octahedral (CSO) network and chain structures such as perovskites, tungsten bronzes and titanite-related structures (e.g., $MTiO_3$ (M = Ca, Sr, Ba), Δ = 9-12% and $KNbO_3$, Δ = 10%), (4) edge-shared Fe^{3+} and Mn^{3+} structures (ESO) such as goethite (FeOOH, Δ = 6%) and (5) compounds exhibiting fast-ion conductivity, showed systematic deviations between observed and calculated polarizabilities and thus were excluded from the regression analysis. The refinement for ~2600 polarizability values using 76 cation polarizabilities with values for $Li^+ \rightarrow Cs^+$, Ag^+, $Be^{2+} \rightarrow Ba^{2+}$, $Mn^{2+/3+}$, $Fe^{2+/3+}$, Co^{2+}, $Cu^{+/2+}$, Zn^{2+}, $B^{3+} \rightarrow In^{3+}$, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, $Lu^{3+} \rightarrow La^{3+}$, $C^{4+} \rightarrow Sn^{4+}$, $Ti^{3+/4+}$, Zr^{4+}, Hf^{4+}, Th^{4+}, V^{5+}, Mo^{6+}, and W^{6+} in varying CN's, yields a standard deviation of the least squares fit of 0.27 (corresponding to an R^2 value of 0.9997) and no discrepancies between observed and calculated polarizabilities, $\Delta > 3\%$.

Using $n = \sqrt{\frac{4\pi\alpha}{(2.26-\frac{4\pi}{3})\alpha+V_m} + 1}$ the mean refractive index can be calculated from the chemical composition and the polarizabilities of ions determined here. The calculated

mean values of <n_D> for 54 common minerals and 650 minerals and synthetic compounds differ by less than 2% from the observed values.

In a comparison of polarizability analysis with 68 Gladstone-Dale Compatibility Index (CI) (Mandarino 1979, 1981) values rated as fair or poor,we find agreement in 32 instances. However, the remaining 36 examples show polarizability Δ values less than 3%. Thus, polarizability analysis may be a more reliable measure of the compatibility of a mineral's refractive index, composition and crystal structure.

Introduction

Importance of refractive indices

Refractive indices (RI's) are important properties of minerals (Feklichev 1992; Nesse 2013). They are required for the description of a mineral and they help understand chemical trends in structural families such as andalusites, adularia, cordierites and zeolites (Gunter and Bloss 1982; Selkregg and Bloss 1980; Gunter and Ribbe 1993; Palmer and Gunter 2000) and can help determine H_2O content of hydrated minerals and zeolites (Medenbach et al. 1980; Gunter and Ribbe 1993).

In addition to being of interest in mineralogy, refractive indices are also widely used in the field of optics to help characterize optical materials. Predicting optical properties from the chemical composition is of value in developing new materials. Specifically, prediction of the refractive indices of borate optical crystals from polarizabilities plays an important role in the search for new linear and nonlinear optical materials (Qin and Li 2011). Refractive index is a fundamental parameter of lasers. It is required for the analysis of the radiative properties of Ln^{3+}

ions, for the calculation of the nonlinear and thermal refractive index contributions and for the design of antireflection coatings and optical waveguide structures (Han et al. 2012).

Polarizabilities – General

Electronic polarizabilities have many uses from calculation of refractive indices to optical activity of polar crystals. Derivation of static polarizabilities, representing polarizabilities at wavelengths extrapolated to $\lambda = \infty$, and references to many of their uses are described in detail in Shannon and Fischer (2006), hereafter referred to as SF2006. Dynamic polarizabilities derived from refractive indices in the visible region of light can be used to predict mean refractive indices in individual minerals. Symbols used in equations and text are listed in Table 1.

Total polarizabilities calculated from Lorenz-Lorentz, Gladstone-Dale and Drude relations. Polarizabilities are important properties for characterization of materials and in particular, minerals. Three commonly used expressions that relate polarizabilities to refractive indices (Anderson and Schreiber 1965; Anderson 1975; Eggleton 1991) are: the Lorenz-Lorentz (LL, Lorenz 1880; Lorentz 1880, eqn. 1a), Gladstone-Dale (GD, Gladstone and Dale 1863; Jaffe 1988; Fowler et al.1991) and Drude relationships Many other publications list the expressions in terms of refractivity; for our purposes it is more useful to list them in terms of polarizability, as do Renn (1974), Anderson (1975), Jaffe (1988), Fowler and Tole (1991), Dimitrov and Sakka (1996), and Heaton et al. (2006).

Static electronic polarizabilities, α, far below electronic resonances are described by the Lorenz-Lorentz (LL) equation:

$$\alpha_{LL} = \frac{1}{b} V_m \cdot \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \qquad \text{(1a)}$$

with the Lorentz factor, $b = 4\pi/3$ for compounds with cubic symmetry, V_m = molar volume in Å^3, and n_∞ = the mean static refractive index at $\lambda = \infty$. It will be shown later that this equation can be applied to the visible region of light as well.

Anderson (1975) modified the Lorenz-Lorentz relationship to include the effects of electron overlap in a general polarizability equation. Eggleton (1991) expressed this approach in the following relationship

$$\alpha = \frac{(n^2-1)V_m}{4\pi+\left(\frac{4\pi}{3}-c\right)(n^2-1)} \qquad (1b)$$

with the Lorentz factor $4\pi/3$ and c as the electron overlap factor. When $c = 0$ (no electron overlap), we obtain the LL equation (1a); when $c = 4\pi/3$ (strong electron overlap), we obtain Drude's equation (2). For some classes of compounds with partial electron overlap this factor was experimentally determined as $c = 3.69$ for borosilicate glasses (Ritland 1955), $c = 3.57$ (Anderson and Schreiber 1965) and $c = 2.99$ (Marler 1988) for SiO_2 polymorphs. For 570 rock-forming minerals (n_D = 1.5 – 1.9), Anderson and Schreiber (1965) obtained $c = 2.19$ and for 574 silicates (n_D = 1.4 – 1.8) whereas Eggleton (1991) found $c = 2.26$.

Drude equation: $$\alpha_{Dr} = \frac{(n^2-1)V_m}{4\pi} \text{ for } c = 4\pi/3 \text{ in (1b)} \qquad (2)$$

Gladstone-Dale equation: $$\alpha_{GD} = 3\pi/4\ V_m\ (n-1) \qquad (3)$$

Anderson-Eggleton equation[1]: $$\alpha_{AE} = \frac{(n^2-1)V_m}{4\pi+\left(\frac{4\pi}{3}-2.26\right)(n^2-1)} \qquad (4a)$$

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[1] The special case with $c = 2.26$ determined by Eggleton (1991) and used extensively in this study, will be referred to as the Anderson-Eggleton (AE) relationship. These relations have been discussed by Larsen (1909), Anderson and Schreiber (1965), Anderson (1975), Mandarino (1976, 1978, 1979, 1981), Marler (1988), Eggleton (1991) and Fowler et al. (1991). Although Anderson and Schreiber concluded that (1) from a study of silica polymorphs (n_D = 1.42 - 1.85) the Drude equation fits the data slightly better than the LL equation for the silica polymorphs, Anderson later showed from plots of n_D vs. density for a more extensive set of 570 rock-forming minerals that it was not possible to favor the choice between the LL ($c = 0$), Drude ($c = 4\pi/3$), or

Eqn. (4a) solved for n:

$$n_{AE} = \sqrt{\frac{4\pi\alpha_{AE}}{(c-b)\alpha_{AE}+V_m} + 1} \tag{4b}$$

with $c = 2.26$ and b = 4π/3.

Several aspects of the Gladstone-Dale relation have been questioned (Bloss et al. 1983; Eggleton 1991; Fowler et al.1991). Mandarino (1981) and Bloss et al. (1983) pointed out the structure dependency of the GD constants. In addition, Fowler et al. (1991) pointed out that "the polarisabilities produced by the LL and GD approaches are different, and clearly cannot both be correct". They point out that *ab initio* calculations of LiF, BeO, and MgO polarizabilities agree quite well with the LL equation but show larger discrepancies with the GD and Drude relations.

Figure 1 shows the polarizabilities calculated from refractive indices by the different approaches. The α_{LL} values are significantly lower than the α_{GD} values especially towards higher RI's while the α_{AE} values with $c = 2.26$ are somewhere intermediate. Eggleton (1991) found this value by trial and error methods and described it to approach α_{GD} values but actually it is closer to α_{LL} as shown in Figure 1. The α_{Dr} values are closer to α_{GD} with a crossover point at $n = 2$. The values are approximately equidistant between $n = 1.5$ and 1.6 representing a range of RI'stypical for silicate minerals.

Figure 2 shows what we propose to be a theoretical relationship between covalence and LL, AE, and GD relations. As covalence increases, calculated polarizabilities increase in the order LL→AE→GD. The effects of the intermediate nature of oxide and silicate covalence on

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intermediate relations (c = 2.2-3.0). The Drude equation has not been used for minerals but the GD equation has been used extensively by mineralogists to evaluate experimental refractive indices (Mandarino 1976; 1978; 1979;1981; Bloss et al. 1983; Jaffe, 1988; Eggleton 1991; Gunter and Ribbe 1993).

refractive index was pointed out by Jaffe (1988, p.131). We believe most minerals are best described by the AE relationship although the more covalent carbonates, nitrates, sulfates and perchlorates fall outside the AE region. It will be shown later that an oxygen polarizability correction must be made to obtain a good fit between observed and calculated polarizabilities.

Cation and anion polarizabilities.

We assume that the total molar electronic polarizability α_T of a compound can be calculated as a linear combination of individual ion electronic polarizabilities, α_e(ion), then it can be expressed as

$$\alpha_T = \sum_{i=1}^{N} m_i \cdot \alpha_{ei}(ion) \quad (5)$$

Here, i varies over the total number (N) of types of ions in the formula unit, and m_i is the number of ions of type i in the formula unit. So, as an example, the total polarizability of albite ($NaAlSi_3O_8$) could be calculated according to $\alpha_T(\text{albite}) = \alpha_e(Na^+) + \alpha_e(Al^{3+}) + 3\alpha_e(Si^{4+}) + 8\alpha_e(O^{2-})$. Consequently, ion polarizabilities, α_e(ion), can be used as a set of refinable parameters in a least-squares procedure that minimizes the function in Eqn (9). Such sets of empirical electronic ion polarizabilities were derived by several authors (e.g., Tessman and Kahn 1953; Pirenne and Kartheuser 1964; Boswarva 1970; Jain et al. 1975; Pohl 1978) and most pertinent to this study including primarily mineral refractive indices by Lasaga and Cygan (1982) who derived a set of electronic polarizabilities from a variety of mineral polarizabilities.

Anion polarizabilities.

While cation polarizabilities are strictly additive after taking account of cation coordination, anion polarizabilities are correlated with the volume occupied by the anion which could be expressed by the volume of the unit cell divided by the number of anions, and therefore is related by inference to the interatomic distances.

The various approaches that have been used by various authors to correct for the anion polarizabilities are discussed in detail in SF2006. In this paper we use

$$\alpha_- = \alpha_-^o \cdot 10^{-N_o/V_{an}^n} \tag{6}$$

with α_-= anion polarizability, α_-^o = free-ion polarizability, and V_{an} = anion molar volume. In SF2006 the exponent n = 2/3 was used to be consistent with Fowler and Madden (1984, 1985) and Fowler and Tole (1991). In this work, we tried a variety of exponents from 0.666 to 1.33. The value of n = 1.20 yielded the smallest deviations between observed and calculated total polarizabilities and was therefore used throughout the calculations.

Cation polarizabilities.

Jemmer et al. (1998) analyzed the effects of coordination number and interatomic distance on anion polarizabilities using a light-scattering model with the polarizability given as $a = q/k$ where q is a bound charge and k being a function of the nearest-neighbor-distance R according to

$$k(R) = a_1 + a_2 CN_{ca} e^{-a_3 R} + a_4 CN_{aa} e^{-\sqrt{2} a_5 R} \tag{7}$$

with CN_{ca} = number of nearest neighbor ions (cation-anion interactions), CN_{aa} = number of second nearest neighbor ions (anion-anion interactions), and a_{1-5} being constants. Neglecting second nearest neighbors and considering the approximately linear relationship between CN and R as shown in SF2006, eqn. (7) can be reduced to

$$\alpha(CN) = (a_1 + a_2 CN e^{-a_3 CN})^{-1} \tag{8}$$

with a_1, a_2, and a_3 being refinable parameters. The procedure and further details on the dependence of static polarizabilities on cation coordination is described in SF2006.

This work

In an earlier study, a set of empirical ***static*** electronic polarizabilities was developed for use in oxides, hydroxides, oxyfluorides and oxychlorides, using 534 total polarizabilities from 387 compounds. These polarizabilities, derived using the LL equation in conjunction with the polarizability additivity rule and a light scattering model of cation polarizability to give a smooth decrease of polarizability with cation coordination, were useful in calculating a variety of physical properties but they were not useful in predicting the value of the refractive index, n_D, at 589.3 nm.

Because the LL equation has a theoretical basis and the Drude and empirical GD relationships show larger discrepancies (Table 2) from the ab initio polarizabilities of LiF, BeO, and MgO, we originally chose to use the LL equation for our derivation of n_D polarizabilities. However, the LL polarizabilities did not fit the refractive index data as well as the AE polarizabilities, probably because of the covalent character of borates, silicates, phosphates, arsenates and sulphates [50-90%, Pauling 1939; Allred and Rochow 1958]. We also make the assumption that the LL and AE equations are valid for n_D as well as for n_∞. Although Lorentz (1880) states that the LL equation is valid only for light of infinite wavelengths, Born and Wolf (1975) state that Eqn (1a) is valid for light of any wavelength.

In this paper with the aid of the AE relationship, [Eqn (4a)], and the polarizability additivity rule in conjunction with ~2600 total dynamic polarizabilities derived from the refractive indices n_D, at 589.3 nm of ~1200 minerals and 675 synthetic compounds, we develop a universal set of cation and anion polarizabilities. This new set of polarizabilities is useful in calculating the mean refractive index of most minerals and synthetic oxides if the composition, unit cell and crystal structure are known.

Experimental

Data Base

The data necessary for this analysis are the refractive indices, crystal structure, unit-cell dimensions and chemical composition. Refractive indices were taken from Gaines et al. (1997), Deer, Howie and Zussman (1963a, 1963b, 1978, 1982, 1986, 1996), Doelter (1914, 1917), Anthony et al. (2015), Hintze (1897, 1915, 1933, 1938, 1960, 1968), Hellwege and Hellwege (1962, 1969, 1979, 1981), Nelson (1996), McLune (1989), Medenbach and Shannon (1997), Shannon et al. (2002), Swanson et al. (1962-1981), Webmineral (2015), Winchell (1931), Winchell and Winchell (1964), the powder diffraction files of the International Centre for Diffraction Data (ICDD), and descriptions of minerals in mineralogical journals (up to the end of 2015). In general the above publications were used to locate the refractive indices and the original publications. Original publications were preferred in order to provide refractive indices, crystal structure, unit-cell dimensions and chemical composition on the same sample. Occasionally, unit-cell dimensions and composition were taken from the Inorganic Crystal Structure Database (Belsky et al. 2002).

The complete data set (DS1) consists of approximately ~4000 refractive index measurements on 3000 minerals and 1000 synthetic compounds. Included in DS1 are 425 compounds containing lone-pair ions and 120 compounds containing uranyl ions, 650 RI measurements on the same mineral, 35 corner-shared octahedral (CSO) network and chain structures such as perovskite (ABO_3), and tungsten bronze ($SrNb_2O_6$), 40 compounds containing edge-sharing Fe^{3+} and Mn^{3+} octahedra (ESO) such as $LiFeO_2$, goethite (FeOOH), and hausmannite (Mn_3O_4), 40 alkali ion conductors, and 120 sterically-strained (SS) structures with strong bond valence deviations. Some minerals show considerable zoning within individual grains and also significant grain-to-grain compositional differences, depending on details of paragenesis. Where this is the case, there may be significant differences between the average composition given and that of the grain used to determine the refractive indices, unless the composition of that grain is analyzed by electron microprobe. Approximately 100 minerals and compounds were deleted from DS1 because of this problem. Table 3 summarizes the reasons for deletion of minerals from the dataset. Removal of the above compounds from DS1 resulted in DS2 with 2600 entries that were used for derivation of the polarizability parameters. This reduced dataset DS2 contains approximately 1800 minerals and 800 synthetic compounds. Included in DS2 are refractive index measurements on oxides, hydroxides, oxyfluorides, oxychlorides , ~200 F-containing compounds, 65 Cl-containing compounds, 115 carbonates, 20 nitrates, ~250 sulfates, 15 perchlorates, 650 non-hydrogen-bonded hydroxyl-containing compounds, ~300 moderately strong hydrogen-bonded hydroxyl-containing compounds, and 35 minerals with very strong H-bonded hydroxides.

Two separate data sets, DSF, containing refractive index measurements on 36 fluorides and DSCl, containing refractive index measurements on 48 chlorides were used for the refinements of α(F$^-$) and α(Cl$^-$), respectively.

The mineral and oxide data set uses the compositions, mean total polarizabilities, molar anion volumes, V_{an}, and the weight given to the compound in the refinement ($w_{\mathrm{i}} = \sigma_i^2$, where σ_i is the estimated % error in the experimental refractive index.

Procedure

Calculations. The calculation and experimental procedure is similar to that described in SF2006. The reader can refer to that publication for further details with the proviso that the considerations specific to “free ion” and “static polarizabilities” do not apply here.

If it is assumed that the total molar electronic polarizability α_T of a compound can be calculated (α_{calc}) as a linear combination of individual ion electronic polarizabilities, α_e (ion), according to the additivity rule [eqn (5)], then the ion polarizabilities, α_e (ion), can be used as a set of refinable parameters in a least-squares procedure that minimizes the function:

$$\sum_{i=1}^{M} w_i (\alpha_{obs} - \alpha_{calc})^2 \qquad (9)$$

where i varies over the number of measurements of α_{obs} for a variety of compounds and w_{i} = σ_i^{-2} with σ_i being the estimated % error in the experimental refractive index.

The least-squares refinement program POLFIT originally used for dielectric polarizability analysis (Shannon 1993) was modified and improved to allow simultaneous refinement of α_e

(ion) for cations and for O^{2-}, OH^-, H_2O, F^-, and Cl^- as a function of anion volume [eqns (6) and (8)] using a Levenberg-Marquardt algorithm (Levenberg 1944; Marquardt 1963).

The results of least-squares refinements were evaluated by examining the weighted variance of fit (F) representing the residual sums of squares for the final parameter estimates:

$$F = \frac{\sum_i w_i \left[(\alpha_{obs})_i - (\alpha_{calc})_i\right]^2}{\sum_i w_i} \tag{10}$$

The square root of the weighted variance, i.e., the standard deviation, SD, of the fit is reported further on as an estimate for the goodness of fit.

The standard deviation of a refined value of α_e(ion) is calculated as:

$$\sigma[\alpha_e(ion)] = M_I^{-1/2} \tag{11}$$

where M_I is the diagonal element of the inverted normal matrix corresponding to the ion polarizability for ion "I" varied in the least-squares procedure.

In the further discussion we will use the deviation of observed from calculated total polarizabilities (%) as an additional measure for the quality of the fit. In general, we just consider deviations less than 3% to be highly significant and do not discuss compounds with deviations greater than 3% unless they have sterically-strained structures: $Ca_{12}Al_{14}O_{33}$ (mayenite), $Na_{4.4}Ca_{3.8}Si_6O_{18}$ (combeite), $Ca_3MgSi_2O_8$ (merwinite), $NaScSi_2O_6$ (jervisite), silicate and germanates with the melilite structure, $Ca_2Al_3Si_3O_{12}OH$ (zoisite and clinozoisite), $CaSO_4$ (anhydrite) or are part of a series showing systematic changes, e.g., corner-shared octahedral structures such as (1) perovskites including $KNbO_3$ and $KTaO_3$, (2) shared-edge covalent compounds with Fe^{3+}, Mn^{3+}, Y^{3+}, Ti^{4+}, Mo^{6+} and W^{6+} face and edge-shared polyhedra, and (3) certain tungsten bronze compounds e.g., $Sr_{0.5}Ba_{0.5}Nb_2O_6$.

Anion parameters in oxides, fluorides, chlorides, hydroxides, and hydrates. As discussed in SF2006, ab initio calculations show that anion polarizabilities in crystals are considerably reduced from their "free-ion" values and depend on interatomic distances. For example α_- (O^{2-}) is smaller in SiO_2 than in BaO. Because it is not practical in complex oxides and fluorides to use interatomic distances as an independent variable, following Tessman and Kahn (1953), we have chosen to use the molar anion volume, V_{an},. In most compounds with ions having similar polarizabilities such as Be_2SiO_4, $MgAl_2O_4$, or Al_2SiO_5, the system provides a reasonably accurate correlation to mean interatomic distances, but in those compounds containing a large ion in a matrix of smaller ions, e.g., $BaSi_2O_5$ where $V_{an}(BaO) = 42.5$ Å^3, $V_{an}(SiO_2) = 18.8$ Å^3, and $V_{an}(BaSi_2O_5) = 24.10$ Å^3, some uncertainty arises.

As explained in the chapter on anion polarizabilities in the Introduction we are using eqn. (6) with $n = 1.20$ in the exponent as being most appropriate for n_D data. Figure 3 shows the dependence of AE polarizabilities on V_{an} for simple oxides.

a. Oxide polarizability.

The first step in the refinement procedure was to obtain anion parameters α_- (O^{2-}) and N_o for oxygen. Refinements were begun using the small cation oxides BeO, B_2O_3, SiO_2 and P_2O_5 where most of the polarizability is derived from the oxide ion. With α (Be^{2+}), α ($^{[3]}B^{3+}$), $\alpha(Si^{4+})$ and α (P^{5+}) fixed at their values from SF2006, (0.22 Å^3, 0.009 Å^3, 0.333 Å^3, and 0.266 Å^3) an initial value of α_- (O^{2-}) = 1.76 Å^3 with $N_o = -1.80$ was obtained.

Values of calculated "in-crystal" α_{-}^{o} (O^{2-}) from first-principles range from 1.90 Å^3 (MgO) to 3.35 Å^3 (BaO), (Pearson et al. 1984), 1.83 Å^3 (MgO), (Fowler and Madden 1985), 1.30 Å^3 (BeO) (Fowler, Munn and Tole 1991) and 1.68 Å^3 (MgO) to 3.54 Å^3 (K_2O), (Fowler and Tole 1991). A more recent analysis of oxygen polarizabilities in complex aluminates, silicates, and sulphates, (Ray et al.1996), indicated α_{-} (O^{2-}) = 1.3 – 2.8 Å^3. These values are much lower than "free-ion" values but are significantly larger than values of α_{-} (O^{2-}) using methods other than "first-principles" methods. For example, the values of α_{-} (O^{2-}) in Table VII of SF2006 range from 0.55 - 2.40 Å^3 (mean value = 1.3 Å^3) and values obtained from electric field gradient measurements (Kirsch et al. 1974) in spinels range from 0.5 to 1.5 Å^3.

Using the entire data set of ~2600 polarizabilities resulted in oxygen parameters α_{-} (O^{2-}) = 1.79Å^3, N_o = -1.776 [in eqn. (6)]. Our oxygen polarizabilities ranging from 1.44 Å^3 in SiO_2 (stishovite) to 1.71 Å^3 in BaO with values for BeO (1.50 Å^3), B_2O_3 (1.53 Å^3), SiO_2 (1.58 Å^3) and P_2O_5 (1.60 Å^3) fall within the ranges quoted above (1.3 Å^3 -3.35 Å^3) for the calculated α_{-}^{o} (O^{2-}) "in-crystal" polarizabilities.

b. Fluoride and chloride polarizabilities.

To obtain initial anion parameters for F^-, a set of 36 spectral refractive index measurements from 35 fluorides was used. This data set contained the F^- anion and 31 cations with approximate polarizabilities obtained from a general least squares fit using the entire ~2600 experimental polarizabilities. This refinement resulted in a refined value of α_{-}^{o} (F^-) = 0.85 Å^3 and N_o(F^-) = -1.9. Further refinement using the entire data set of ~2600 polarizabilities resulted in a value of α_{-}^{o} (F^-) = 0.82 Å^3 and N_o(F^-) = -3.00. The fluoride parameters α_{-}^{o} (F^-) = 0.82 Å^3 and N_o(F^-)

= -3.00 were retained for subsequent refinements. Although these polarizabilities are valid for oxyfluorides, they are not, in general, valid for the highly ionic pure fluorides.

Fowler and Tole (1991) found the empirical values of 0.9 – 2.4 Å^3. Our fluoride polarizabilities ranging from 0.64 Å^3 in LiF to 0.75 Å^3 in KF and BaF_2 with values for CaF_2 (0.68 Å^3), LaF_3 (0.66 Å^3), and Cs_2SiF_6 (0.73 Å^3) are all smaller than the ranges quoted above (0.9 Å^3 – 2.4 Å^3) for the calculated α (F$^-$) "in-crystal" polarizabilities.

Using 48 chlorides, a value of α^o_- (Cl$^-$) = 4.0 Å^3 and N$_o$(Cl$^-$) = -1.7 was obtained using cation values found in the fluoride refinement. The final values found to best fit the entire data set of ~2600 polarizabilities data by manually adjusting α^o_- (Cl$^-$) was 3.88 Å^3 and N$_o$(Cl$^-$) = -1.80. Our chloride polarizabilities ranging from 3.63 Å^3 in LiCl, 3.77 Å^3 in KCl, to 3.79 Å^3 in CsCl with values for $Ca_5P_3O_{12}Cl$ (3.44 Å^3), $BaCl_2$ (3.70) Å^3, and K_2SnCl_6 (3.69 Å^3) are in the range of the Wilson and Curtis (1970) values of 2.9 - 4.8 Å^3 and in the upper end of the ranges quoted by Pearson et al. (1984), 3.1 – 3.7 Å^3 and by Fowler and Tole (1991), 2.9 – 3.6 Å^3. These parameters are valid for oxychlorides but are not, in general, valid for the highly ionic pure chlorides.

c. Hydroxide and hydrate polarizabilities.

Initial α^o_- (OH$^-$) values were assumed to be similar to α^o_- (O^{2-}). Later analysis using the complete data set (omitting the 175 moderately strong H-bonded hydroxides) and refinement of all cation parameters showed a good fit for α^o_- (OH$^-$) with the value of 1.79Å^3, N$_o$ = -1.792, similar to α^o_- (O^{2-}) with values of 1.79Å^3, N$_o$.= -1.776. This value is smaller than the value of 2.03 Å^3 from SF2006 (which was derived assuming the ionic L-L eqn (1a)) and the calculated "free-ion" values of 2.9 - 6.5 Å^3 in Table III of SF2006. Comparison of the refined values of α_-^o(OH$^-$) to those of α_-^o(O^{2-}) in Mg(OH)$_2$ [brucite] (1.59 Å^3) and MgO (1.58 Å^3) confirms the close identity of α_-^o(OH$^-$) and α_-^o(O^{2-}) but differing from SF2006, where α_-^o(OH$^-$) was found to be slightly greater than α_-^o(O^{2-}).

At a later stage in the refinement process it was confirmed that using the α_-^o(OH$^-$) value of 1.79 Å^3, for calculation of the polarizability of sassolite [B(OH)$_3$] results in a calculated polarizability that is higher than the observed polarizability by about 4%. We assumed from this result that hydrogen bonded OH's have a lower polarizability, about 4-5% lower than the normal OH's. Because the same effect was observed in ~175 other H-bonded hydroxyl compounds, we concluded it was a general effect and thereafter assigned the values of α_-^o(OH$^-$) = 1.73Å^3 and N$_o$ = -2.04 to moderately strong hydrogen-bonded hydroxyls (d(OH….O) = 2.6 - 2.9 Å). Setting of α_-^o(OH$^-$) = 1.73A^{3}for the many H-bonded hydroxides almost always gives better agreement than the value of 1.79 A^3.

Generally, minerals with OH…O distances between 2.6 Å and 2.9 Å require use of α_-^o(OH$^-$) = 1.73 Å$^{3.}$ However, when the hydroxyl is very strongly H-bonded, such as in cubic HBO$_2$ (metaborite), AlOOH (diaspore), NaCa$_2$Si$_3$O$_8$(OH) (pectolite), CaHPO$_4$ (monetite) and KH$_2$AsO$_4$, α_-^o(OH$^-$) = 1.79 Å^3 results in a better fit. There are ~35 structures that contain very strongly bonded hydroxyl ions defined here by OH…O distances less than ~<2.6 Å >. Wiedemann (1976) shows that very strongly bonded hydroxyls behave differently from moderately H-bonded hydroxyls. It is possible the different values of very strong and moderate H-bonds result from the tendency of the very strong H-bonds to be more symmetrical than moderate H-bonds.Wiedemann (1976) shows that the polarizability goes up as the bond becomes more symmetrical.

In SF2006, setting α^o (H_2O) to the free ion value of 1.432 Å^3 gave good results; variation of N_o resulted in a value of 0.03 indicating little or no dependence of α^o (H_2O) on cell volume (interatomic distance). Using the complete data set with the higher AE polarizability values and refinement of all cation parameters, a value of α^o (H_2O) = 1.620Å^3 was obtained and, as in SF2006, with N_o = 0.0.

Cation parameters.

Using α^o_- (O^{2-}) = 1.79 Å^3, refinement of α (Be^{2+}), α(Si^{4+}) and α (P^{5+}) gave initial values 0.19 Å^3, 0.30 Å^3, and 0.030 Å^3, respectively. In SF2006, we showed that cation polarizabilities are coordination dependent so that further polarizability refinements were made for each ion in a specific coordination.

The next refinement using the small ions Li^+, Be^{2+}, Mg^{2+}, B^{3+}, Al^{3+}, Si^{4+}, and P^{5+} with α^o_- (O^{2-}) fixed at 1.79 Å^3, resulted in the provisional polarizabilities α ($^{[4]}Li^+$) = 0.50 Å^3, α ($^{[6]}Li^+$) = 0.56 Å^3, α (Be^{2+}) = 0.18Å^3, α ($^{[4]}Mg^{2+}$) = 0.82Å^3, α ($^{[6]}Mg^{2+}$) = 0.72Å^3, α ($^{[3]}B^{3+}$) = 0.12 Å^3, α ($^{[4]}B^{3+}$) = 0.04 Å^3, α ($^{[4]}Al^{3+}$) = 0.40Å^3, α ($^{[5]}Al^{3+}$) = 0.43Å^3, α ($^{[6]}Al^{3+}$) = 0.47 Å^3, α (Si^{4+}) = 0.32 Å^3, and α (P^{5+}) = 0.17 Å^3. To be in accordance with other cation CN dependences, α ($^{[3]}B^{3+}$) of three-coordinated B (based on RI of B_2O_3) was assigned a value of 0.12 Å^3 and α ($^{[4]}B^{3+}$) of four-coordinated B a value of 0.03 Å^3. The procedure of gradually adding the cations Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Ga^{3+}, Ge^{4+}, Zr^{4+}, Y^{3+}, RE ions, etc., to individual refinements was followed until all 76 cations in various coordinations, H_2O, and the anions F^-, Cl^-, OH^- were included. During these refinements, $\alpha_-^o(F^-)$, $\alpha_-^o(Cl^-)$, and $\alpha^o(H_2O)$ were held constant at 0.82 Å^3, 3.88 Å^3, and 1.620 Å^3, respectively. In addition to B^{3+}, F^-, Cl^-, and H_2O, the polarizabilities of the small cations S^{6+} and Cl^{7+} were fixed at their free-ion values of 0.011 Å^3 and 0.0075 Å^3 (Johnson et al. 1983). In instances when there were not many examples of compounds containing the cations $^{[4\text{-}9]}Ag^+$, $^{[6]}As^{5+}$, $^{[6]}Cr^{6+}$, Hg^{2+}, $^{[6]}I^{7+}$, $^{[5]}Mn^{3+}$, $^{[8],[9]}Pu^{4+}$, Rh^{3+}, and $^{[6]}Ti^{3+}$ least-squares analysis was ineffective, and polarizabilities were obtained by manually adjusting α_+^o to best fit each compound and holding them constant in subsequent refinements.

As established in SF2006 for static polarizabilities, α decreases upon increasing CN and for isovalent cations with similar electron configurations α increases upon increasing ionic size. We have assumed similar behavior for dynamic polarizabilities. These relationships were used to obtain approximate polarizabilities for some of the cations in the periodic table. In particular, the polarizabilities of the rare earth ions were fitted to the cube of the ionic radius, in Figure 4, in a manner similar to that shown in Figure 1 of SF2006. We have no explanation for the deviation of Y from the regular behavior shown by the rare earth ions also observed in SF2006.

Similarly, $\alpha_+^o(Hf^{4+})$ was adjusted to be smaller than $\alpha_+^o(Zr^{4+})$ in accordance with $r^3(Hf^{4+}) = 0.572$ Å^3 and $r^3(Zr^{4+}) = 0.593$ Å^3: $\alpha_+^o(^{[8]}Hf^{4+}) = 3.10$ Å^3 and $\alpha_+^o(^{[8]}Zr^{4+}) = 3.74$ Å^3. Note, however, the polarizabilities are not proportional to r^3**.**

In a final step cation polarizabilities were adjusted to be in accordance with the results of the light-scattering (LS) model proposed by Jemmer et al. (1998) applied here in its reduced form [eqn. (8)]. When there are only a few observed data points, a_2 and a_3 of eqn. (8) are based on the two most reliable data points in each data set calculated by least squares fits. In SF2006, the free-ion value, α^o, was used as a data point but this procedure is not valid for dynamic polarizabilities. Here we use as an approximate value of α^o the value obtained at high CN's andionic radius-CN data from Shannon (1976). The resulting fits for Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Y^{3+}, (Lu^{3+}-La^{3+}), Zr^{4+}, and Th^{4+} (see Figure 5a - 5d for plots of α_{AE} vs. CN for Na^+, Ca^{2+}, La^{3+}, and Zr^{4+}) show reasonably good agreement with the observations although dependent on the accuracy of the α^o parameters.

The final refinement was carried out on a data set identical to the one above but which excluded the above compounds with either questionable refractive indices or compositions. The results are shown in the last columns of Table 4 utilizing ~2600 measurements on 1550 compounds with SD = 0.273 and all deviations of observed from calculated total polarizabilities <3%. This represents our most complete and accurate set of polarizabilities.

Results and discussion

Polarizability values

Table 4 lists 270 dynamic polarizabilities for 76 cations in various coordinations representing 66 elements, 5 H_xO_y species [$(H_3O)^+$,$(H_5O_2)^+$, $(H_3O_2)^-$, $(H_4O_4)^{4-}$,$(H_7O_4)^-$], and NH_4^+ derived in this study. No. is a relative measure of the reliability of the polarizability value. For example, $^{[4]}$Al (No. = 227), $^{[6]}$Al (No. = 570), $^{[7]}$Ca (No. = 224), $^{[8]}$Ca (No. = 383), $^{[6]}Fe^{2+}$ (No. = 248), $^{[6]}$Mg (No. = 403), $^{[6]}Mn^{2+}$ (No. = 239), $^{[4]}P^{5+}$ (No. = 421), $^{[4]}$Si(No. = 1004) and $^{[4]}S^{6+}$ (No. = 304), are found more commonly in minerals than most other ions and their derived polarizabilities are therefore more reliable.

Calculation of polarizability and mean refractive index

Eqn (4a) can be used to calculate the total polarizability α_{AE} of a mineral and, vice versa, the refractive index n_D at $\lambda = 589.3$ nm can be calculated from eqn (4b). Alternatively, where the total polarizability α_{AE}(calc) can be calculated from the sum of ion polarizabilities listed in Table 4. The ion polarizabilities in Table 4 in conjunction with accurate chemical analyses and structure determinations, are effective in calculating the total polarizability (Eqn 4a) and the mean refractive index (Eqn 4b). It should be emphasized that to obtain reliable values of α_{AE} and $\langle n_D \rangle$, accurate chemical analyses with sums that add up to stoichiometric mineral compositions are important as is accurate determination of cation coordination numbers. In some cases cation coordination, especially of alkaline and alkaline earth ions is not well-defined. In general, higher coordinations seem to be more satisfactory yielding a better fit between observed and calculated polarizabilities. A further variable is H_2O content of hydrates. Generally, the ideal H_2O content is satisfactory.

Table 6 lists values of total polarizability, α_{AE}(obs) and α_{AE}(calc), and mean refractive index, $\langle n_D \rangle$(obs) and $\langle n_D \rangle$(calc) for 54 common minerals. Generally, discrepancies, Δ, between observed and calculated polarizabilities are $< 3\%$ and between observed and calculated mean refractive indices, $\langle n_D \rangle$, are $< 2\%$. Some common minerals such as calcite, dolomite, anhydrite and gypsum were not included in this list because of steric strain caused by overbonded Ca or Mg. Table A1 [supplementary material[2]] gives a more complete list of > 600 minerals and synthetic compounds with corresponding observed and calculated total polarizabilities, $\Delta < 3\%$, and observed and calculated refractive indices with $\Delta < 2\%$. In Table 6 we have listed values of $\langle n_D \rangle$ (calc) taken from Gladstone-Dale calculations in Webmineral (2015). In many cases, these values are quite accurate but in instances of minerals with variable composition, especially those

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[2] Deposit items are available on the American Mineralogist web site (http://www.minsocam.org or current web address)

containing Fe, there is a wide range of calculated <n_D>: augite (1.71-1.8), andradite (1.73-1.81), diopside (1.67-1.73), enstatite (1.63-1.68), epidote (1.82-1.91), jarosite (1.76-1.87), and magnesiohornblende (1.63-1.74) (Webmineral, 2015). To illustrate the application of ion polarizabilities to calculation of complex mineral total polarizabilities and <n_D>, we show the data for 8 minerals (Krivovichev 2013) in Table 7 where the mean deviation of <n_D>(calc) from <n_D>(obs) is 0.3%.[3]

The values, α_{AE} and <n_D> can be used for minerals when RI's are not known or to compare with experimental <n_D> values. Alternatively, they could also be used in place of Gladstone-Dale Compatibility Indices where the reader takes V_m from mineral data and a calculated value of α_{AE} using ion polarizabilities from Table 4.

Comparison of polarizability analysis with Gladstone-Dale Compatibility Indices

The Gladstone-Dale compatibility index (CI = 1 – (K_p/K_c)) allows a measure of the *internal consistency* of the mean index of refraction, the density and the chemical composition using a set of general oxide parameters to define a specific *chemical* refractivity $K_c = \sum_i \frac{k_i p_i}{100}$ where k_i = Gladstone-Dale constants and p_i = weight percentages. This quantity, K_c, is then compared to an experimental *physical* value defined as K_p = (<n> – 1)/density (Mandarino 1979, 1981). The "compatibility" measures the agreement between the two sides of the equation (n-1)/d = $\Sigma k_i p_i$ where "superior" < 2%; excellent 2% - 4%; good 4% - 6%; fair 6% - 8% and poor >8%. The GD compatibility index has been used often in this regard and to predict the mean refractive

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[3] A manuscript in preparation, „Refractive Indices of Minerals and Synthetic Compounds", (Shannon, Lafuente, Shannon, Downs and Fischer) will describe: composition, mineral name, location, refractive indices, mean refractive index,V_m, V_{anion} and reference CODEN for 2000 minerals and 1000 synthetic compounds.

index, <n_D>, when it has not been possible to measure one or more of the refractive indices. It is a required calculation for approval of new mineral species (Nickel and Grice 1998).

However, Bloss et al. (1983) pointed out that the Gladstone-Dale constants, k_i, are *structure dependent* and that the best values of K_c are derived from values of k_i that are specific for each mineral group as demonstrated in their examples with the silica polymorphs, andalusite, sillimanite, kyanite, kanonaite and plagioclase. They pointed out that, even for the simple SiO_2 composition, different structures with varying degrees of covalency require different k_n values that range from 0.188 for stishovite to 0.207 for quartz to 0.222 for silicalite, thus indicating that the greatest weakness of the CI as a measure of internal consistency of physical and chemical data, is the variability of the Gladstone-Dale constants, k_i.

Using Mandarino's (1981) values of the Gladstone-Dale constants for nesosilicates, the deviations Δ (<n_D>, for andalusite, sillimanite and kyanite, respectively, using the Gladstone-Dale values (Mandarino 1981) of $k(SiO_2) = 0.208$ and $k(Al_2O_3) = 0.176$ are 2.5%, 3.2% and 2.0%. Using a different set of Gladstone-Dale values $k(SiO_2) = 0.285$ and $k(Al_2O_3) = 0.153$ *specific to andalusite, sillimanite and kyanite*, Bloss et al. (1983) found Δ<n_D> are 0.6%, 0.5% and 0.7% respectively. These values compare well to the Δ<n_D> values derived from polarizability analysis in Table A1 (see footnote 2) for andalusite, sillimanite and kyanite of 0.2%, 0.5% and 0.1%, respectively. Using polarizability analysis with $\alpha_e(Si) = 0.283$ Å^3 from Table 4, deviations, Δ (<n_D>), of obs and calc refractive indices for the silica polymorphs, quartz, cristobalite, coesite, keatite, melanophlogite and stishovite (Tables A1 and 6) are not greater than 0.5%.

Polarizability analysis provides similar information on minerals and synthetic compounds but it uses values of empirical ion polarizabilities in conjunction with the chemical composition and crystal structure. Thus, we replace the general oxide parameters, k_i, by specific ion parameters, α_e, evaluated for specific ion coordinations and apply them to known crystal structures with specific compositions. This procedure solves, to a large degree, the mineral group problem noted by Bloss et al. (1983).

Eggleton (1991) revised the Gladstone-Dale constants for H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Al^{3+}, Mn^{3+}, Fe^{3+}, Cr^{3+}, Ti^{3+}, Si^{4+}, and Ti^{4+} using data from 574 silicates [94 garnets, 156 orthosilicates, sorosilicates and cyclosilicates, 54 pyroxenes, 129 amphiboles, 74 layer silicates and 65 framework silicates] to incorporate the dependence upon the cation coordination number. These revised values allowed 533 of these silicates (93%) to fall in the Superior category (Mandarino 1981) with better than 2% agreement. Our results with coordination-dependent polarizabilities are consistent with Eggleton's findings. Eggleton's results with 574 silicates are significantly better than the Mandarino (1981) results on 505 silicates where only 70% fell in the Superior category. With the exceptions of $^{[6]}Mg^{2+}$ and $^{[4]}Si^{4+}$ Eggleton's constants varied significantly from Mandarino's constants but he did not specify what the corresponding agreement for his silicates was using Mandarino's constants. Eggleton also stated that his new GD constants yield agreement between observed and calculated mean refractive indices to within 4% but did not show any of these data. These error limits are, however, significantly greater than indicated for polarizability analysis of the large number of minerals in Table 6 and Table A1 (see footnote 2).

In Table 8 we compare the polarizability analysis results for 68 examples for which we have polarizability data to 68 of the 205 examples tabulated as fair or poor by Mandarino (2006, 2007). Polarizabilities with $\Delta > 3\%$ agree with GD values in 32/68 instances. This is to be expected when there is an error in either the composition, crystal structure or the RI. In the remaining 35 examples, polarizability values are <3%. Many minerals that were deemed to have poor compatibilities showed excellent fits with polarizabilities. The GD poor compatibilities may be the result of different compositions used in the CI calculations. Many minerals have variable compositions and we have no information as to which composition was used in Mandarino's CI calculations. In these instances the disagreement may also result from incorrect GD constants k_n, as indicated by Eggleton's data and as observed by Bloss et al. (1983) for andalusite, kanonaite and plagioclases. Polarizability calculations, in contrast, are generally made on minerals with specific compositions, unit-cell dimensions and cation coordinations.

Deviations from polarizability additivity

In SF2006, systematic deviations from additivity of static polarizabilities were observed in (1) sterically-strained (SS) structures and (2) crystal structures containing corner-shared octahedra (CSO). Similarly, systematic deviations from additivity of dynamic polarizabilities are observed in (SS) and (CSO) structures in this study. However, in addition to these two categories, we also observe systematic deviations in (1) crystal structures containing edge-shared Fe^{3+}, Mn^{3+}, Ti^{4+}, Mo^{6+} and W^{6+} octahedra (ESO) and (2) fast-ion conductors. Examples of the discrepancies in the refinement using polarizability analysis are associated with: (1) sterically-strained (SS) structures; (2) CSO network and chain structures such as perovskite (ABO_3), and tungsten bronze ($SrNb_2O_6$) structures; and (3) alkali-rich oxysalts that are frequently associated with fast-ion conduction. Examples of (1) are $Na_{4.4}Ca_{3.8}Si_6O_{18}$ (combeite) $\Delta = 6\%$, $Ca_3Mg_2Si_2O_8$ (merwinite) $\Delta = 4\%$, and the structural families $MM'AlO_4$ (M = Ca, Sr; M' = Y,La, Nd) $\Delta = \sim 7.5\%$ and $Ca_2MSi_2O_7$, M = Mg, Zn (åkermanite), $Ca_2M_2'SiO_7$, M = Al, Ga (gehlenite). Examples of (2) are $MTiO_3$ (M = Ca, Sr, Ba) $\Delta = 9\text{-}12\%$, $KNbO_3$, $\Delta = 10\%$, $KTaO_3 \Delta = 11\%$ and

$Ba_{.5}Sr_{.5}Nb_2O_6$, Δ = 8%. Examples of (3) are the compounds $Li_2B_4O_7$, Δ = -6%, Li_2CO_3, Δ = -11%, $Li_2Ti_3O_7$ (ramsdellite) Δ = -5%, Li_3PO_4, Δ = -7%, and Na_2SO_4, Δ = -7%. These systematic deviations from additivity will be discussed in more detail in a further publication.

Implications

Careful evaluation of more than 2600 sets of refractive indices of minerals and compounds by regression analyses yielded a unique set of individual electronic polarizabilities of ions. The polarizabilities can be used for the interpretation of optical properties. Specifically the following implications arise from this work:

- Refractive indices of minerals and synthetic crystalline compounds can be predicted within less than 2% deviation from experimentally determined values.
- The contribution of cations in various valence states to the optical properties can be inferred from the set of polarizabilities. Thus, details in the chemical composition of minerals like the distribution of Fe^{2+} and Fe^{3+} can be determined.
- The contribution of cations in various coordinations can be inferred from the set of polarizabilities. Thus, the data set can be used to determine possible coordinations of cations in the crystal structure.
- The contribution of the anions to the optical properties of a compound can be determined from an analysis of the polarizability using an exponential function with two parameters for each anion and the molar volume of the anion per formula unit.
- The polarizability analysis is a more reliable measure of the compatibility (as defined by Mandarino 1979, 1981) of a mineral's refractive index, density, and chemical composition.

- The set of electronic polarizabilities can be used to design new materials with specific optical properties.

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Table 1: Selected symbols of parameters used here. “Total” refers to the polarizability of compounds in contrast to individual polarizabilities of ions.

symbol	unit	explanation
AE		Anderson-Eggleton relationship
α_{AE}	Å^3	dynamic polarizability calculated from eqn. (4)
α_{Dr}	Å^3	dynamic polarizability calculated from eqn. (2)
α_{LL}	Å^3	dynamic polarizability calculated from eqn. (1a)
α_{GD}	Å^3	dynamic polarizability calculated from eqn. (3)
α_e	Å^3	electronic polarizability experimentally determined at any wavelength in the visible region of light
$\alpha(D)_e$	Å^3	total electronic (dynamic) polarizability experimentally determined at 589.3 nm
$\alpha(\infty)_e$	Å^3	total static electronic polarizability; electronic polarizability at $\lambda = \infty$ (seealso footnote on p. 2) calculated from n_∞ using eqn (1a)
α_e(ion)	Å^3	individual electronic polarizability of an ion, not to be confused with “ionic polarizability” outside of the visible region. Empirically determined by least squares fits using the additivity rule corresponding to eqn. (3).
α_T	Å^3	total electronic polarizabiliity obtained by the sum of α_e(ion)
α_{obs}	Å^3	experimentally determined total polarizability from LL or AE equation
α_{calc}	Å^3	total polarizability calculated by the sum of individual polarizabilities of ions
α_{-}	Å^3	anion polarizability
α_{+}	Å^3	cation polarizability
α^{o}	Å^3	free ion polarizability; polarizability of a free ion extracted from the structure, determined by *ab initio* calculations
α_{-}^{o}	Å^3	free “in crystal” anion polarizability
CI		compatibility index (Mandarino 1981)
CN		coordination number
CSO		corner-shared octahedra
Dr		Drude relationship
ESO		edge-shared octahedra
GD		Gladstone-Dale relationship
k		Gladstone-Dale constant (Mandarino 1976)
K_c		chemical refractivity (Mandarino 1979)
K_p		physical refractivity (Mandarino 1979)
LL		Lorenz-Lorentz
n_D		dynamic refractive index determined at $\lambda = 589.3nm$
n_∞		static refractive index; refractive index at $\lambda = \infty$, extrapolated from Sellmeier fit of dispersion data
<n>		mean refractive index; $<n> = (2n_o+n_e)/3$ for uniaxial crystals and $<n>=(n_x+n_y+n_z)3$ for biaxial crystals
r	**Å**	effective ionic radius (Shannon 1976)
R	Å	interatomic distance
SS		sterically strained
V_{an}	Å^3	molar volume of an anion, calculated from V_m divided by the number of anions

		in the formula unit
V_m	$Å^3$	molar volume corresponding to the volume of one formula unit

Table 2**.** *Ab initio* polarizabilities for LiF, BeO and MgO compared to polarizabilities determined from the LL, AE, GD, and Drude relationships.

	α(*ab initio*)	α_{LL}	α_{AE}	α_{GD}	α_{Dr}
	Fowler et al. (1991)	$c = 0$ Eqn (1a)	$c = 2.26$ Eqn (4a)	Fowler et al. (1991) Eqn (3)	$c = 4.189$ Eqn (2)
LiF	0.91 Å^3	0.921 Å^3	1.06 Å^3	1.51 Å^3	1.21 Å^3
BeO	1.26 Å^3	1.305 Å^3	1.66 Å^3	2.38 Å^3	2.16 Å^3
MgO	1.75 Å^3	1.789 Å^3	2.28 Å^3	3.19Å^3	2.99 Å^3

Table 3. Some reasons for not including data in the regression analysis.

	Example	Reference
A. Chemical composition		
poor or no analysis – composition uncertain	taikanite	Armbruster et al. (1993)
	cerchiaraite-Mn	Basso et al. (2000)
total amount of elements far below 100 %	haineaultite	McDonald and Chao(2004)
Rare earth ions not specified	thalenite	Fitzpatrick and Pabst (1986)
Fe^{2+}/Fe^{3+} ratio not known	morimotoite	Henmi et al. (1995)
H_2O content uncertain	hydroandradite	Peters (1965)
Crystal not homogeneous, e.g., zoned	morimotoite	Henmi et al.(1995)
	londonite	Simmons et al. (2001)
OH not found or OH:F variable in hydroxyfluorides		
Chemical analysis not determined on the samecrystal used for the refractive index measurement		
B. Crystal structure		
Structure unknown or incorrect	peprossiite-Ce	Callegari et al. (2000)
	fervanite	Hess and Henderson (1931)
Cation CN's or occupancies incorrect	khibinskite	Chernov et al. (1970)
C. Refractive index		
inaccurate nD	not common	
Not all indices measured	liebenbergite	DeWaal and Calk (1973)
wavelength is not λ(D) = 589 nm	Fe_3BO_6n(λ=630 nm)	Abe et al. (1980)
crystal reacts with immersion fluid	millosevichite	Miura et al. (1994)
nD calculated, not measured	$RbSr_4B_3O_9$	Xia and Li (2013)

Table 4. Dynamic polarizabilities of cations and H_xO_y species. Columns 1-4 show the ion with its coordination, the cube of the effective ionic radius *r* (Shannon 1976) indicating the relative size of the ion, the number noof data used in deriving the polarizability and, finally, the AE dynamic polarizability α(D).

ion	r^3[Å^3] ^{a}	No.^{b}	α(D) (Å^3)
$^{[4]}$Ag^{+}	1.00	2	3.50
$^{[6]}$Ag^{+}	1.52	3	3.00
$^{[7]}$Ag^{+}	1.82	0	2.80
$^{[8]}$Ag^{+}	2.10	0	2.70
$^{[9]}$Ag^{+}		1	2.60
$^{[4]}$Al^{3+}	0.06	227	0.533
$^{[5]}$Al^{3+}	0.11	28	0.500
$^{[6]}$Al^{3+}	0.15	570	0.468
$^{[4]}$As^{5+}	0.04	165	1.630
$^{[6]}$As^{5+}	0.10	1	1.50
$^{[3]}$B^{3+}	0.00	172	0.12
$^{[4]}$B^{3+}	0.00	111	0.03
$^{[6]}$Ba^{2+}	2.46	10	3.680
$^{[7]}$Ba^{2+}	2.63	11	3.550
$^{[8]}$Ba^{2+}	2.86	28	3.410
$^{[9]}$Ba^{2+}	3.18	27	3.300
$^{[10]}$Ba^{2+}	3.51	32	3.190
$^{[11]}$Ba^{2+}	3.87	13	3.090
$^{[12]}$Ba^{2+}	4.17	33	3.000
$^{[3]}$Be^{2+}	0.00	0	0.25
$^{[4]}$Be^{2+}	0.02	99	0.164
$^{[3]}$C^{4+}		115	0.001
$^{[5]}$Ca^{2+}		1	1.910
$^{[6]}$Ca^{2+}	1.00	180	1.790
$^{[7]}$Ca^{2+}	1.19	224	1.670
$^{[8]}$Ca^{2+}	1.40	383	1.570
$^{[9]}$Ca^{2+}	1.64	111	1.480
$^{[10]}$Ca^{2+}	1.86	33	1.390
$^{[11]}$Ca^{2+}		1	1.320
$^{[12]}$Ca^{2+}	2.41	10	1.250
$^{[6]}$Cd^{2+}	0.86	24	2.700
$^{[7]}$Cd^{2+}	1.09	1	2.50
$^{[6]}$Ce^{3+}	1.03	2	4.400
$^{[7]}$Ce^{3+}	1.23	3	4.220
$^{[8]}$Ce^{3+}	1.49	10	4.070
$^{[9]}$Ce^{3+}	1.71	34	3.920
$^{[10]}$Ce^{3+}	1.95	22	3.780
$^{[11]}$Ce^{3+}			3.650
$^{[12]}$Ce^{3+}	2.41	9	3.550
$^{[6]}$Ce^{4+}	0.66	2	7.80
$^{[8]}$Ce^{4+}	0.91	3	7.20
$^{[9]}$Ce^{4+}	1.06	1	6.90
$^{[12]}$Ce^{4+}	1.48		6.00
$^{[4]}$Cl^{7+}	0.00	14	0.007
$^{[4]}$Co^{2+}		2	1.9

$^{[6]}\mathrm{Co}^{2+}$	0.27	24	1.710
$^{[6]}\mathrm{Cr}^{3+}$	0.23	27	3.020
$^{[4]}\mathrm{Cr}^{6+}$	0.02	7	5.400
$^{[6]}\mathrm{Cs}^{+}$	4.66	3	3.800
$^{[7]}\mathrm{Cs}^{+}$		1	3.650
$^{[8]}\mathrm{Cs}^{+}$	5.27	5	3.500
$^{[9]}\mathrm{Cs}^{+}$	5.64	8	3.350
$^{[10]}\mathrm{Cs}^{+}$	5.93	6	3.200
$^{[11]}\mathrm{Cs}^{+}$	6.33	11	3.000
$^{[12]}\mathrm{Cs}^{+}$	6.64	30	2.900
$^{[2]}\mathrm{Cu}^{+}$	0.10	1	4.42
$^{[4SQ]}\mathrm{Cu}^{2+\ c}$	0.19	16	2.300
$^{[5]}\mathrm{Cu}^{2+}$	0.27	24	2.260
$^{[6]}\mathrm{Cu}^{2+}$	0.39	125	2.230
$^{[6]}\mathrm{Dy}^{3+}$	0.76	2	3.500
$^{[7]}\mathrm{Dy}^{3+}$	0.91	2	3.350
$^{[8]}\mathrm{Dy}^{3+}$	1.08	3	3.220
$^{[9]}\mathrm{Dy}^{3+}$	1.27	1	3.100
$^{[10]}\mathrm{Dy}^{3+}$			2.980
$^{[12]}\mathrm{Dy}^{3+}$		2	2.770
$^{[6]}\mathrm{Er}^{3+}$	0.71	6	3.280
$^{[7]}\mathrm{Er}^{3+}$	0.84	1	3.130
$^{[8]}\mathrm{Er}^{3+}$	1.01	6	2.990
$^{[9]}\mathrm{Er}^{3+}$	1.20	1	2.860
$^{[10]}\mathrm{Er}^{3+}$			2.750
$^{[12]}\mathrm{Er}^{3+}$		2	2.550
$^{[8]}\mathrm{Eu}^{2+}$	1.95	1	3.95
$^{[9]}\mathrm{Eu}^{2+}$	2.20	1	3.80
$^{[6]}\mathrm{Eu}^{3+}$	0.85	2	3.880
$^{[7]}\mathrm{Eu}^{3+}$	1.03		3.750
$^{[8]}\mathrm{Eu}^{3+}$	1.21	1	3.600
$^{[9]}\mathrm{Eu}^{3+}$	1.40		3.470
$^{[10]}\mathrm{Eu}^{3+}$			3.330
$^{[12]}\mathrm{Eu}^{3+}$		2	3.070
$^{[4P}\mathrm{Fe}^{2+}$	0.26	2	2.70
$^{[4SQ]}\mathrm{Fe}^{2+\ c}$	0.25	7	2.30
$^{[5]}\mathrm{Fe}^{2+}$		10	2.110
$^{[6]}\mathrm{Fe}^{2+}$	0.47	248	2.040
$^{[7]}\mathrm{Fe}^{2+}$		4	2.000
$^{[8]}\mathrm{Fe}^{2+}$	0.78	50	1.970
$^{[4]}\mathrm{Fe}^{3+}$	0.12	8	3.950
$^{[5]}\mathrm{Fe}^{3+}$	0.20	3	3.900
$^{[6]}\mathrm{Fe}^{3+}$	0.27	234	3.850
$^{[4]}\mathrm{Ga}^{3+}$	0.10	44	1.750
$^{[6]}\mathrm{Ga}^{3+}$	0.24	34	1.500
$^{[6]}\mathrm{Gd}^{3+}$	0.83	9	3.770
$^{[7]}\mathrm{Gd}^{3+}$	1.00	2	3.620
$^{[8]}\mathrm{Gd}^{3+}$	1.17	22	3.500
$^{[9]}\mathrm{Gd}^{3+}$	1.36	2	3.390
$^{[10]}\mathrm{Gd}^{3+}$		1	3.270
$^{[12]}\mathrm{Gd}^{3+}$		4	3.10
$^{[4]}\mathrm{Ge}^{4+}$	0.06	22	1.65
$^{[5]}\mathrm{Ge}^{4+}$	0.06		1.62
$^{[6]}\mathrm{Ge}^{4+}$	0.15	12	1.580

H_3O^+		4	1.45
$H_3O_2^{-1}$		2	2.67
$H_4O_4^{-4}$		14	6.40
$H_5O_2^+$		2	3.10
$H_7O_4^{-1}$		1	9.50
$^{[6]}Hf^{4+}$	0.36	6	3.400
$^{[7]}Hf^{4+}$	0.44	2	3.250
$^{[8]}Hf^{4+}$	0.57	2	3.100
$^{[6]}Hg^{+}$	1.68	1	7
$^{[6]}Hg^{2+}$	1.06	3	6
$^{[6]}Ho^{3+}$	0.73	1	3.380
$^{[7]}Ho^{3+}$		2	3.240
$^{[8]}Ho^{3+}$	1.05	2	3.120
$^{[9]}Ho^{3+}$	1.23	1	2.980
$^{[12]}Ho^{3+}$		2	2.640
$^{[4]}I^{7+}$	0.07	3	3.10
$^{[6]}I^{7+}$	0.15	1	3.00
$^{[6]}In^{3+}$	0.51	5	2.52
$^{[4]}K^{+}$	2.57	1	1.600
$^{[5]}K^{+}$		2	1.550
$^{[6]}K^{+}$	2.63	28	1.500
$^{[7]}K^{+}$	3.11	19	1.450
$^{[8]}K^{+}$	3.44	67	1.400
$^{[9]}K^{+}$	3.72	52	1.350
$^{[10]}K^{+}$	4.02	42	1.300
$^{[11]}K^{+}$		3	1.250
$^{[12]}K^{+}$	4.41	70	1.200
$^{[6]}La^{3+}$	1.10	6	4.450
$^{[7]}La^{3+}$	1.33	9	4.320
$^{[8]}La^{3+}$	1.56	28	4.180
$^{[9]}La^{3+}$	1.80	30	4.050
$^{[10]}La^{3+}$	2.05	26	3.900
$^{[11]}La^{3+}$		2	3.770
$^{[12]}La^{3+}$	2.52	8	3.650
$^{[4]}Li^{+}$	0.21	40	0.44
$^{[5]}Li^{+}$		5	0.33
$^{[6]}Li^{+}$	0.44	69	0.24
$^{[8]}Li^{+}$	0.78	5	0.15
$^{[6]}Lu^{3+}$	0.64	9	2.940
$^{[7]}Lu^{3+}$			2.790
$^{[8]}Lu^{3+}$	0.93	7	2.650
$^{[9]}Lu^{3+}$	1.10		2.530
$^{[12]}Lu^{3+}$		1	2.25
$^{[4]}Mg^{2+}$	0.19	47	0.835
$^{[5]}Mg^{2+}$	0.29	3	0.710
$^{[6]}Mg^{2+}$	0.37	403	0.651
$^{[7]}Mg^{2+}$		3	0.615
$^{[8]}Mg^{2+}$	0.71	34	0.600
$^{[4]}Mn^{2+}$	0.29	2	2.350
$^{[5]}Mn^{2+}$	0.42	7	2.200
$^{[6]}Mn^{2+}$	0.57	239	2.074
$^{[7]}Mn^{2+}$	0.73	13	2.000
$^{[8]}Mn^{2+}$	0.88	33	1.950
$^{[4]}Mn^{3+}$			4.05

$^{[5]}\mathrm{Mn}^{3+}$	0.20	1	3.94
$^{[6]}\mathrm{Mn}^{3+}$	0.27	32	3.830
$^{[4]}\mathrm{Mo}^{6+}$	0.07	17	4.560
$^{[6]}\mathrm{Mo}^{6+}$	0.21		3.70
$^{[3]}\mathrm{N}^{5+}$		23	0.001
$^{[4]}\mathrm{Na}^{+}$	0.97	17	0.760
$^{[5]}\mathrm{Na}^{+}$	1.00	27	0.650
$^{[6]}\mathrm{Na}^{+}$	1.06	207	0.560
$^{[7]}\mathrm{Na}^{+}$	1.40	97	0.490
$^{[8]}\mathrm{Na}^{+}$	1.64	197	0.430
$^{[9]}\mathrm{Na}^{+}$	1.91	49	0.380
$^{[10]}\mathrm{Na}^{+}$		25	0.340
$^{[11]}\mathrm{Na}^{+}$		5	0.300
$^{[12]}\mathrm{Na}^{+}$	2.69	9	0.270
$^{[6]}\mathrm{Nb}^{5+}$	0.26	42	5.78
$^{[6]}\mathrm{Nd}^{3+}$	0.95	2	4.20
$^{[7]}\mathrm{Nd}^{3+}$		4	4.05
$^{[8]}\mathrm{Nd}^{3+}$	1.36	11	3.900
$^{[9]}\mathrm{Nd}^{3+}$	1.57	12	3.750
$^{[10]}\mathrm{Nd}^{3+}$		6	3.600
$^{[11]}\mathrm{Nd}^{3+}$		1	3.45
$^{[12]}\mathrm{Nd}^{3+}$	2.05	2	3.35
$^{[6]}\mathrm{NH_4}^{+}$		4	2.29
$^{[7]}\mathrm{NH_4}^{+}$		2	2.23
$^{[8]}\mathrm{NH_4}^{+}$		30	2.18
$^{[9]}\mathrm{NH_4}^{+}$		4	2.13
$^{[10]}\mathrm{NH_4}^{+}$		9	2.08
$^{[11]}\mathrm{NH_4}^{+}$			2.03
$^{[12]}\mathrm{NH_4}^{+}$		7	1.98
$^{[6]}\mathrm{Ni}^{2+}$	0.33	31	1.710
$^{[4]}\mathrm{P}^{5+}$	0.00	421	0.036
$^{[6]}\mathrm{Pr}^{3+}$	0.97		4.24
$^{[7]}\mathrm{Pr}^{3+}$		1	4.09
$^{[8]}\mathrm{Pr}^{3+}$	1.43	1	3.97
$^{[9]}\mathrm{Pr}^{3+}$	1.64	1	3.82
$^{[10]}\mathrm{Pr}^{3+}$			3.68
$^{[11]}\mathrm{Pr}^{3+}$		1	3.56
$^{[12]}\mathrm{Pr}^{3+}$		1	3.42
$^{[8]}\mathrm{Pu}^{4+}$	0.88	2	4.60
$^{[9]}\mathrm{Pu}^{4+}$		2	4.00
$^{[6]}\mathrm{Rb}^{+}$	3.51		2.370
$^{[7]}\mathrm{Rb}^{+}$	3.80	2	2.200
$^{[8]}\mathrm{Rb}^{+}$	4.17	19	2.020
$^{[9]}\mathrm{Rb}^{+}$	4.33	14	1.870
$^{[10]}\mathrm{Rb}^{+}$	4.57	8	1.700
$^{[12]}\mathrm{Rb}^{+}$	5.09	7	1.400
$^{[4]}\mathrm{Re}^{7+}$	0.05	3	3.20
$^{[6]}\mathrm{Rh}^{3+}$	0.29	2	4.02
$^{[4]}\mathrm{S}^{6+}$	0.00	304	0.011
$^{[6]}\mathrm{Sb}^{5+}$	0.22	24	3.100
$^{[6]}\mathrm{Sc}^{3+}$	0.41	25	2.32
$^{[7]}\mathrm{Sc}^{3+}$		2	2.23
$^{[8]}\mathrm{Sc}^{3+}$	0.66	1	2.15
$^{[4]}\mathrm{Se}^{6+}$	0.02	20	1.510

$^{[4]}\mathrm{Si}^{4+}$	0.02	1004	0.284
$^{[6]}\mathrm{Si}^{4+}$	0.06	10	0.20
$^{[6]}\mathrm{Sm}^{3+}$	0.88		3.950
$^{[7]}\mathrm{Sm}^{3+}$	1.06	1	3.850
$^{[8]}\mathrm{Sm}^{3+}$	1.26	4	3.710
$^{[9]}\mathrm{Sm}^{3+}$	1.45	1	3.600
$^{[10]}\mathrm{Sm}^{3+}$		2	3.480
$^{[12]}\mathrm{Sm}^{3+}$	1.91	3	3.250
$^{[6]}\mathrm{Sn}^{4+}$	0.33	33	2.910
$^{[6]}\mathrm{Sr}^{2+}$	1.64	4	2.640
$^{[7]}\mathrm{Sr}^{2+}$	1.77	19	2.420
$^{[8]}\mathrm{Sr}^{2+}$	2.00	26	2.210
$^{[9]}\mathrm{Sr}^{2+}$	2.25	23	2.040
$^{[10]}\mathrm{Sr}^{2+}$	2.52	24	1.900
$^{[11]}\mathrm{Sr}^{2+}$		5	1.760
$^{[12]}\mathrm{Sr}^{2+}$	2.99	14	1.650
$^{[6]}\mathrm{Ta}^{5+}$	0.26	17	5.20
$^{[6]}\mathrm{Tb}^{3+}$	0.79	1	3.610
$^{[7]}\mathrm{Tb}^{3+}$	0.94		3.460
$^{[8]}\mathrm{Tb}^{3+}$	1.12	4	3.350
$^{[9]}\mathrm{Tb}^{3+}$	1.31		3.230
$^{[12]}\mathrm{Tb}^{3+}$		2	2.860
$^{[6]}\mathrm{Te}^{6+}$	0.18	2	4.43
$^{[6]}\mathrm{Th}^{4+}$	0.83	1	4.70
$^{[8]}\mathrm{Th}^{4+}$	1.16	13	4.44
$^{[9]}\mathrm{Th}^{4+}$	1.30	9	4.35
$^{[10]}\mathrm{Th}^{4+}$	1.44	1	4.29
$^{[12]}\mathrm{Th}^{4+}$	1.77	2	4.20
$^{[6]}\mathrm{Ti}^{3+}$	0.30	2	3.60
$^{[5]}\mathrm{Ti}^{4+}$	0.13	11	4.350
$^{[6]}\mathrm{Ti}^{4+}$	0.22	118	5.010
$^{[6]}\mathrm{Tm}^{3+}$	0.68	3	3.130
$^{[7]}\mathrm{Tm}^{3+}$			3.000
$^{[8]}\mathrm{Tm}^{3+}$	0.98	2	2.870
$^{[9]}\mathrm{Tm}^{3+}$	1.16		2.770
$^{[10]}\mathrm{Tm}^{3+}$			2.650
$^{[12]}\mathrm{Tm}^{3+}$		2	2.460
$^{[8]}\mathrm{U}^{4+}$	1.00	8	5.00
$^{[6]}\mathrm{V}^{3+}$	0.26	22	2.960
$^{[5]}\mathrm{V}^{4+}$	0.15	4	2.700
$^{[6]}\mathrm{V}^{4+}$	0.20	11	2.600
$^{[4]}\mathrm{V}^{5+}$	0.04	31	4.450
$^{[5]}\mathrm{V}^{5+}$	0.10	1	4.00
$^{[6]}\mathrm{V}^{5+}$	0.16	8	3.40
$^{[4]}\mathrm{W}^{6+}$	0.07	14	3.960
$^{[6]}\mathrm{W}^{6+}$	0.22	3	3.500
$^{[6]}\mathrm{Y}^{3+}$	0.73	17	2.820
$^{[7]}\mathrm{Y}^{3+}$	0.88	7	2.780
$^{[8]}\mathrm{Y}^{3+}$	1.06	41	2.740
$^{[9]}\mathrm{Y}^{3+}$	1.24	7	2.700
$^{[10]}\mathrm{Y}^{3+}$		1	2.650
$^{[6]}\mathrm{Yb}^{3+}$	0.65	6	3.000
$^{[7]}\mathrm{Yb}^{3+}$	0.79	2	2.860
$^{[8]}\mathrm{Yb}^{3+}$	0.96	4	2.730

$^{[9]}Yb^{3+}$	1.13	1	2.630
$^{[12]}Yb^{3+}$		2	2.360
$^{[4]}Zn^{2+}$	0.22	58	1.720
$^{[5]}Zn^{2+}$	0.31	17	1.710
$^{[6]}Zn^{2+}$	0.41	81	1.700
$^{[6]}Zr^{4+}$	0.37	61	4.220
$^{[7]}Zr^{4+}$	0.47	4	3.960
$^{[8]}Zr^{4+}$	0.59	12	3.740
$^{[9]}Zr^{4+}$	0.70	4	3.560

[a] empty fields are not listed in Shannon (1976)

[b] number of ions > 0.3 a.p.f.u in minerals and compounds

[c] 4SQ indicates a square planar cooradination

Table 5. Dynamic polarizabilities of anions and H_2O. The values in columns α_-^o and N_o refer to eqn (6).

ion	α_-^o	N_o
Cl^-	3.88	1.800
F^-	0.82	3.000
H_2O	1.62	0.000
O^{2-}	1.79	1.776
O^{2-} in sulfates	1.76	1.780
O^{2-} in perchlorates	1.63	1.900
O^{2-} in nitrates	1.73	1.700
O^{2-} in carbonates	1.72	1.730
O^{2-} in borates	1.75	1.580
OH^-	1.79	1.792
OH^- H-bonded	1.73	2.042

Table 6. Polarizabilities and mean refractive indices of 52 minerals and compounds. Numbers in brackets refer to the number of minerals in the respective group.

Mineral / Compound	Composition	Origin	α_{obs} (Å^3)	α_{calc} (Å^3)	$\Delta\alpha$	$<n_D>$ calc^a	$<n_D>$ obs	$<n_D>$ calc	Δn
SILICA POLYMORPHS [6]									
melanophlogite	SiO_2	Racalmuto, Sicily	3.551	3.57	-0.5%	1.45	1.425	1.427	-0.2%
cristobalite	SiO_2	alpha-cristobablite	3.460	3.51	-1.5%	1.48	1.485	1.492	-0.5%
keatite	SiO_2	synthetic	3.468	3.48	-0.4%		1.519	1.521	-0.1%
quartz	SiO_2	synthetic Bell Labs	3.441	3.46	-0.5%	1.55	1.547	1.550	-0.1%
coesite	SiO_2	synthetic	3.401	3.41	-0.2%		1.596	1.598	-0.1%
stishovite	SiO_2	synthetic	3.114	3.09	0.9%	1.89	1.808	1.801	0.5%
OXIDES [3]									
periclase	MgO	synthetic	2.284	2.24	2.1%	1.75	1.735	1.719	0.9%
corundum	Al_2O_3	synthetic	5.393	5.47	-1.4%	1.84	1.765	1.778	-0.7%
ice 1h			1.647	1.62	1.6%	1.31	1.305	1.300	0.4%
HYDROXIDES [3]									
gibbsite	$Al(OH)_3$	Chester, Massachusetts	5.088	5.09	0.5%	1.60	1.574	1.575	0.0%
boehmite	AlOOH	Ratnapura, Ceylon	3.544	3.48	1.8%		1.658	1.646	0.7%
diaspore	$Al_{0.99}Fe_{0.01}OOH$	Turkey	3.562	3.54	0.5%	1.77	1.725	1.722	0.2%
BORATES [4]									
kernite	$Na_2B_4O_7$ $4H_2O$	Kern Cnty, California	18.743	19.04	-1.6%	1.47	1.471	1.479	-0.5%
borax	$Na_2B_4O_5(OH)_{4.8}H_2O$		28.635	28.84	-0.7%	1.46	1.463	1.466	-0.2%
colemanite	$CaB_3O_4(OH)_{3.}H_2O$	Death Valley, California	13.970	14.30	-2.3%	1.58	1.597	1.611	-0.8%
ulexite	$CaNaB_5O_6(OH)_6$ $5H_2O$	Boron, California	29.018	29.21	-0.7%	1.50	1.505	1.508	-0.2%
CARBONATES [2]									

thaumasite	$Ca_3Si(SO_4)(CO_3)(OH)_6\ 12H_2O$	Tschwinning mine, So. Africa	44.084	44.62	-1.2%	1.49	1.485	1.490	-0.4%
malachite	$Cu_2[CO_3](OH)_2$	Copper Queen Mine, AZ	12.229	12.18	0.4%	1.74	1.813	1.809	0.2%
SILICATES [32]									
spodumene	$Li_{0.95}Na_{0.05}AlSi_2O_6$	Maharitra, Madagascar	10.822	10.59	2.1%	1.68	1.667	1.653	0.9%
nepheline	$Na_{0.69}K_{0.16}Ca_{0.06}Al_{0.98}Si_{1.02}O_4$	Monte Somma, Mt. Vesuvius, xtal #2	8.141	7.93	2.6%	1.53	1.537	1.524	0.9%
albite	$Na_{0.97}K_{0.02}Ca_{0.01}Al_{0.97}Fe_{0.01}Mg_{0.02}Si_3O_8$	Rischuna Alp, Switzerland	14.804	14.80	0.1%	1.54	1.534	1.533	0.0%
labradorite	$Na_{0.312}K_{0.01}Ca_{0.657}Fe_{0.01}Fe^{3+}_{0.01}Al_{1.657}Si_{2.335}O_8$	Lake County, Oregon	15.850	15.78	0.5%	1.57	1.567	1.564	0.2%
aegirine	$Na_{0.959}K_{0.011}Ca_{0.013}Fe^{3+}_{0.955}Fe_{0.021}Ti_{0.018}Al_{0.006}Si_{1.997}O_6$	Gout Creek, So. Westland, New Zealand	14.087	14.27	-1.3%	1.86	1.792	1.802	-0.6%
aegirine-augite	$Na_{0.77}Ca_{0.14}K_{0.02}Fe^{3+}_{0.52}Fe_{0.24}Al_{0.08}Ti_{0.08}Mn_{0.03}Mg_{0.02}$ $Nb_{0.02}Si_{1.95}Al_{0.03}Be_{0.02}O_{5.85}(OH)_{0.09}F_{0.06}$	Seal Lake, Labrador	13.834	13.72	0.8%		1.764	1.758	0.4%
elbaite	$Na_{0.74}Ca_{0.01}\ Al_{8.11}Li_{1.05}Fe_{0.01}Mn_{0.01}(BO_3)_3\ Si_{5.94}O_{18}$ $(OH)_{3.63}\ O_{0.32}\ F_{0.05}$	San Diego, California	54.481	54.47	-0.0%	1.65	1.635	1.635	0.0%
dravite	$Na_{0.73}K_{0.12}Ca_{0.07}Mg_{2.70}Al_{6.35}Mn_{0.08}Fe_{0.04}Ti_{0.02}(BO_3)_3$ $Si_{5.88}\ O_{18}\ (OH)_{3.70}\ O_{0.20}\ F_{0.10}$	Dobrowa,Slovenia	55.354	55.87	-0.9%	1.65	1.628	1.634	-0.4%
cordierite	$Na_{0.04}Mg_{1.72}Fe_{0.27}Al_{3.97}Fe^{3+}_{0.03}Si_5O_{18.}(H_2O)_{0.49}$ $(CO_2)_{0.07}$	Madagascar	35.048	35.44	-1.1%	1.54	1.540	1.546	-0.4%
marialite	$Na_{2.664}K_{0.243}Ca_{0.870}Fe_{0.028}Ti_{0.005}Al_{3.767}Si_{8.232}C_{0.016}O_{24.5}$ $Cl_{0.843}$	Los Molles, Argentina	50.403	50.80	-0.8%	1.54	1.547	1.552	-0.3%
meionite	$Na_{0.195}Ca_{3.666}K_{0.094}Mg_{0.018}Sr_{0.01}Fe_{0.02}Al_{5.73}Si_{6.27}O_{24}$ $(CO_3)_{0.93}(SO_4)_{0.026}Cl_{0.027}$	Monte Somma, Mt. Vesuvius	55.061	54.52	1.0%	1.56	1.586	1.580	0.4%
orthoclase	$K_{0.92}Na_{0.08}Al_{0.97}Fe_{0.03}Si_3O_8$	Madagascar	15.708	15.74	-0.2%	1.52	1.522	1.524	-0.1%
microcline	$K_{0.82}Na_{0.18}Al_{1.02}Si_{2.98}O_8$	Bedford, New York	15.651	15.72	0.4%	1.53	1.522	1.524	0.1%
sanidine	$K_{0.90}Na_{0.07}Ca_{0.03}Al_{0.84}Fe_{0.13}Mg_{0.03}Si_3O_8$	Wasatch Mt., Utah	16.099	16.12	-0.2%	1.52	1.530	1.531	0.0%
muscovite 2M	$K_{1.856}Na_{0.29}Ca_{0.015}Mg_{0.142}Fe_{0.261}Cr_{0.226}Ti_{0.172}Al_{3.113}$ $Al_{1.967}Si_{6.033}O_{20}(OH)_4$	Acworth Township, New Hampshire	45.169	45.13	0.1%	1.59	1.584	1.583	0.0%
enstatite	$Mg_{1.962}Ca_{0.036}Na_{0.001}Fe_{0.007}Al_{0.013}Si_{1.987}\ O_6$	Hvittis meteorite	11.432	11.33	0.9%	1.65	1.657	1.651	0.4%
pyrope	$Mg_{1.95}Fe_{0.99}Ca_{0.09}Mn_{0.01}Al_{1.98}Si_3O_{12}$	Madagascar	23.730	23.57	0.7%	1.76	1.752	1.747	0.3%
forsterite	$Mg_{1.80}Fe_{0.225}Ni_{0.01}SiO_4$	San Carlos, AZ	8.219	8.24	-0.2%	1.67	1.675	1.677	-0.1%

magnesio-hornblende	$Mg_{2.91}Na_{0.30}K_{0.10}Ca_{1.90}Fe_{1.29}Mn_{0.08}Al_{0.14}Ti_{0.10}Fe^{3+}_{0.49}Si_{7.03}Al_{0.97}O_{22}(OH)_{1.85}F_{0.08}Cl_{0.01}$	Mt.Givens granodiorite Sierra Nevada batholith	50.666	50.92	-0.5%		1.661	1.664	-0.2%
phlogopite	$Mg_3K_{0.77}Na_{0.16}Ba_{0.05}Al_{1.05}Si_{2.95}O_{10}(OH)_{0.70}F_{1.30}$	Franklin, New Jersey	22.340	22.50	-0.7%	1.57	1.549	1.553	-0.3%
lizardite	$Mg_{2.884}Al_{0.036}(Fe_3+)_{0.042}Si_{1.916}O_5(OH)_{4.124}$	New Idria, San Benito County, California	16.975	16.94	0.2%	1.58	1.564	1.563	0.1%
antigorite	$Mg_{2.806}Fe_{0.02}Fe^{3+}_{0.03}Si_{1.95}Al_{0.05}O_5(OH)_{3.68}$	Cross River, Kokonui, New Zealand	16.141	16.20	-0.4%	1.56	1.562	1.564	-0.1%
anorthite	$CaAl_2Si_2O_8$	Vesuvius	16.262	16.21	0.3%	1.57	1.581	1.580	0.1%
tremolite	$Ca_{1.79}Na_{0.04}K_{0.07}Na_{0.11}Mg_5Si_8O_{22}(OH)_2$	Gouverneur, N.Y.	46.448	46.63	-0.4%	1.64	1.614	1.616	-0.1%
diopside	$CaMg_{0.92}Fe_{0.08}Si_2O_6$	Ala Valley,Italy	12.499	12.38	1.4%		1.683	1.676	0.4%
grossular	$Ca_{2.92}Mn_{0.04}Fe_{0.135}Al_2Si_3O_{12}$	Asbestos, Quebec	25.525	25.52	0.0%	1.74	1.738	1.738	0.0%
andradite	$Ca_{3.00}Fe_{1.99}Mg_{0.02}Al_{0.01}Si_{2.98}O_{12}$	Val Malenco, Italy	32.071	32.19	-0.4%		1.886	1.890	-0.2%
epidote	$Ca_{1.90}Mg_{0.04}Fe_{0.06}Al_{2.4}Fe_{0.6}Si_3O_{12}OH$	Pfarreb, Zoptau	27.957	27.55	1.4%		1.738	1.727	0.6%
staurolite	$Fe_{1.48}Mg_{0.44}Mn_{0.01}Al_{8.78}Zn_{.01}Ti_{0.06}Si_{3.878}O_{22}(OH)_2$	Galax, Virgina	45.659	45.89	-0.5%	1.76	1.742	1.746	-0.2%
almandine	$Fe_{2.207}Ca_{0.441}Mn_{0.200}Mg_{0.139}Al_{1.814}Fe^{3+}_{0.113}Ti_{0.071}Al T_{0.106}Si_{2.894}O_{12}$	Pizzo Robone, Ali area, Peloritani Mtns,Sicily	26.419	26.62	-0.7%	1.83	1.821	1.827	-0.4%
zircon	$ZrSiO_4$	Chantaboon, Thailand	10.234	10.24	0.0%		1.945	1.946	0.0%
kaolinite	$Al_{42.005}Si_{1.97}Fe_{0.01}Fe^{3+}_{0.02}Mg_{0.01}Ca_{0.02}O_5(OH)_4$	Mikawo mine, Niigata, Japan	15.570	15.79	-1.4%	1.59	1.565	1.573	-0.5%
PHOSPHATES [2]									
vivianite	$Fe_2P_2O_8\ 8H_2O$	Catavi, Llallagua, Bolivia	31.209	31.89	-2.3%	1.61	1.603	1.617	-0.8%
fluorapatite	$Ca_{10}P_6O_{24}F_{1.96}Cl_{0.02}(OH)_{0.02}$	Kiglapait intrusion Labrador	55.454	56.02	1.0%	1.62	1.634	1.641	-0.4%
SULFATES [2]									
alunite	$KAl_3(SO_4)_2(OH)_6$		23.673	23.84	-0.7%		1.579	1.583	-0.3%
jarosite	$KFe^{3+}_3(SO_4)_2(OH)_6$	Cyprus	35.011	34.27	2.1%		1.793	1.776	1.0%

[a] mean refractive index <nD> taken from Webmineral (2015)

Table 7. Selected minerals (Krivovichev 2013) with a complex chemical composition.

Mineral / Compound	Composition	Origin	α_{obs} (Å^3)	α_{calc} (Å^3)	Δα	<n$_D$> obs	<n$_D$> calc	Δn	ref.
rogermitchellite	$Na_{12}Sr_{21.16}Na_{1.17}Ca_{0.21}Ba_4Zr_{25.33}Ti_{0.93}Si_{77.02}B_{0.98}B_{12}O_{246}(OH)_{24} \cdot 18H_2O$	Mt. St. Hilaire, Quebec,Canada	655.788	661.51	-0.9%	1.648	1.653	-0.3%	McDonald et al. 2010
bannisterite	$K_{0.4}Na_{0.1}Ca_{0.4}Mn_{6.2}Fe_{1.4}Mg_{1.4}ZnFe^{3+}_{0.2}Si_{14.4}Al_{1.4}O_{38}(OH)_8 \cdot 6H_2O$	Franklin, NJ	107.148	107.82	-0.6%	1.573	1.576	-0.2%	Smith et al. 1968
giuseppettite	$Na_{5.3}K_2Ca_{0.67}Al_6Si_6O_{24}(SO_4)_{1.25}Cl_{0.25} \cdot 0.625 H_2O$	Sacrofano, Italy	62.518	61.28	2.0%	1.496	1.487	0.6%	Mazzi et al. 1981;Bonaccorsi, 2004
sobolevite	$Na_{13.62}Ca_{1.63}Sr_{0.03}Mg_{0.39}Mn_{1.02}Fe_{0.1}Ti_{2.42}Nb_{0.51}Zr_{0.09}Si_4P_4O_{33.08}F_{2.92}$	Khibina-Lovozero complex, Kola Peninsula, Russia	86.419	86.06	0.4%	1.668	1.665	0.2%	Sokolova et al. 2005
polyphite	$Na_{8.72}Ca_{1.4}Sr_{0.03}Mg_{0.3}Mn_{0.68}Fe_{0.07}Ti_{1.41}Nb_{0.19}Zr_{0.19}P_{2.96}Si_{2.04}O_{20.94}F_{2.06}$	Khibina-Lovozero complex, Kola Peninsula, Russia	53.626	54.47	-1.6%	1.643	1.653	-0.6%	Sokolova et al. 2005
quadruphite	$Na_{13.59}Ca_{1.44}Sr_{0.06}Mg_{0.5}Mn_{0.85}Fe_{0.10}Ti_{2.55}Nb_{0.44}Zr_{0.47}Si_4P_4O_{33.89}F_{2.11}$	Khibina-Lovozero complex, Kola Peninsula, Russia	86.742	87.35	-0.7%	1.668	1.668?	?0.0%	Sokolova et al. 2001
nechelelyustovite	$Na_{4.2}Ca_{0.5}Ba_{1.3}Sr_{0.5}K_{0.3}Mn_{1.4}Ti_{4.1}Nb_{1.4}Fe^{3+}_{0.1}Si_8 0_{28}(OH)_{2.9}F_{1.1} \cdot 6H_2O$	Lovozero alkaline massif, Kola peninsula, Russia	108.952	108.79	0.1%	1.715	1.714	0.0%	Németh et al. 2009
apjohnite	$Mn_{0.64}Mg_{0.28}Zn_{0.06}Fe_{0.02}Al_2(SO_4)_4 \cdot 22H_2O$	Terlano, Bolzano, Italy	63.315	63.48	-0.3%	1.481	1.482	-0.1%	Menchetti and Sabelli 1976

Table 8. Comparison of polarizability analyses for 68 out of 205 examples where the compatibility index (CI) is listed as fair or poor by Mandarino (2006, 2007). Numbers in brackets refer to the number of minerals in the respective group.

Mineral	Composition	CI from Webmineral 2015	CI from Manda-rino 1981	α_{AE} (obs)	α_{AE} (calc)	$\Delta\alpha$
CARBONATES [5]						
tuliokite	$Na_6BaTh_{0.95}Fe^{3+}_{0.05}(CO_3)_6 \cdot 8H_2O$	CI calc= 0.09 (Poor)	fair	48.194	47.36	1.7%
mguinnessite	$Mg_{1.06}Cu_{0.94}(CO_3)(OH)_2$	CI calc= -0.146 (Poor)	poor	10.249	10.28	-0.3%
comblainite	$Ni_{6.1}Co_{2.9}(CO_3)(OH)_{18} \cdot 4H_2O$	CI calc= 0.068 (Fair)	fair	55.679	55.76	-0.2%
nullaginite	$Ni_{1.93}Mg_{0.05}Cr_{0.01}(CO_3)(OH)_2$	CI calc= 0.081 (Poor)	poor	10.584	10.84	-2.5%
azurite	$Cu_3[CO_3OH]_2$	CI calc= -0.08 (Poor)	poor	19.495	19.05	2.3%
BORATES [9]						
hambergite	$Be_2BO_3(OH)_{0.96}F_{0.04}$	CI calc= -0.04 (Good)	poor	6.513	6.54	-0.5%
azoproite	$Mg_{1.82}Fe_{0.13}Fe^{3+}_{0.37}Ti_{0.36}Mg_{0.25}BO_5$	CI calc= 0.092 (Poor)	poor	11.665	12.77	-9.5%
wightmanite	$Mg_{4.7}Ca_{0.2}Fe_{0.1}BO_4(OH)_5 \cdot 2H_2O$	CI calc= 0.095 (Poor)	poor	18.892	21.21	-12.3%
				19.475	21.28	-9.2%
pinakiolite	$Mg_{1.75}Mn_{0.25}Mn^{3+}_{0.75}Sb^{3+}_{0.22}Al_{0.01}BO_5$	CI calc= -0.323 (Poor)	poor	14.676	13.64	7.0%
warwickite	$Mg_{1.33}Al_{0.21}Ti_{0.34}Fe^{3+}_{0.12}OBO_3$	CI calc= 0.241 (Poor)	poor	8.963	9.45	-5.4%
nordenskioldine	$CaSnB_2O_6$	CI calc= 0.029 (Excellent)	excellent	13.457	14.42	-7.1%
solongoite	$Ca_2B_3O_4Cl(OH)_4$	CI calc= 0.185 (Poor)	poor	15.762	18.69	-18.5%
garrelsite	$Ba_3NaSi_2B_7O_{16}(OH)_4$	CI calc= 0.066 (Fair)	fair	40.007	41.95	-4.8%
peprossite-Ce	$Ce_{0.4}La_{0.32}r_{0.09}Nd_{0.05}Th_{0.02}Ca_{0.09}Al_2B_3O_9$	CI calc= 0.019 (Excellent)	poor	20.281	20.27	0.1%
SILICATES [4]						
lomonosovite	$Na_{9.5}Mn_{0.16}Ca_{0.11}Ti_{2.83}Nb_{0.51}Mn_{0.27}Zr_{0.11}Mg_{0.11}Fe_{0.1}Fe^{3+}_{0.06}Si_4O_{14}\ P_2O_8\ O_{3.5}F_{0.5}$	CI calc= 0.064 (Fair)		66.577	67.44	-1.3%
baghdadite	$Ca_3Zr_{0.83}Ti_{0.15}Si_{1.99}Al_{0.01}Fe_{0.01}O_9$	CI calc= 0.118 (Poor)		24.206	24.29	-0.3%
zunyite	$Al_{13}Si_{4.69}Ti_{0.13}P_{0.12}O_{20}(OH)_{14.29}F_{3.59}Cl_{0.96}$	CI calc= 0.069 (Fair)		66.935	66.76	0.3%
huttonite	$Th_{0.96}U_{0.01}Y_{0.01}Ce_{0.02}SiO_4$	CI calc= 0.279 (Poor)		11.166	11.02	1.3%
PHOSPHATES [19]						
kidwellite	$Na_{0.7}Fe_9(PO_4)_6(OH)_{10}5H_2O$	CI calc= 0.093 (Poor)	poor	92.144	95.13	-3.2%
viitaniemiite	$Na_{0.9}Ca_{0.6}Mn_{0.4}AlPO_4F_{1.6}OH_{1.3}$	CI calc= 0.087 (Poor)	fair	11.816	12.18	-3.1%

kosnarite	$K_{0.9}Na_{0.2}Zr_{1.8}Mn_{0.1}(PO_4)_3$	CI calc= -0.047 (Good)	fair	28.820	28.83	0.0%
tiptopite	$K_2Li_{2.88}Na_{1.68}Ca_{0.66}(Be_6(PO_4)_6(OH)_2 \cdot 4H_2O$	CI calc= -0.064 (Fair)	fair	51.028	49.10	3.8%
jahnsite	$Mg_{3.5}Ca_{2.0}Mn_{2.3}Fe_{3.3}Al_{0.8}(OH)_{4.1}(PO_4)_8 \cdot 15.8H_2O$	CI calc= 0.019 (Excellent)	superior	108.778	106.50	2.1%
attakolite	$Ca_{0.8}Sr_{0.2}MnAl_{3.6}Fe^{3+}{}_{0.4}Si_{0.7}P_{0.3}O_3(PO4)_3(OH)_5$	CI calc= 0.062 (Fair)	fair	36.604	37.50	-2.4%
zodacite	$Ca_4Mn_{0.8}Mg_{0.1}Fe^{3+}{}_{2.2}Al_{1.8}(PO_4)_6(OH)_4 \cdot 12H_2O$	CI calc= 0.142 (Poor)	fair	77.444	77.58	-0.2%
wilhelmvierlingite	$Ca_{0.85}Zn_{0.13}MnFe^{3+}{}_{0.95}(PO_4)_2(OH) \cdot 4H_2O$	CI calc= -0.087 (Poor)	poor	27.710	28.39	-2.4%
kastningite	$Mn_{0.7}Fe_{0.3}Al_2(PO_4)_2 (OH) \cdot 8H_2O$	CI calc= 0.005 (Superior)	poor	31.922	31.86	0.2%
metaswitzerite	$Mn_{2.2}Fe_{0.6}Fe^{3+}{}_{0.2}(PO_4)_2 \cdot 4H_2O$	CI calc= 0.096 (Poor)	poor	24.776	25.92	-4.6%
switzerite	$Mn_{2.8}Fe_{0.2}(PO_4)_2 \cdot 7H_2O$	CI calc= 0.031 (Excellent)	excellent	29.970	30.51	-1.8%
barbosalite	$FeFe^{3+}{}_2(PO_4)_2(OH)_2$	CI calc= 0.119 (Poor)	poor	23.701	25.53	-7.7%
roscherite	$Fe_{2.64}Ca_{1.2}Mn_{0.04}Be_{2.5}(PO_4)_3(OH)_3 \cdot 3H_2O$	CI calc= -0.055 (Good) -	poor	33.138	36.51	-10.2%
benauite	$Sr_{0.67}Ba_{0.16}Pb_{0.07}Fe^{3+}{}_{2.90}Al_{0.03}P_{1.48}As_{0.04}S_{0.48}O_7(OH)_7$	CI calc= 0.053 (Good)	poor	36.975	35.35	4.4%
strengite	$FePO_4 \cdot 2H_2O$	CI calc= 0.038 (Excellent)	fair	13.099	13.44	-2.6%
tavorite	$LiFePO_4OH$	CI calc= 0.073 (Fair)	fair	11.909	11.96	-0.5%
cheralite-Ce	$Ca_{1.027}Th_{1.15}U_{0.148}Ce_{0.71}La_{0.306}Nd_{0.338}Sm_{0.100}Pr_{0.07}Gd_{0.02}P_{3.67}Si_{0.333}O_{16}$	CI calc= 0.14 (Poor)	poor	38.767	38.78	0.0%
petersite-Y	$Y_{0.41}Ce_{0.28}Nd_{0.23}Sm_{0.13}La_{0.11}Fe_{0.20}Ca_{0.79}Cu_{12.07}(PO_4)_6(OH)_{12} \cdot 6H_2O$	CI calc= -0.079 (Fair)	fair	51.869	50.35	2.9%
monazite-Sm	$Sm_{0.18}Gd_{0.16}Th_{0.15}Ce_{0.15}Ca_{0.12}Nd_{0.09}La_{0.03}Y_{0.03}Pb_{0.02}Pr_{0.02}Tb_{0.02}Dy_{0.02}P_{0.94}Si_{0.06}O_4$	CI calc= -0.005 (Superior)	poor	9.569	9.91	-3.6%
ARSENATES[10]						
agardite-Ce	$Ce_{0.32}Ca_{0.22}La_{0.15}Nd_{0.15}Y_{0.08}Sm_{0.03}Gd_{0.03}Eu_{0.02}Dy_{0.01}Cu_{5.62}Fe_{0.05}As_{2.8}Si_{0.17}S_{0.05}O_{12.08}(OH)_6 \cdot 3H_2O$	CI calc= -0.108 (Poor)	fair	58.971	52.97	10.2%
arseno-crandallite	$Ca_{0.61}Sr_{0.29}Ba_{0.14}Bi_{0.05}Al_{2.79}Cu_{0.11}Fe^{3+}{}_{0.07}Zn_{0.02}A._{0.99}P_{0.75}Si_{0.26}O_4(OH)_5 H_2O$	CI calc= 0.249 (Poor)	poor	26.062	27.51	-5.6%
weilite	$CaHAsO_4$	CI calc= -0.035 (Excellent)	poor	9.391	9.65	-2.28%
zalesiite	$Ca_{0.81}Y_{0.13}Al_{0.05}La_{0.01}Cu_{5.75}Ca_{0.15}As_{1.95}P_{0.05}O_4AsO_3OH(OH)_6 \cdot 3H_2O$	CI calc= -0.079 (Poor)	fair	55.707	53.55	3.9%
arsenogoyazite	$Sr_{0.5}Ca_{0.25}Ba_{0.25}Al_3As_{1.2}P_{0.6}O_8(OH)_4F \cdot H_2O$	CI calc= 0.025 (Excellent)	poor	26.661	26.21	1.7%
dussertite	$BaFe^{3+}{}_{2.52}Sb^{5+}{}_{0.483}As_2O_8(OH)_6$	CI calc= 0.023 (Excellent)	fair	39.233	39.34	-0.3%
bradaczekite	$Na_{1.16}K_{0.05}Cu_{3.74}Zn_{0.07}Fe^{3+}{}_{0.03}As_3O_{12}$	CI calc= -0.01 (Superior)	poor	34.899	33.29	4.6%

symplesite	$Fe_3As_2O_8 \cdot 8H_2O$	CI calc= 0.18 (Poor)	fair	36.243	35.17	3.0%
clinoclase	$Cu_3AsO_4(OH)_3$	CI calc= -0.068 (Fair)	fair	19.884	19.48	2.0%
olivenite	Cu_2AsO_4OH	CI calc= -0.047 (Good)	fair	14.100	14.09	-0.1%
SULFATES [15]						
alunite	$KAl_3(SO_4)_2(OH)_6$	CI calc= 0.268 (Poor)	poor	23.673	23.84	-0.7%
caminite	$Mg_3(SO_4)_2(OH)_2$	CI calc= 0.214 (Poor)	fair	15.943	17.72	-11.0%
caminite	$Mg_7(SO_4)_5(OH)_4 \cdot H_2O$	CI calc= 0.214 (Poor)	fair	15.896	17.52	-10.0%
bassanite	$2CaSO_4 \cdot H_2O$	CI calc= -0.026 (Excellent)	fair	8.257	8.71	-5.6%
bentorite	$Ca_{5.88}Cr_{1.61}Al_{0.32}Fe^{3+}_{0.02}(SO_4)_3(OH)_{12} \cdot 26H_2O$	CI calc= 0.033 (Excellent)	poor	92.726	95.69	-3.2%
argentojarosite	$AgFe_3(SO_4)_2(OH)_6$	CI calc= 0.084 (Poor)	fair	36.401	36.06	1.0%
cesanite	$Ca_{2.92}Sr_{0.06}Na_{6.98}K_{0.04}(SO_4)_6(OH)_{0.88}Cl_{0.12} \cdot 0.88H_2O$	CI calc= -0.081 (Poor)	fair	50.433	49.81	1.2%
chalcocyanite	$CuSO_4$	CI calc= -0.076 (Fair)	poor	8.300	8.37	-0.7%
dolerophanite	Cu_2OSO_4	CI calc= -0.117 (Poor)	poor	12.748	12.31	3.4%
chalcoalumite	$CuAl_4SO_4(OH)_{12} \cdot 3H_2O$	CI calc= 0.047 (Good)	fair	34.151	33.57	1.7%
fedotovite	$K_2Cu_3O(SO_4)_3$	CI calc= -0.054 (Good)	poor	29.699	29.79	-0.3%
kamchatkite	$KCu_3(SO_4)OCl$	CI calc= -0.068 (Fair)	poor	26.414	25.85	2.1%
millosevichite	$Al_{1.5}Fe_{0.5}(SO_4)_3$	CI calc= 0.144 (Poor)	fair	21.924	21.35	2.6%
felsobanyite	$Al_4(SO_4)(OH)_{10} \cdot 4H_2O$	CI calc= 0.064 (Fair)	poor	30.627	30.54	-0.1%
walthierite	$Ba_{0.5}Al_3(SO_4)_2(OH)_6$	CI calc= 0.01 (Superior)	fair	24.073	24.11	0.2%
CHROMATES [1]						
chromatite	$CaCrO_4$	CI calc= 0.072 (Fair)	poor	11.204	12.46	-11.2%
MOLYBDATES [5]						
mendozavilite	$Na_{1.2}K_{1.1}CaFe^{3+}_{0.5}Ca_{0.4}Fe^{3+}_{2.9}Al_{0.1}Mo_{7.77}P_{1.95}O_{31.62}(OH)_2Cl_{0.09} \cdot 19.6H_2O$	CI calc= 0.193 (Poor)	poor	151.403	139.48	7.9%
obradovicite	$K_{1.72}Cu^{2+}_{0.58}Na_{0.38}Cu^{2+}Mo_8As_{1.53}Fe^{3+}_{2.64}O_{31.11}(OH)_{5.89} \cdot 18.25H_2O$	CI calc= -0.011 (Superior)	poor	163.741	144.50	11.7%
betpakdalite	$Ca_{1.89}Na_{0.42}K_{0.09}Cu^{2+}_{0.03}Mg_{1.01}Fe^{3+}_{3.01}Mo_8As_{1.8}P_{0.06}Si_{0.04}O_{36}(OH)1 \cdot 23H_2O$	CI calc= -0.071 (Fair)	poor	169.427	144.02	14.9%
bamfordite	$Fe^{3+}Mo_2O_6(OH)_3 \cdot H_2O$	CI calc= -0.067 (Fair)	fair	31.438	27.15	13.6%
lindgrenite	$Cu_3Mo_2O_8(OH)_2$	CI calc= -0.087 (Poor)	poor	33.784	31.90	5.7%

TUNGSTATES [4]						
scheelite	$CaWO_4$	CI calc= 0.152 (Poor)	poor	11.887	11.91	-0.2%
paraniite-Y	$Ca_{1.64}Y_{1.13}Gd_{0.03}Dy_{0.08}Er_{0.07}Yb_{0.03}As_{1.07}W_{0.93}O_{12}$	CI calc= 0.143 (Poor)	poor	32.661	30.76	5.8%
yttrotungstite-Y	$YW_2O_6(OH)_3$	CI calc= 0.067 (Fair)	poor	26.439	23.99	9.3%
yttrotungstite	$Y_{1.1}Nd_{0.17}Ce_{0.15}Dy_{0.09}RE_{0.3}Al_{0.2}W_{3.7}O_{11.4}(OH)_{6.6}$	CI calc= 0.067 (Fair)	poor	53.074	47.54	10.4%
tungstibite	Sb_2WO_6	CI calc= -0.091 (Poor)	poor	27.796	23.34	16.0%
COMPLEX STRUCTURES [10]						
farnesite	$Na_{36.43}K_{9.18}Ca_{8.75}Si_{42.50}Al_{41.50}O_{213.72}F_{0.16}Cl_{0.48} \cdot 3H_2O$	**CI calc= 0.038 (Excellent)**		443.929	430.65	3.0%
giuseppetite	$Na_5K_{1.8}CaAl_{6.05}Si_{5.95}O_{24}(SO_4)_{1.8}Cl_{0.25}$	**CI calc= -0.029 (Excellent)**		62.518	61.24	2.0%
megacyclite	$Na_8KSi_9O_{18}(OH)_9 \cdot 19H_2O$	**CI calc= -0.016 (Superior)**		86.600	84.23	2.7%
nechelelyrusto-vite	$Na_4Ba_2Mn_{1.5}Ti_5NbSi_80_{28}(OH)_3F \cdot 6H_2O$	CI calc= 0.113 (Poor)		108.952	108.73	0.2%
polyphite	$Na_{8.72}Ca_{1.4}Sr_{0.03}Mg_{0.3}Mn_{0.68}Fe_{0.07}Ti_{1.41}Nb_{0.19}Zr_{0.19}P_{2.96}Si_{2.04}O_{20.94}F_{2.06}$	**CI calc= 0.004 (Superior)**		53.626	54.47	-1.6%
quadruphite	$Na_{13.59}Ca_{1.44}Sr_{0.06}Mg_{0.5}Mn_{0.85}Fe_{0.10}Ti_{2.55}Nb_{0.44}Zr_{0.47}Si_4P_4O_{33}F_{2.6}$	**CI calc= 0.059 (Good)**		86.742	86.54	0.2%
roger-mitchellite	$Na_{12}Sr_{21.16}Na_{1.17}Ca_{0.21}Ba_4Zr_{25.33}Ti_{0.93}Si_{77.02}B_{0.98}B_{12}O_{246}(OH)_{24} \cdot 18H_2O$			655.788	661.85	-0.9%
sobolevite	$Na_{13.62}Ca_{1.63}Sr_{0.03}Mg_{0.39}Mn_{1.02}Fe_{0.1}Ti_{2.42}Nb_{0.51}Zr_{0.09}Si_{4.1}P_4O_{33.08}F_{2.92}$	**CI calc= 0.013 (Superior)**		86.419	86.02	0.5%
bannisterite	$Ca_{0.40}K_{0.44}Na_{0.05}Mn_{6.22}Fe_{1.45}Mg_{1.43}Zn_{1.01}Fe^{3+}_{0.18}Si_{14.42}Al_{1.43}O_{38}(OH)_8 \cdot 6H_2O$	**CI calc= 0.02 (Excellent)**		107.148	107.83	-0.6%
apjohnite	$Mn_{0.64}Mg_{0.28}Zn_{0.06}Fe_{0.02}Al_2(SO_4)_4 \cdot 22H_2O$	**CI calc= -0.009 (Superior)**		63.315	63.48	-0.3%

Figure captions

Figure 1. Comparison of polarizabilities calculated by the four different algorithms. Arbitrarily, a V_m of 100 Å^3 was assumed.

Figure 2. Polarizability vs. covalence (%) using electronegativity values from Allred and Rochow (1958). Covalence is calculated according to cov [%] = $100 \cdot e^{-\frac{1}{4}\cdot(x_a - x_b)^2}$

Figure 3. Relationship between AE polarizabilities (eqn. 1b) and anion volume V_{an} of simple oxides.

Figure 4. Relationship between polarizabilities α and the cube of the ionic radii (Shannon 1976) of rare earth ions.

Figure 5: Cation polarizabilities α plotted vs. coordination number CN. a) Na, b) Ca, c) La, d) Zr. Numbers above the curves refer to the numbers of examples of minerals and compounds containing ions in specific coordinations on the abscissa.

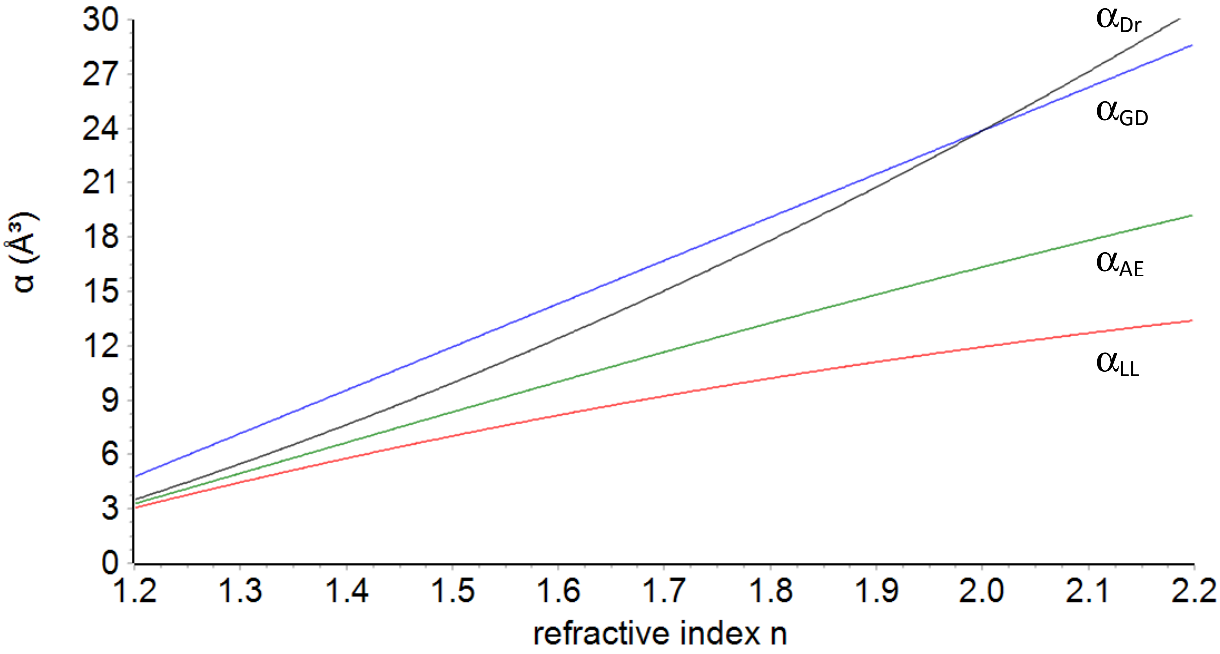


Figure 1. Comparison of polarizabilities calculated by the four different algorithms. Arbitrarily, a V_m of 100 Å^3 was assumed.

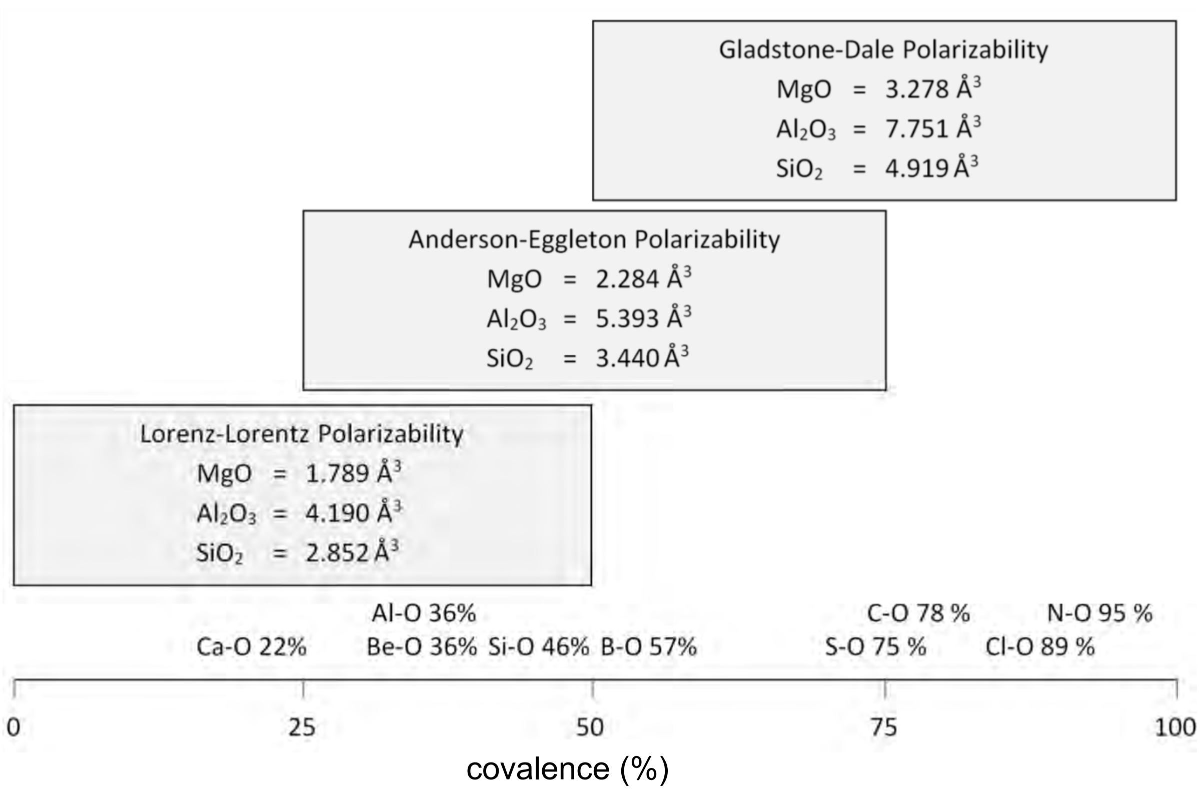


Figure 2. Polarizability vs. covalence (%) using electronegativity values from Allred and Rochow (1958). Covalence is calculated according to cov [%] = $100 \cdot e^{-\frac{1}{4}\cdot(X_a - X_b)^2}$

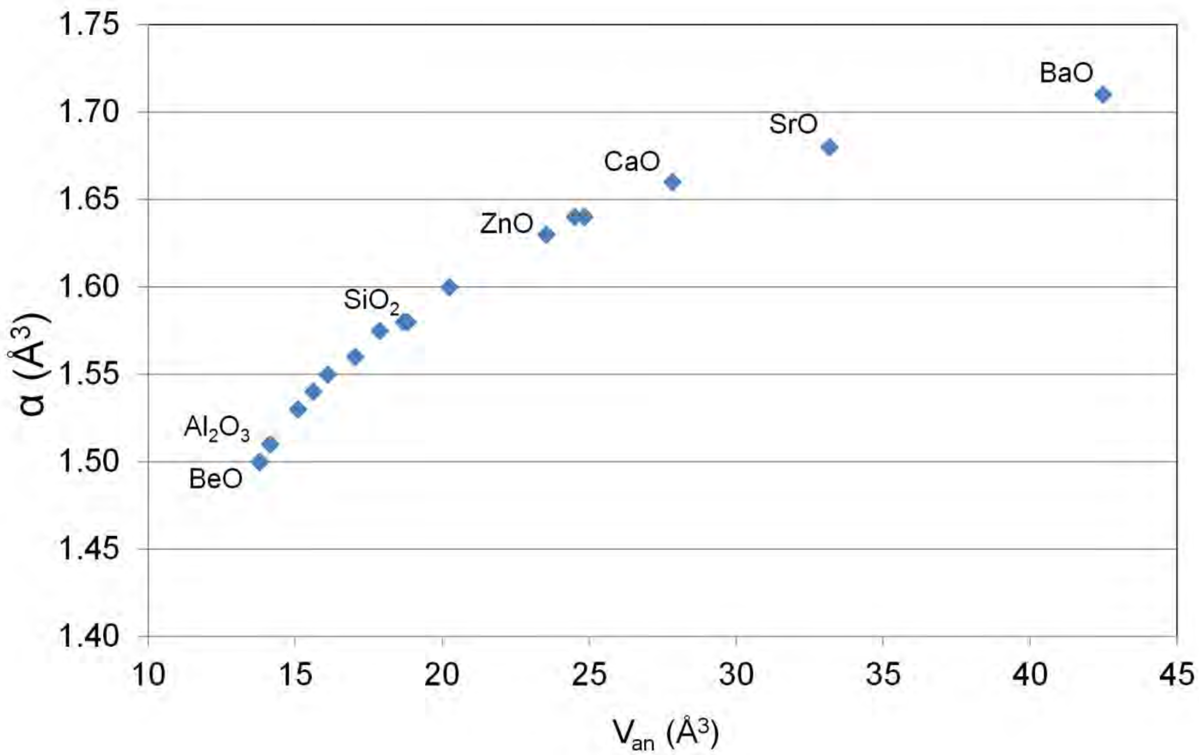


Figure 3. Relationship between AE polarizabilities (eqn. 1b) and anion volume V_{an} of simple oxides.

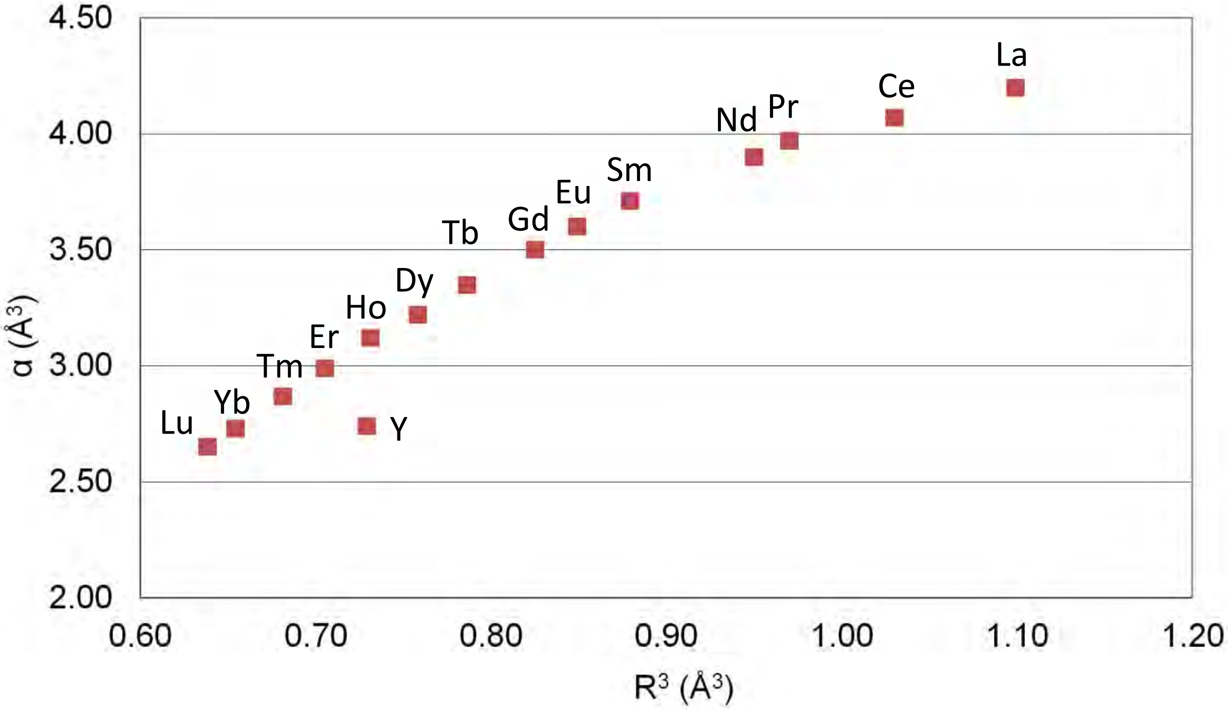
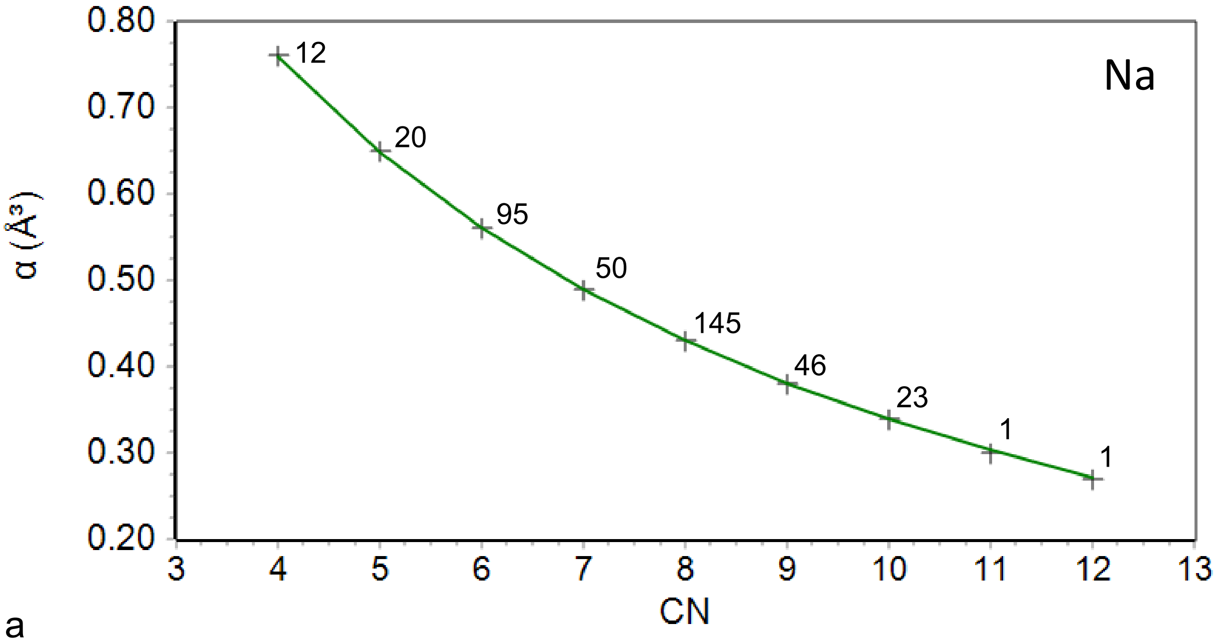
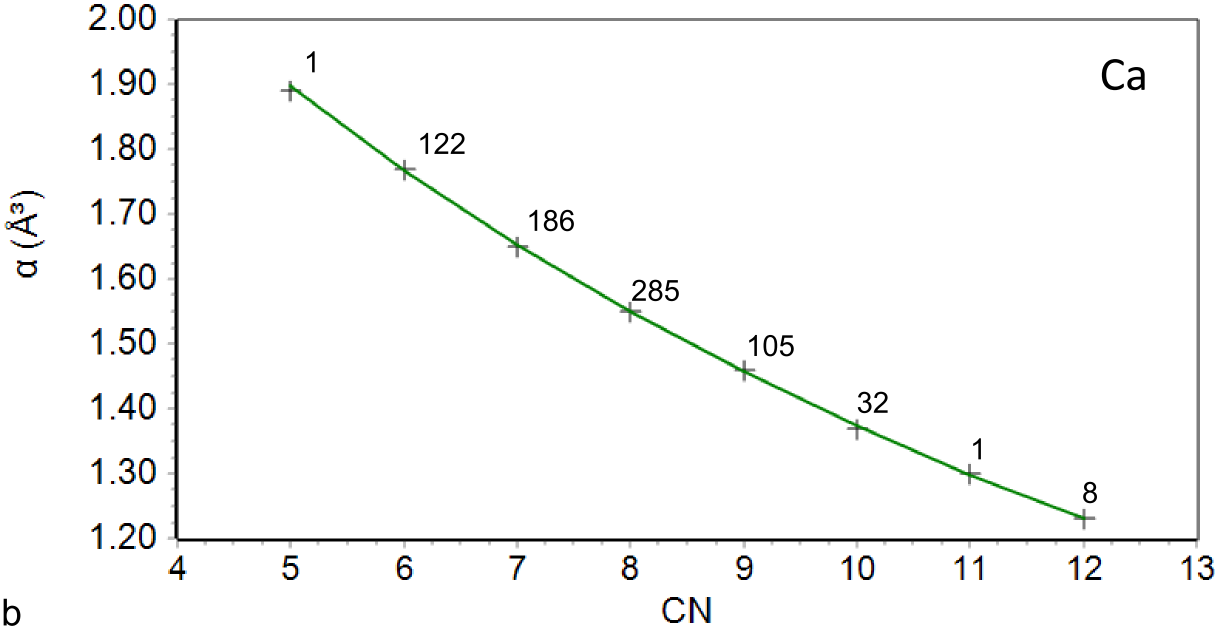


Figure 4. Relationship between polarizabilities α and the cube of the ionic radii (Shannon 1976) of rare earth ions.


Na
α (Å³)
0.80
0.70
0.60
0.50
0.40
0.30
0.20
CN
3
4
5
6
7
8
9
10
11
12
13
12
20
95
50
145
46
23
1
1

a


Ca
α (Å³)
2.00
1.90
1.80
1.70
1.60
1.50
1.40
1.30
1.20
CN
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105
32
1
8

b

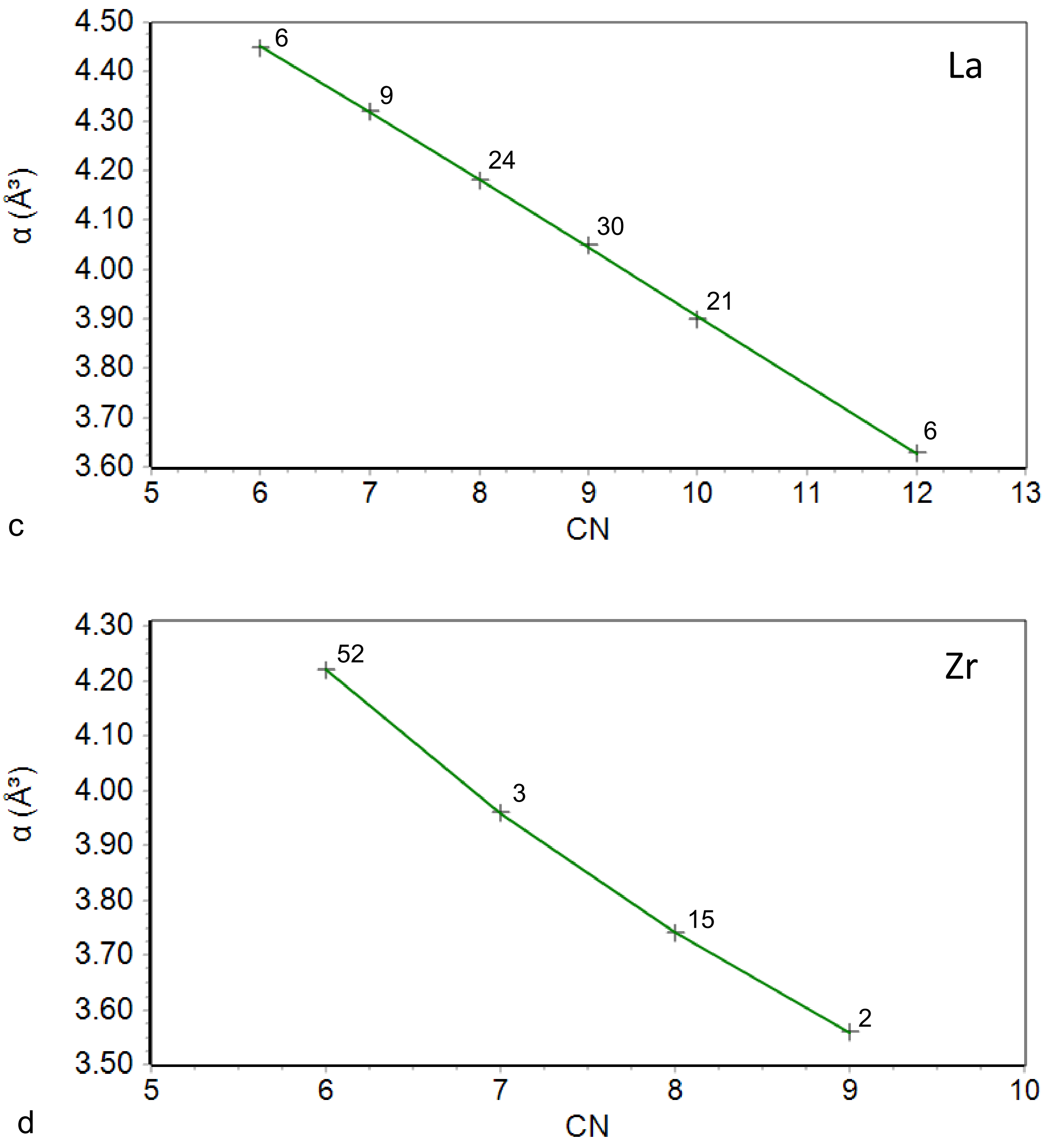

Figure 5: Cation polarizabilities α plotted vs. coordination number CN. a) Na, b) Ca, c) La, d) Zr. Numbers above the curves refer to the numbers of examples of minerals and compounds containing ions in specific coordinations on the abscissa.