Letter (Revision 1)

POLARIO, a computer program for calculating refractive indices from chemical compositions

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Abstract

POLARIO is a computer program to calculate total electronic polarizabilities, refractive energies, and refractive indices of transparent minerals and synthetic crystalline compounds from their chemical composition and molar volume. If measured refractive indices or observed polarizabilities are entered, POLARIO also allows calculation of the deviation between observed and calculated values and determines the compatibility index as a measure of agreement. The density of the compound is calculated from the chemical composition and the molar volume of a formula unit. Atom parameters can be read in cif format to determine possible coordination numbers of cations and to compose the entire input necessary to do the calculations. It displays a table of interatomic distances and angles, and it shows the chemical composition with superscripted coordination numbers and valencies. The program is written in Delphi XE6 for WINDOWS operating systems and contains 5,300 constants and parameters to do the calculations.

Keywords: Refractive index, total electronic polarizabilities, refractive-index calculation, Anderson-Eggleton relationship, Gladstone-Dale relationship, computer program.

Introduction

Refractive indices *n* are routinely used to describe the properties of minerals and other transparent compounds. They are defined as the velocity *c* of light in vacuum divided by the velocity c_m in the medium according to $n = c / c_m$. If light propagates from a medium with n_1 into a medium with n_2, it changes its direction according to Snell's law, $n_1 \cdot \sin\alpha = n_2 \cdot \sin\beta$, with the angle α of incidence (= angle between incident beam and normal on interface between the two media) and the angle β of refraction (= angle between refracted beam and normal). Thus, the refractive indices can be simply determined by measuring the angles, most accurately on a prism using the minimum-deviation method (see, e.g., Medenbach and Shannon 1997). Alternatively, immersion methods can be used for small crystals (< about 1 mm) to obtain a match in refraction between the crystal (or other transparent media) and the liquid in which it is embedded.

Physically, the effect of refraction is caused by dipole moments *p* induced by the electromagnetic wave on entering the crystal being proportional to the electric field *E* according to $p = \alpha \cdot E$, where the polarizability α represents the factor of proportionality between the dipole moment and the electric field. In the visible region of light, the dipole moment originates in the displacement of electrons relative to the protons, and α is called the "electronic polarizability". It was shown independently by Lorenz (1880) and Lorentz (1880) that the polarizabilities are related to the refractive indices according to

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

known as the Lorenz-Lorentz (LL) relation, 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 $\lambda = \infty$ which means that this equation is strictly valid only for infinite wavelength. However, in common practice, this relation is used in the visible region of light as well, and it is also applied to noncubic crystals (for details see discussion in Shannon and Fischer 2016). In our work, we use a modified equation described in the section for calculating refractive indices from electronic polarizabilities of ions.

Gladstone and Dale (1863) found a relation between the chemical composition of a liquid and its refractive index by assigning "specific refractive energies" to its component elements and summing them weighted by the proportional weight contributions of the elements. This concept was applied by Larsen (1921) to minerals and later on refined by Mandarino (1976, 1978, 1979, 1981, 2006, 2007), providing a comprehensive set of refractive energies for the ions (listed as oxides in the Mandarino publications). The Gladstone-Dale (GD) compatibility index ($CI = 1 - (K_p/K_c)$, see below) was introduced by Mandarino (1979) as a measure of internal consistency of the mean index of refraction.

Here, we introduce POLARIO, a computer program to calculate refractive indices from electronic polarizabilities of the ions after Shannon and Fischer (2016) and from refractive energies (Gladstone-Dale constants) after Mandarino (1976, 1981). As listed in Table 5 in Shannon and Fischer (2016) different electronic polarizabilities are assigned to oxygen in borates, carbonates, nitrates, sulfates and perchlorates to reflect the more covalent nature of these compounds.

Calculating refractive indices from electronic polarizabilities of ions

Using the electronic polarizabilities of cations and anions from Tables 4 and 5 in Shannon and Fischer (2016), the total polarizability of a mineral or compound can be calculated by applying the additivity rule. Thus, the total polarizability α_{tot} is calculated as the sum of the cation and anion contributions which can be expressed as

$$\alpha_{tot} = \sum_{i=1}^{Ncat} m_i \cdot \alpha_{ei}(\text{cation}) + \sum_{i=1}^{Nan} n_i \cdot \alpha_{ei}(\text{anion}). \qquad (2)$$

Polarizabilities and refractive indices depend on the coordination numbers (CN) of the cations being higher for low CN and lower for high CN. In general, higher coordinations for calculated polarizabilities seem to be more satisfactory yielding a better fit between observed and calculated polarizabilities (Shannon and Fischer, 2016). Whereas the cation polarizabilities are strictly additive, the anion polarizabilities α_{an} including H_2O molecules are correlated with the volume occupied by the anion expressed by the volume of the formula unit divided by the number of anions. Similar to Shannon and Fischer (2006) for the calculation of polarizabilities at infinite wavelength, we use the relation in Shannon and Fischer (2016):

$$\alpha_{an} = \alpha_{-}^{o} \cdot 10^{-N_o/V_{an}^{1.2}} \qquad (3)$$

with V_{an} = anion molar volume, α_{-}^{o} = free-ion polarizability, and N_o is taken from Table 5 in Shannon and Fischer (2016).

The mean refractive index n_D at $\lambda = 589.3$ nm is then calculated from the total polarizability using the Anderson-Eggleton relationship (Anderson 1975; Eggleton 1991; Shannon and Fischer 2016)

$$\alpha_{AE} = \frac{(n^2-1)V_m}{4\pi + \left(\frac{4\pi}{3} - 2.26\right)(n^2-1)} \qquad (4)$$

solved for n according to

$$n_{\mathrm{AE}} = \sqrt{\frac{4\pi\alpha_{\mathrm{AE}}}{\left(2.26-\frac{4\pi}{3}\right)\alpha_{\mathrm{AE}}+\mathrm{V_m}} + 1}. \tag{5}$$

This equation is similar to the Lorenz-Lorentz relation but covers a more appropriate range of compounds with interatomic bonds having an intermediate character between covalent and ionic bonds as discussed by Shannon and Fischer (2016).

Using the example of orthoclase ($KAlSi_3O_8$) from Shannon et al. (2017), representing a typical example for a silicate, the following results are obtained:

Cation polarizabilities are taken from Table 4 in Shannon and Fischer (2016), being $\alpha(^{[9]}K^+)$ = 1.35 Å^3, $\alpha(^{[4]}Al^{3+})$ = 0.533 Å^3, and $\alpha(^{[4]}Si^{4+})$ = 0.284 Å^3. Thus, the total cation contribution is calculated as to $\alpha(K) + \alpha(Al) + 3 \cdot \alpha(Si) = 1.35 + 0.533 + 3 \cdot 0.284 = 2.735$ Å^3. Similarly, the anion contribution is calculated using the anion volume V_m=22.51 Å^3 and the parameters from Table 5 in Shannon and Fischer (2016) as to $8 \cdot \alpha(O) = 8 \cdot 1.79 \cdot 10^{\frac{-1.776}{22.51^{1.2}}} = 8 \cdot 1.79 \cdot 0.9071 = 12.990$ Å^3, summing to $\alpha(\mathrm{tot})$ = 2.735 Å^3 + 12.990 Å^3 = 15.725 Å^3. Using eqn. (5) and the molar volume V_m = 180.10 Å^3 (corresponding to $8 \cdot V_{an}$) for one formula unit, the mean refractive index is then calculated to be $\langle n_D \rangle$ = 1.523, in close agreement with the experimentally determined value of 1.524 (see orthoclase entry in supplemental Table S1 in Shannon et al. 2017).

Calculating refractive indices from refractive energies of ions

Following the approach of Gladstone and Dale (1863), Mandarino (1976, 1981) determined a set of parameters k_i (Gladstone-Dale constants) to define a specific *chemical* refractivity (cm^3/g)

$$K_c = \sum_i \frac{k_i p_i}{100} \tag{6}$$

where p_i = weight percentages of the oxide contents in the respective compounds. This quantity, K_c, is then compared to an experimental *physically* derived value defined as $K_p = \langle n \rangle - 1/D$ with the density D (Mandarino 1979, 1981). The "compatibility" measures the agreement between the two sides of the equation $(n\text{-}1)/D = \Sigma k_i p_i/100$ where "superior" < 2%; excellent 2% - 4%; good 4% - 6%; fair 6% - 8% and poor >8%. Replacing K_c in eqn. (6) by K_p allows the calculation of the mean refractive index according to

$$\langle n_D \rangle = \sum_i \frac{k_i p_i}{100} \cdot D + 1 \qquad (7)$$

Using again the example of the orthoclase, the calculation is as follows:

The chemical refractivity Kc is calculated using eqn. (6):

$$K_c = \frac{k(K_2O)\cdot p(K_2O)}{100} + \frac{k(Al_2O_3)\cdot p(Al_2O_3)}{100} + \frac{k(SiO_2)\cdot p(SiO_2)}{100} = 0.196 \cdot 0.1692 + 0.207 \cdot 0.1832 + 0.208 \cdot 0.6476 = 0.2058\ \text{cm}^3/\text{g}.$$

The mean refractive index is then calculated using eqn. (7) as

$\langle n_D \rangle = 0.2058\ \text{cm}^3/\text{g} \cdot 2.566\ \text{g/cm}^3 + 1 = 1.528$.

For compounds other than oxides, e.g. halides, the sum of the molecular weights of the oxides plus the sum of the atomic weights of the halides is decreased by the number of halide ions multiplied by half of the atomic weight of oxygen (the charge of half an oxygen ion corresponds to the charge of one halide ion). The weight fractions are then calculated with the reduced sum of molecular weights. The sum of the product $k_i p_i$ of the refractive energies and the weight fractions is decreased by the the number of halide ions multiplied by half of the atomic weight of oxygen times the weight fraction of the oxygen equivalent multiplied by the refractive energy of oxygen $k(O) = 0.203$ (Mandarino 1979, 1981) (for further details see the examples on p. 74 in Mandarino 1979).

Input data and program handling

The only data necessary to calculate refractive indices from polarizabilities are the chemical composition and the molar volume V_m. If coordination numbers CN are omitted, mean values for the cation polarizabilities are used. The total polarizability of the compound is calculated using eqn. (2) and the mean refractive index is calculated according to eqn. (5). Similarly the corresponding values derived from the Gladstone-Dale refractive energies are calculated using eqns. (6) and (7) where the density is calculated from the molar volume. Input and output handling is shown in Figure 1. Dark fields cannot be edited by hand. Numbers in parentheses in the following description refer to the numbers in Figure 1. The chemical composition (23) can be entered up to 32 elements including coordination numbers of cations and valences of ions. After entering the molar volume V_m (Å^3) (10), the density (14), the anion volume V_{an} (Å^3) (11), the total polarizability (16 top), and the refractive energy (16 bottom) are calculated. From these values, the mean refractive index (18), the refractive index (19) calculated from ion polarizabilities averaged over different coordination numbers, and the corresponding n(GD) value (20) using the Gladstone-Dale (GD) constants are calculated (6). It can be chosen (7) if all GD constants are taken from Mandarino (1981) or if a subset for certain silicates is taken from Eggleton (1991). The type of silicate can be selected using the pulldown menu (12). If observed values for either total polarizability (15) or refractive index (17) (or both) are entered, POLARIO also calculates the deviation between observed and calculated values, and it determines the compatibility index (20) as defined by Mandarino (1979, 1981). Alternatively, atom parameters can be read (1, 2) from cif formatted files allowing for distance calculations (2) with a suggestion for possible coordination numbers. The space-group symbol needed for the calculation is then displayed in (9). If present in the cif file, additional information on the compound is displayed in

(8, 22). Results, error messages, and warnings are written into field (21) and can be stored using the button in (1). The chemical composition from (23) is formatted with subscripts and superscripts in html format in (24) and can be copied, e.g., into word-processing programs. Additional tools (3, 4, 5) facilitate the program handling. A detailed description of the program can be found in the user manual.

Limitations of POLARIO

The program does not contain polarizability values for uranyl ions and for ions having lone-pair electrons (Tl^+, Sn^{2+}, Pb^{2+}, As^{3+}, Sb^{3+},Bi^{3+}, S^{4+}, Se^{4+}, Te^{4+}, Cl^{5+}, Br^{5+}, I^{5+}) which do not fit the simple additivity scheme of polarizabilities.

Calculated values of $<n_D>$ generally deviate from observed $<n_D>$ by less than Δ = (n(obs)-n(calc))/n(obs) of 1-2% (Shannon and Fischer 2016; Shannon et al. 2017) with the exception of some groups of compounds showing systematic deviations from this scheme. Compounds that are ion conductors, generally alkali-ion rich, typically show calculated refractive indices, $<n_D>$, 0.7-3% larger than observed refractive indices: e.g., for thenardite, Na_2SO_4, $<n_D>$ calc = 1.51 and $<n_D>$ obs = 1.474 with Δ = -2.4%. Compounds containing edge- and corner-sharing octahedra (M = Fe^{3+}, In^{3+}, Y^{3+}, Ti^{4+}, Nb^{5+}, Ta^{5+}, V^{5+}, Mo^{6+}, and W^{6+}) typically show calculated refractive indices, $<n_D>$ of 5-30% smaller than observed refractive indices: e.g. for $CaTiO_3$ <nD> calc = 2.25 and $<n_D>$ obs = 2.407 with Δ = 6.5% and for elsmoreite, $WO_3 \cdot 0.5H_2O$, $<n_D>$ calc = 1.80 and <nD> obs = 2.240 with Δ = 19.6%. Similarly, compounds showing steric strain, where incident bond valences show positive or negative deviations from the valence-sum rule, can show calculated refractive indices, <nD> smaller or larger than observed refractive indices, depending on the type and degree of steric strain (Gagné et al. 2017). An example of a negative deviation is kieserite, $MgSO_4 \cdot H_2O$ where $\langle n_D \rangle$ calc = 1.57 and $\langle n_D \rangle$ obs = 1.551 with Δ = -1.2%.

Technical specifications and availability

The program is written in DELPHI using the Embarcadero XE6 version running on WINDOWS operating systems. It contains 5,300 constants and parameters taken from Shannon and Fischer (2016) (parameters for 76 cations in various coordinations, H_xO_y species, NH_4^+, and 4 anions) and from Mandarino (1981) and Eggleton (1991) with values for VO_2 from Mandarino (2005). Atomic weights and molecular weights of the oxides calculated thereof are from Wieser et al. (2013). Symmetry operators are derived from the space-group symbol using a routine from Burzulaff and Hountas (1982) translated to Pascal (Delphi) as implemented in our programs BRASS (Birkenstock et al. 2014) and STRUPLO (Fischer and Messner 2015). The routine reading cif files was written by Thomas Messner also implemented in the two programs mentioned above. POLARIO can be downloaded free of charge from the website www.brass.uni-bremen.de.

Implications

The calculation of refractive indices from chemical compositions is important for mineralogists and materials scientists. It is required for new-mineral proposals submitted to the International Mineralogical Association (IMA) and it is a valuable tool for designing new materials with specific optical properties. However, it is a tedious procedure if calculated by hand. POLARIO provides two different routes to calculate mean refractive indices, based on electronic polarizabilities and on refractive energies, respectively. It evaluates atom parameters to determine possible coordination numbers, and it calculates densities, total electronic polarizabilities, chemical refractive energies, and the compatibility index. Thus, it represents a fast and easy-to-use tool to determine optical properties from chemical compositions.

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Figure 1. POLARIO form. For explanations see text.