

## 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  $\lambda = 589.3$  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

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

where  $\alpha_T$  = the total polarizability of a mineral or compound,  $n_D$  = the refractive index at  $\lambda = 589.3$  nm,  $V_m$  = molar volume in  $\text{\AA}^3$ , 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,  $\text{H}_2\text{O}$ , 5  $\text{H}_x\text{O}_y$  species [ $(\text{H}_3\text{O})^+$ ,  $(\text{H}_5\text{O}_2)^+$ ,  $(\text{H}_3\text{O}_2)^-$ ,  $(\text{H}_4\text{O}_4)^4-$ ,  $(\text{H}_7\text{O}_4)^-$ ],  $\text{NH}_4^+$ , and 4 anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{O}^{2-}$ ).

Anion polarizabilities are a function of anion volume,  $V_{\text{an}}$ , according to  $\alpha_- = \alpha_-^0 \cdot 10^{-N_0/V_{\text{an}}^{1.20}}$  where  $\alpha_-$  = anion polarizability,  $\alpha_-^0$  = free-ion polarizability, and  $V_{\text{an}}$  = 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  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Y}^{3+}$ ,  $(\text{Lu}^{3+}\text{-La}^{3+})$ ,  $\text{Zr}^{4+}$ , and  $\text{Th}^{4+}$ . Compounds with: (1) structures containing lone-pair and uranyl ions; (2) sterically strained (SS) structures [e.g.,  $\text{Na}_{4.4}\text{Ca}_{3.8}\text{Si}_6\text{O}_{18}$  (combeite),  $\Delta = 6\%$  and  $\text{Ca}_3\text{Mg}_2\text{Si}_2\text{O}_8$  (merwinite),  $\Delta = 4\%$ ]; (3) corner-shared octahedral (CSO) network and chain structures such as perovskites, tungsten bronzes, and titanite-related structures [e.g.,  $\text{MTiO}_3$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ),  $\Delta = 9\text{--}12\%$  and  $\text{KNbO}_3$ ,  $\Delta = 10\%$ ]; (4) edge-shared  $\text{Fe}^{3+}$  and  $\text{Mn}^{3+}$  structures (ESO) such as goethite ( $\text{FeOOH}$ ,  $\Delta = 6\%$ ); 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  $\text{Li}^+ \rightarrow \text{Cs}^+$ ,  $\text{Ag}^+ \rightarrow \text{Be}^{2+} \rightarrow \text{Ba}^{2+}$ ,  $\text{Mn}^{2+/3+}$ ,  $\text{Fe}^{2+/3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{+/2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{B}^{3+} \rightarrow \text{In}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Lu}^{3+} \rightarrow \text{La}^{3+}$ ,  $\text{C}^{4+} \rightarrow \text{Sn}^{4+}$ ,  $\text{Ti}^{3+/4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Hf}^{4+}$ ,  $\text{Th}^{4+}$ ,  $\text{V}^{5+}$ ,  $\text{Mo}^{6+}$ , and  $\text{W}^{6+}$  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

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

the mean refractive index can be calculated from the chemical composition and the polarizabilities of ions determined here. The calculated mean values of  $\langle n_D \rangle$  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  $\Delta$  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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