

Electronic polarizability of oxygen and optical basicity of single component oxides for nonlinear optics

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비선형광학을 위한 단성분 산화물에서의 산소의 전자분극률과 광학 염기도

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Abstract Average oxygen polarizabilities and optical basicity of single component oxides has been estimated on the basis of two different properties such as refractive index and energy gap in order to design the third-order nonlinear optical materials. We made an attempt to compare numerically the data of average oxygen polarizabilities and optical basicity from the two different properties by introducing the Lorentz-Lorenz equation and Duffy's semiempirical formular. For the first time, a good correspondence can be observed the average oxygen polarizabilities and optical basicity data obtained by independent initial quantities, respectively.

요약 3차 비선형광학 재료를 설계하기 위해 단성분 산화물에서의 산소의 평균 전자분극률과 광학 염기도를 굴절율, 에너지 갭의 각기 다른 물성을 통해 산출하였다. Lorentz-Lorenz 식과 Duffy의 반실험식을 도입하여 산소의 평균 전자분극률과 광학 염기도를 두가지 다른 물성으로부터 계산하여 비교하였다. 처음으로 독립적인 초기값에서 계산한 각각의 산소의 평균 전자분극률과 광학 염기도 사이에 좋은 상응관계가 있음을 확인하였다.

1. Introduction

Nonlinear optical properties of materials have steadily increased in importance since the invention of high-power laser and have recently stimulated great interest because of their high potential for optical functional devices [1]. For instance, optical modulators, optical switches, fiber lasers and optical memories were demonstrated using optical nonlinearity. For this purpose, materials of higher optical nonlinearity have to be seek for or designed on the basis of the correlation of optical nonlinearity with some other electronic properties which are well understood and easily accessible.

Since the optical nonlinearity is caused by electronic polarization of the material upon exposure to intensive light beam, linear polarizability including the oxide polarizability ($\alpha_{o^{2-}}$) is one of the most important properties which govern the nonlinear response of the materials.

The oxygen polarizability is closely related to many macro- and microscopic physical and chemical properties of substances such as the optical nonlinearity, optical basicity, optical absorption of transition elements, ferroelectricity and refractivity. Therefore, it will be valuable to estimate the value of oxygen polarizability. On the other hand, optical basicity as proposed by Duffy and Ingram [2] is used as a measure of acid-base property of oxides. The optical basicity can be experimentally determined, however the application of the method is rather limited. Therefore, it is desirable to derive the

value for many single component oxides based on the similarity of element.

In this paper, average oxygen polarizabilities and optical basicity of many single component oxides has been estimated on the basis of refractive index (n) and energy gap (E_g). We made an attempt to compare numerically the data of average oxygen polarizabilities and optical basicity from the two different properties.

2. Electronic polarizability of oxygen ions based on the refractive index

At optical frequencies where the refractive index is measured, the dielectric constant arises almost entirely from electronic polarizability is expressed by the following expression,

$$\alpha_e = \frac{e^2}{4\pi^2 m} \cdot \sum_i i \frac{f_i}{v_i^2 - v^2} \quad (1)$$

where e is the electronic charge, m is the electronic mass, f_i represents the oscillator strength, v_i is the electronic frequency and v is the frequency of the incident photons. According to Maxwell's theory, the relationship $n_{\lambda \rightarrow \infty}^2 = \epsilon$ holds for infinity long waves. The Clausius-Mossott relation is expressed by,

$$\begin{aligned} \frac{4\pi N\alpha}{3M} &= \frac{\epsilon - 1}{\epsilon + 2} = \frac{n^2 - 1}{n^2 + 2} \\ &= N \frac{e^2}{12\epsilon_0\pi^2 m} \cdot \sum_i \frac{f_i}{v_i^2 - v^2} \end{aligned} \quad (2)$$

where N is the number of electrons in the solid. As indicated in eq. (2), refractive

index depends upon the composition of an optical materials; the more polarizable the outer electrons, the higher the refractive index. When eq. (2) is expressed in terms of the specific mass and density, the electronic polarizability of simple oxide, A_pO_q can be calculated through the following expression,

$$R_m = \frac{n^2 - 1}{n^2 + 1} \cdot \frac{M}{d} = \frac{n^2 - 1}{n^2 + 1} \cdot V_m \quad (3)$$

where n is linear refractive index, d is the density, M is the molecular weight and V_m is the molar volume. By introducing Avogadro number (N_A), the molar refractivity (R_m) can be expressed as a function of polarizability (α_m) of the molecule,

$$R_m = \frac{4}{3} \pi \cdot \alpha_m \cdot N_A \quad (4)$$

with α_m in (\AA^3) this equation can be transformed to,

$$R_m = 2.52 \cdot \alpha_m \quad (5)$$

Assuming that R_m and α_m are additive quantities as,

$$R_m = pR_i + qR_{o^{2-}} = 2.52(p\alpha_i + q\alpha_{o^{2-}}) \quad (6)$$

where R_i is the ionic refractivity of the cation, $R_{o^{2-}}$ is the ionic refractivity of the oxygen ion, α_i is the polarizability of the cation and $\alpha_{o^{2-}}$ is the polarizability of the oxygen ion. The ionic refractivity of the oxygen ion can be calculated by subtracting the ionic refractivity of the respective cations from the molar refraction. This approach has been ap-

plied by Kordes [3] to Li_2O , MgO , CaO , SrO , BaO , ZnO , CdO , B_2O_3 , SiO_2 , SnO_2 and TiO_2 Tessman and Shockley [4] to Li_2O , MgO , CaO , SrO , BaO , ZnO , CdO , Al_2O_3 , SiO_2 , SnO_2 , PbO and TiO_2 and Duffy [2] to Li_2O , MgO , CaO , SrO , BaO , B_2O_3 , Al_2O_3 , SiO_2 , TiO_2 and ZrO_2 . For example oxides with common formula A_pO_q , we have calculated the values of $\alpha_{o^{2-}}$ (n) using the following expression on the basis of equations (1)-(6),

$$\alpha_{o^{2-}}(n) = \left[\frac{V_m}{2.52} \cdot \frac{(n^2 - 1)}{(n^2 + 2)} - p\alpha_i \right] / q \quad (7)$$

where p and q are the number of the cations and oxygen ions in the chemical formula A_pO_q , respectively. The polarizabilities of the cations was obtained using the values of calculated ionic refraction shown by Kordes [3], except those for Cu^{2+} , Sb^{3+} , Bi^{3+} and Te^{4+} for which the data was cited in the references [5,6]. The data of the refractive index, molecular weight and density were taken from the references [7-11].

The calculated values of the polarizability of oxygen ions as a function of refractive index are plotted in Fig. 1. In this study, the values of $\alpha_{o^{2-}}$ (n) for ten oxides of Ga, Y, Ge, Sb, Te, Mo, W, Mn, Fe and Ni are added over these listed by Kordes, Tessman and Shockly, and Duffy. It is seen that there is a general trend in which $\alpha_{o^{2-}}$ (n) increases with increasing refractive index, but the scattering of the data points is pretty large, indicating that no direct relation is found between $\alpha_{o^{2-}}$ and (n). This is evident from eq. (7) which shows that the polarizability of the oxygen ion depends not

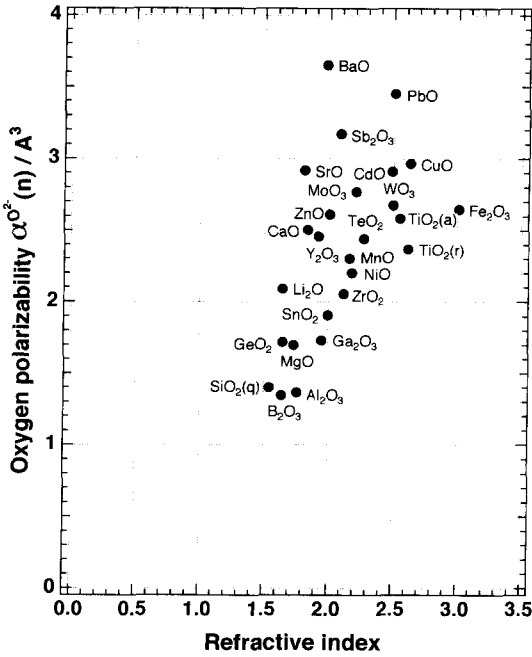


Fig. 1. The relationship between the polarizability of oxygen ions as a function of refractive index ($\alpha_{O^{2-}}(n)$) and linear refractive index.

only on the refractive index but also on the molar volume and polarizability of cation.

3. Electric polarizability of the oxygen ion based on the energy gap

Discussion concerning the relationship between polarizability and onset of metallization have indicated that if the molar volume is below a certain critical value, then a polarization occurs at which point the valence electrons become itinerant and metallic conduction occurs. Equation (2) indicates that when R_m/V_m approaches unity, ϵ becomes

infinite. In other words, a material is nonmetallic for R_m/V_m less than unity, but is metallic when $R_m/V_m = 1$. In the tight binding approach to the band theory [12, 13], the onset of metallization is when the valence band and conduction band merge into each other. Since the valence band is composed essentially of anion orbitals and the conduction band of cation orbitals for a binary compound like a simple oxide, the merging of the two bands into each other can be thought of as the stage at which the minimum energy of transferring an electron from the anion to cation becomes zero. In terms of the polarizability approach, this is when the electrons become itinerant and $R_m/V_m = 1$. Thus, for simple oxides, the nonmetal to metal transition is approached more closely as the energy E and the quantity $(1 - R_m/V_m)$ both approach zero. Duffy plotted $\sqrt{E_g}$ against $(1 - R_m/V_m)$ for a large number of simple oxides, obtaining a good linear correlation between these two distinct quantities. From the plots he proposed the relation,

$$E_g = 20(1 - R_m/V_m)^2 \quad (8)$$

Since this equation is valid for a large number of oxides, we use the equation to estimate the polarizability of the oxygen ion from the energy gap. The expression of eq. (8) gives the explicit expression of R_m ,

$$R_m = V_m(1 - \sqrt{E_g/20}) \quad (9)$$

Substitution of eq. (9) in eq. (6) gives

polarizability, $\alpha_{O^{2-}}(E_g)$ of a simple oxide with common formula A_pO_q .

$$\alpha_{O^{2-}}(E_g) = \left[\frac{V_m}{2.52} \cdot \left(1 - \sqrt{\frac{E_g}{20}} \right) - p\alpha_i \right] / q \quad (10)$$

This equation indicates that the polarizability of the oxygen ion in a simple oxide can be calculated from the data of the energy gap, the molar volume and the polarizability of the cation.

The energy gap data for oxides of Cu, Mg, Ca, Sr, Ba, Zn, Cd, Ga, In, Sc, Ge, Sn, Ti, Ce, Sb, Mo, Mn, Fe, Co and Ni are cited from ref. 12. Those for Pb, Zr, Bi, V, Nb, Ta and W are cited from ref. 14. The energy gap data for SiO_2 and TeO_2 are cited from ref. 15 and 16 respectively. The relationship between the obtained $\alpha_{O^{2-}}(E_g)$ and the energy gap are plotted in Fig. 2. It can be seen that generally $\alpha_{O^{2-}}(E_g)$ increases with decreasing energy gap, but with a large scattering.

The calculated values of $\alpha_{O^{2-}}(n)$ are plotted against $\alpha_{O^{2-}}(E_g)$ in Fig. 3. It is remarkable that a good relation exists between these two distinct quantities. The relationship between the data for the refractive index and the energy gap E_g of numerous simple oxides are presented in Fig. 4. It can be seen that refractive index decrease with increasing of energy gap. The direct dependence between these different quantities is one complementary argument for the possibility of an use of energy gap for calculation of the oxygen ion polarizability of the solids.

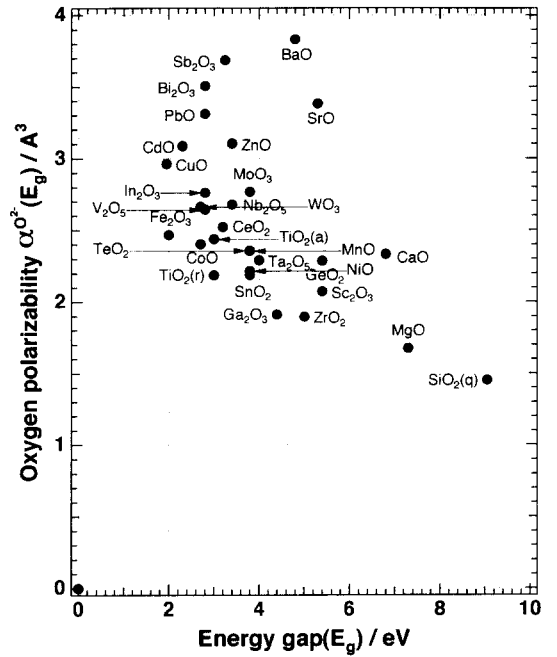


Fig. 2. The relationship between the polarizability of oxygen ions as a function of energy gap ($\alpha_{O^{2-}}(E_g)$) and energy gap.

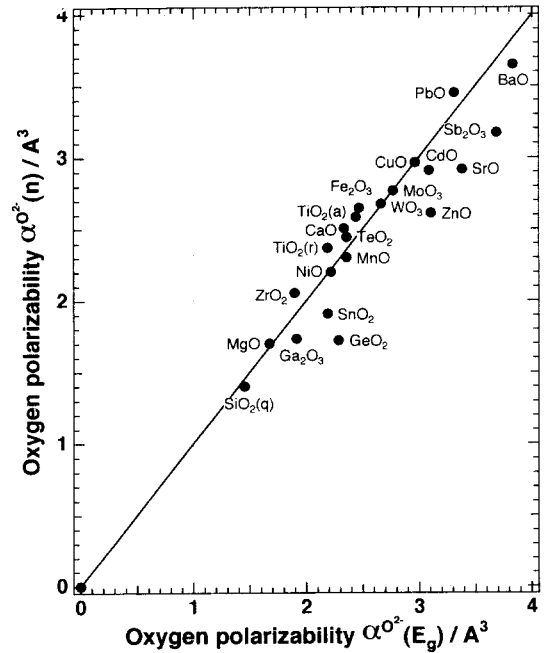


Fig. 3. The relationship between the calculated ($\alpha_{O^{2-}}(n)$) and the ($\alpha_{O^{2-}}(E_g)$).

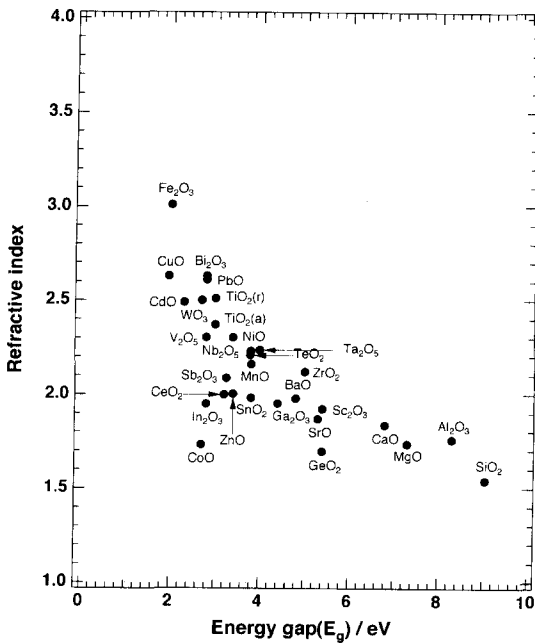


Fig. 4. The relationship between the linear refractive index and the energy gap.

4. Optical basicity of the oxides

Duffy has established the following relation between the optical basicity and electronic polarizability of the oxygen ion [17],

$$A = 1.67 \left(1 - \frac{1}{\alpha_{O^{2-}}} \right) \quad (11)$$

It has concluded that this relationship represents a general tendency toward the increase of the oxygen polarizability with increasing the optical basicity. Equation (11) was used by us for calculation of the optical basicity of the oxides on the basis of obtained the values of $\alpha_{O^{2-}}$ from the refractive index and energy gap. New data for the oxides of Cu, Zn, Cd, Ga, In, Sc, Y, Sn, Ce, Sb, Bi, V, Nb, Ta, Te, Mo, W, Mn, Fe, Co, Ni are obtained. The comparatively relationship

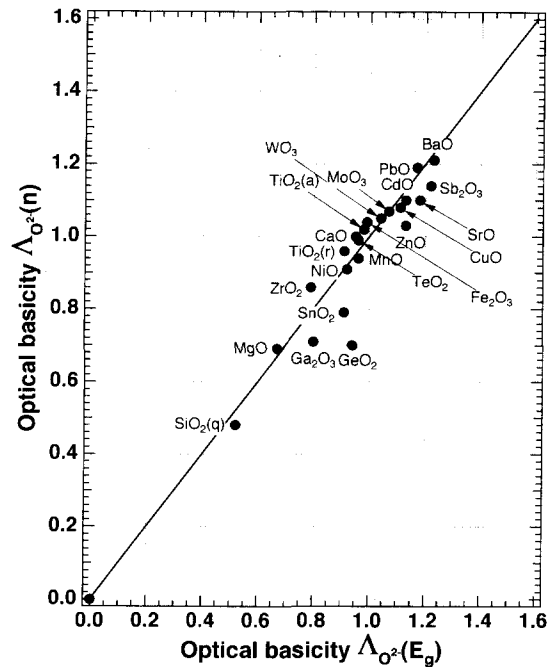


Fig. 5. The relationship between the optical basicity calculated from the refractive index ($\Lambda_{O^{2-}}(n)$) and the optical basicity obtained by the energy gap ($\Lambda_{O^{2-}}(E_g)$) of the oxides.

between the optical basicity calculated from the refractive index and the optical basicity obtained by the energy gap of the oxides is plotted in Fig. 5. A good correspondence can be observed between the optical basicity data obtained by independent initial quantities.

5. Discussion

The polarizabilities of oxygen ion in simple oxides can be classified into the three oxides groups. The first group includes SiO_2 , B_2O_3 , Al_2O_3 , GeO_2 , Ga_2O_3 , MgO with low pola-

rizability of oxygen ion in 1 to 2 Å³ range. These are mainly light *p*- and *s*-block elements. The cations possess a small polarizability and large positive charge. Their unit field strength are very large [18]. They exert a strong influence on the electron charge cloud of the oxygen ion.

The second group consists mainly of *d*-transition oxides with oxygen polarizability between 2 and 3 Å³. The relatively high polarizability of the oxygen ion can be attributed to the existence of empty *d*-states of the corresponding cation [19]. On the other hand, the high coordination number toward the oxygen ion in transition oxides (usually 6) and very often the presence of asymmetric metal-oxygen polyhedra decrease the unit field strength of the transition cation. This leads to decreasing of the polarizing effect of the cation on the average oxygen ion. It is of significance that the cation polarizability by Kordes of the transition elements takes intermediate place in relation to cations of the first and third groups in the present classification. The values of the oxygen polarizability in 2 to 3 Å³ range determine the value of the optical basicity for the transition oxides around unit near to that of CaO. This is in good agreement of the previously results of Duffy [20] for TiO₂ and ZrO₂.

The oxides of Cd²⁺, Pb²⁺, Ba²⁺, Sb³⁺ and Bi³⁺ are presented in the third group with oxygen polarizability above 3 Å³. These are oxides of heavy *s*- and *p*-block elements and their covalent bond radii is large (1.41 ~ 1.98 Å). The magnitude of cation unit field

strength is very small in the same order as alkaline-earth cations. Meanwhile, these cations possess very high polarizability. On the other hand, it is interesting to notice that Pb²⁺, Sb³⁺, Bi³⁺ and Te⁴⁺ ions possess lone pair in the valence shells. According to Gillespie [21], a repulsion exists between the different electron pairs in the coordination polyhedra of the cation. It is known that the repulsion of the bond pair-bond pair is smaller than that of the bond pair-lone pair. This may lead to an additional relaxation of the cation polarizing effect on the oxide ion. Since the distance of the cation-lone pairs increases from Pb²⁺ (1.16 Å) to Sb³⁺ (1.18 Å) and Te⁴⁺ (1.26 Å) [22], the repulsion of the bond pair-bond pair decreases in the same order of magnitudes and resulting in an increases of the polarizing effect of the cation. This assumption may be supported by the decreases of the distance M-O_{ax} (axial bonds) and M-O_{eq} (equatorial bonds) from PbO (2.22 Å ; 2.19 Å) to TeO₂ (2.09 Å ; 1.92 Å). This may explain the polarizability of the oxygen ion in TeO₂ which is smaller than those for PbO, CdO, Sb₂O₃ and Bi₂O₃. On the basis of these result, the important point is that the polarizing effect of the cation and oxygen relating to unit structure is a serious parameter in order to design the nonlinear optical materials with high nonlinearity.

6. Conclusion

The average polarizability of the oxygen

ion has been determined in 34 single oxides on the basis of refractive index and energy gap data. The optical basicity of the oxides has been calculated by introducing the Duffy's theory. A good correspondence can be observed the average oxygen polarizabilities and optical basicity data obtained by independent initial quantities, respectively. The single oxides have been classified into three group on the basis of the polarizability of the oxygen ion and specific characteristics of structural unit.

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