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Relationship between the activation energy of ion migration and the heat of transport in some ionic conductors

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ABSTRACT

The heat of transport determined from the thermopower measurement provides important information to know the ion transport processes occurring in solid electrolytes. Recently, we have proposed a theoretical model for the heat of transport in ionic conductors. According to the model, the relationship between the heat of transport and the activation energy of ion conduction is determined by the participation degree of different phonon modes. In the present study, some behavior expected from the model is compared with experimental observations. It is shown that the predictions of the model are consistent with the experimental data.

1. Introduction

In ionic conductors, ions diffuse from site to site by hopping mechanisms and carry electrical charge and heat. When a temperature gradient exists in the system, the ions move and generate the voltage. This is the well known thermoelectric or Seebeck effect. Earlier studies in thermoelectric materials have focused on metals that exhibit thermopower values of about tens of μV/K. In the mid-twentieth century, interests were focused on semiconductors with high thermopower. Since the research of Terasaki et al. in 1997 [1], oxide semiconductor materials have attracted attention as one of the significant thermoelectric materials. These oxide materials show many advantages. For instance, oxides with the perovskite structure allow the synthesis of solid solution containing various ions. Their properties can be modified in a wide range with defect formations generated by substitution. Therefore, many investigations have been performed to improve the properties of oxide materials, not only as semiconductors [2–4] but also as mixed conductors [5–8]. Concerning the thermoelectric effects in ionic conductors, although some studies have been actively done in the 1970s to 1990s, its understanding from the fundamental point of view is not clear. For example, in superionic conductors, it is experimentally known that the heat of transport Q is nearly equal to the activation energy for ion transport E_a. However, its origin is not known exactly. By looking at the experimental data carefully, some materials such as Ag_2HgI_4 show $Q < E_a$ [9], whereas others such as AgI–AgBr systems exhibit $Q > E_a$ [10]. Theoretically, the free ion model predicts $Q = E_a$ [11], whereas the polaron gas model [12] and the lattice gas model [13] predict $Q < E_a$. Therefore, there were no theory that explains the relative magnitudes between Q and E_a.

Recently, we proposed a model for the heat of transport in ionic conductors [14]. The model suggests that the relation between the heat of transport Q and the activation energy E_a is controlled by the participation degree of different phonon modes. In this study, some behavior expected from the model is compared with experimental observations. It will be shown that the predictions of the model are in good agreement with experimental data.

2. Theory

2.1. Model for the heat of transport

The transport phenomenon in ionic conductors is governed wholly or partly by mobile ions. The elementary step for ion conduction occurs by thermally activated hopping between adjacent sites in the potential barrier profile. The magnitude of the potential barrier is described by the activation energy.

When one end of a conductor is at a different temperature from the other, it results in energy flow by phonons and mobile ions to reach the thermal equilibrium. In our model, we have shown that the relationship between the heat of transport and the activation energy of ion conduction is determined by the participation degree of different phonon modes, in particular the short wavelength phonons to the atomic jump processes.

In terms of superposition of lattice modes, the displacement of an ion from the equilibrium lattice sites is written as [15]:

$$q = \sum_i \alpha_i M_i = \sum_i \alpha_i \varepsilon_i^{1/2} \cos \omega_i t. \quad (1)$$

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Here ε_i is the energy of the mode M_i and α_i is the weight factor of the mode that has frequency ω_i. The ion jumps when its amplitude q of vibration exceeds a critical value q_0, leading to ionic current $\vec{j}$. Considering that the jumping rate is expressed by the vibration amplitude, and that the energy of the mode ε_i in a temperature gradient is obtained by solving the Boltzmann transport equation, the ion flow $\vec{j}$ is written as:

$$\vec{j} = na_0\bar{f}\exp\left[-\frac{E_a}{k_BT}\right]\left\{\frac{2E_al}{k_BT^2}\right\}\mathrm{grad}T, \tag{2}$$

$$l = \frac{\sum \alpha_i^2\tau_i v_i}{\sum \alpha_i^2}, \tag{3}$$

where n is the ion concentration, a_0 is the interatomic distance, $\bar{f}$ is the mean vibrational frequency and k_B is the Boltzmann constant. l is a quantity that is written in terms of the velocity v_i and the relaxation time τ_i of the mode as given in Eq. (3).

According to the laws of irreversible thermodynamics, when a gradient of temperature T exist and there is no gradient of ion concentrations n in the system, the ion flow density $\vec{j}$ is written as [16]:

$$\vec{J} = -D\left(\frac{Qn}{k_BT^2}\mathrm{grad}T\right), \tag{4}$$

where D is the diffusion coefficient, written as $D = a_0^2\bar{f}\exp[-E_a/k_BT]$. Comparing this phenomenological relation with the expression given by Eq. (2), we obtain the following relationship between the heat of transport Q and the activation energy E_a.

$$Q = \frac{2l}{a_0}E_a. \tag{5}$$

2.2. Discussion and theoretical predictions

The result of our model shown in Eq. (5) indicates that the ratio between Q and E_a is determined by the quantity l defined in (3). Note that the interatomic distance a_0 is a material constant and l has the dimension of length. According to the relation between Q/E_a and l given in Eq. (5), $Q > E_a$ is satisfied when l takes a large value. In contrast, a small value of l gives $Q < E_a$. The model suggests that the analysis of the data through Eq. (5) could provide many insights to understand the fundamental properties of ion transport in solids.

As discussed previously [14], the modes that contribute effectively to the ion jumping processes seem to be short wavelength phonons, because, these types of motions create an elongated space near the jumping ion. If the contribution of these short wavelength phonons dominate the atomic displacements described by (1), the quantity l will take a small value, because the group velocity v_i of these phonons is very small. On the other hand, the vibration mode could be of both types, acoustic and optical modes. The model suggests the importance of acoustic modes. This observation arises from the positive value of l.

A schematic picture of ion jumping processes is shown in Fig. 1. To avoid confusion, it is illustrated in one dimension. When the short wavelength phonon is dominant, ions jump individually as shown in Fig. 1(a). On the other hand, as shown in Fig. 1(b) the ions move collectively when the weight factor of the long-wavelength phonons increases. These observations provide an understanding to the ion transport mechanism in superionic conductors. It has been recognized that superionic conductors are characterized by their low energy barrier for ion migration and from their collective motions that these ions exhibit. The low energy barrier has its origin in the peculiar nature of chemical bonding [17]. The model proposed previously suggests that the ions overcome collectively the barrier with the help of phonons. The interesting point that should be noted is that superionic conducting materials exhibit a relatively flat phonon dispersion curve when compared with other non-superionic materials [18]. The flat phonon band implies that many phonon modes have almost the same energy. This feature might be related to the participation degree of different phonon modes in the collective ion dynamics of superionic conductors.

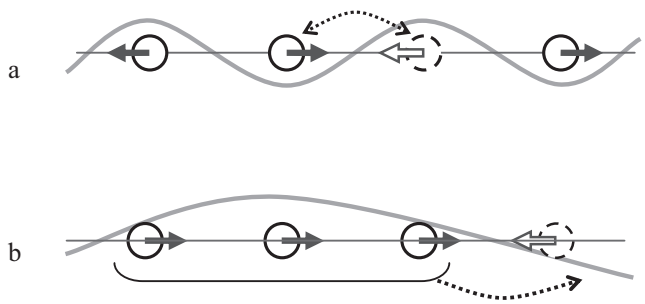

Fig. 1. Schematic view of ion jumping processes. (a) Ions jump individually with the help of short wavelength phonons. (b) The collective motion of ions arises with the contribution of long-wavelength phonons.

The above discussion make possible to draw the following predictions:

(1) Good ionic conductors will show large value of Q/E_a.
(2) In bad ionic conductors such as alkali halides, ions move individually and the heat of transport takes a small value, because in these materials, the dominant phonons related with ion migration are short wavelength phonons.
(3) By increasing temperature, different phonons with large group velocities start to participate in the ion transport processes. Therefore, the value of Q/E_a will increase with the increase of temperature.

In order to verify the above predictions, we have collected some experimental data from the literature.

3. Comparison with experiments

3.1. Q/E_a and ionic conductivity

Fig. 2 shows the relationship between the ratio Q/E_a and the ionic conductivity. The experimental data of ionic conductivity, activation energy and heat of transport are all taken in a limited temperature range, 400–555 K to avoid the temperature effect as

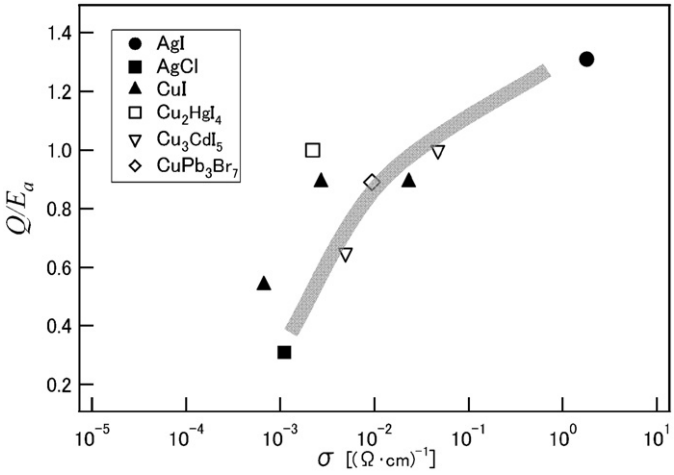

Fig. 2. Relationship between the ratio Q/E_a and the ionic conductivity in some ionic conductors in the temperature range 400–555 K. The curve is a guide to the eyes.