# Nonlinear optical constants of ionic conductors: a study based on the Sheik-Bahae equation

**Shosuke Ikeda**[*,1] **and Masaru Aniya**[**,2]

[1] HUREC, Kumamoto University, 860-8555, Kumamoto, Japan
[2] Department of Physics, Graduate School of Science and Technology, Kumamoto University, 860-8555, Kumamoto, Japan

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Guided by the prediction of the bond fluctuation model of superionic conductors, the relation between the nonlinear optical constants and the ion transport properties in ionic conductors has been studied. Since the measured values of nonlinear optical constants in ionic conductors are very limited, they have been evaluated through the Sheik-Bahae equation. Using such values, it is shown that the activation energy of ion transport and the superionic transition temperature decrease with the increase of the nonlinear refractive index. It is also pointed out that the band gap energy and the linear refractive index in superionic conductors are relatively weakly correlated when compared with non-superionic materials. The development of a new field of study that could be called photoionics is suggested.

**1 Introduction** The advents of optical-fiber communication networks have motivated much study on nonlinear optical materials [1]. On the other hand, new materials and new functionalities have been searched in battery technology related materials such as solid electrolytes [2]. However, no attention has been paid to link these two properties. That is, optical nonlinearity from one hand, and ionic conduction from the other hand. Needless to say, if these properties are interrelated, new developments in multifunctional materials become possible. In the present paper, a fundamental study on nonlinear optical constants in ionic conductors is reported.

At a glance, it seems that optical nonlinearity has no relation with ionic conduction. However, that is not true. According to the bond fluctuation model of superionic conductors that explains many aspects of ionic conducting materials, the fast ion movement in solids is accompanied by local change of the chemical bond [3, 4]. Since the bonding nature of a solid is intimately related with its local structure, the local fluctuation of the bonding can induce the movement of other ions that surround the bond fluctuating site. That is, when an ion moves in the solid, it influences the surrounding by creating new bond fluctuating sites. Therefore, the model explains in a natural way the origin of the highly correlated ion dynamics, which is a characteristic of superionic conductors. Thus, the model suggests that there must be a close relationship between the electronic polarizability which reflects the bonding nature of the material and the ionic conduction in solids. In other words, the model suggests the possibility that ionic conduction is related with high optical nonlinearity.

Guided by this model, and with an objective to gain further understanding on the properties of superionic conductors, studies on nonlinear optical constants in superionic conductors has been started [5, 6]. As expected from the predictions of the bond fluctuation model, in Ag ion conducting glasses such as $(AgX)_y$-$(Ag_2O$-$B_2O_3)_{1-y}$ (X = Cl, Br, I), a correlation between the ionic conduction and the nonlinear optical constants was found. That is, the nonlinear optical constant increases with the increase of the ionic conductivity.

In order to consolidate the above finding, in the present contribution, further evidence of the above correlation is presented. In addition, since the measured values of nonlinear optical constants in ionic conductors are very limited, evaluation has been done based on the Sheik-Bahae equation [7], an equation used successfully to analyze the nonlinear optical constants in semiconductors and insulators.

**2 Estimation of the non-linear optical constants of ionic conductors** The refractive index $n$ is described as

$$n = n_0 + n_2 I\,, \tag{1}$$

where $n_0$ and $n_2$ are the linear and nonlinear refractive indexes, respectively, and $I$ is the light-intensity. According to the expression for the nonlinear refractive index derived by Sheik-Bahae et al. based on two-photon excitation process and the nonlinear Kramers-Kronig equation, $n_2$ is given by [7]

$$n_2 = K' \frac{G_2(\hbar\omega / E_g)}{n_0 E_g^4}\,, \tag{2}$$

where $K'$ is a constant and $G_2$ is a function that depends on frequency and bang gap energy $E_g$. $G_2$ is written explicitly as

$$G_2(x) = \frac{-2 + 6x - 3x^2 - x^3 - 3/4x^4 - 3/4x^5 + 2(1-2x)^{3/2}\Theta(1-2x)}{64x^6}\,, \tag{3}$$

where $\Theta$ is a step function.

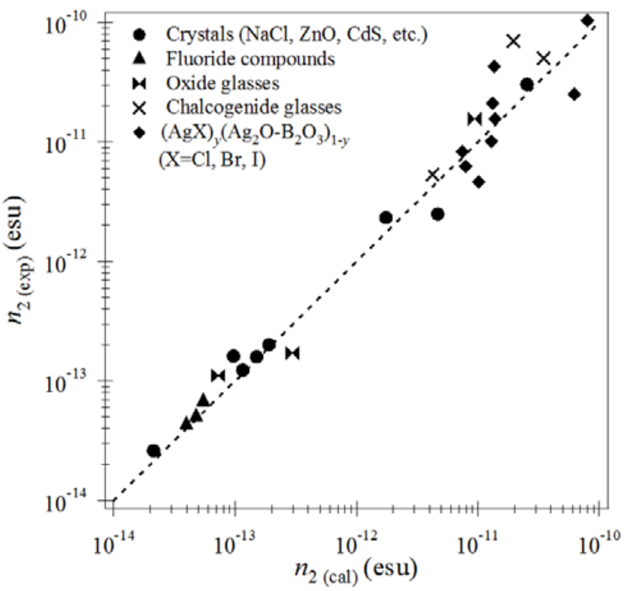


**Figure 1** Comparison between the experimental and calculated nonlinear refractive indexes $n_2$ for various compounds.

The Sheik-Bahae equation has been originally developed for crystalline materials. The usefulness of this equation in the estimation of nonlinear optical constants has been verified in ionic crystals and crystalline II-VI and III-V semiconductors [7]. Recent studies have shown that it could be applied as a rough approximation to glasses and amorphous films as well. Examples of applications have been shown for the cases of oxide and chalcogenide glasses [8, 9]. A new list of application could be added from the comparison shown in Fig. 1. Here, the values of $n_2$ for superionic glasses $(AgX)_y(Ag_2O\text{-}B_2O_3)_{1-y}$ (X = Cl, Br, I) calculated based on the Sheik -Bahae equation are compared with the experimental values. For their evaluation, the materials parameters have been obtained from [10]. We can see that the agreement is reasonable. For the sake of comparison, other compounds such as NaCl, ZnO, CdS, oxide and chalcogenide glasses, etc. are also shown.

**3 Relation between the nonlinear optical constant and the activation energy of ion transport in ionic conductors** As mentioned in the Introduction, the bond fluctuation model of superionic conductors predicts that ionic conduction is related with high optical nonlinearity. In a previous study, it has been shown that the nonlinear optical constant in $(AgX)_y\text{-}(Ag_2O\text{-}B_2O_3)_{1-y}$ (X = Cl, Br, I) increases with the increase of ionic conductivity [6]. To consolidate that finding, further evidence should be given. However, unfortunately, few measured values of $n_2$ for ionic conductors are available. But now, we have the Sheik-Bahae equation which provides a tool to estimate the nonlinear optical constants with reasonable accuracy.

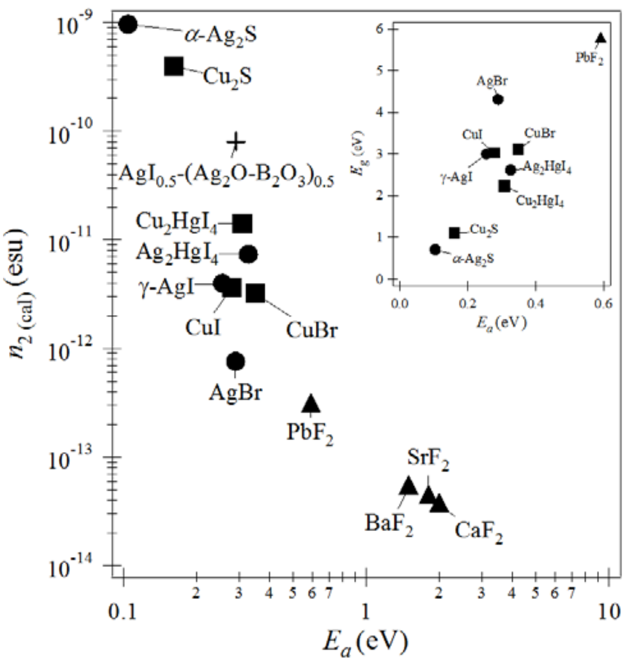


**Figure 2** Relationship between the nonlinear refractive index $n_2$ and the activation energy of ion transport $E_a$ in typical ionic conductors. The inset shows the relationship between the band gap energy $E_g$ and $E_a$. The experimental data are taken from [7, 11-13].

In Fig. 2, the relationship between the nonlinear refractive index and the activation energy of ion transport in typical ionic conductors is shown. The mobile species are $Ag^+$, $Cu^+$ or $F^-$ ions. Datum of $(AgI)_{0.5}\text{-}(Ag_2O\text{-}B_2O_3)_{0.5}$ glass is also included for comparison. In the figure, with the exception of fluoride compounds and $(AgI)_{0.5}$-$(Ag_2O$-$B_2O_3)_{0.5}$ glass, we have used calculated values of $n_2$. The figure indicates clearly that there is a material trend. The activation energy decreases with the increase of the nonlinear optical constant. The result is in accord with the previous finding [6].

The origin of the trend can be understood as follows. The decrease of $E_a$ is related with the weakening of the interatomic interaction between the mobile atom and its surroundings. If the electronic distribution around the mobile specie is tight, the atom is strongly bonded and difficult to migrate. Therefore, in this case, the activation energy for migration is large, and at the same time, the electronic polarizability is low due to the tight electronic distribution, resulting in the low value of optical constant. On the other hand, easy deformation of the electronic distribution results in the lowering of the activation energy and increase of the electronic polarizability. To avoid misunderstanding, a comment should be given here. The above discussion does not imply that materials exhibiting high optical nonlinearity should exhibit high ionic conductivity. For instance, the ionic conductivity of chalcogenide glasses such as $As_2Se_3$ is negligible, whereas it exhibit high value of optical constant. For the appearance of ionic conductivity, the material must fulfil some conditions such as low coordination, easiness of structural transformation, atomic size, availability of free volume, etc. [3, 4, 14]. The point that we want to stress here is that good ionic conductors exhibit also a high value of nonlinear optical constants as have been reported previously [6, 7, 10].

It should be informative to mention the relationship between the optical band gap $E_g$ and the activation energy of ion transport $E_a$. Such relationship is shown in the inset of Fig. 2. We can note that $E_g$ increases with the increase of $E_a$. This behaviour is expected, because the electronic polarizability increases with the decrease of $E_g$. From the mechanistic point of view, the decrease of $E_g$ is also favourable for the occurrence of bond fluctuation processes, because it leads to an easy formation of different hybrid orbitals [3].

Fig. 3 shows the relation between the superionic transition temperature $T_c$ and the nonlinear optical constant $n_2$. We can see that the transition temperature decreases with the increase of $n_2$. The result provides another support to the picture discussed above. It also reinforces the conjecture of the bond fluctuation model of superionic conductors. That is, the fast ion movement is related with the instability of the chemical bonding. The results shown in Figs 2 and 3 provide clear evidence that optical nonlinearity is related with ion transport properties. The results suggest also that a new field of study that could be called photoionics can be developed.

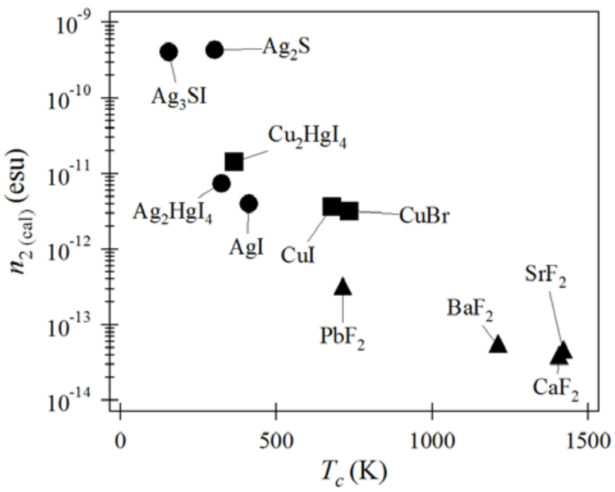


**Figure 3** Relationship between the nonlinear refractive index $n_2$ and the transition temperature to the superionic state $T_c$. The experimental data of $T_c$ are taken from [12].

**4 Relation between the optical parameters** In the previous section we have shown the intimate correlation between the optical constants and the ion transport properties. In this section an interesting trend of the optical parameters is shown. The function $G_2(x)$ of the Sheik-Bahae equation given in Eq. (3) describes the frequency dependence of the nonlinear refractive index $n_2$. It is a smoothly varying function that exhibit a maximum near $x = 0.5$. Its range of variation is confined approximately between 0.07 and -0.03. Therefore, according to Eq. (2) the magnitude of $n_2$ is controlled mainly by the factor $n_0E_g^4$. Explicitly, small value of $n_0E_g^4$ results in large value of $n_2$. This is an interesting observation when we consider superionic conductors, because the bond fluctuation process is facilitated with the reduction of the band gap energy as mentioned briefly in the previous section.

The relation between the linear refractive index $n_0$ and the band gap energy $E_g$ has been discussed widely in the literature [15-17]. In the following, an analysis based on an empirical relation proposed by Reddy et al. [17] is presented. It is expressed as

$$n_0 = -\ln(AE_g)\,, \qquad (4)$$

where $A$ is considered to be a constant that depends weakly on the materials. Fig. 4 shows the result of the analysis. We can see that not all the materials can be fitted with a single value of $A$ as suggested in [17]. It is interesting to note that superionic materials are best fitted by adopting a larger value of $A$. More interesting, superionic materials at temperature above transition temperature $T_c$ seem to follow a curve with $A$ even more larger. This observation points out that in superionic conductors, $E_g$ and $n_0$ are weakly correlated when compared with other materials. From the figure, we note that in superionic conductors, large variation in $n_0$ results in relatively small variation in $E_g$. The exact origin of the behaviour is not known at present. However, undoubtedly it is providing a hint to understand better the mechanism of ion transport in solids.

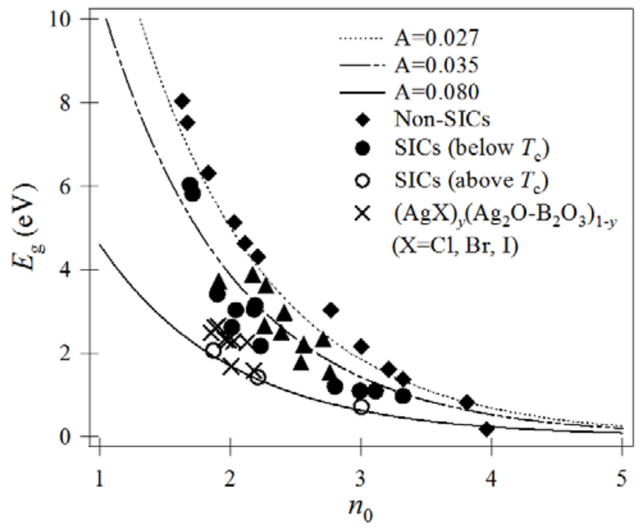


**Figure 4** Relationship between the band gap energy $E_g$ and the linear refractive index $n_0$. Experimental data are taken from [10, 11].

The above observation is reinforced with the result shown in Fig. 5, where the relationship between the activation energy of ion transport and the parameter $A$ is shown. We can see clearly that the activation energy decreases with the increase of $A$.

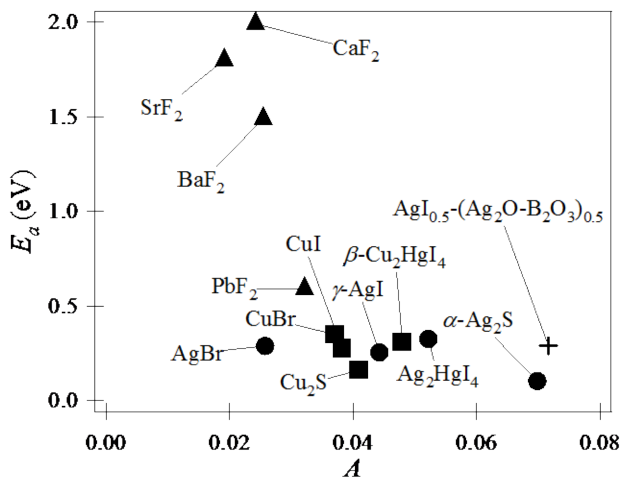


**Figure 5** Relationship between the parameter $A$ of Eq. (4) and the activation energy of ion transport in some typical ionic conductors.

**5 Conclusion** The bond fluctuation model of superionic conductors predicts that there must be a close relationship between the polarizability and the ionic conduction in solids. Guided by this model, the relation between the nonlinear optical constants and the ion transport properties in ionic conductors has been studied. Since measured values of nonlinear optical constants in ionic conductors are very limited, they have been evaluated using the Sheik-Bahae equation. In the study, it has been shown that the activation energy of ion transport and the superionic transition temperature decrease with the increase of the nonlinear refractive index. Analysis based on the Reddy relation indicated that in superionic conductors, large variation in linear refractive index results in relatively small variation of band gap energy, when compared with other materials. The results presented in this study suggest that a new field of study that could be called photoionics can be developed.

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