

Electrical properties of silver iodide nanoparticles system embedded into opal porous matrix

A E Lukin, E N Ivanova, S V Pan'kova, V G Solovyev, V L Veisman

Pskov State University, Lenin square, 2, 180000 Pskov, Russia

E-mail: richardstone@yandex.ru

Abstract. Opal-based composite with silver iodide nanoparticles (AgI/opal) has been prepared by host-guest technology. Temperature and frequency dependences of electrical conductivity and those of dielectric permittivity of AgI/opal samples were measured. Size effects in this opal-based nanocomposite have been discussed.

1. Introduction

Silver iodide is a well-known model superionic compound in solid state physics [1-3]. At room temperature AgI is a mixture of low-conducting β (wurtzite) and γ (zinc blende) phases. At transition temperature $T_t \approx 420$ K the phase transition to the high-conducting (superionic) α -AgI occurs. In this high-temperature α phase large iodine anions form a body-centred cubic (bcc) lattice, whereas small silver cations move over numerous sites, forming “liquid-like” system.

In last decades, superionic conductor AgI has been thoroughly studied under restricted geometry conditions. A giant dielectric permittivity values as well as significant broadening of the melting-freezing phase transitions were found, in particular, in opal-based composites containing nanoparticles of AgI and those of other ionic compounds [4-6]. To discover new size effects as well as to design novel switching and memory devices operating at lowered temperatures, silver iodide nanoparticles [7-11], nanowires [12, 13], nanoplates [14, 15] and thin films [16-18] have been investigated.

In this work, we use regular porous opal matrix for preparing nanosize objects within the regular systems of voids. This idea proposed by Bogomolov and co-workers [19-21] was successfully used in [7-9] where silver iodide particles were prepared in voids and channels of molecular sieves MCM-41 and SBA-15, porous glasses and opals by chemical synthesis [8, 9] or high-pressure technique [7]. Unlike these technologies, we filled opal matrix directly with silver iodide melt under the ambient conditions.

A three-dimensional ordered face centered cubic (fcc) structure of self-assembled artificial opal matrix [22] is formed by closely packed silica globes with their volume filling factor $\rho = \pi\sqrt{2}/6 \approx 0.74$ and the first-order porosity $f_1 = 1 - \rho \approx 0.26$. One can also find smaller voids and channels in some types of “open” (fractal) opal structures with high order ($m \geq 1$) porosity:

$$f_m = (1 - \rho)(1 + \rho + \dots + \rho^{m-1}) = 1 - \rho^m. \quad (1)$$

2. Experimental procedure

To prepare AgI/opal nanocomposite (i.e., host opal matrix filled with silver iodide guest substance) we inserted initial opal matrix into the melt of silver iodide ($T = (836 \pm 3)$ K) for three hours. Then the



sample ($5 \times 5 \times 0.7 \text{ mm}^3$ plate) was cleaned and polished mechanically and its opposite plane surfaces were covered with graphite (used as electrode material).

In our experiments the gravimetric density of the polished composite sample was found to be $\rho_c = 3.3 \text{ g/cm}^3$, so one can calculate the volume fraction of the guest substance in the composite:

$$\frac{\rho_c - \rho_o}{\rho_{AgI}} \approx 0.35, \text{ where } \rho_{AgI} = 5.7 \text{ g/cm}^3 \text{ and } \rho_o = 1.3 \text{ g/cm}^3 \text{ are the gravimetric densities of bulk}$$

AgI and bare opal, correspondingly. Thus, the sample under study possessed not only the first-order porosity, but partially the second-order one (see formula (1)). According to this estimation, the concentration of nanostructured silver iodide in our composite based on “open” opal structure was about 40% more than that in the sample obtained by high-pressure technique in [7] and one order of magnitude higher than that in the sample synthesized chemically in [8].

Electrical measurements of the samples under study (initial opal host matrix, bulk AgI guest substance and AgI/opal nanocomposite) were carried out at the frequency of 1 kHz by an E7-13 impedance meter as well as by impedance bridge MPP300 and generator Philips GM6012 within the frequency range 100 Hz – 300 kHz. Direct current was measured by electrometer Keithley 6517B and micro ammeter M95. The temperature dependences of all the electric sample characteristics were measured upon continuous heating or cooling with a rate of 1 to 2 degrees per minute.

3. Results

Temperature dependences of alternating-current (AC) ionic conductivity of AgI/opal nanocomposite material (AC frequency $\nu = 1 \text{ kHz}$) are shown in figures 1 and 2. It is clearly seen that the temperature of the phase transition to the superionic state upon heating of the nanocomposite sample (figure 1, curve 1) is close to the corresponding temperature in the bulk guest material ($T_i \approx 420 \text{ K}$). On the other hand, the T_i value shifts to approximately 400 K upon cooling (figure 1, curve 2). This rather wide hysteresis loop, as well as the values of activation energy in the Arrhenius plot (figure 2) agrees with recently published data [8]. On the other hand, the AC ionic conductivity values measured in [8] at $\nu = 1.5 \text{ kHz}$ are much smaller ($\sigma_{AC} \approx (10^{-4} - 10^{-3}) \text{ S/m}$ above the temperature of the phase transition) than corresponding σ_{AC} values plotted in figure 1. This fact as well as the nonmonotonic temperature dependence $\sigma_{AC}(T)$ observed in [8] at middle and low frequencies is probably due to the low concentration and nonhomogeneous distribution of silver iodide nanoparticles chemically synthesized within opal pores.

In figure 3 direct-current (DC) ionic conductivity values for bulk silver iodide (figure 3, *a*) and those for AgI/opal nanocomposite with much more pronounced hysteresis (figure 3, *b*) are displayed. It should be noted that contrary to AC conductivity demonstrating distinct step-like conductivity enhancement at elevated temperature (figure 1), estimated DC conductivity values are much lower, decreasing monotonically during measurement process and showing only peaks at corresponding temperatures (figure 3). In our opinion, these effects are due to the polarisation processes.

Nevertheless, DC conductivity of AgI/opal nanocomposite at $T = 450 \text{ K}$ is at least five orders of magnitude higher than that of initial opal host matrix [6].

Figure 4 illustrates, in addition, the low-temperature shift of the phase transition point for AgI/opal nanocomposite upon cooling when compared with that for the bulk guest substance. The shift value $\Delta T_i \approx 20 \text{ K}$ also agrees with the result published in [8] for AgI/opal nanocomposite. It should be mentioned that for AgI nanowires grown with the usage of porous alumina template this shift is much larger ($\Delta T_i \approx 70 \text{ K}$) and it is thought that plenty of stacking defects and adsorption/segregation of Ag^+ ions at the alumina surface could be the main factors for abnormal phase transition in this composite structure [12].

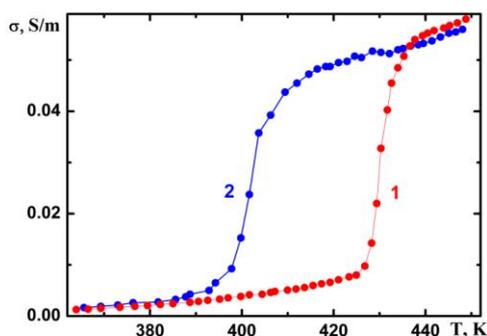


Figure 1. Temperature dependence of AC ionic conductivity ($\nu = 1$ kHz) of AgI/opal nanocomposite (1 - heating, 2 - cooling).

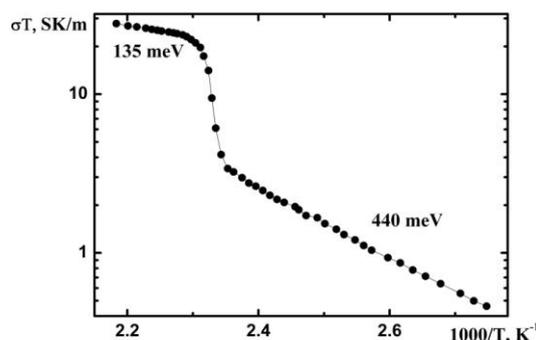


Figure 2. Arrhenius plot of AC ionic conductivity ($\nu = 1$ kHz) of AgI/opal (heating). Activation energies are shown for two linear segments.

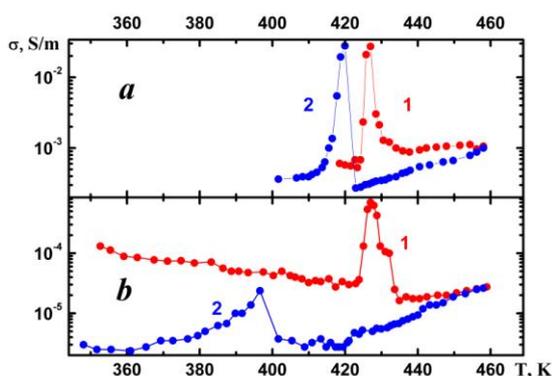


Figure 3. Temperature dependence of DC ionic conductivity of *a*) bulk AgI and *b*) AgI/opal (1 - heating, 2 - cooling)

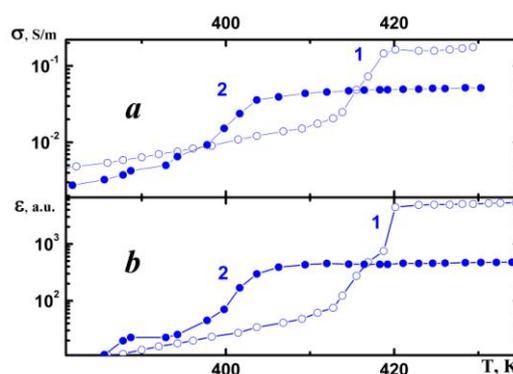


Figure 4. Temperature dependences of AC ionic conductivity (*a*) and dielectric permittivity (*b*) of bulk AgI (1) and those of AgI/opal nanocomposite (2) on cooling ($\nu = 1$ kHz).

The frequency dependence $\varepsilon(\nu)$ of dielectric permittivity within the frequency range from 10^2 to 10^5 Hz is in agreement with the power law approximation ($\varepsilon(\nu) = C\nu^{-n}$), which is typical for ionic compounds dispersed within the voids of opal matrices [6].

4. Acknowledgments

The authors are grateful to Dr. S.G. Romanov for providing bulk opal matrices.

This work was supported by the Ministry of Education and Science of Russian Federation according to the program “Development of Scientific Potential of Higher Educational Institutions”.

References

- [1] Mott N F and Gurney R F 1948 *Electronic processes in ionic crystals* (Oxford)
- [2] Lidiard A 1957 *Ionic conductivity* (Berlin: Springer)
- [3] Salamon M B, Beyeler H U, Boyce J B *et al* 1979 *Physics of superionic conductors*

ed M B Salamon (Berlin: Springer)

- [4] Pan'kova S V, Poborchii V V, Solov'ev V G 1996 *Journal of Physics: Condensed Matter* **8** L203
- [5] Fokin A V, Kumzerov Yu A, Okuneva N M *et al* 2002 *Physical Review Letters* **89** 175503
- [6] Solovyev V, Kumzerov Y, Khanin S 2011 *Physics of regular matrix composites (Electrical and optical phenomena in nanocomposite materials based on porous dielectric matrices)* (Saarbrücken, Germany: LAP, in Russian)
- [7] Il'inskii A V, Aliev R A, Kurdyukov D A *et al* 2006 *Physica Status Solidi A* **203** 2073
- [8] Vergent'ev T Yu, Koroleva E Yu, Kurdyukov D A *et al* 2013 *Physics of the Solid State* **55** 175
- [9] Baryshnikov S V, Tien C, Charnaya E V *et al* 2008 *Physics of the Solid State* **50** 1342
- [10] Wang Y, Huang L, He H *et al* 2003 *Physica B* **325** 357
- [11] Yamasaki S, Yamada T, Kobayashi H *et al* 2013 *Chemistry. An Asian Journal* **8** 73
- [12] Liang C, Terabe K, Hasegawa T *et al* 2007 *Journal of Applied Physics* **102** 124308
- [13] Liang C, Terabe K, Tsuruoka T *et al* 2007 *Advanced Functional Materials* **17** 1466
- [14] Guo Yu G, Lee J S and Maier J 2005 *Advanced Materials* **17** 2815
- [15] Guo Yu G, Lee J S, Hu Y S *et al* 2007 *Journal of the Electrochemical Society* **154** K51
- [16] Tappertzhofen S, Valov I and Waser R 2012 *Nanotechnology* **23** 145703
- [17] Liang X F, Chen Y, Shi L *et al* 2007 *Journal of Physics D: Applied Physics* **40** 4767
- [18] Furusawa S and Sakai Y 1999 *Journal of the Physical Society of Japan* **68** 976
- [19] Bogomolov V N 1978 *Soviet Physics Uspekhi* **21** 77
- [20] Astratov V N, Bogomolov V N, Kaplyanskii A A *et al* 1995 *Il Nuovo Cimento* **17D** 1349
- [21] Kumzerov Y and Vakhrushev S 2004 *Encyclopedia of Nanoscience and Nanotechnology* (vol 7) ed H S Nalwa (American Scientific Publishers) pp 811–849
- [22] Balakirev V G, Bogomolov V N, Zhuravlev V V *et al* 1993 *Crystallography Reports* **38** 348