Electronic and ionic polarizabilities of silicate minerals

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Abstract

Molecular polarizabilities of silicate minerals are obtained using the Lorentz–Lorenz relation at optical frequencies and the Clausius–Mosotti relation at "static" frequencies. These polarizabilities are used to obtain a universal table of both electronic and static ion polarizabilities. Use of this set of polarizabilities shows that the additivity rule works rather well for complex silicates, *i.e.*, the measured polarizability can be obtained from the appropriate sum of the ion polarizabilities in one formula unit. Therefore, the set of ion polarizabilities can be used in model calculations on the structure and bonding of silicates.

Introduction

The treatment of silicate mineralogy from solid state principles requires an understanding of the nature of the bonds in the crystals. In many instances the crystal can be considered to be composed of ions with the chemical bonds being suitably described as ionic bonds. The major contribution to the lattice cohesion energy of a perfect ionic crystal is the coulomb energy, arising from all the coulomb interactions between the ions. In addition, the repulsion between nearby ions must also be included in the calculation of cohesion energy. For two ions of charge z_i and z_j a simple interion potential consisting of a coulomb term and an exponential repulsion term

$$V(r) = z_i z_j \frac{e^2}{r} + A e^{-\alpha r}$$

suffices to describe the ionic bond. For example, if the constants A and α are obtained from the equilibrium bond distance and the vibrational frequency of *gaseous* NaCl, the bond energy of the NaCl molecule is predicted rather well *i.e.*, 3.87 ev *versus* an experimental value of 4.22 ev (Karplus and Porter, 1970). Furthermore, a similar treatment of the NaCl crystal yields a lattice energy of 178.6 Kcal/mole (7.75 ev), which compares very well with the experimental value of 182.6 Kcal/mole (7.92 ev) (Kittel, 1976). Thus, this simple description of ionic bonds is reasonable for some crystals.

However, if there are defects in a crystal or if a crystal interacts with electromagnetic fields (*e.g.*,

light), additional potential terms must be included in the treatment of the ionic bonds. The important new aspect of these ionic interactions is the inducement of dipole moments (polarization) in the ions by either external electric fields or by internal fields, such as those arising from defects in minerals. The polarization of ions accounts for the difference between the predicted ($\mu = er_0 = 11.34$ Debye) and observed (9.00 Debye) dipole moments of the Na^+Cl^- molecule, where r_0 is the equilibrium bond distance. In silicates these polarization effects give rise to the measured dielectric constants and refractive indices. Several papers (Tessman *et al.*, 1953; Roberts, 1949; Shanker and Agrawal, 1978; Niwas *et al.*, 1977; Agrawal *et al.*, 1977) have related observed dielectric constants of simple crystals (*e.g.* alkali halides and alkaline-earth-dihalides) to molecular polarizabilities and ultimately to the individual polarizabilities of each ion in the lattice.

The polarizabilities of individual ions are fundamental quantities, which are needed in any theoretical treatment of the ionic lattices as well as in numerous mineralogical calculations. Crystal defect analyses and calculations of diffusion coefficients are two such examples where the introduction of the polarization energy is essential. Recently Lasaga (1980) has demonstrated the existence of a large decrease in the defect formation energies for forsterite once the polarization effect is taken into account. The polarization energy can reach values up to 75% of the coulombic attractive energy in the olivine defect calculations.

Inclusion of polarization in the treatment of ionic

bonds bridges the gap between purely ionic and purely covalent bonds. A covalent bond can be viewed as an extreme polarization of the ionic charge between two ions such that the electrons are now considered to be "shared" between the atoms. This bridge between ionicity and covalency afforded by the polarization of the oxygen ions was used by Ramberg (1954) to analyze the relative stability of simple silicates. A similar concept has been invoked by Greenwood (1968).

While ionic radii have played an important role in predicting and understanding mineral structures, the influence of polarization has been generally neglected. Yet, ion polarizabilities reflect the local environment surrounding a particular ion and can afford a new understanding of ionic interactions and the character of silicates. Of course, the first basic question is whether there exists a univeral set of ion polarizabilities, which can be transferred from mineral to mineral in the same manner as ionic radii. This paper presents polarizability values for ions in a variety of minerals using experimental dielectric constant data and analyzes the additivity and universality of the ion polarizabilities.

Basic theory

The polarizability of an ion, α_1, relates the induced dipole moment on the ion, μ_i, and the total electric field acting on that ion, E_{loc}:

$$\mu_i = \alpha_i E_{loc} \tag{1}$$

The electronic polarizability of an ion, therefore, measures the susceptibility of the ion's electron density to distortion by the applied electrical field. A quantity, such as the polarizability, relating two vectors is in general a second rank tensor. However, for most ions isotropy reduces the polarizability tensor to a proportionality constant. The units of α_i, as defined in equation (1), are volume units, and it is usual to give α_i in $\mathring{A}^3$. In fact, the magnitude of the polarizability is proportional to the volume or size of the ions.

The polarization of a crystal, P, is defined as the induced dipole moment per unit volume. Therefore, if there are N crystal formula units per unit volume, the polarization can be written as,

$$P = N \, \mu_{induced} \tag{2}$$

where $\mu_{induced}$ is the induced dipole moment per crystal formula unit. If there are several ions in the crystal formula unit, P can be expressed as,

$$P = N \sum_i \alpha_i E_{loc} \tag{3}$$

summing over the ions in the formula unit and utilizing the initial relation given by equation (1). Equation (3) can be rewritten as,

$$P = N\alpha_{tot}E_{loc} \tag{4}$$

where,

$$\alpha_{tot} = \sum_i \alpha_i \tag{5}$$

Therefore, the molecular polarizability, α_{tot}, of a crystal such as a silicate can be expressed as the summation of the polarizabilities of the constituent ions in one formula unit. Karplus and Porter (1970) and Kittel (1976) provide excellent reviews of these electric field and polarization concepts.

In the presence of an electric field, the induced dipole moment in an ionic crystal may result from several mechanisms. Part of the induced dipole moment is the result of distortions of the symmetrical electronic charge distributions relative to the nucleus of each ion; this induced dipole moment defines the electronic polarizability. However, part of the induced dipole moment may also arise by the relative displacements of the entire ion from its normal lattice site; this latter induced dipole moment defines the ionic polarizability. The ionic polarizability arises from the *relative displacement* of the various ions in the crystal, which occurs because cations and anions move in opposite directions when acted upon by an electric field. Therefore, the ionic polarizability depends on the repulsive forces between nearest neighbors in the crystal. In addition, an orientation or dipolar polarizability may occur for materials possessing permanent dipoles (*e.g.*, organic crystals). A fourth mechanism, interfacial polarization, is the result of space charges, defects or inhomogeneities in the mineral. Each of these mechanisms may contribute to the total polarization of the mineral.

The electromagnetic frequency dependence of the crystal polarizability allows the experimentalist to sort out the different polarization mechanisms. At high optical frequencies (10^{16} cycles per second, Hz) only electronic distortions contribute to the polarizability. These frequencies are too great to allow any other response (*e.g.* ion displacement) to the quickly alternating applied field. If the frequency is decreased below the infrared region (10^{14} Hz),
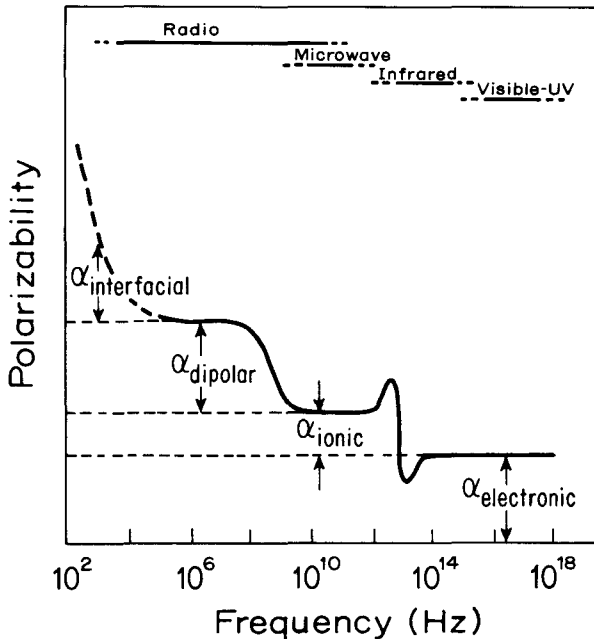
Fig. 1. Typical response of the total polarizability of a crystal as a function of electric field frequency.

displacements of the entire ions can then contribute to the total polarizability (ionic polarizability). The infrared frequency region corresponds to the vibrational frequencies of the ions in solids and hence to the rate of movement of the ions. Therefore, the moving ions can respond to an electric field which is varying more slowly than the infrared frequency. At these low frequencies, the total polarizability (*i.e.*, the sum of the electronic and ionic polarizabilities) is termed the *static* polarizability. If the applied field frequency is decreased still further to the radio wave section of the spectrum (10^3–10^6 Hz), the dipolar and interfacial polarizability responses, if present, would be observed. The dipolar polarizability is not usually present in silicate minerals. Figure 1 summarizes the dependence of the polarizability on the frequency of the electric field.

Molecular polarizabilities in crystals can be determined from dielectric data by use of the Clausius–Mosotti relation:

$$\alpha_{tot} = \frac{3V}{4\pi} \frac{\epsilon - 1}{\epsilon + 2} \qquad (6)$$

where V is the molecular volume and ϵ is the real component of the dielectric constant. Equation (6) is usually an approximation since it assumes an isotropic crystal lattice (see Appendix). The frequency dependence of α_{tot} is obtained from the

frequency dependence of ϵ. At optical frequencies the dielectric constant is the square of the optical refractive index, n, and the Clausius–Mosotti relation can be rewritten as,

$$\alpha_{tot} = \frac{3V}{4\pi} \frac{n^2 - 1}{n^2 + 2} \qquad (7)$$

This relation is known as the Lorentz–Lorenz equation. See the Appendix for the derivation of these two important equations.

Using the known silicate mineral refractive index data, the Lorentz-Lorenz relation makes it possible to obtain the electronic polarizability of silicates. Static dielectric values of silicate minerals, those obtained at infrared or microwave frequencies, will provide the combined ionic and electronic polarizability by the use of the Clausius–Mosotti relation, equation (6). From these two calculations the individual values of the ionic polarizability and the electronic polarizability of silicate minerals can be determined.

Electronic polarizabilities for minerals are easily generated because the optical refractive index is known for almost all minerals. On the other hand, there is a deficiency of single crystal static dielectric data for a variety of minerals. Reported static dielectric constants for minerals are normally obtained from capacitance measurements of polycrystalline samples of questionable purity. In addition, the precision of dielectric measuring techniques is varied. Therefore, it is not uncommon to see a wide range of static dielectric constants reported for a single mineral.

Polarizability and the additivity rule

The Clausius–Mosotti equation, equation (6), along with molar volumes and dielectric data yield the molecular polarizability of a crystal. For example, in the case of forsterite, equation (6) will give the value of $\alpha_{Mg_2SiO_4}$, where Mg_2SiO_4 is one molecule (a neutral unit) of the crystal. It is important to ask whether the molecular polarizability can be further resolved into a contribution from each of the ions in the crystal as in equation (5):

$$\alpha_{Mg_2SiO_4} = 2\alpha_{Mg^{2+}} + \alpha_{Si^{4+}} + 4\alpha_{O^{2-}} \qquad (8)$$

Unfortunately, the individual values of the polarizabilities (electronic or ionic) are not easily measured or derived. The significance or relevance of such a decomposition as in (8) derives from the possibility of obtaining a *universal* set of polarizability values

α_i. Thus $\alpha_{Mg^{2+}}$ used in equation (8) could also be used in any other silicate with octahedral magnesium ions. This universality is the tenet of the additivity rule. However the decomposition in equation (8) is also important because a solid state treatment of ionic crystals (*e.g.* Lasaga, 1980) requires the values of the individual ionic polarizabilities. Finally, if the additivity rule holds and the individual polarizabilities are transferable, we can predict the polarization behavior and dielectric constants of new materials.

This technique has been successfully utilized by Tessman *et al.* (1953) and later by Pirenne and Kartheuser (1964) for predicting the electronic polarizabilities of the alkali halides and other simple AB type crystals. The additivity rule has also been incorporated by Roberts (1949) to successfully predict the static polarizability, which includes both electronic and ionic components, for simple AB crystals. Jonker and van Santen (1947) and Roberts (1949) enjoyed similar success in applying the additivity rule utilizing component oxide polarizabilities such as in equation (9) below.

Silicate mineral polarizabilities, which have been previously avoided by the chemical physicists due to the complex crystal structure of silicates, can now be investigated utilizing the additivity rule as originally suggested by Cygan and Lasaga (1979). Silicates are a complex mixture of oxides, therefore the additivity rule can be initially written using oxide components:

$$\alpha_{mineral} = \sum \alpha_{oxides} \qquad (9)$$

For example, in the case of forsterite, the polarizability now becomes:

$$\alpha_{Mg_2SiO_4} = 2\alpha_{MgO} + \alpha_{SiO_2} \qquad (10)$$

The polarizabilities of the individual oxides can be obtained from the oxide dielectric data, and so equation (9) contains the simplest check on the additivity rule. We will concern our discussion first with the electronic polarizability. All optical refractive index values were obtained from Kerr (1977) and were averaged when reported for an anisotropic mineral. In the vast majority of cases the average was very close to all the refractive indices of the anisotropic mineral. The molecular volume data was obtained from Robie *et al.* (1967). As an example, forsterite, Mg_2SiO_4, can be related to the two simple oxides MgO and SiO_2. The electronic polarizabilities obtained for these minerals are

MgO–1.79Å^3, SiO_2–2.86Å^3 and Mg_2SiO_4–6.35Å^3. Introducing the simple oxide values into equation (10), the predicted optical polarizability for forsterite is 6.44Å^3, which agrees well with the actual measured value (6.35Å^3). The static polarizability values for MgO and SiO_2 are respectively 3.32Å^3 and 4.84Å^3 utilizing the Clausius–Mosotti equation with the dielectric data of Westphal and Sils (1972). Inserting these values into equation (10) produces a predicted static polarizability for forsterite of 11.48Å^3 which is in excellent agreement with that obtained for the pure mineral using either the dielectric data of Olhoeft (1979), (11.44Å^3; polycrystalline sample) or that obtained in our laboratories (11.55Å^3; single crystal, average for three orientations). Note that in each case the predicted polarizability agrees with the measured value within the approximate 5% uncertainty associated with the dielectric measurements for each value. It is noteworthy also to emphasize the difference between the optical and static values. As mentioned earlier, the higher static polarizability is the result of contributions from *both* ionic and electronic polarizations, whereas the lower optical polarizability is generated from only the electronic response. It is the static polarizability which is of importance in determining the crystal energy due to the polarization from point defects (Lasaga, 1980).

Table 1 presents polarizability data for numerous binary oxides at both static and optical frequencies as calculated from the available dielectric data of Keller (1966), Westphal and Sils (1972), Young and Frederikse (1973) and Olhoeft (1979) and the refractive index data of Weast (1971) and Kerr (1977). Assuming the additivity rule, these values are then utilized to predict the static and optical polarizabilities of several silicate minerals. A comparison of predicted and measured polarizabilities for silicates at 25°C is given in Table 2. Reasonable agreement occurs for almost every silicate mineral.

Ultimately, the additivity rule must be tested using *ion* polarizabilities. The question now is whether one set of these ion polarizabilities can adequately predict all the various molecular polarizabilities of minerals, including those of the oxides. Table 3 provides a listing of the best individual electronic and static polarizabilities. The table was constructed by examining the optical and static polarizabilities of over 40 rock-forming silicates and their corresponding oxide minerals. Due to the ubiquitous presence of oxygen in these compounds, we have optimized the oxygen anion polarizability

Table 1.   Polarizabilities of oxides at 25°C in units of Å^3

Oxide	α_{opt}	α_{stat}
Li_2O.	2.13	-
BeO	1.31	2.15
MgO	1.79	3.32
Al_2O_3	4.19	7.70
SiO_2	2.86	4.84
CaO	2.97	5.20
TiO_2	5.13	7.18
Cr_2O_3	7.49	9.04
MnO	2.84	4.46
FeO	2.97	3.89
Fe_2O_3	8.87	10.67
NiO	2.64	3.41
Cu_2O	6.54	6.39
ZnO	2.88	4.47
GeO_2	3.58	4.51
As_2O_3	8.30	-
SeO_2	4.58	-
SrO	3.97	7.03
ZrO_2	4.64	7.62
CdO	3.96	-
Sb_2O_3	11.48	-
BaO	5.24	9.74
HgO	4.86	-
K_2O*	5.27	10.91
Na_2O*	3.59	7.63

*from individual ions (e.g. 2K + O)

Table 2.   Silicate mineral polarizabilities as predicted from oxide additivity rule at 25°C in units of Å^3

Mineral	Formula	Optical		Static	
		Pred.	Meas.	Pred.	Meas.
foresterite	Mg_2SiO_4	6.44	6.35	11.48	11.55
fayalite	Fe_2SiO_4	8.80	8.33	12.62	12.12
orthoclase	$KAlSi_3O_8$	13.31	13.11	23.83	25.98
enstatite	$MgSiO_3$	4.65	4.56	8.16	7.96
diopside	$CaMgSi_2O_6$	10.48	9.85	18.20	18.78
tephroite	Mn_2SiO_4	8.54	8.26	13.76	14.45
phenakite	Be_2SiO_4	5.48	5.46	9.14	8.51
willemite	Zn_2SiO_4	8.62	8.08	13.78	14.35
monticellite	$CaMgSiO_4$	7.62	7.52	13.36	14.54
rhodonite	$MnSiO_3$	5.70	5.62	9.30	10.45
zircon	$ZrSiO_4$	7.50	7.55	12.46	11.67
hedenbergite	$CaFeSi_2O_6$	11.66	10.95	18.77	22.89
jadeite	$NaAlSi_2O_6$	9.61	8.84	17.35	17.96
leucite	$KAlSi_2O_6$	10.45	10.46	18.99	23.09
nepheline	$NaAlSiO_4$	6.75	6.71	12.51	13.46
microcline	$KAlSi_3O_8$	13.31	13.23	23.83	26.61
albite	$NaAlSi_3O_8$	12.47	12.25	22.19	26.37
anorthite	$CaAl_2Si_2O_8$	12.88	13.35	22.58	26.49
almandine	$Fe_3Al_2Si_3O_{12}$	21.68	20.07	33.89	23.93
spessartine	$Mn_3Al_2Si_3O_{12}$	21.29	20.02	35.60	32.20
sillimanite	Al_2SiO_5	7.05	7.36	12.54	15.22
beryl	$Be_3Al_2Si_6O_{18}$	25.28	26.32	43.19	53.02
sphene	$CaTiSiO_5$	10.96	10.42	17.22	19.18
wollastonite	$CaSiO_3$	5.83	5.62	10.04	11.35

the predicted and measured polarizabilities for the major silicates as generated by this technique. Agreement among the values is reasonable for each case at both optical and infrared frequencies.

A refinement of the individual ion polarizabilities would require the analysis of the effect of coordination number changes of the ion just as is done with ionic radii. This particular effect may be difficult to analyze in light of the present lack of precision in reported dielectric measurements especially at low frequencies.

to obtain a universal table capable of predicting mineral polarizabilities.

There are some important features to emphasize in Table 3. The electronic polarizability measures the distortion of the ion's electron cloud. Ions with large electron clouds, which have their charge spread over a large volume, should distort more easily. As a consequence, anions tend to have much larger polarizabilities than cations in Table 3. Because the purely ionic bond was created by the transfer of charge from cations to anions, the much larger anion polarizability enables some of this charge to be returned or "shared" with the cations. In this manner, polarization takes into account bonds which are more "covalent", such as between a small cation and a large anion. Table 3 also shows that the cation polarizabilities increase with increasing ion size and decreasing charge.

The total polarizability of a silicate mineral at either optical or static frequencies can now be predicted by the additivity rule utilizing the *individual* ion polarizabilities in Table 3. Table 4 compares

Table 3.   Polarizabilities of major individual ions at 25°C in units of Å^3

Ion	α_{opt}	α_{stat}
O^{2-}	1.31	2.37
Si^{4+}	0.08	0.10
Al^{3+}	0.13	0.29
Mg^{2+}	0.48	0.94
Ca^{2+}	1.66	2.83
Mn^{2+}	1.53	2.08
Na^+	1.14	2.63
K^+	1.98	4.27
Cs^+	2.12	2.78
Be^{2+}	0.05	0.14
Li^+	0.03	0.10

Table 4. Silicate mineral polarizabilities as predicted from ion additivity rule at 25°C in units of Å^3

Mineral	Formula	Optical		Static	
		Pred.	Meas.	Pred.	Meas.
forsterite	Mg_2SiO_4	6.28	6.35	11.46	11.55
monticellite	$CaMgSiO_4$	7.46	7.52	13.35	14.54
spessartine	$Mn_3Al_2Si_3O_{12}$	20.81	20.02	35.56	32.20
diopside	$CaMgSi_2O_6$	10.16	9.85	18.19	18.78
rhodonite	$MnSiO_3$	5.54	5.62	9.29	10.45
wollastonite	$CaSiO_3$	5.67	5.62	10.04	11.35
orthoclase	$KAlSi_3O_8$	12.83	13.11	23.82	25.98
albite	$NaAlSi_3O_8$	11.99	12.25	22.18	26.37
anorthite	$CaAl_2Si_2O_8$	12.56	13.35	22.57	26.49
enstatite	$MgSiO_3$	4.49	4.56	8.15	7.96
tephroite	Mn_2SiO_4	8.38	8.26	13.74	14.45
phenakite	Be_2SiO_4	5.42	5.46	9.86	8.51
jadeite	$NaAlSi_2O_6$	9.29	8.84	17.34	17.96
leucite	$KAlSi_2O_6$	10.13	10.46	18.98	23.09
nepheline	$NaAlSiO_4$	6.59	6.71	12.50	13.46
beryl	$Be_3Al_2Si_6O_{18}$	24.47	26.32	44.26	53.02

Preliminary high temperature dielectric measurements have been performed on single crystals of several silicate minerals in order tò document the polarizability change at reasonable geologic conditions. Although the experimental work is incomplete at this time, the results suggest that the additivity rule holds at temperatures approaching 1000°C, at least for olivine.

A caution should be expressed with respect to the application of the mineral dielectric and refractive index data. Polarizabilities were calculated with the assumption that the minerals possessed a high degree of symmetry. This assumption was made in the derivation of both the Clausius–Mosotti and the Lorentz–Lorenz equations. Therefore we are restricted in applying the polarizabilities and polarizability additivity rule to minerals whose anisotropy is small. Most of the minerals and compounds that are dealt with in this study have much less than 5% anisotropy in the optical region. All such minerals required averaging of their dielectric (when presented for a single crystal) and refractive index values before the determination of their polarizabilities.

Conclusion

The Clausius–Mosotti and Lorentz–Lorenz equations can be used to obtain molecular polarizabilities for a variety of minerals. These polarizabilities depend on the frequency of the electric field; in particular we have tabulated both the electronic and static polarizabilities of these minerals. Since the polarizabilities of *individual* ions are needed in many theoretical treatments, a table of ion polariza-

bilities was then constructed. Use of this table shows that the molecular polarizabilities of minerals can be closely approximated by summing over the values of a *universal* set of ion polarizabilities. These ion polarizabilities, then, are common to the various minerals just as the universal set of ionic radii. The feasibility of these universal polarizability values simplifies their use in solid state treatments of minerals.

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Appendix: derivation of the Clausius–Mosotti and Lorentz–Lorenz polarizability relations

The dielectric constant, ϵ, of a material is defined as,

$$\epsilon = 1 + 4\pi \ (P/E) \tag{A1}$$

where E is the applied electric field and P is the polarization. Solving for P, we obtain,

$$P = \frac{E}{4\pi} (\epsilon - 1) \tag{A2}$$

By introducing this polarization into the original polarizability relation, equation (4), we obtain after rearranging,

$$\alpha = \frac{\dfrac{E}{4\pi}(\epsilon - 1)}{N \ E_{loc}} \tag{A3}$$

Lorentz (1909) demonstrated that for cubic or highly symmetric crystal lattices,

$$E_{loc} = E + \frac{4\pi}{3} P \tag{A4}$$

where E_{loc} is the total effective electric field which includes the applied electric field plus the field generated by the polarization of the material. It is assumed that there is negligible contribution of the induced dipoles interacting among each other in the material. By substituting equation (A2) for P into equation (A4) and then the expression for E_{loc} into equation (A3) we arrive, after rearranging, at the Clausius–Mosotti relation:

$$\alpha = \frac{3}{4\pi N} \frac{\epsilon - 1}{\epsilon + 2} = \frac{3V}{4\pi} \frac{\epsilon - 1}{\epsilon + 2} \tag{A5}$$

(*viz.* equation 6) where V is the molecular volume. The Lorentz–Lorenz polarizability relation, to be used at optical frequencies, is easily obtained knowing,

$$\epsilon = n^2 \tag{A6}$$

where n is the refractive index of the concerned material. This provides us with the following optical polarizability equation (*viz.* equation 7):

$$\alpha = \frac{3V}{4\pi} \frac{n^2 - 1}{n^2 + 2} \tag{A7}$$