Nonlinear Optical Constants of Superionic Conductors -A Study from the Bond Orbital Theory-

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According to the bond fluctuation model of superionic conductors, the polarizability of a material that exhibit high ionic conductivity must be large. That is, the model predicts that ion conducting materials must have large values of optical constants. This prediction has been confirmed recently, through a comparative study of the nonlinear optical constants of ion conducting and non-conducting glasses. In the present report, the values of the nonlinear optical constants $\chi^{(3)}$ of R_2O-B_2O_3 (R=Rb, Cs, Ag) glasses have been estimated by using the bond orbital theory. For the Rb_2O-B_2O_3 and Cs_2O-B_2O_3 glasses, a good agreement between the calculated and the measured values has been found. On the other hand, for the Ag_2O-B_2O_3 system, a deviation was observed. Such a disagreement has been explained by taking into account the contribution of d-electrons of the Ag ions, which plays also a fundamental role in the ion transport mechanism.

KEYWORDS: superionic conducting glasses, nonlinear optical constants, bond orbital theory

1. Introduction

Superionic conductors are known for their high ionic conductivity that exhibit in the solid phase. In some cases, the magnitude of the ionic conductivity exceeds those observed in the liquid phase. Superionic conductors have attracted the interest of many researchers from both, academic and applied points of views. The academic interest arises from the fact that the mechanism of ion transport is not well understood yet. The bond fluctuation model[1)] explains the ionic conduction from a chemical bond point of view. According to the model, in superionic conductors, the local changes of the electronic cloud distribution are induced easily as events of lattice dynamical processes. The bond fluctuations occur more frequently in materials with intermediate covalent-ionic bonds. A field of forces to move the ions originates from the instability of the bonding. The local fluctuation of the bonding can trigger the movement of other ions that surround the fluctuating site. The model predicts that superionic conductors should have high electronic polarizability. Based on this background, a new field of research, named “Photoionics” was initiated. The aim is to explore the interrelation between the optical property and the ionic diffusion in the materials. As a first step towards photoionics, the interrelation between the ionic conduction and the nonlinear optical phenomena has been studied. In a recent work[2)] a preliminary study on the relationship between the ionic conductivity and the nonlinear optical constants in glasses were performed. There, it has been found that glasses with high ionic conductivity show large nonlinear optical properties in accord with the prediction of the bond fluctuation model. In order to understand the physical background of the finding, in the present report, the values of the third-order susceptibility $\chi^{(3)}$ for R_2O-B_2O_3 (R=Rb, Cs, Ag) glasses is estimated by using the bond orbital theory[3)]. The analysis supports the idea that fast ionic diffusion is related with large nonlinear optical constants.

2. Calculation for R_2O-B_2O_3 system (R=Rb, Cs, Ag)

The third-order susceptibility $\chi^{(3)}$ has been considered in many theories. Among these, there is a theory proposed by Lines, which is based on the bond orbital theory.

According to Lines’s approach[4)], $\chi^{(3)}$ is given by

$$\chi^{(3)} = \frac{25}{3\pi}\frac{f_L^3 d^2 (n^2-1)E_0^6}{(E_0^2-\hbar^2\omega^2)^4}\times 10^{-13} esu, \tag{1}$$

where d is the average bond length, $f_L=(n^2+2)/3$ is the Lorentz local-field factor, n is the long-wavelength limit of the refractive index, and E_0 is the oscillator energy. In the present report, as a first approximation, it is assumed that the value of the bond length d is the average of R-O and B-O bonds in BO_4 and BO_3. For the evaluation of $\chi^{(3)}$, the values of E_0 and n obtained from ref. 5 and d obtained from ref. 6 were used.

Fig. 1 shows a comparison between the calculated and the measured values of $\chi^{(3)}$. The chemical compositions of the data points are given in Table I. Fig. 1, indicates that the agreement between the calculated and the measured values for Rb_2O- and Cs_2O-B_2O_3 glasses are good. On the other hand, for the Ag_2O-B_2O_3 glasses, deviations are observed. In addition, for these systems, the experimental values are larger than the calculated ones. What does this behavior mean? The interesting point that must be noted is that the Ag_2O-B_2O_3 system is a material that exhibits high ionic conduction. This peculiar characteristic has been already

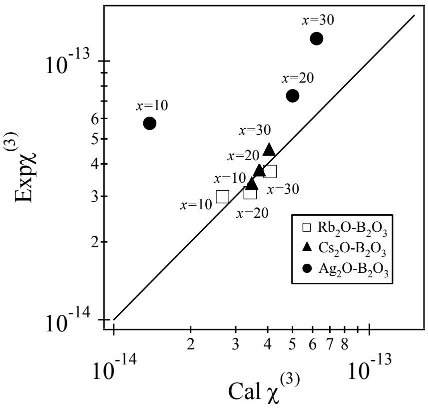

Fig. 1. Calculated and measured values of the nonlinear optical constants for xR_2O-$(100-x)B_2O_3$ glasses.

Table I. Calculated and measured values of the nonlinear optical constants for some glasses.

	$\chi^{(3)}\times10^{-14}$ (esu)	
Glasses	Cal	Exp[5)]
$10Rb_2O$-$90B_2O_3$	2.66	2.99
$20Rb_2O$-$80B_2O_3$	3.42	3.1
$30Rb_2O$-$70B_2O_3$	4.08	3.74
$10Cs_2O$-$90B_2O_3$	3.47	3.31
$20Cs_2O$-$80B_2O_3$	3.71	3.73
$30Cs_2O$-$70B_2O_3$	4.05	4.48
$10Ag_2O$-$90B_2O_3$	1.38	5.74
$20Ag_2O$-$80B_2O_3$	5.01	7.34
$30Ag_2O$-$70B_2O_3$	6.22	12.2

pointed out in our previous preliminary work.

3. Results

Why the $\chi^{(3)}$ of Ag_2O-B_2O_3 glasses deviates from the expected theoretical value? This question will be considered in the following subsection by analyzing the factors that influences the value of $\chi^{(3)}$.

3.1 Factors determining the optical constants

According to Wemple[7)], the refractive index n is given by

$$n^2-1=\frac{E_dE_0}{E_0^2-(\hbar\omega)^2}, \qquad (2)$$

$$E_d=\beta N_cZ_aN_e, \qquad (3)$$

where E_d is the dispersion energy, N_c is the coordination number of the cation, Z_a is the formal chemical valence of the anion and N_e is the total number of valence electrons per anion. β is a constant that depends on the bonding character of the materials ($\beta\approx0.26$ eV for ionic materials, $\beta\approx0.37$ eV for covalent materials). Table 2 shows the calculated values of E_d for R_2O-B_2O_3 glasses estimated through Eq. (2) by using the experimental data of n[5)]. It is noted that Ag_2O-B_2O_3 glasses have large values of E_d. According to Eq. (2), the large value of E_d results in the large value of n. Concerning the Ag_2O-B_2O_3 system, E_d exhibits a minimum at the composition of x=20. It is interesting to note that in the same composition range, the average bond length of Ag-O exhibit a peaked behavior[6)]. It is quite probable that these two behaviors are correlated.

It is known that the Ag-O bonds in a Ag_2O-B_2O_3 glass forms p (anion)-d (Ag) hybridization[8)]. In this case, the d-electrons are included in the total number of electrons N_e. Therefore, N_e in Ag_2O-B_2O_3 is larger than that in Cs_2O- and Rb_2O-B_2O_3. N_e is 8 in alkali halides, 18 in copper halides and 14 in silver halides[9).] In these Ag-compounds, with the exception of AgF, the d-level energy lies 2 to 4 eV below the anion p-level and the hybridization is less strong than in copper halides. Therefore, it is not surprising that Ag halides have smaller N_e than Cu halides. That is, the increase of E_d in Ag_2O-B_2O_3 arises from the increased value of N_e through the consideration of d-electrons of Ag.

Table II. Dispersion energy for some glasses.

R	Rb	Cs	Ag
Glasses	E_d (eV)	E_d	E_d
$10R_2O$-$90B_2O_3$	9.79	8.47	18.00
$20R_2O$-$80B_2O_3$	10.25	9.41	14.10
$30R_2O$-$70B_2O_3$	10.25	10.22	16.60

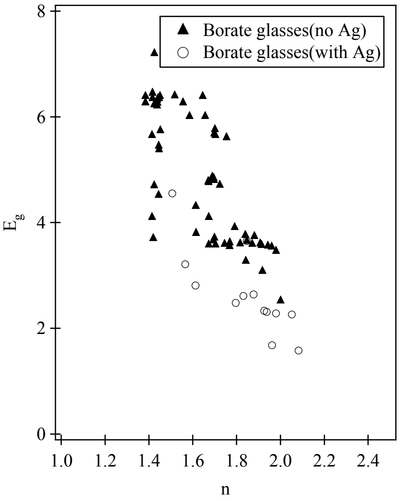

Fig. 2. The relation between the refractive index n and the energy gap E_g in some borate glasses. Triangles are glasses without silver. Circles are glasses contain silver. Experimental data are taken from ref. 10.

The oscillator energy E_0 is defined as the transition energy from the bonding orbital to the anti-bonding orbital[7)]. Therefore, the oscillator energy E_0 and the energy gap E_g are intimately related. In simple systems such as C, Si, etc., E_0 is approximated as $E_0\approx E_g$. Fig. 2 shows the correlation between the refractive index and the energy gap in some glasses. From Fig.2, it is noted that glasses with low values of energy gaps have large values of refractive indexes. E_g and n are related by the so-called Moss equation[11)],

$$nE_g^4=const. \qquad (4)$$

The low values of E_g in Ag_2O-B_2O_3 glasses are related with the p-d hybridization, which also results in the increase of the refractive index and the decrease of oscillator energy. Fig. 3 shows the relation between the energy gap and the oscillator energy in R_2O-B_2O_3 glasses. It is noted that the oscillator energy in Ag_2O-B_2O_3 glasses is sensitive to the composition and that it increases with the energy gap. On the other hand, the oscillator energies in Cs_2O- and Rb_2O-B_2O_3 glasses depend only slightly on the composition

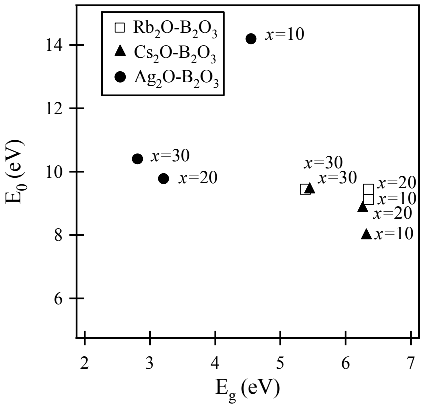

Fig. 3. The relation between the oscillator energy E_0 and the energy gap E_g in $x$$R_2O$-(100-$x$)$B_2O_3$ glasses.

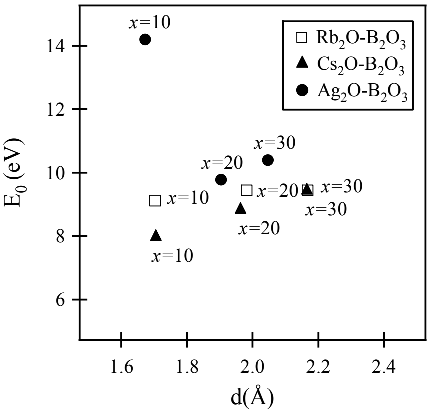

Fig. 4 The relation between the bond length d and the oscillator energy E_0 in xR$_2$O-(100-x)B$_2$O$_3$ glasses.

and it decreases with the energy gap. Accordingly, the oscillator energy is largely influenced by the energy gap and the p-d hybridization.

In crystals, the existence of a correlation between bond length d and oscillator energy E_0 has been proposed by Wemple[9]. The same relation determined for the R$_2$O-B$_2$O$_3$ glasses is shown in Fig. 4. It is seen that for the Rb$_2$O- and Cs$_2$O-B$_2$O$_3$ glasses, E_0 increases monotonically with d. The Cs-O and Rb-O bonds have high ionic character and the bond length is longer than the B-O bond. When B$_2$O$_3$ glass is doped with Cs or Rb, the average bond length and the ionicity in Rb- and Cs$_2$O-B$_2$O$_3$ glasses increases. In addition, the increase of the ionicity results in the decrease of the bond overlap and the increase of E_0. On the other hand, for the case of Ag$_2$O-B$_2$O$_3$, both E_g and E_0 exhibit decreasing trends with the increase in the amount of Ag or the increase of d. The different behavior between the Rb$_2$O- (Cs$_2$O-) and the Ag$_2$O- systems is interpreted to arise from the absence or presence of the p-d hybridization.

The p-d hybridization of Ag-O bond causes the increase of E_d and the decrease of E_0. These two factors together increase the refractive index given by Eq. (2). The above observations suggest that the contribution of the Ag-O bonding to the nonlinear optical constant is larger than the Cs-O, Rb-O or B-O bonding.

3.2 Optical constant of Ag$_2$O-B$_2$O$_3$ glasses

In the calculation shown in Fig. 1, the bond length d used was the averaged value of all the bond length (R-O and B-O). On the other hand, in the previous subsection it was shown that the optical properties of Ag$_2$O-B$_2$O$_3$ glasses are largely determined by the Ag-O bond. Therefore, the effect of replacement of the average bond length by the bond length of Ag-O has been studied. The result is shown in Fig. 5. It clearly shows that the agreement between the theoretical and the experimental values increases.

From this result, we recognize that the nonlinear optical constants of Ag$_2$O-B$_2$O$_3$ glass are dominated by the p-d hybridization of the Ag-O bond. This finding is important and interest, because it has been suggested that the p-d hybridization plays a fundamental role in the ion transport mechanism in ion conductors containing Ag or Cu such as Ag$_2$O-B$_2$O$_3$ glasses[12, 13]. According to the bond fluctuation model of superionic conductors[1], the time fluctuating creation and annihilation of different type of bonds triggers the ion movement. The p-d hybridization is an important type of bonding that participates in the bond fluctuation processes. This observation reinforces our previous finding that ion conducting materials have large value of nonlinear optical constants.

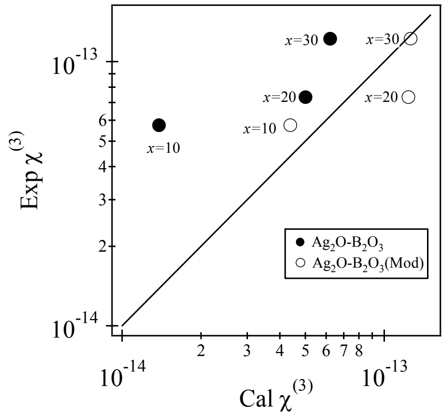

Fig. 5. Calculated and measured values of the nonlinear optical constants for xAg$_2$O-(100-x)B$_2$O$_3$ glasses. Black circles are the values shown in Fig. 1. White circles are the modified values.

4. Conclusion

We have estimated the nonlinear optical constant $\chi^{(3)}$ of R$_2$O-B$_2$O$_3$ (R=Rb, Cs, Ag) glasses by using the bond orbital theory. The agreement between the calculated and the measured values of Rb$_2$O- and Cs$_2$O-B$_2$O$_3$ glasses are good. For the case of Ag$_2$O-B$_2$O$_3$ glasses, a deviation was observed. The disagreement has been explained by taking into account the d-electrons of the Ag ions, which plays also a fundamental role in the ion transport mechanism.

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