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.

Keywords: heat of transport, thermoelectric power, ionic conductors, phonons

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 $\mu V/K$. 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]

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

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

$$\vec{j} = n a_0 \bar{f} \exp\left[-\frac{E_a}{k_B T}\right]\left\{\frac{2E_a l}{k_B T^2}\right\} \mathrm{grad}T , \tag{2}$$

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

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]

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

where D is the diffusion coefficient, written as $D = a_0^2 \bar{f} \exp\left[-E_a/k_B T\right]$. 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.

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 small as possible [10,19-21]. As discussed in the previous section, the model predicts that good ionic conductors will show large value of Q/E_a. According to the data reported, the conductivity of AgI is $\sigma_{Ag} = 1.8\,\text{Scm}^{-1}$ and $Q/E_a \approx 1.3$ at $T = 555\text{K}$ [10], whereas for AgCl, they are $\sigma_{Ag} = 1.1 \times 10^{-3}\,\text{Scm}^{-1}$ and $Q/E_a \approx 0.3$ [19,20]. Regarding the Cu based superionic system, we recognize from Fig. 2 that Q/E_a increases with the increase of ionic conductivity. This behavior is consistent with the prediction of our model, which states that the degree of collective motion in ionic conductors will increase with the increase of Q/E_a.

3.2 Relation between Q and E_a

The relationship between the heat of transport and the activation energy of ion conduction in some materials is shown in Fig. 3. The data of Q and E_a for a particular material group is taken at the same temperature, but not all the materials are taken at the same temperature. Among the AgI-based superionic conductors ($\bigcirc$), we include α-AgI, Ag_4RbI_5, $Ag_4NH_4I_5$, Ag_4KI_5, $Ag_{1.1}Hg_{0.3}Se_{1.4}I_{0.9}$, α-$Ag_2HgI_4$, etc. [9]. Amorphous solid electrolyte AgI-Ag_2O-V_2O_5-P_2O_5 ($\square$) has very high ionic conductivity [22], and their data follows the relation $Q = E_a$. Concerning the Cu based superionic solids ($\blacktriangle, \blacktriangledown$), they were considered also in Fig.2. [21]. Most superionic (SI) solids show a phase transition from low to high conducting phase by increasing temperature. In Fig. 3, these phases are denoted as non-superionic (non-SIC) and superionic (SIC), respectively. From the figure, we can recognize that there is a material trend in the behavior. Superionic conductors are located near the line denoted by $Q = E_a$. In contrast, typical ionic crystals like alkali halides are located far

from the line. For these materials, the activation energy are much larger compared to those of superionic systems. The material trend observed in Fig. 3 supports the prediction (2) mentioned in section 2.2. In Fig. 3, it is interesting to note that the heat of transport of Cu based materials exhibit relatively larger values than Ag-based conductors. This observation is interpreted to be related to the mixed conducting nature that the Cu compounds exhibit. The heat of transport Q is related to the transference number of the ions as

$$Q = \frac{eT}{t_+}\left(-\theta + H\right).$$
(6)

where e is the charge of the mobile ion, T is the temperature, t_+ is the cationic transference number, θ is the thermopower which is proportional to the potential difference measured, and H is a term due to the electrode contact potential [9, 23]. The above relation indicates that the decrease of cationic transference number leads to the increase of Q.

Related to the above observations, the electronic conductivities of AgI-based superionic conductors considered in Fig. 3 are very low, that is, negligible compared with their high ionic conductivities. For these compounds, the value of transport number of Ag^+ is ≈ 1 [9]. On the other hand, the cationic transference number of Cu based superionic conductor is low when compared with Ag systems [9,24,25]. In particular, it has been reported by Wagner that the electronic conductivity in Cu-halide materials is non-negligible below 573K [24]. Takahashi et al. [25] have also reported that the electronic conductivity of CuI-CdI_2 is of the order of $10^{-4} \sim 10^{-5}$ (Scm^{-1}) whereas in AgI-CdI_2 is less or equal to 10^{-10} (Scm^{-1}), both at 500 K.

3.3 Temperature dependence of Q/E_a

Table 1 shows the temperature dependence of Q/E_a for some materials. For each material, it is noted that Q/E_a increases with temperature. According to the model, when the temperature is increased, different phonons with large group velocities start to take part in the ion transport processes, resulting in the increase of l and Q/E_a.

Another interesting point that should be noted is that, at the same temperature, the multicomponent copper halide $Cu_{16}Rb_4I_7Cl_{13}$ show larger value of Q/E_a than the binary CuI system. This behavior can be understood as follows. The bonding type of rubidium iodide is ionic. When rubidium iodide is mixed with copper halide, the local bonding becomes unstable, which develops into the superionic behavior as suggested in the bond fluctuation model of superionic conductors [17].

4. Conclusion

The ion transport processes are discussed according to our model for the heat of transport in ionic conductors proposed previously. In particular, it was shown that there is a material trend when the heat of transport Q is plotted against the activation energy E_a of ion transport. Good ionic conductors are located near the line $Q = E_a$, whereas bad ionic conductors deviate from the line and follow $Q < E_a$. Concerning the temperature dependence, it is shown that Q/E_a, will increase with temperature. According to the model, these behaviors are related to the difference in the participation degree of different phonon modes to the ion transport and to the increase of phonons with large group velocities, respectively. The experimental data support the predictions of the model.

5. Acknowledgement

References

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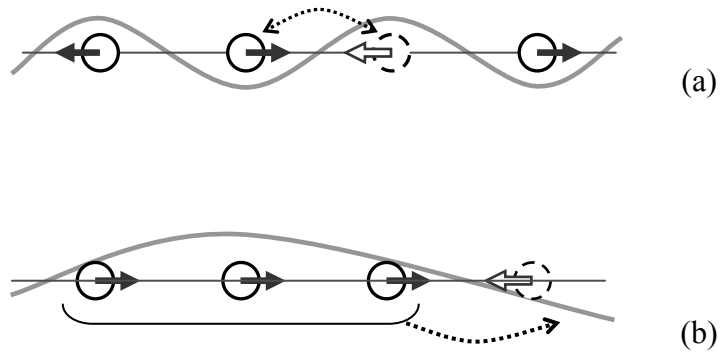[25] T. Takahashi and O. Yamamoto, Denki Kagaku 31 (1963) 678.

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.
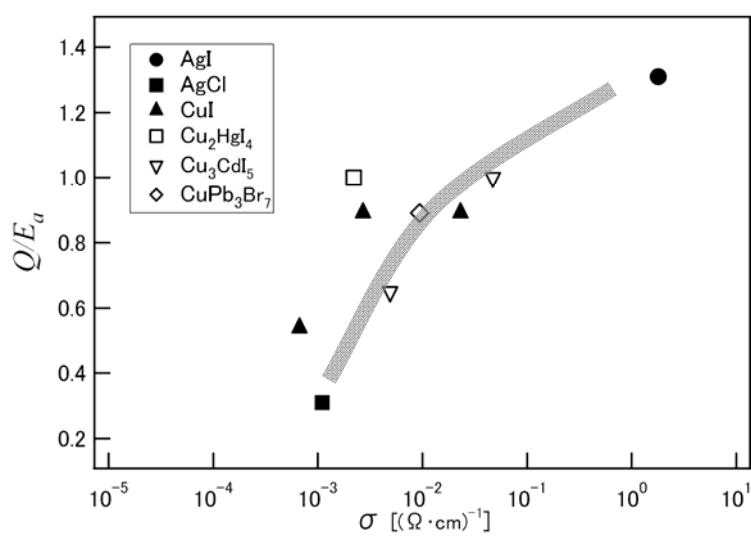
Fig. 2.   Relationship between the ratio Q/E_a and the ionic conductivity in some ionic conductors in the temperature range 400-555 [K]. The curve is a guide to the eyes.
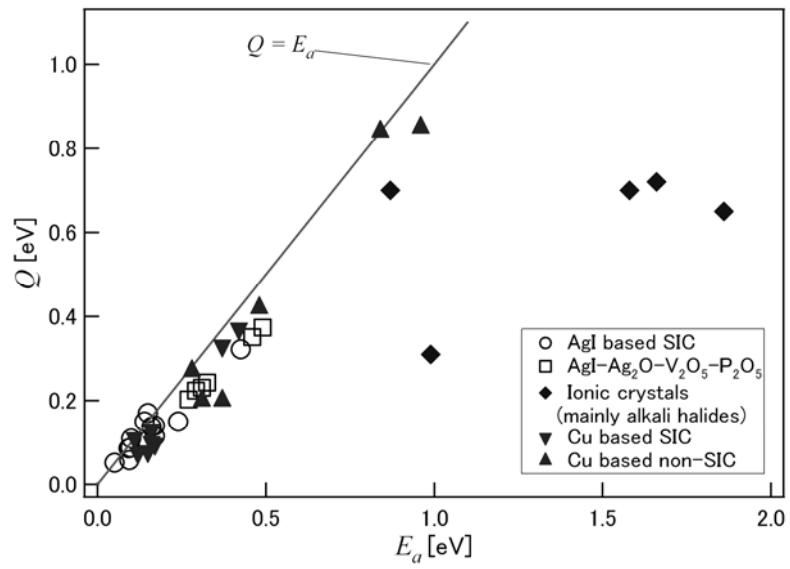
Fig. 3. Relationship between the heat of transport and the activation energy of ion conduction in some materials. The solid line represents the line $Q = E_a$.

Compound	T(K)	Q/E_a	Phase
CuI	435	0.54	non-SIC
	572	0.89	non-SIC
Cu_3CdI_5	395	0.65	non-SIC
(non-superionic)	470	1.00	non-SIC
$Cu_7(C_6H_{12}N_4CH_3)Br_8$	322	0.63	SIC
	372	0.88	
$Cu_{16}Rb_4I_7Cl_{13}$	360	0.63	SIC
	437	0.81	

Table 1. The values of Q/E_a at different temperatures for some cuprous halide systems. SIC and non-SIC denote superionic and non-superionic conducting phases, respectively.