Nonlinear Optical Constants of Fluoride Ion Conductors
— *Analysis by the Sheik-Bahae Equation* —

Shosuke IKEDA and Masaru ANIYA

Department of Physics, Kumamoto University, Kumamoto 860-8555

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Study on the correlation between ionic conduction and nonlinear optical (NLO) constants has been extended to fluoride materials. It is found that the activation energy of ion transport decreases with the increase of the NLO constants. To understand the origin of the relationship, the NLO constants of fluoride ion conductors are investigated by using the Sheik-Bahae equation, which has been used successfully in the study of nonlinear refractive indexes of semiconductors. The analysis reveals that the bond fluctuation model of superionic conductors provides a basis to understand the observed behavior.

§1. Introduction

According to the bond fluctuation model of superionic conductors, the fast ion movement in solids is triggered by a local instability of the chemical bond.[1] 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 fluctuating site. That is, when an ion moves in the solid, it influences the surrounding by creating a new bond fluctuating site. Therefore, the model explains in a natural way the origin of the highly correlated ion dynamics, which is a characteristic of superionic conductors.[2] The above model suggests that there must be a close relationship between the polarizability and the ionic conduction in solids.

Guided by this model, and with an objective to gain further understanding on the properties of superionic conductors, studies on nonlinear optical (NLO) constants in superionic glasses has been started.[3] As expected from the predictions of the bond fluctuation model, in Ag ion conducting glass, a correlation between the ionic conduction and the NLO constants was found. In this report, the study is extended to fluoride materials. It is shown that the activation energy for ion transport decreases with the increase of the NLO constants. To understand the obtained relationship, the NLO constants of fluorides are estimated by the Sheik-Bahae equation.[4] The result reveals that the analysis of the NLO constants by the Sheik-Bahae equation provides a hint to understand why ionic conductors have high values of the NLO constants.

§2. The nonlinear optical constant and the activation energy of ion transport in fluoride ion conductors

Figure 1 shows the relationship between the nonlinear refractive index[5] and the activation energy of ion transport[6] in some fluoride materials that exhibit superionic conduction (CaF_2, SrF_2, BaF_2 and CdF_2). In these materials, the mobile species is the F^- ion. It is noted that the activation energy decreases with the increase of the NLO constants. In the followings, to investigate the origin of the observed relationship, the NLO constants of fluoride materials are analyzed by the Sheik-Bahae equation which has been used successfully in the study of semiconducting materials.

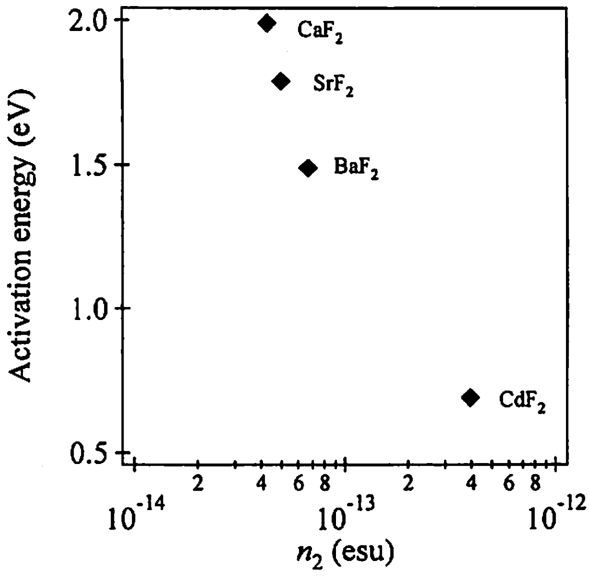

Fig. 1. Relationship between the nonlinear refractive index n_2 and the activation energy in fluorides.

§3. Analysis of fluoride ion conductors by the Sheik-Bahae equation

The refractive index n is described as

$$n = n_0 + n_2 I, \tag{3.1}$$

where n_0 and n_2 are the linear and nonlinear refractive indices, respectively, and I is the light-intensity. Some years ago, an expression[4)] was deduced for the nonlinear refractive index n_2 based on two-photon excitation processes and the nonlinear Kramers-Kronig equation. The Sheik-Bahae equation for n_2 is given by

$$n_2 = K' \frac{G_2(\hbar\omega/E_g)}{n_0 {E_g}^4}, \tag{3.2}$$

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

$$G_2(x) = \frac{-2 + 6x - 3x^2 - x^3 - 3/4\,x^5 + 2(1-2x)^{3/2}\Theta(1-2x)}{64x^6}, \tag{3.3}$$

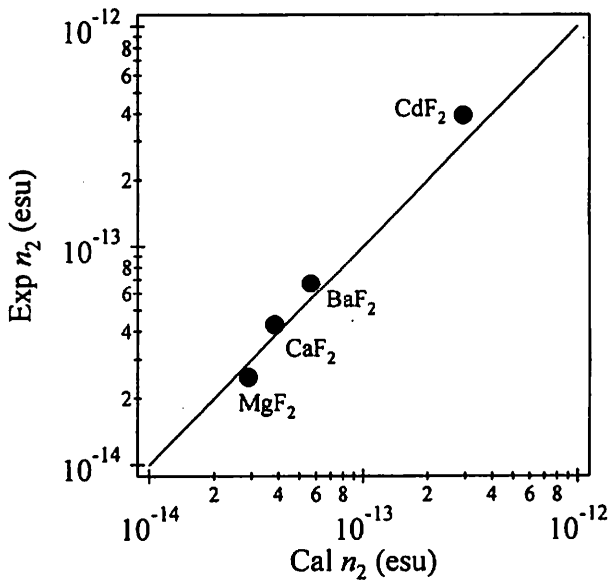

Fig. 2. Comparison between the experimental nonlinear refractive index n_2 and the calculated nonlinear refractive index n_2 in fluorides.

where Θ is a step function.

Figure 2 shows a comparison between the calculated values of n_2 through the Sheik-Bahae equation and the experimental values. We note that the agreement between both quantities is good. Based on this agreement, we can use the Sheik-Bahae equation to analyze the NLO constants of fluorides. According to the Sheik-Bahae equation, the NLO constant is inversely proportional to $n_0 E_g{}^4$. That is, small values of $n_0 E_g{}^4$ results in a large value of the NLO constants.

In order to clarify which factor, n_0 or E_g controls the enhanced values of the NLO constants, we have studied the correlation that exists between n_0 and E_g. A convenient empirical expression to study the correlation between n_0 and E_g has been proposed as[7)]

$$n_0 = -\ln(AE_g), \tag{3.4}$$

where A is a constant that depends weakly on the materials. The analysis based on the Reddy equation (3.4) shows that the increase of A results in the reduction of $n_0 E_g{}^4$. One of the factors which cause the increase of the NLO constant is related with this observation. In addition, E_g of a material decreases with the increase of A. The decrease of E_g is also favorable for the occurrence of bond fluctuation processes mentioned in the introduction. Therefore, the fast ion movements are related with the increase of A.

Figure 3 shows the relation between the activation energy of ion transport and A for fluoride materials. As expected, the activation energy decreases with the increase of A. That is, in fluoride systems, the increase of A in the Reddy equation causes the increase of the NLO constant and the ionic diffusion in solids.

The bond fluctuation model of superionic conductors has been proposed origi-

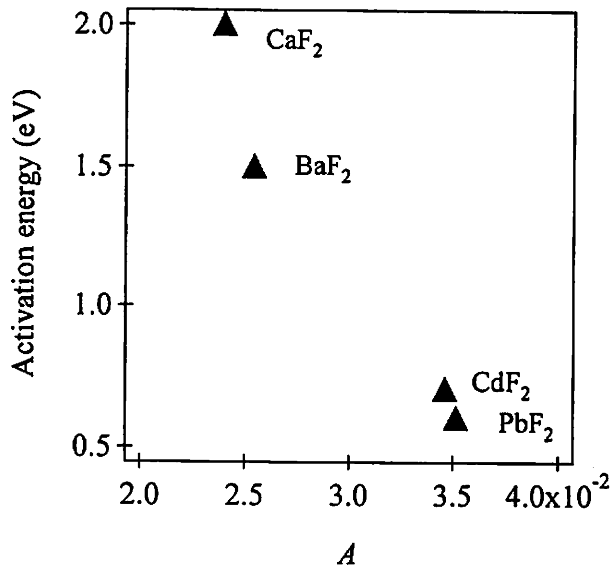

Fig. 3. Relationship between A and the activation energy of ion transport in fluoride crystals.

nally to understand the mechanism of ion transport in compounds such as Ag and Cu halides or chalcogenides. The results of the analysis presented in this paper suggest that the concept of this model is also applicable to fluoride compounds.

§4. Conclusion

The NLO constants of fluorides (CaF_2, SrF_2, BaF_2 and CdF_2) were estimated by the Sheik-Bahae equation. The calculated NLO constants for these materials showed a good agreement with the experimental values. According to the Sheik-Bahae equation, the increase of the NLO constant is related with the decrease of $n_0 E_g{}^4$. The decrease of $n_0 E_g{}^4$ is also related with the increase of A in the Reddy equation. On the other hand, the bond fluctuation model of superionic conductors suggests that the high ionic conduction is related with the easy change of the electronic cloud distribution, that is, with a large value of A. As expected from the model, it was shown that the activation energy for ion transport decreases with the increase of A.

Acknowledgements

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