A Study on the Relationship between Nonlinear Optical Constants and the Ionic Conductivity in Glasses

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Abstract. The bond fluctuation model of superionic conductors predicts that the polarizability of solids that exhibit high ionic conduction is large. Based on this background, a study on the nonlinear optical constants in superionic glasses has been started. As a first step, the relationship between the third-order susceptibility $\chi^{(3)}$ and the linear susceptibility $\chi^{(1)}$ of various kinds of glasses has been studied. It is found that the values of $\chi^{(3)}$ of superionic conducting glasses exceed considerably the values predicted by the usual Miller rule. The deviation arises from the increase of the ionic coordinate dependent electronic polarizability, which plays also an important role in the ion transport processes.

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. To explain the origin of the high ionic conductivity, the bond fluctuation model of superionic conductors has been proposed [1]. This model has been proposed based on the observation that many superionic conducting materials have intermediate covalent-ionic bonds. A field of forces to move the ions appears from the instability of the bonding. The local fluctuation of the bonding triggers the movement of other ions that surround the fluctuating site. According to the model, in superionic conductors the local change of the electronic cloud distribution is induced easily. Therefore, the model predicts that superionic conductors should have high electronic polarizability [2]. Based on this prediction, we have studied the correlation between the ionic conduction and the nonlinear optical properties in glasses [3], [4].

2. Miller rule in borate glasses

When an electric field E is applied to a material, it induces a polarization. In the case of a strong electric field, the polarization P is written as

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \cdots, \tag{1}$$

where $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ are the linear, second-order and third-order nonlinear optical susceptibilities. For the case of amorphous materials with optical isotropy, usually $\chi^{(2)}$ is not observed. Therefore, the lowest and most important non-linear term is $\chi^{(3)}$.
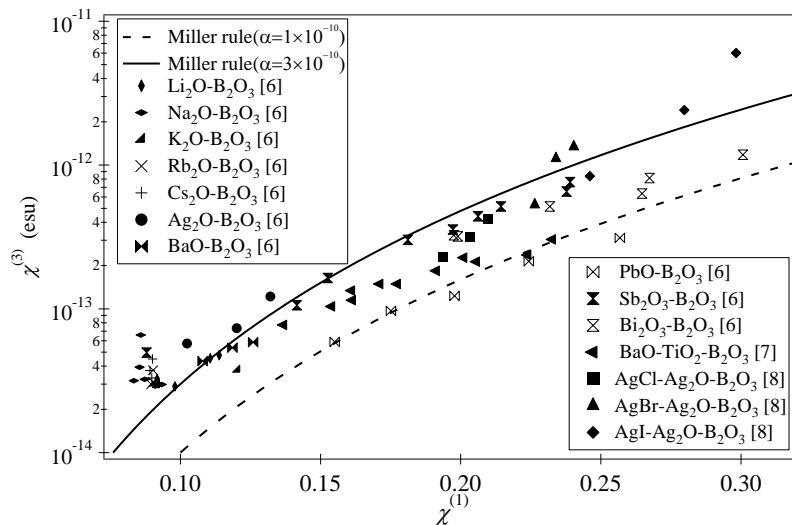
Figure 1. Relationship between the linear $\chi^{(1)}$ and the third-order optical susceptibility $\chi^{(3)}$ in borate glasses.

It is known that $\chi^{(1)}$ and $\chi^{(3)}$ are related by the so-called Miller rule [5]

$$\chi^{(3)} = \alpha \left(\chi^{(1)} \right)^4 \quad \text{(esu)},\tag{2}$$

where α is a constant. Equation (2) is a semi-empirical rule. Figure 1 shows the plots of $\chi^{(3)}$ against $\chi^{(1)}$ of borate glasses. The experimental data were obtained from references [6]-[8]. In the present study, the trend of figure1 is analyzed by using the Miller coefficient α. From the figure, it is observed that the value of α for most borate glasses is between 1×10^{-10} and 3×10^{-10}. However, for glasses that exhibit high ionic conductivity we note the following characteristics.

- The $\chi^{(3)}$ of R_2O-B_2O_3 (R=Li, Na, K, Rb, Ag) glasses are smaller than those of other glasses. However, these glasses have large values of α. In other words, they show large deviation from the usual Miller rule. It is interesting to note that these glasses exhibit R-ion conduction.
- The nonlinear optical susceptibilities of superionic conducting glasses AgX-Ag_2O-B_2O_3 (X=Cl, Br, I) are large. These glasses have also large value of α. The ordering of α in AgX-Ag_2O-B_2O_3 glasses is $\alpha_{Cl} < \alpha_{Br} < \alpha_I$, and α increase with the increase of the concentration of doped Ag-halides. These trends are similar to the trend observed in the ionic conductivity of AgX-Ag_2O-B_2O_3 glasses.

As expected from the bond fluctuation model of superionic conductors, figure 1 indicates that superionic conducting glasses have large nonlinear optical constants. Figure 2 shows the relationship between the ionic conductivity σ_i [9] and the nonlinear optical constants in AgX-Ag_2O-B_2O_3 glasses. The increase of σ_i with the increase of $\chi^{(3)}$ is clearly recognized.

3. Correlation between the Miller rule and the ionic conductivity in AgX-Ag₂O-B₂O₃ glasses

An expression for the third-order susceptibility $\chi^{(3)}$ can be deduced from the Three-Dimensional Two-Coupled Anharmonic Oscillator model [10]. According to this model, $\chi^{(3)}$ is written as

$$\chi^{(3)}(\omega) = -\frac{12\varepsilon_0^3 \left[\chi_e^{(1)}(\omega) \right]^3}{N^3 e_e^3} \left[\frac{A\chi_e^{(1)}(\omega)}{e_e} + \frac{B\chi_i^{(1)}(\omega)}{e_i} \right],\tag{3}$$

where the subscripts e and i indicate the electronic and ionic components, respectively. e is the charge, and N is the number of electronic oscillator per unit volume. A gives the departure from the harmonic electronic potential. B stands for a kind of nonlinearity in which a change in the ionic coordinate affects the electronic polarizability. Since $\chi_i^{(1)} \ll \chi_e^{(1)}$, the term containing B is usually neglected.

However, it has been shown that B could be large when different bonds coexist [10]. For example, the magnitudes of B in KCl:Cd^{2+} and KCl:Mn^{2+} are 10^5 times larger than that of KCl. This behaviour has much in common with the behaviour expected from the bond fluctuation model of superionic conductors mentioned in the introduction. The above observations indicate that the deviation from the Miller rule is reflected in the increase of B.

In order to analyze the result shown in figures 1 and 2, we should discuss how the deviation from the Miller rule is influenced by the bonding nature of AgX-Ag$_2$O-B$_2$O$_3$ glasses. The evaluation of the bonding nature in glasses is in general difficult, because, in addition to the amorphous structure, the chemical composition can be changed continuously and they are usually multi-component systems. A convenient scale to overcome this difficulty is the average electronegativity, χ_m which is calculated from the chemical composition of the glasses and the electronegativity of the constituent elements [11]. It has been shown that χ_m influences σ_i and the medium range structure of superionic conducting glasses [11]. If the chemical formula of a glass is written as A$_x$B$_y$C$_z$ …, where A, B, C, …are the elements and $x, y, z,…$are their compositions, the average electronegativity is given by

$$\chi_m = \left(\chi_A^x \cdot \chi_B^y \cdot \chi_C^z \cdots\right)^{1/(x+y+z\cdots)}. \tag{4}$$

The equation generalizes the postulate used by Sanderson to describe the principle of electronegativity equalization [12]. This principle has been proved to be very efficient to understand the bond formation in ionic-covalent crystals. The validity of the expression was verified mainly in binary compounds. However, recent study revealed that the principle described by the equation (4) has more general validity and could be applied to multicomponent systems.

Figure 3 shows the relation between α and χ_m in AgX-Ag$_2$O-B$_2$O$_3$ glasses. It is noted that α increases with the decrease of χ_m. In addition, it is noted that the decrease of χ_m arises from the increase in the concentration of Ag halides. The silver halides are known for their high silver ion conductivity. It has been suggested that when Ag$_2$O-B$_2$O$_3$ glasses are doped with silver halides, the number of bond fluctuating sites increase and results in the increase of the ionic conductivity [11]. Therefore, both, the bond fluctuation model and the average electronegativity suggest that the electrons are loosely bound in these systems. In other words, the increase of the polarizability is reflected in the decrease of χ_m. On the other hand, as discussed in the previous section, the electronic polarizability increases with the value of B. That is, the Miller coefficient will increase with the decrease of χ_m. The result shown in figure 3 confirms this situation. The relationship between σ_i and α in AgX-Ag$_2$O-B$_2$O$_3$ glasses is shown in figure 4. As expected, it is noted that glasses with high ionic conductivity have large values of α. The result indicates that ionic conduction and nonlinear optical property are intimately related as predicted from the bond fluctuation model of superionic conductors.
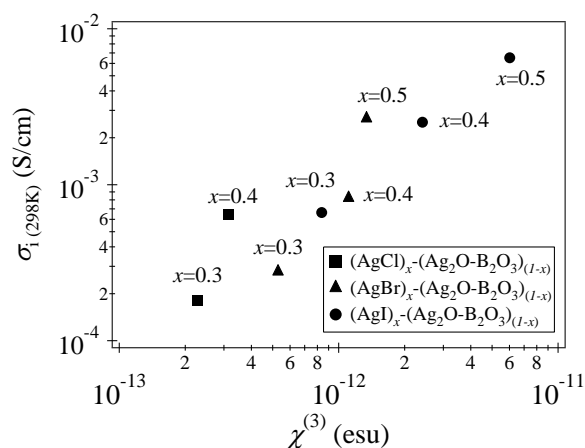

Figure 2. Relationship between the ionic conductivity σ_i and the third-order susceptibility $\chi^{(3)}$ in AgX-Ag$_2$O-B$_2$O$_3$ glasses.
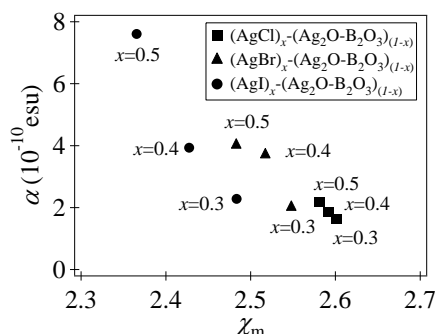
Figure 3. Relationship between the average electronegativity χ_m and the Miller coefficient α.
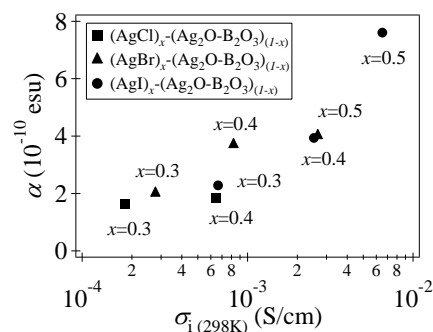
Figure 4. Relationship between the ionic conductivity σ_i and the Miller coefficient α.

To avoid misunderstanding, it should be pointed out however, that not all the glasses shown in Figure 1 follow the same trend. Among the glasses in consideration, the relations shown in Figures 3 and 4 are obeyed by glasses containing Ag halides that have large values of B, that is, glasses characterized by bond fluctuation processes.

4. Conclusion

The correlation between the ionic conductivity and the nonlinear optical constants in glasses has been studied from the point of view of bond fluctuation model of superionic conductors. The main results are summarised as follows.

- The data of ionic conducting glasses deviate from the usual Miller rule that links the third-order $\chi^{(3)}$ and the linear $\chi^{(1)}$ optical susceptibilities.
- AgX-Ag$_2$O-B$_2$O$_3$ (X=Cl, Br, I) glasses have large values of α. The composition dependence of α in AgX-Ag$_2$O-B$_2$O$_3$ glasses is similar to the composition dependence of the ionic conductivity.
- The materials trend of the above deviation has been related with a parameter of the coupled oscillator model which reflects the ionic coordinate dependent electronic polarizability.
- The values of α increase with the decrease of the average electronegativity of AgX-Ag$_2$O-B$_2$O$_3$ glasses. This behaviour is related with the loose bound of the electrons to the ions which leads to the high ionic conductivity.

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