

## Analysis of the AC Ionic Conductivity in $(\text{AgI})_{0.4}(\text{AgPO}_3)_{0.6}$ Glass by Using the Logarithmic Mixing Rule

Jean Leopold NDEUGUEU and Masaru ANIYA

*Department of Physics, Kumamoto University, Kumamoto 860-8555*

(Received September 30, 2008)

The ac ionic conductivity of the glassy system  $(\text{AgI})_{0.4}(\text{AgPO}_3)_{0.6}$  has been analyzed by the logarithmic mixing rule. The analysis reveals that the rule is also applicable to AgI-based oxide superionic glasses.

### §1. Introduction

Many materials that exhibit the power law dispersion in the ac conductivity consist of phases with different conductivity. The overall conductivity increases with frequency. At lower frequencies, transport must extend over longer distances and is limited by poorly conducting regions. At higher frequencies, localized charge carrier motion contributes to a maximum in the well conducting regions.<sup>1)</sup> Almond et al. have modeled the ac conductivity by a randomly connected resistance-capacitance network where the conductive phase is represented by resistors and the dielectric phase by capacitors.<sup>2),3)</sup> According to the logarithmic mixing rule, the complex conductivity of the network  $\sigma^*$  with  $x$  components can be expressed by<sup>4)</sup>

$$\ln \sigma^* = \sum \alpha_x \ln \sigma_x^*, \quad (1.1)$$

where  $\sigma_x^*$  and  $\alpha_x$  are the complex conductivity and volume fraction of the  $x$ -th component, respectively. The measurable bulk ac conductivity  $\sigma_{meas}$  (real component of  $\sigma^*$ ) can be deduced from Eq. (1.1) as

$$\sigma_{meas} = (\omega\epsilon\epsilon_0)^\alpha (\sigma_c)^{1-\alpha} \cos(\alpha\pi/2), \quad (1.2)$$

where  $\sigma_c$  and  $\epsilon$  are the conductivity and relative permittivity of the conductive and dielectric phases, respectively.  $\epsilon_0$  is the permittivity of free space, and  $\alpha$  is the fractional volume of the material occupied by the dielectric phase.

The interesting point of the logarithmic mixing rule given by Eq. (1.2) is that it leads to a power law frequency dependence of ac conductivity which is characterized by the Jonscher's universal relaxation law<sup>5)</sup>

$$\sigma(\omega) = \sigma(0) + A\omega^n, \quad (1.3)$$

where  $\sigma(0)$  is the low frequency plateau in conductivity. This is often considered to be the dc conductivity of the material.  $n$  is the power law exponent varying roughly between 0.6 and 0.7 at room and higher temperatures<sup>6)</sup> but is found universally to rise to 1.0 at low temperatures.<sup>7)</sup>  $A$  is a constant given by

$$A = \omega_c^{-n} \sigma(0), \quad (1.4)$$

where  $\omega_c$  represents the onset frequency of the dispersive behavior.

## §2. Analysis of the ac ionic conductivity by using the logarithmic mixing rule

Recently, Almond and Bowen have presented an experimental examination of the R-C network approach by comparing the measured electrical properties of a carefully selected and characterized real material system with those predicted by the logarithmic mixing rule for a random R-C network.<sup>2)</sup> The two materials selected to form the test system are the ferroelectric ceramic lead zirconate titanate (PZT) as the dielectric phase and water as the conductive phase. An independent measurement of the conductivity of water has been made, and it has been shown that at critical frequency  $\omega_c$ , the percolation conductivity of water through the PZT pore system is a factor  $\approx 20$  smaller than that of the water. They have also suggested the use of this factor to estimate the actual conductivity in other systems. At the critical frequency, the measurable bulk ac conductivity  $\sigma_{\text{meas}}$  given by Eq. (1.2) has been approximated as 10 times the dc conductivity  $\sigma(0)$ , i.e.,

$$\sigma_{\text{meas}} \approx 10\sigma(0). \quad (2.1)$$

Inserting Eq. (2.1) into Eq. (1.2), the value of  $\alpha$  has been extracted for the water-PZT system. The obtained results ( $\alpha = 0.78$ ) are found to be in excellent agreement with measurements.

Based on this finding, we have verified the applicability of the suggestions made by Almond and Bowen in the  $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$  glass system (with  $x = 0.4$ ). In this case the relationship between the conductivity of AgI,  $\sigma_c$ , and the dc conductivity  $\sigma(0)$  is written as

$$\sigma_c = \beta\sigma(0), \quad (2.2)$$

where  $\beta$  is a constant. A widely employed practice has been used to fit experimental data by adding the dc conductivity to the measurable bulk ac conductivity.<sup>1),8),9)</sup> Thus Eq. (1.2) can be written as

$$\sigma_{\text{meas}} = (\omega\epsilon\epsilon_0)^\alpha (\sigma_c)^{1-\alpha} \cos(\alpha\pi/2) + \sigma(0). \quad (2.3)$$

The fractional volume occupied by  $\text{AgPO}_3$  has been calculated from

$$\alpha = \frac{(1-x)M_1}{(1-x)M_1 + x(\rho_1/\rho_2)M_2}, \quad (2.4)$$

where  $M_1$  and  $M_2$  are the molar weights,  $\rho_1$  and  $\rho_2$  are the mass densities of  $\text{AgPO}_3$  and AgI, respectively,  $x$  is the mole fraction of  $\text{AgPO}_3$ . Data of  $\rho_1$  and  $\rho_2$  have been taken from Refs. 10 and 11, respectively. The relative permittivity  $\epsilon$  has been taken from Refs. 11 and 12. The results obtained for different values of  $\beta$  are shown in Fig. 1. A comparison with experimental data<sup>12)</sup> is also indicated.

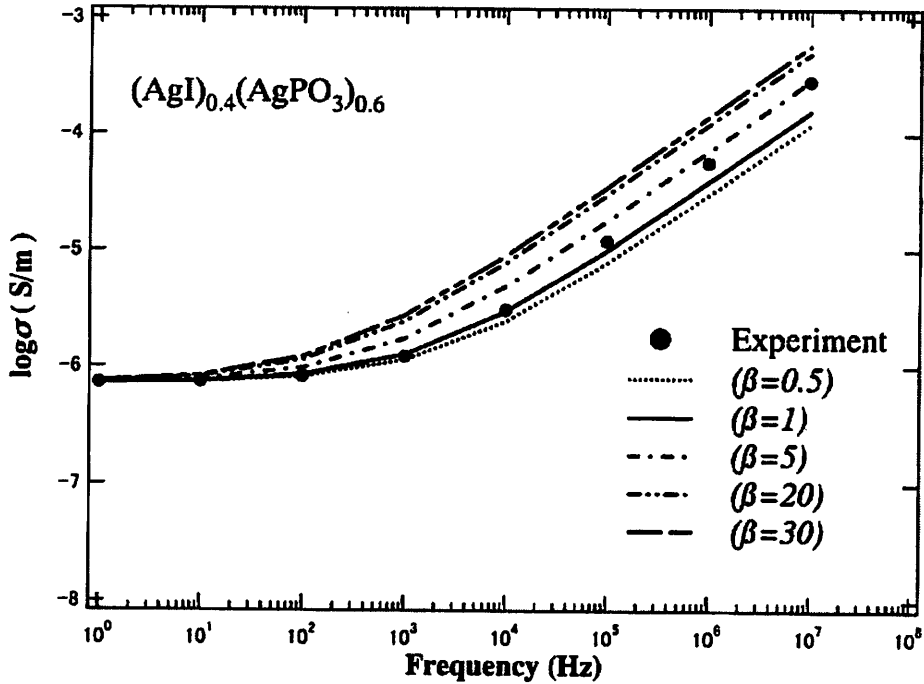


Fig. 1. The ac conductivity of  $AgI_{0.4}(AgPO_3)_{0.6}$  at 151.8 K. Solid and broken lines are calculated from Eq. (2.3) for different values of  $\beta$ .

### §3. Discussion

The explanation of the power law (mixing rule) has been based on the following conditions:<sup>2)</sup>

- 1) The material must have a microstructure, i.e., a network of interconnected conductive and dielectric phases.
- 2) These phases must be well characterized and frequency independent in the low frequency range.
- 3) Commonly, in the frequency range  $\approx 10^5 - 10^7$  Hz, the power law dispersion must occur.

Although the glass system  $AgI_{0.4}(AgPO_3)_{0.6}$  under consideration is not an ideal mixture of conductive and dielectric phases, Eq. (2.3) can reproduce quite well the experimental data if we choose  $\beta = 1$ . From the study on the water-PZT system, Almond and Bowen have suggested that at critical frequency, the actual conductivity of other systems can be estimated as 20 times the dc conductivity  $\sigma(0)$ . As it can be observed in Fig. 1, this suggestion is not compatible with our results. In addition to the case of water-PZT, the validity of the assumption  $\sigma_c = 20\sigma(0)$  has been also verified in the systems of Na- $\beta$  alumina,  $Na_2O-3SiO_2$  glass,  $LiCl-H_2O$ , 12 mol% Ytria-zirconia, and Carbon black in thermoset resin.<sup>2)</sup> It will be interesting to investigate to what extent this relation is valid in different materials systems.

#### §4. Conclusion

We have analyzed the ac conductivity in glassy  $\text{AgI}_{0.4}(\text{AgPO}_3)_{0.6}$  by using the logarithmic mixing rule. A good agreement with experimental data has been found. A relationship between the actual conductivity of the conductive phase and the dc conductivity has been proposed to better fit the experiment data for the materials which exhibit the power law ac conductivity. This work reconfirms the suggestion made by Almond et al. that the power law dispersion found in the electrical response of materials can be satisfactorily explained by using the logarithmic mixing rule.

#### Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (No. 19560014) and by a Grant-in-Aid for Scientific Research on Priority Area, "Nanoionics (439)" from the Ministry of Education, Culture, Sports, Science and Technology of Japan. J.L.N. acknowledges the Monbukagakusho Scholarship.

#### References

- 1) J. C. Dyre and T. B. Schröder, *Rev. Mod. Phys.* **72** (2000), 873.
- 2) D. P. Almond and C. R. Bowen, *Phys. Rev. Lett.* **92** (2004), 157601.
- 3) D. P. Almond and B. Vainas, *J. Phys. Condens. Matter* **11** (1999), 9081.
- 4) V. T. Truong and J. G. Ternan, *Polymer* **36** (1995), 905.
- 5) A. K. Jonscher, *Nature* **267** (1977), 673.
- 6) D. L. Sidebottom, P. F. Green and R.K.Brow, *J. Non-Cryst. Solids* **183** (1995), 151.
- 7) W. K. Lee, J. F. Liu, and A. S. Nowick, *J. Mat. Sci.* **19** (1984), 3236.
- 8) A. G. Hunt, *Philos. Mag. B* **81** (2001), 875.
- 9) E. Tuncer, Y. V. Serdyuk and S. M. Gubanski, *IEEE Trans. Dielectr. Electr. Insul.* **9** (2002), 809.
- 10) P. Benassi, A. Fontana and P. A. M. Rodrigues, *Phys. Rev. B* **43** (1991), 1756.
- 11) Landolt-Börnstein, **17(b)**, Springer Verlag (1982), p.301.
- 12) D. L. Sidebottom, *Phys. Rev. B* **61** (2000), 14507.