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Dual percolation transition of an ionic conductor in the AgI–BN composite system

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Abstract

The electrical conductivity of the AgI + BN composite system was measured both at 298 and at 453 K. The electrical conductivity increases with the increase of the volume fraction of AgI at both temperatures. The behaviour of ionic conductivity was analysed based on the generalized effective medium (GEM) theory. The threshold values of the volume fraction for the percolation of ionic conduction were 16% at 298 K and 17% at 453 K respectively. These threshold values as well as the determined power indexes agree with those given by computer simulations for the percolation.

The electrical properties of conductor–insulator composite systems have been studied for many years. They have attracted considerable attention for practical reasons. The materials are frequently employed not in the pure state but in the mixed states in which both components are present as a heterogeneous phase with each other [1]. In some materials, the grains or grain boundaries, which can also be treated as a heterogeneous phase, contribute to the electrical conduction [2]. The behaviour of the electrical conductivity or the dielectric constant for these heterogeneous materials has been discussed based on the percolation theory [3]. In addition to these, the percolation theory has been discussed with relation to the mechanism of metal–insulator transitions [4]. Therefore, artificial composite materials have been studied intensively. The effective medium theory has also been valid to explain the behaviour of the electrical conductivity and the dielectric constant for heterogeneous systems [5]. Particularly, McLachlan [6] presented the theory for the electrical conduction of inhomogeneous systems composed of two phases by coupling the effective medium theory with the percolation theory. The results [7, 8] of application are successful for various composites, particularly for metal–insulator composites. However, the composites studied have been mainly couples of an electron

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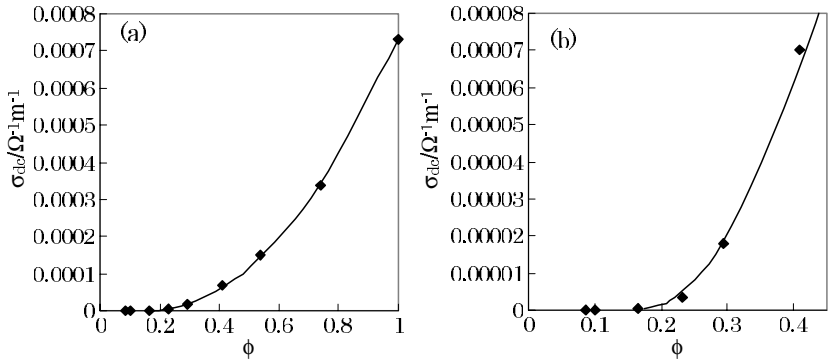

Figure 1. (a) Dc conductivity, σ_{dc}, at 298 K as a function of the volume fraction of AgI, ϕ (closed squares), and the fitted curve to equation (2) (curve) in the range from $\phi = 0$ to 1. (b) Dc conductivity, σ_{dc}, at 298 K as a function of the volume fraction of AgI, ϕ (closed squares), and the fitted curve to equation (2) (curve) in the range from $\phi = 0$ to 0.45.

conduction material and an insulator. To date, there have been almost no studies of binary composites between an ionic conduction material and an insulating one.

The purpose of this research is to study the electrical conductivity of the composite formed by AgI and BN powders. The former is a well known superionic conductor and the latter is a well known insulator.

The reagents, AgI and BN, were ground together in a mortar with the use of a pestle into fine powders. The AgI used was a special grade (over 99%) from Kojundo Chemical Laboratory Co. Ltd. The BN used was also a special grade (over 99%) from Wako Pure Chemical Co. Ltd. The obtained fine powders were pressed into a cylindrical pellet with a 3 mm depth and a 13 mm diameter together with thin Ag powder layers (as electrodes) on both sides. The concentration range studied was $x = 0$–1 for $(AgI)_x$–$(BN)_{1-x}$. The impedance measurements were made for this pellet by using a HIOKI 3532-20 high tester in the frequency range from 47 Hz to 5 MHz. In this experiment, the temperatures were kept at two values, 298 and 453 K, by the electric furnace. The former temperature was selected as the temperature of β-AgI and the latter was chosen as that of α-AgI. The dc part of the electrical conductivity, σ_{dc}, was extracted from the measured impedance by the conventional method. The density was calculated from values of the mass, the surface area, and the thickness of the pellet.

Figure 1(a) shows the dc conductivity, σ_{dc}, of AgI–BN composite at 298 K as a function of volume fraction, ϕ, of AgI (closed squares) between $\phi = 0$ and 1. The σ_{dc} increases rapidly with an increase of the volume fraction of AgI around 0.2. This behaviour can be seen more clearly in figure 1(b), which illustrates the ϕ dependence of σ_{dc} in the range from $\phi = 0$ to 0.45. Figure 2(a) shows the ϕ dependence of σ_{dc} at 453 K in the whole volume fraction range. The dc conductivity at 453 K also increases rapidly around $\phi = 0.2$. This can also be seen clearly in figure 2(b), which depicts the ϕ dependence of this σ_{dc} between $\phi = 0$ and 0.45.

As shown in figures 1 and 2, two percolation behaviours were obtained at 298 and 453 K for the same AgI–BN composite. The value of σ_{dc} at 453 K in figure 2 is far larger than that at 298 K in figure 1. Since the α–β transition temperature of AgI is known to be 420 K, the large value of σ_{dc} in figure 2 is derived from the superionic conductor phase of AgI, that is α-AgI. However, the small value of σ_{dc} in figure 1 is derived from the low conducting phase, β-AgI.

Many theoretical expressions, such as the Maxwell equation and the Bruggeman one, have been given for the electrical conductivity of binary composites [9]. However, the applicability of these theories has been limited [9]. The effective medium (EM) theory [5] is known for its

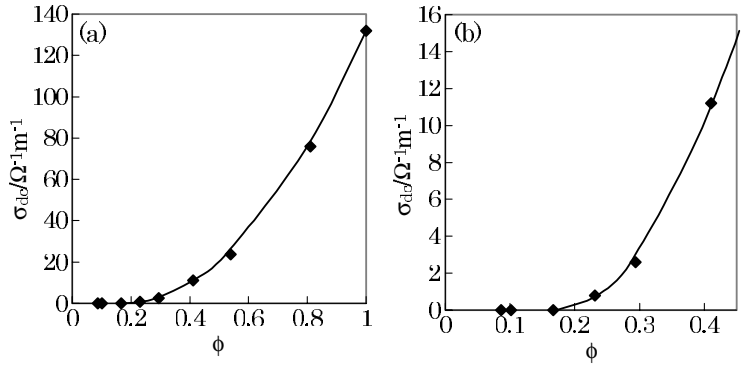

Figure 2. (a) Dc conductivity, σ_{dc}, at 453 K as a function of the volume fraction of AgI, ϕ (closed squares), and the fitted curve to equation (2) (curve) in the range from $\phi = 0$ to 1. (b) Dc conductivity, σ_{dc}, at 453 K as a function of the volume fraction of AgI, ϕ (closed squares), and the fitted curve to equation (2) (curve) in the range from $\phi = 0$ to 0.45.

wide applicability. According to this theory, the electrical conductivity of binary composite systems, σ_m, is given by the following equation:

$$\phi\left(\frac{\sigma_1 - \sigma_m}{\sigma_1 + 2\sigma_m}\right) + (1-\phi)\left(\frac{\sigma_2 - \sigma_m}{\sigma_2 + 2\sigma_m}\right) = 0. \tag{1}$$

In this equation, σ_m, σ_1, and σ_2 are respectively the electrical conductivity of the composite system, that of a high conductivity phase, and that of a low conductivity phase; ϕ is the volume fraction of the high conducting phase. It is well known that the threshold value of the volume fraction ϕ, ϕ_c, is one-third in the EM theory. The present studied system showed an abrupt increase of σ_{dc} around $\phi = 0.2$, as shown in figures 1 and 2. Therefore, the EM theory is not applicable to the present system straightforwardly.

McLachlan [8] has presented the generalized effective medium (GEM) theory, in which the scaling law of the percolation theory [10] was introduced into the EM theory (equation (1)). The explicit equation for the GEM theory is written as follows:

$$\phi\left(\frac{\sigma_1^{1/t} - \sigma_m^{1/t}}{\sigma_1^{1/t} + A\sigma_m^{1/t}}\right) + (1-\phi)\left(\frac{\sigma_2^{1/s} - \sigma_m^{1/s}}{\sigma_2^{1/s} + A\sigma_m^{1/s}}\right) = 0. \tag{2}$$

In this equation, the power indices s and t relate respectively to the power law behaviour of the percolation for the appearance of the conductivity and that for its disappearance. In addition, $A = \frac{1-\phi_c}{\phi_c}$, where ϕ_c is the threshold value of the volume fraction of the highly conducting phase for the percolation of electrical conduction. Equation (2) reduces to the various classical equations for the composite materials proposed to date, when the appropriate limit is applied [6]. In addition, equation (2) is known to be valid in a wide range of conductivity at least for the binary composite composed of electronic conduction and insulating phases [8].

At first, equation (2) was applied to the behaviour of σ_{dc} at 298 K exhibited in figure 1. Phases 1 and 2 are considered to be β-AgI and BN phases respectively. For σ_1, the value obtained in the present experiment ($\phi = 1.0$), 0.000 73 Ω^{-1} m^{-1}, was employed. For simplicity, the value of σ_2 for the BN phase was taken to be zero because of its extremely low value. The solid curve in figure 1 indicates the fitted curve to equation (2). The critical volume fraction of the β-AgI phase for the percolation of ionic conduction, ϕ_c, was determined as 0.16 ± 0.003 and t was determined as 2.0 ± 0.04. In addition, a similar fitting procedure was performed for the behaviour of σ_{dc} at 453 K exhibited in figure 2. For σ_1, the value obtained

in the present experiment ($\phi = 1.0$), 132 Ω^{-1} m^{-1}, was employed. The value of σ_2 for the BN phase was taken to be zero, as before. The critical volume fraction of the α-AgI phase for the percolation of ionic conduction, ϕ_c, and the power index, t, at 453 K was determined as 0.17 ± 0.003 and 2.00 ± 0.04 respectively. For both cases, the determined values for ϕ_c and t are in good agreement with the characteristic values of the percolation given by computer simulations, $\phi_c = 0.16 \pm 0.02$ and $t = 2.00 \pm 0.04$.

On the Monte Carlo computer simulation of the site model, each site is assumed to be occupied with a probability p [11, 12]. It is said that a cluster is formed if two adjacent sites are occupied. On increasing p, a cluster of infinite size is formed at p_c; at this moment the electrical conduction is considered to appear macroscopically. Zallen [3] and Scher and Zallen [13] converted the threshold value p_c to the another threshold value, ϕ_c. p_c and ϕ_c are defined respectively as the threshold value of the probability of occupation of the site, p, and that of the volume fraction of conducting phase(site), ϕ. They found that ϕ_c is dependent only on the dimensionality and independent of the crystal structures. In the three-dimensional case, $\phi_c = 0.16 \pm 0.02$. The critical exponents, t and s, were determined respectively, for example, by the resistor network model [10, 14, 15]. In this model, each bond of the percolation lattice is considered as the circuit element with a conductance σ, whose value is assumed to be either $\sigma = \sigma_H$ with probability p or $\sigma = \sigma_L$ with probability $1 - p$ (σ_H, the electrical conductivity of the high conducting bond; σ_L, that of the low conducting one). The universal values accepted for t and s are 2.0 [10] and 0.87–0.89 [10, 16] respectively.

Up to now, the percolation view has been applied for ionic conduction systems of macroscopically homogeneous ionic glasses [17–20]. However the reported ϕ_c values (critical volume fraction of a conducting phase) or x_c values (critical mole fraction of a conducting phase) are around 0.3. These large ϕ_c or x_c values of AgI may indicate that a considerable number of Ag^+ ions or AgI may be required for the formation of the ionic conduction domain, whose connection may produce the ion conducting path in homogeneous glasses. Quite recently, an attempt to apply the GEM theory to the (yttria-stabilized zirconia)–yttria ceramic composites [21] was made. Obtained percolation thresholds were found to be around 0.28. This large ϕ_c was attributed to the existence of the intrinsic blocking of carriers at the interface (mainly non-conducting grain boundary regions) of zirconia-based solid electrolytes.

As described above, the present result is in excellent agreement with the prediction of the computer simulations for the percolation of electrical conduction. Therefore, the present result is the first successful application of the GEM to the binary composite with ionic conduction. This indicates that the present AgI–BN composite is an ideal binary composite system composed of good ionic conductors and insulators.

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