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

$$\alpha_T = \frac{\left(n_D^2 - 1\right)V_m}{4\pi + \left(\frac{4\pi}{3} - c\right)\left(n_D^2 - 1\right)}$$

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 $\alpha_- = \alpha_-^0 \cdot 10^{-N_O/V_{an}^{1.20}}$ 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 $\alpha_{(CN)} = \left(a_1 + a_2 CN e^{-a_3 CN}\right)^{-1}$ 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, Δ > 3%.

Using

$$n_D = \sqrt{\frac{4\pi\alpha}{\left(2.26 - \frac{4\pi}{3}\right)\alpha + V_m} + 1}$$

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 <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 <3%. Thus, polarizability analysis may be a more reliable measure of the compatibility of a mineral's refractive index, composition, and crystal structure.

Keywords: Electronic polarizabilities, refractive indices, Gladstone-Dale relationship, Anderson-Eggleton relationship, Lorenz-Lorentz relationship, Drude relationship, optical properties

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