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# The evolution of the ionic conduction of $(\text{AgI})_x-(\text{Ag}_2\text{O})_y-(\text{B}_2\text{O}_3)_{1-(x+y)}$ glasses containing nanocrystallites of $\alpha$ -AgI

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## Abstract

The dc electrical conductivity,  $\sigma_{\text{dc}}$ , was measured at room temperature by the ac impedance method for  $(\text{AgI})_x-(\text{Ag}_2\text{O})_y-(\text{B}_2\text{O}_3)_{1-(x+y)}$  ( $x = 0.75\text{--}0.85$ ;  $y = 0.09\text{--}0.15$ ) glasses, which were prepared by the twin-roller rapid quenching method. X-ray and scanning electron microscope analyses showed that, together with  $\beta$ -AgI crystallites with poor  $\sigma_{\text{dc}}$ , nanocrystallites of  $\alpha$ -AgI with high  $\sigma_{\text{dc}}$  were dispersed in the glass matrix with low  $\sigma_{\text{dc}}$ . The volume fraction of  $\alpha$ -AgI phase,  $\phi_1$ , was determined successfully from the measured  $^{109}\text{Ag}$  NMR spectrum and the density. The value of  $\sigma_{\text{dc}}$  increases with the increase of  $\phi_1$ . The behaviour of  $\sigma_{\text{dc}}$  was analysed based on the generalized effective medium theory for the coexisting system of three phases. A supplementary analysis was performed based on a power law in the percolation theory. A threshold value of 0.144 was obtained for the ionic conduction,  $\phi_c$ . Values of the critical exponents were determined as  $t = 1.98$  and  $s = 0.86$ , respectively. These characteristic values of percolation were in good agreement with the universal values, which have been predicted by computer simulations for the percolation of electrical conduction.

## 1. Introduction

The superionic conductors are ionic solids or ionic glasses with far higher electrical conductivities than those of ordinary solid ionic conductors. In the extreme case of  $\alpha$ -AgI crystal, its ionic conductivity amounts to that of an electrolyte solution. Much attention has been focused on the mechanism and the application of this high ionic conductivity. However, solid AgI is in the highly conductive phase, the  $\alpha$ -phase, only in the high temperature range (above 420 K) [1]. It is greatly desired to obtain such a high ionic conductivity in a low

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temperature range, such as at room temperature. Tatsumisago *et al* [2] presented a pioneering study for the preparation of superionic conductors containing nanocrystallites of  $\alpha$ -AgI in a glass matrix at room temperature. Because of the existence of these nano  $\alpha$ -AgI crystallites, the ionic conductivity is considerably high. However, the analysis of the electrical conductivity has not always been performed. Particularly, up to now, the effect of the variation of AgI concentration has not been clarified.

The glass containing  $\alpha$ -AgI precipitates is interesting because of its heterogeneous feature; crystal particles with high ionic conductivity are dispersed in the glass matrix with low conductivity. This situation may provide a good example of the percolation theory [3–5] or the effective medium theory [6] for ionic conduction systems. Electrical conduction in heterogeneous systems has been reviewed by Bergman and Stroud [7], Ce-Ben Nan [8], Kirkpatrick [9], and Clerc *et al* [10]. To date, the percolation theory has been employed to explain the behaviour of electrical conduction in heterogeneous materials or ‘artificial composites’ which are composed of electronically highly conductive materials and insulators (or poorly conductive materials). Here, the term ‘artificial composites’ means composite materials obtained ‘artificially’, that is ‘composites’ prepared simply by pressing a mixture of two constituent materials. In this respect, the  $\alpha$ -AgI precipitated glass should be called a ‘spontaneous composite’ because it is prepared in the cooling process from the melt ‘spontaneously’.

The dc electrical conductivity of heterogeneous systems increases rapidly with the increase of the volume fraction of highly conductive phase,  $\phi$ , when it exceeds the critical volume fraction, or the threshold value of the volume fraction,  $\phi_c$ . According to the percolation theory [3–5], the dc electrical conductivity,  $\sigma_{dc}$ , can be expressed as two power laws. One is  $\sigma_{dc} = \sigma_H(\phi - \phi_c)^t$ , which is valid for  $\phi > \phi_c$  (‘over  $\phi_c$ ’). In this equation,  $\sigma_H$  indicates the dc electrical conductivity of the highly conductive phase and the critical exponent  $t$  represents the approaching tendency of  $\sigma_{dc}$  to  $\sigma_H$  over  $\phi_c$ . Another is  $\sigma_{dc} = \sigma_L(\phi_c - \phi)^{-s}$ , which is valid for  $\phi < \phi_c$  (‘below  $\phi_c$ ’). In this equation,  $\sigma_L$  is the dc electrical conductivity of the poorly conductive phase and the critical exponent  $s$  represents the increasing tendency of  $\sigma_{dc}$  from  $\sigma_L$  below  $\phi_c$ . Historically, the electrical conduction in heterogeneous systems has also been discussed from the effective medium (EM) theory. Recently McLachlan [11, 12] proposed the generalized effective medium (GEM) theory, whose expression includes two power law behaviours,  $\sigma_{dc} = \sigma_L(\phi_c - \phi)^{-s}$  and  $\sigma_{dc} = \sigma_H(\phi - \phi_c)^t$  respectively, as two limiting cases,  $\sigma_{dc} \approx \sigma_L$  and  $\sigma_{dc} \approx \sigma_H$ . Thus, the GEM formula can be applicable to all the range of volume fraction. The behaviour of the electrical conductivity of a heterogeneous system can be characterized by  $\phi_c$ ,  $t$  and  $s$ .

Scher and Zallen [5] and Zallen [13] revealed that  $\phi_c$  is dependent only on the dimensionality if  $\phi_c$  is evaluated from  $p_c$ , which is given by computer simulations for various crystal forms [3, 4] as the threshold value of the probability of the occupancy on the site. Therefore,  $\phi_c$  can be considered to be universal. The universal value of  $\phi_c$  for the three-dimensional case is  $0.16 \pm 0.02$  [5, 13]. It has also been considered that for the critical exponents,  $t$  and  $s$ , there exist universal values, which are 2.0 for  $t$  and 0.87–0.89 for  $s$  respectively [3, 4, 7, 10–12]. However, it is quite incredible that, to date, the set of characteristic values of percolation,  $(\phi_c, t, s)$ , has not yet been determined completely for real materials, as discussed in detail in section 4. Therefore, it is very interesting to investigate whether the determined threshold value and the critical exponents of glass containing  $\alpha$ -AgI precipitates agree with the universal values [3, 4, 7, 10–12] or not.

The purpose of this study is to investigate from a viewpoint of percolation the behaviour of the dc electrical conductivity for the  $(\text{AgI})_x-(\text{Ag}_2\text{O})_y-(\text{B}_2\text{O}_3)_{1-(x+y)}$  system, which is a ‘spontaneous’ composite between the glass matrix and precipitates of nanocrystallites of

$\alpha$ -AgI. The dc electrical conductivity was analysed as a function of volume fraction of highly conductive  $\alpha$ -AgI phase,  $\phi_1$ , successfully based on the GEM theory [11, 12]. The previous GEM theory was limited to the binary composite and in this study the GEM theory was extended to the ternary composite. A supplementary analysis was also performed based on the power law in the percolation theory.

## 2. Experimental details

The superionic conductor glass containing nanocrystallites of  $\alpha$ -AgI,  $(\text{AgI})_x-(\text{Ag}_2\text{O})_y-(\text{B}_2\text{O}_3)_{1-(x+y)}$ , was prepared in the following way. The reagents used are Aldrich 99.999% for AgI and the special grade of Wako Pure Chemical for  $\text{Ag}_2\text{O}$  and  $\text{B}_2\text{O}_3$ . The reagents,  $\text{Ag}_2\text{O}$ ,  $\text{B}_2\text{O}_3$ , and AgI, were mixed together into fine powders in a mortar with the use of a pestle. The mixture of these fine powders was melted at 923 K in an electric furnace. Then, the homogeneous liquid was quenched with the use of a twin-roller rapid quenching apparatus [14]. The sample preparation was performed for  $(\text{AgI})_x-(\text{Ag}_2\text{O})_y-(\text{B}_2\text{O}_3)_{1-(x+y)}$  ( $x = 0.7\text{--}0.9$ ,  $y = 0.05\text{--}0.20$ ).

The rapidly quenched samples obtained were investigated with x-ray diffraction analysis, scanning electron microscope (SEM) analysis, impedance measurements, and  $^{109}\text{Ag}$  NMR measurements. The x-ray diffraction analysis was performed on thin films of rapidly quenched samples at room temperature by using a Rigaku MultiFlex with a  $\text{Cu K}\alpha$  x-ray source. The impedance measurements were performed on pellet samples of  $(\text{AgI})_x-(\text{Ag}_2\text{O})_y-(\text{B}_2\text{O}_3)_{1-(x+y)}$  ( $x = 0.75\text{--}0.85$ ,  $y = 0.09\text{--}0.15$ ) at room temperature by using an HP4291A impedance analyser in the frequency range from 20 Hz to 1 MHz. The pellet samples for the impedance measurements were prepared by pressing an assemblage of the rapidly quenched samples with thin silver powder layers (as electrodes) on both sides [15]. The dc (direct current) part of the electrical conductivity,  $\sigma_{\text{dc}}$ , was extracted from the measured impedance by the conventional method. The  $^{109}\text{Ag}$  NMR spectrum was obtained at 13.9 MHz with the use of a Bruker MSL-300 spectrometer. The magic angle spinning method [16] was adopted. Typical repetition time was 1 s. A dead time of 150–200  $\mu\text{s}$  was adopted. The  $^{109}\text{Ag}$  NMR was determined by the accumulation of 30 000–60 000 times. A 10 M aqueous solution of  $\text{AgNO}_3$  was used as the reference of the chemical shift.

In this study an accurate value of  $\phi_1$  was important for the analysis of the behaviour of  $\sigma_{\text{dc}}$ . By coupling the data of the density and the peak area of  $^{109}\text{Ag}$  NMR signals,  $\phi_1$  was evaluated. The density was determined from the volume and the weight of the sample pellet prepared for the density measurements. The volume of this sample pellet was calculated from its surface area and thickness. The mass of this sample pellet was determined by weighing. This density determination was performed with an accuracy over 99.9% judging from the comparison between the density determined for the AgI pellet prepared and that in the literature [17]. A typical example of a  $^{109}\text{Ag}$  NMR signal is shown in figure 1, which shows that there are three  $^{109}\text{Ag}$  NMR peaks. These three peaks are derived from  $\text{Ag}^+$  ions in the  $\alpha$ -AgI and the  $\beta$ -AgI phases and the glass matrix phase respectively, as explained in section 3. The peak areas in the  $^{109}\text{Ag}$  NMR signal were evaluated after the deconvolution of peaks.

The volume fraction of three phases ( $\alpha$ -AgI phase,  $\beta$ -AgI phase, and glass matrix phase) was evaluated as follows: the Ag mass ratio among these three phases was determined by the ratio of the corresponding peak area in the  $^{109}\text{Ag}$  NMR signal; the mass of the respective phase in the sample pellet for the density measurements was determined by considering this Ag mass ratio, the total weight and the weight of both AgI and  $\text{Ag}_2\text{O}$  of the rapidly quenched sample, and the weight of this sample pellet; the volume of  $\alpha$ -AgI phase and that of  $\beta$ -AgI phase in this sample pellet were calculated by using their density data [17] and their evaluated mass

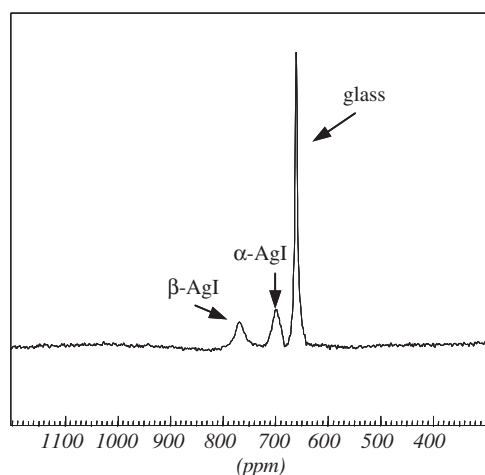


Figure 1. Typical  $^{109}\text{Ag}$  NMR spectrum for the glass containing nanocrystallites of  $\alpha\text{-AgI}$ .

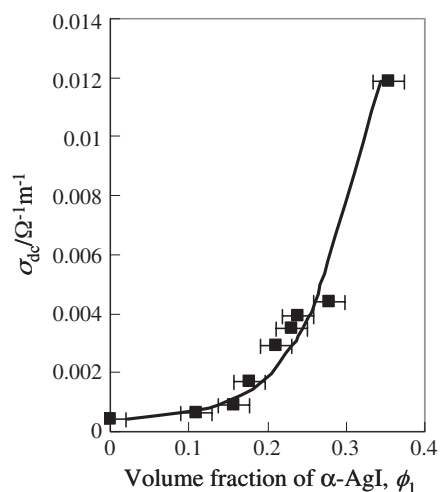
data; the volume of the glass matrix was calculated from the difference between the measured volume of this sample pellet and the sum of volume of both  $\alpha\text{-AgI}$  phase and  $\beta\text{-AgI}$  one. From these volumes, the evaluation was performed for the volume fraction of  $\alpha\text{-AgI}$  phase,  $\phi_1$ , that of  $\beta\text{-AgI}$  phase,  $\phi_2$ , and that of glass matrix phase,  $\phi_3$ . The determined set ( $\phi_1, \phi_2, \phi_3$ ) was adopted for the analysis of the measured conductivity. Needless to say, the same sample was employed for all series of present experiments, the x-ray diffraction analysis, the SEM analysis, the impedance measurements, and the  $^{109}\text{Ag}$  NMR measurements.

It was important for the exact evaluation of the set ( $\phi_1, \phi_2, \phi_3$ ) to evaluate the peak area in the  $^{109}\text{Ag}$  NMR signal accurately because the density determination was performed with a sufficient accuracy, as described above. The reliability of the determination of the peak area was over 98% judging from the reproducibility of the evaluation of the peak area by fitting a Gaussian function to the peaks in the  $^{109}\text{Ag}$  NMR signal. The error bar of volume fraction was estimated to be 2% at the maximum. This error bar was explicitly attached to the data points in figures 2–4.

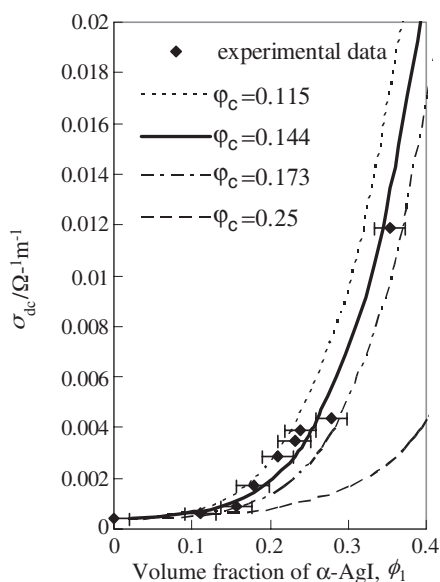
### 3. Results

The preparation of the superionic glass containing nanocrystallites of  $\alpha\text{-AgI}$  was confirmed qualitatively by the x-ray analysis; the Bragg peaks corresponding to the precipitated phases of  $\alpha\text{-AgI}$  and  $\beta\text{-AgI}$  respectively were observed in the halo pattern of the glass phase. The SEM analysis showed that the particle size of  $\alpha\text{-AgI}$  with almost round shape was a few 10 nm and that of  $\beta\text{-AgI}$  was a few  $\mu\text{m}$ . Also from the  $^{109}\text{Ag}$  NMR signals, it was possible to confirm quantitatively that the three phases ( $\alpha\text{-AgI}$  and  $\beta\text{-AgI}$  crystallites, and glass matrix) exist in the samples prepared. Three separate peaks can be seen in the  $^{109}\text{Ag}$  NMR spectrum shown in figure 1. The positions of three peaks were in good agreement with the  $^{109}\text{Ag}$  peak positions of  $\alpha\text{-AgI}$  single phase,  $\beta\text{-AgI}$  single phase, and homogeneous glass phase containing AgI respectively [16]. Therefore, it was concluded that these three peaks are derived from the  $\alpha\text{-AgI}$  and the  $\beta\text{-AgI}$  crystallites and the glass matrix, respectively.

By the rapid quenching technique, four kinds of glass were prepared,  $\alpha\text{-AgI}$  precipitated glass,  $\beta\text{-AgI}$  precipitated glass, both  $\alpha\text{-AgI}$  and  $\beta\text{-AgI}$  precipitated glass, and homogeneous glass. Among these samples, selected compositions for the dc conductivity measurements

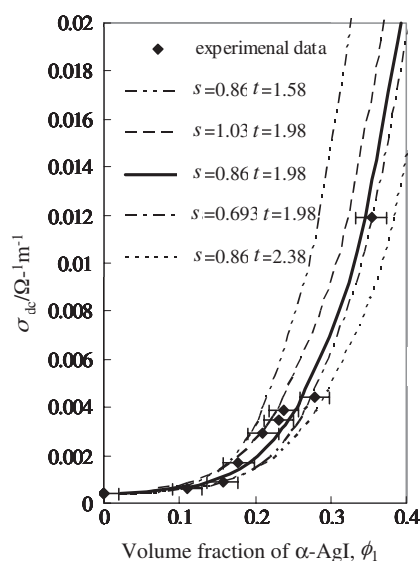


**Figure 2.** The dc electrical conductivity,  $\sigma_{dc}$ , at room temperature as a function of the volume fraction of  $\alpha$ -AgI,  $\phi_1$ ; closed squares: experimental data; line: the curve fitted to equation (1).



**Figure 3.** The effect of the variation of the threshold value,  $\phi_c$ , on the predicted curve of the dc electrical conductivity,  $\sigma_{dc}$ , by equation (1) ( $t = 1.98$ ,  $s = 0.86$ ).

were (0.85, 0.10, 0.05), (0.85, 0.09, 0.06), (0.83, 0.11, 0.06), (0.82, 0.13, 0.05), (0.80, 0.14, 0.06), (0.79, 0.11, 0.10), (0.79, 0.15, 0.06), (0.77, 0.15, 0.08), and (0.75, 0.15, 0.10); in this notation  $a$ ,  $b$ , and  $c$  in  $(a, b, c)$  correspond to the mole fraction of  $\text{AgI}_{(x)}$ ,  $\text{Ag}_2\text{O}_{(y)}$ , and  $\text{B}_2\text{O}_3_{(1-(x+y))}$ , respectively. The corresponding volume fractions of each phase evaluated for these nine samples are respectively (0.354, 0.183, 0.463), (0.287, 0.152, 0.561), (0.238, 0.078, 0.684), (0.231, 0.077, 0.692), (0.210, 0.175, 0.615), (0.178, 0.00, 0.822), (0.173, 0.137, 0.690), (0.110, 0.105, 0.785), and (0.00, 0.00, 1.00), with the notation of the set  $(\phi_1, \phi_2, \phi_3)$ .



**Figure 4.** The effect of the variation of critical exponents,  $t$  and  $s$ , on the predicted curve of the dc electrical conductivity,  $\sigma_{dc}$ , by equation (1) ( $\phi_c = 0.144$ ).

As shown in figure 2, the measured dc conductivity (solid circles),  $\sigma_{dc}$ , was well summarized as a function of the  $\phi_1$  irrespective of  $\phi_2$ . The value of  $\sigma_{dc}$  increases rapidly around  $\phi_1 = 0.16$  with the increase of  $\phi_1$ .

#### 4. Discussions and conclusions

The behaviour of the  $\sigma_{dc}$  obtained in the present study encouraged us to perform a percolation analysis or a GEM analysis. At first the analysis was performed based on the GEM theory, which can describe the conductivity behaviour in the whole range of volume fraction. The GEM form for the binary composite has been successfully applied to several systems though the systems studied were limited to electronic conduction systems [11, 12, 18–21]. It is expected that the GEM theory is also applicable to ionic systems. As already described, the present ionic system is composed of three phases, the high, poor and low conductive phases of  $\alpha$ -AgI,  $\beta$ -AgI and glass matrix respectively. Therefore, the GEM theory was extended to the case of ternary composite. The explicit derivation is given in the appendix. The GEM formula for a ternary composite is written as follows:

$$\phi_1 \left( \frac{\sigma_1^{1/t} - \sigma_m^{1/t}}{\sigma_1^{1/t} + A\sigma_m^{1/t}} \right) + \phi_2 \left( \frac{\sigma_2^{1/s} - \sigma_m^{1/s}}{\sigma_2^{1/s} + A\sigma_m^{1/s}} \right) + \phi_3 \left( \frac{\sigma_3^{1/s} - \sigma_m^{1/s}}{\sigma_3^{1/s} + A\sigma_m^{1/s}} \right) = 0. \quad (1)$$

In this equation,  $\sigma_i$  is the dc electrical conductivity of phase  $i$  ( $i = 1, 2$  and  $3$ ), and  $\sigma_m$  is that of effective medium composed of phases, 1, 2, and 3. The critical exponents,  $t$  and  $s$ , have the same meaning as those in the power laws. In addition, the symbol  $A$  is defined as  $A = \frac{1-\phi_c}{\phi_c}$  ( $\phi_c$ : the threshold value of the volume fraction of phase 1 with the largest electrical conductivity) [22].

In the application of equation (1), the phases, 1, 2, and 3, are assumed to correspond to the  $\alpha$ -AgI, the  $\beta$ -AgI, and the glass matrix phase respectively. The characteristic values of percolation,  $\phi_c$ ,  $t$ , and  $s$ , were determined by fitting equation (1) to the experimental

$\phi_1$  dependence of the  $\sigma_{dc}$  by the least squares method. As  $\sigma_1$ ,  $16.7 \Omega^{-1} \text{ m}^{-1}$  was adopted by extrapolating the temperature dependence of  $\sigma_{dc}$  for  $\alpha$ -AgI over 420 K [1] to room temperature. As  $\sigma_2$ , the adopted value was  $0.0002 \Omega^{-1} \text{ m}^{-1}$ , which was the measured value in the present experiment. As  $\sigma_3$ , the adopted value was  $0.0423 \Omega^{-1} \text{ m}^{-1}$ , which was taken from the measured  $\sigma_{dc}$  for the homogeneous glass containing the solubility limit of AgI.

The solid line in figure 2 shows the curve fitted to equation (1). This fitted curve was obtained as follows: the set,  $(\phi_1, \phi_2, \phi_3)$ , corresponding to the experimental dc electrical conductivity,  $\sigma_m^{\text{Exp}}(\phi_1, \phi_2, \phi_3)$ , was already presented in section 3; the set  $(\sigma_1, \sigma_2, \sigma_3)$  is given as described above; if the set  $(\phi_c, t, s)$  is given,  $\sigma_m$  can be calculated by using equation (1) and this calculated  $\sigma_m$  is denoted as  $\sigma_m^{\text{Try}}(\phi_1, \phi_2, \phi_3)$ ; the best set of  $(\phi_c, t, s)$  is obtained by minimizing the square of the standard deviation,  $\sum_{(\phi_1, \phi_2, \phi_3)} (\sigma_m^{\text{Try}}(\phi_1, \phi_2, \phi_3) - \sigma_m^{\text{Exp}}(\phi_1, \phi_2, \phi_3))^2$ . The GEM values,  $\sigma_m^{\text{GEM}}$ , can be obtained from equation (1) by inserting the best fitted set of  $(\phi_c, t, s)$  and nine sets of  $(\phi_1, \phi_2, \phi_3)$  corresponding to  $\sigma_m^{\text{Exp}}(\phi_1, \phi_2, \phi_3)$ . The curve fitted to equation (1) was drawn by using these  $\sigma_m^{\text{GEM}}$ .

From this analysis, the obtained  $\phi_c$  was 0.144. The determined critical exponents were  $t = 1.98$  and  $s = 0.86$ , respectively. These determined values are in good agreement with universal values,  $\phi_c = 0.16 \pm 0.02$  [5, 13],  $t = 2.0$  [3, 4, 10–12] and  $s = 0.87\text{--}0.89$  [3, 4, 10–12], which are given by the computer simulations.

To verify the accuracy of this least squares determination by using the GEM theory, the deviation of the curve from the experimental points was investigated by adopting values of  $(\phi_c, t, s)$  slightly different from the best set. As can be seen in figure 3, a considerable deviation was observed in the case of  $\phi_c$  being different from the best fitted value. This indicates the reliability of the determination of  $\phi_c$ . As can be seen in figure 4, the reliability is confirmed also for the determination of  $t$ . However, figure 4 shows that the determination of  $s$  seems to be performed in a slightly insensitive manner in the present study, though the best fitted value of  $s$  itself remains as 0.86.

A power law analysis was also performed for the present experimental result. The best set  $(\phi_c, t)$  was determined for the  $\log(\sigma_{dc} - \sigma_3) - \log(\phi_1 - \phi_c)$  plot. In this case, the extrapolated value of  $\sigma_{dc}$  of  $\alpha$ -AgI at room temperature,  $16.7 \Omega^{-1} \text{ m}^{-1}$ , was also adopted as the data for  $\phi_1 = 1$  in addition to the present nine sets of experimental data,  $(\phi_1, \sigma_{dc})$ . The  $\phi_c$  and  $t$  obtained by the least squares method are 0.146 and 1.80, respectively. The value of  $\phi_c$  is in good agreement with 0.144 obtained by the GEM analysis. Therefore, the reliability was confirmed for the  $\phi_c$  obtained by the GEM analysis together with the adopted value of  $\sigma_{dc}$  for  $\alpha$ -AgI at room temperature. On the other hand, 1.80, given for  $t$  by the power law, was slightly smaller than the value of  $t$  given by the GEM analysis, 1.98, which is in good agreement with the universal value. According to Lin [23], a value smaller than 2 can be obtained as the critical exponent  $t$  by a power law analysis for a composite in which the conductivity difference between the constituent phases is not so large. The present smaller value of  $t$  in the power law analysis,  $t = 1.8$ , seems to correspond to the case pointed out by Lin.

Needless to say, it is better to determine the characteristic values of percolation by using as many data points as possible. In the present experiment, the  $\alpha$ -AgI precipitated glass was prepared only in a limited  $\phi_1$  range. In spite of this limitation,  $\phi_c$  seems to be determined accurately by using the GEM theory. The percolation theory or the power law is correct only over  $\phi_c$  or below  $\phi_c$ . Thus, in the percolation theory or the power law, the characteristic values of percolation,  $\phi_c$ ,  $t$  and  $s$ , must be determined in the  $\phi$  range over  $\phi_c$  or below  $\phi_c$ . This requires many data points for the accurate determination of  $\phi_c$  and  $t$  or  $\phi_c$  and  $s$ . It must be stressed that the GEM formula incorporates these power laws over  $\phi_c$  and below  $\phi_c$  as limiting cases. Thus, it is valid in the whole range of the volume fraction (0–1). In addition, on determining  $\phi_c$ ,  $t$



and  $s$  by using the GEM theory, the values of  $\sigma_{dc}$  for  $\phi = 0$  and 1 are inserted beforehand as input data. Therefore, as shown in figures 3 and 4, the determination of  $\phi_c$ ,  $t$  and  $s$  by the GEM theory may be reasonably correct under the present condition, using nine data points. The good agreement of  $\phi_c$ ,  $t$  and  $s$  with universal values may be reliable.

To date, reported characteristic values of percolation have not always been in agreement with the universal values. This unpleasant situation can be seen in table 1 of Clarke *et al* [24]. They showed that even  $\phi_c$  varies from 0.07 to 0.75 though  $\phi_c \cong 0.15$  can be seen most frequently. The situation for  $t$  is worse. There were not so many systems for which the value of  $t$  had been reported. In addition, the values of  $t$  vary in a wide range between 0.38 and 2.0. McLachlan and co-researchers [11, 12, 18, 19, 25] have extensively developed the GEM analysis of the characteristic values of percolation,  $\phi_c$ ,  $t$  and  $s$ , for ‘artificial composites’. In the case of such ‘artificial composites’, the volume fraction of constituent phases can be determined easily with the knowledge of the density and the weight of constituent phases. The determined  $\phi_c$  was in many cases around 0.15, though there were some exceptions. However, obtained  $t$  and  $s$  values depended on the sample measured and differed from the universal values. Recently, quite low values of  $\phi_c$ , below 1%, were reported for composite systems between carbon black (fibre) and polymer [26–29]. The polymer material is not conductive. The highly conductive carbon black (CB) particles have complex structures: hollow semi-spheres of a few graphite layers, 1.0–1.5 nm in thickness, with a diameter of 30 nm [27]. These small values of  $\phi_c$  indicate that the ideal percolation analysis may be insufficient for the composite system with ‘complicated structure’.

The systems discussed above are materials with electronic conduction. The ionic conduction system itself is fundamentally appropriate for the study of percolation phenomena because of the lack of ‘scattering phenomena’ or ‘tunnelling phenomena’ at the boundary between the highly conductive phase and the poorly conductive one. Such complex phenomena usually appear for composites with electronic conduction. Nevertheless, this unsatisfactory situation has been present for the study of composites with ionic conduction. To date, many applications of percolation theory to ionic conduction systems have been limited to homogeneous glasses [15, 30–33]. In such cases, the detail of the ‘evaluation of the volume fraction of conductive phase’ is not always clear in their original references. In addition, the reported  $\phi_c$  or  $x_c$  (the critical mole fraction of percolation) for these homogeneous glasses is around 0.3, which is different from the universal value,  $0.16 \pm 0.02$  [5, 13]. The percolation behaviour with two thresholds ( $x_c = 0.2$  and 0.9) was found for AgI–Al<sub>2</sub>O<sub>3</sub> composites [34]. In this study, the ‘modification of the interface’ was stressed. Recently, an experimental study was performed for the composite material, (ZrO<sub>2</sub>: 8 at.% Y<sub>2</sub>O<sub>3</sub>) + m mol.% Y<sub>2</sub>O<sub>3</sub>, with ionic conduction [35]. The reported  $\phi_c$  is around 0.28, which was obtained based on the simplified GEM theory ( $t = s$  in equation (A.2)). This rather large  $\phi_c$  was attributed to the ‘dependence of the grain size and the porosity on the volume fraction’. On the other hand, two characteristic values of percolation close to the universal values,  $\phi_c = 0.16$  and  $t = 2.0$ , were reported by the present authors [36] for the ‘artificial composite with ionic conduction’ composed of  $\alpha$ -AgI and BN, which do not react with each other. This study implies that the universal values may be valid for the characteristic values of percolation,  $\phi_c$ ,  $t$ , and  $s$ , when there are no chemical reactions between constituent phases and no complex grain structures.

Under these situations, the present study provided the universal values for  $\phi_c$ ,  $t$  and  $s$ . This may be derived from the fact that the present glass containing  $\alpha$ -AgI precipitates is ‘spontaneous composite’, which may be characterized by the almost absence of chemical reactions, and by the clear interface between constituent phases. Almost all the  $\alpha$ -AgI precipitates in the present glass show a round shape with nearly the same size of a few 10 nm, as already described. This may be derived from their origin, namely they may evolve as

liquid droplets in the two liquid phase separation process [37], which is included in the rapid quenching process. In the case of a composite with ‘wide distribution of size and shape of well conductive domain’ in a poorly conductive medium,  $\sigma_{dc}$  may depend not only on the volume fraction but also on this distribution. However, the present system may be free from the problems of ‘complicated structure’, ‘scattering phenomena’, ‘tunnelling phenomena’, ‘modification of the interface’, ‘dependence of the grain size and porosity on the volume fraction’, and ‘wide distribution of size and shape of well conductive domain’ though they are themselves interesting as physics. In addition, it is noteworthy that in the present study the ‘evaluation of the volume fraction of conductive phase’ was rigorously performed by combining the  $^{109}\text{Ag}$  NMR spectra and the density data. For these reasons, a good agreement of  $\phi_c$  with the universal value was obtained in the present study. In other words, the superionic glass containing spontaneous precipitates of nano  $\alpha$ -AgI crystallites seems to be an ideal percolation system.

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### Appendix. The derivation of GEM theory for the dc electrical conductivity of three phase case

According to the EM theory [6, 22], the dc electrical conductivity of the effective medium,  $\sigma_m$ , for a heterogeneous system composed of two phases, 1 and 2, is related to the volume fractions and the electrical conductivities of these phases,  $\phi_i$  and  $\sigma_i$  ( $i = 1$  or  $2$ ). The relation,  $\sigma_1 > \sigma_2$ , can be assumed. The explicit equation of  $\sigma_m$  is as follows:

$$\phi_1 \left( \frac{\sigma_1 - \sigma_m}{\sigma_1 + A\sigma_m} \right) + \phi_2 \left( \frac{\sigma_2 - \sigma_m}{\sigma_2 + A\sigma_m} \right) = 0. \quad (\text{A.1})$$

In this equation,  $A = \frac{1-\phi_c}{\phi_c}$  ( $\phi_c$ : the threshold value of the volume fraction of phase 1); the case of  $\phi_c = 1/3$  ( $A = 2$ ) corresponds to the heterogeneous system composed of spherical spheres (phase 1) and the homogenous matrix (phase 2) [12]. McLachlan [11, 12] derived the GEM theory from this EM theory by taking into account the power law behaviours [3, 7–9, 11, 13]. The explicit form of the GEM theory for the binary composite is written as follows:

$$\phi_1 \left( \frac{\sigma_1^{1/t} - \sigma_m^{1/t}}{\sigma_1^{1/t} + A\sigma_m^{1/t}} \right) + \phi_2 \left( \frac{\sigma_2^{1/s} - \sigma_m^{1/s}}{\sigma_2^{1/s} + A\sigma_m^{1/s}} \right) = 0. \quad (\text{A.2})$$

In this equation, the critical exponents,  $s$  and  $t$ , relate respectively to the increasing tendency of electrical conductivity below  $\phi_c$  and approaching tendency to  $\sigma_1$  over  $\phi_c$  with the increase of  $\phi_1$ . These critical exponents are believed to be universal [3, 4, 10–12]. The extension of equation (A.1) into an  $n$ -phase system is straightforward. The condition of zero for the electric polarization [6] reduces to the following equation [22].

$$\sum_{i=1}^n \phi_i \left( \frac{\sigma_i - \sigma_m}{\sigma_i + A\sigma_m} \right) = 0. \quad (\text{A.3})$$

The extension of equation (A.2) into the ternary composite may be given in a straightforward manner. However, at first sight, it seems to be a little difficult because of the

existence of the critical exponents,  $t$  and  $s$ , in equation (A.2). Therefore, a simple derivation is tried here for this extension. At first, it is assumed that the ternary composite is a mixture of binary composites,  $A$  and  $B$ . The volume fractions of system  $A$  and  $B$  are respectively  $\phi_A$  and  $\phi_B$ ;  $\phi_A + \phi_B = 1$ . The system  $A$  is composed of two phases, 1 and 2, whose volume fractions are  $\phi_{A1}$  and  $\phi_{A2}$  respectively;  $\phi_{A1} + \phi_{A2} = 1$ . The electrical conductivity of phase  $i$  is  $\sigma_i$  ( $i = 1, 2$ ). The system  $B$  is composed of two phases, 1 and 3, whose volume fractions are  $\phi_{B1}$  and  $\phi_{B3}$ , respectively;  $\phi_{B1} + \phi_{B3} = 1$ . The electrical conductivity of phase 3 is  $\sigma_3$ . The only limitation for the notation of phases, 1, 2 and 3, is that the electrical conductivity of phase 1 is largest among these three phases. Then, it is possible to assume that both systems,  $A$  and  $B$ , possess the same electrical conductivity as the effective medium, namely  $\sigma_m$ . Because of the universality, the same critical exponents,  $t$  and  $s$ , can be adopted for both systems,  $A$  and  $B$ .

The GEM theories for systems,  $A$  and  $B$ , are written as follows:

$$\phi_{A1} \left( \frac{\sigma_1^{1/t} - \sigma_m^{1/t}}{\sigma_1^{1/t} + A\sigma_m^{1/t}} \right) + \phi_{A2} \left( \frac{\sigma_2^{1/s} - \sigma_m^{1/s}}{\sigma_2^{1/s} + A\sigma_m^{1/s}} \right) = 0; \quad (\text{A.4})$$

$$\phi_{B1} \left( \frac{\sigma_1^{1/t} - \sigma_m^{1/t}}{\sigma_1^{1/t} + A\sigma_m^{1/t}} \right) + \phi_{B3} \left( \frac{\sigma_3^{1/s} - \sigma_m^{1/s}}{\sigma_3^{1/s} + A\sigma_m^{1/s}} \right) = 0. \quad (\text{A.5})$$

Noting the relations,  $\phi_1 = \phi_A\phi_{A1} + \phi_B\phi_{B1}$ ,  $\phi_2 = \phi_A\phi_{A2}$ , and  $\phi_3 = \phi_B\phi_{B3}$ , equations (A.4) and (A.5) reduce to a single equation, namely equation (1) in the text.

$$\phi_1 \left( \frac{\sigma_1^{1/t} - \sigma_m^{1/t}}{\sigma_1^{1/t} + A\sigma_m^{1/t}} \right) + \phi_2 \left( \frac{\sigma_2^{1/s} - \sigma_m^{1/s}}{\sigma_2^{1/s} + A\sigma_m^{1/s}} \right) + \phi_3 \left( \frac{\sigma_3^{1/s} - \sigma_m^{1/s}}{\sigma_3^{1/s} + A\sigma_m^{1/s}} \right) = 0. \quad (1)$$

It is easy to extend this equation to the general  $n$ -phase ( $n > 3$ ) case. In addition, the present method is also valid for the derivation of equation (A.3) in the EM theory under the assumption that the  $\sigma_1$  is the largest among the  $\sigma_i$  ( $i = 1, 2, 3, \dots, n$ ).

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