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Superionic phase transition in AgI embedded in molecular sieves

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Abstract

Superionic AgI particles embedded in MCM-41 and SBA-15 molecular sieves with different pore sizes were studied using NMR and dielectric methods. The measurements confirmed that the structure of the confined particles did not change noticeably compared to that in bulk AgI. A regular increase in the temperature of the superionic phase transition with decreasing pore size was observed and treated on the basis of the Landau theory of thermodynamic size effects. The maximum increase found upon warming and cooling was about 10 and 8 K, respectively. The ionic conductivity in β -AgI under confinement was shown to be due to silver mobility on the particle surface.

1. Introduction

Studies of the physical properties of materials embedded in solid nanoporous matrices are of high priority in modern science. The dimensions of particles within pores are limited to the size of the pores. This provides a unique possibility to create arrays of particles of well defined sizes and interparticle distances. Therefore, filled porous matrices are considered as prospective nanocomposite structures for technical applications. On the other hand, because of small pore diameters, the properties of confined particles, in particular phase transitions, are expected to be influenced by various size effects.

Composites on the base of nanoporous matrices filled with liquid crystals, simple and organic liquids, metals, polymers and ferroelectrics were fabricated and studied recently (see [1–8] and references therein). The melting and freezing phase transitions, glass formation, atomic and molecular diffusion, superconductivity, ferroelectricity and phase transformations in liquid crystals were found to be

affected by nanoconfinement. It was further suggested ([9] and references therein) that composites comprising porous insulator matrices and ionic conductors should show an improved electrical conductivity. Properties of LiI and AgI within Al_2O_3 and SiO_2 porous matrices were studied [10–14] recently. A strong increase in conductivity was observed for porous alumina–AgI and LiI composites [11, 13] while a pronounced decrease or slight increase in conductivity was found for AgI embedded in SiO_2 porous glasses [10]. Optical properties of AgI and Ag nanoclusters formed in zeolite–Y were studied at room temperature in [15]. No special efforts were made to reveal size effects in the superionic phase transitions under confinement. Single results obtained for alterations of the phase transition temperature for confined AgI were controversial. The phase transition temperature was found to increase for AgI within porous alumina [13], to decrease for AgI particles within pores of an opal photonic crystal [16] and slightly increase and then decrease with decreasing pore size from 50 to 10 nm for AgI-loaded porous glasses [17].

In the present paper we report the results of dielectric and NMR studies of AgI particles confined within pores of

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Table 1. Parameters of molecular sieves used to produce the samples under study and the activation enthalpy H_a of ionic mobility evaluated from linear parts of the plots in figure 3.

Molecular sieve	SBA-15		MCM-41			
Pore size (Å)	52	37	26.1	24.3	23.8	20.3
H_a (eV)	0.23	0.33	0.25	0.25	0.30	0.26

molecular sieves MCM-41 and SBA-15 with various pore sizes from 2.0 to 5.2 nm. The well controlled diameter and geometry of regular cylindrical pores in molecular sieves are advantages of such matrices over other kinds of porous material. Note also that AgI particles confined within pores smaller than 10 nm have to our knowledge not been studied until now.

2. Experimental details

Powder MCM-41 and SBA-15 molecular sieves were used as nanoporous matrices. Both kinds of molecular sieve have an ordered honeycomb structure of cylindrical pores with amorphous silica walls [18, 19]. MCM-41 molecular sieves were synthesized following [18, 20] with a typical pore size from 37 to 20 Å found by electron microscopy and nitrogen adsorption–desorption isotherms. The synthesis of SBA-15 was performed using a method described in [19]. The pore size in the synthesized SBA-15 was estimated using nitrogen adsorption–desorption isotherms as 52 Å. Pore sizes for the matrices used to produce the samples under study are listed in table 1.

The formation of AgI within nanopores was performed by a salt-bridge precipitation method using AgNO_3 and KI aqueous solutions. The filled, washed and dried molecular sieve powder was pressed under a pressure of about 60 kg mm^{-2} to produce pellets of diameter 10 mm.

It is known that pressing can induce formation of the γ modification of bulk AgI at room temperature; however, γ -AgI transforms again to the β phase when heated above the α - β transition (see [13] and references therein). To be sure that mainly β -AgI occurs in our composites below the structural phase transition, the samples were warmed before the measurements up to 170 °C.

X-ray patterns at room temperature of the obtained AgI loaded pellets showed only very weak narrow lines corresponding to the most pronounced peaks for bulk β -AgI. The estimated amount of bulk compound was very small compared to the total amount of AgI used to produce the samples and expected from conductivity or NMR measurements and therefore could not influence the experimental results. No reliable broadened peaks associated with confined small AgI particles were observed.

The pure AgI pellets were also made by pressing powder crystalline AgI under the same conditions as were used for the composite pellets and were warmed before the measurements above the α - β transition to prevent the occurrence of γ -AgI at lower temperatures.

The conductivity and dielectric susceptibility were obtained using a E7-12 immittance meter within the temperature range 295–470 K. The main measurements were

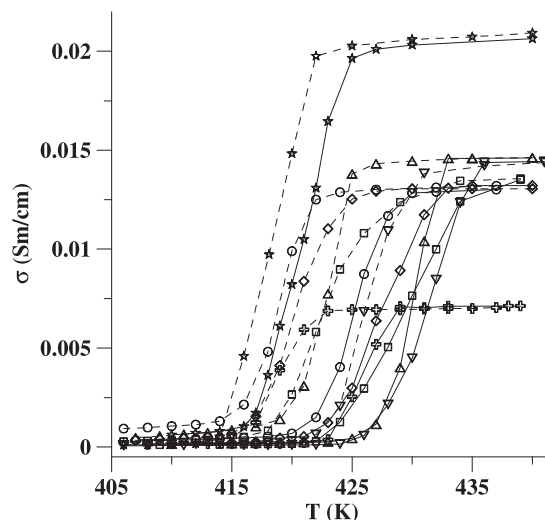


Figure 1. Temperature dependences of the conductivity in the samples under study obtained upon warming and cooling. Stars correspond to bulk AgI. Circles, diamonds, squares, triangles and inverted triangles correspond to the AgI-loaded MCM-41 with pore sizes of 37, 26.1, 24.3, 23.8 and 20.3 Å, respectively. Crosses correspond to SBA-15 filled with AgI. Solid and dashed lines are guides for the eye for data obtained upon warming and cooling, respectively.

carried out at a frequency of 1 MHz. The temperature monitoring was better than 0.1 °C. The temperature changes during the warming and cooling thermal cycles were no faster than 1 K min^{-1} . The measurements were normally performed with coated silver electrodes, but no noticeable difference was found between the results obtained at 1 MHz using the silver and In–Ga eutectic electrodes. To study the frequency dependences of dielectric properties of the composites a Good Will Instrument LCR-819 impedance meter was used with a frequency range of 10 – 10^5 Hz.

^{127}I MAS NMR measurements were carried out using a Bruker Avance 400 NMR pulse spectrometer operating at a Larmor frequency of 80 MHz (in a magnetic field of 9.4 T) at room temperature. The spinning rate was 12 kHz. The position of the central bands was referenced to the ^{127}I NMR signal in a 1 M KI aqueous solution.

3. Results and discussion

Temperature dependences of conductivity measured upon warming and cooling at 1 MHz for all samples under study are shown in figure 1 within the temperature range 405–442 K. The abrupt, step-like changes in conductivity are caused by the superionic phase transition. Because the α - β phase transition is of first order, the transition temperatures observed upon warming and cooling are different, giving rise to a thermal hysteresis. The width of the hysteresis loops is about the same for all composite samples and only slightly broader than in pressed powder crystalline AgI. This result shows that the order of the phase transition in AgI was not affected noticeably by confinement.

The conductivity steps at the phase transition in the composite samples are shifted to high temperature and are

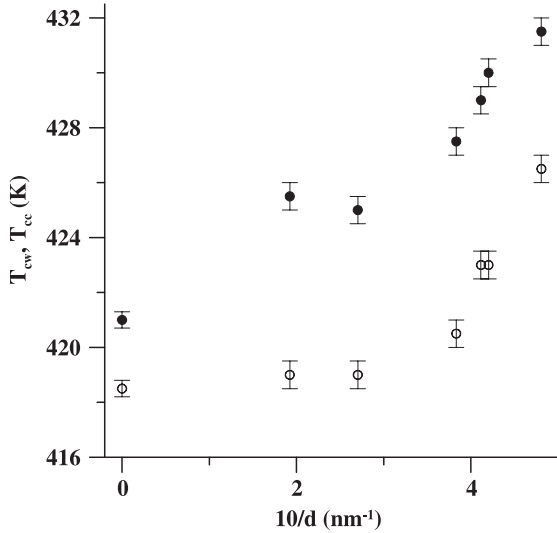


Figure 2. Dependences of the superionic phase transition temperatures upon warming, T_{cw} (closed symbols), and upon cooling, T_{cc} (open symbols), on the inverse pore diameter d .

slightly more diffuse compared to bulk AgI. We defined the phase transition temperature upon warming T_{cw} and cooling T_{cc} as a point where the derivative of conductivity with respect to temperature is maximal. The dependences of T_{cw} and T_{cc} on the inverse pore diameter are shown in figure 2. The phase transition temperatures for the bulk obtained upon warming and cooling are 421 and 418.5 K, respectively. These values agree perfectly with data from other studies (see, for instance, [21–23]). Both T_{cw} and T_{cc} increase steadily with decreasing pore diameter. The increase in the temperatures of the phase transition cannot be caused by stress produced in the composite pellets upon pressing or changing temperature since the superionic phase transition in AgI is known to move to low temperatures with increasing pressure [24]. It was found in [24] that the phase transition temperatures measured upon warming and cooling decreased approximately linearly under increasing pressure with a regression coefficient of about $-14.5 \text{ K kbar}^{-1}$.

As was mentioned in the Introduction, previous studies of AgI embedded in pores of bigger sizes did not reveal any reliable tendency in the phase transition shift [13, 16, 17]. This might be because the pore size was not small enough. On the other hand, assemblies of isolated AgI particles and fine-granular AgI have been produced for a long time (see [25–27] and references therein). The superionic phase transition in granular AgI with grain sizes of 7–9 nm [27] was found to smear out and shift strongly to low temperatures. The results were treated as a transformation of the first-order transition to the second-order one contrary to hysteretic behavior upon warming and cooling.

The ^{127}I MAS NMR spectrum at room temperature for the samples under study consisted of a rather broad strong central band corresponding to the central $1/2 \leftrightarrow -1/2$ transition and weak sidebands arising from satellite transitions $\pm 3/2 \leftrightarrow \pm 1/2$ shifted by first-order quadrupole interactions. The frequency range of the total spectrum is about the same

Table 2. The ^{127}I MAS NMR central band width at half-height and the chemical shift.

Pore size (Å)	Band width (ppm)	Chemical shift (ppm)
Bulk	50	−103
37	75	−107
24.3	75	−106
20.3	54	−105

for the composite and powder samples. The chemical shift and the central band width at half-height are listed in table 2. Very small variations in the chemical shift for confined AgI particles compared to that in the powder sample along with similar total MAS NMR spectra confirm that the crystalline structure and chemical bonding are not noticeably affected by confinement. Therefore, the observed alterations in the superionic phase transition temperature are unlikely to be caused by some structural changes and one can suggest that the shifts of the phase transition are a result of size effects.

One can explain the increase in the superionic phase transition temperatures for fine confined AgI particles using the phenomenological Landau theory similar to that developed for small ferroelectric isolated particles (see [28–30] and references therein). While the Landau theory usually cannot give a comprehensive description of the superionic phase transitions it can still be used for qualitative treatment of thermodynamic size effects.

The order parameter for the superionic phase transition can be defined as a relative number of mobile ions. Such an order parameter η is scalar and non-zero above the phase transition and becomes zero below it. Because of the scalar nature of the order parameter, the free energy expansion allows a cubic invariant in agreement with the first-order phase transition in AgI. The total free energy of a small particle can be written following [28–30] as

$$F = \int \left(\frac{1}{2}A(T_0 - T)\eta^2 + \frac{1}{3}G\eta^3 + \frac{1}{4}B\eta^4 + \frac{1}{2}D(\nabla\eta)^2 \right) dV + \int \frac{1}{2}D\frac{\eta^2}{\delta} dS \quad (1)$$

where the volume and surface integrals correspond to volume and surface energy; A , G , B and D are coefficients in the Landau expansion; T is temperature; T_0 is the upper limit of stability of the non-superionic state in bulk; δ is the extrapolation length which corresponds to the usual boundary condition in the Landau theory [31]

$$\frac{\partial\eta}{\partial\vec{n}} = -\frac{\eta}{\delta} \quad (2)$$

where \vec{n} is the unit normal to the surface. For a superionic particle surrounded by an insulator the correlation length should be positive, which corresponds to disappearance of superionic conductivity in the matrix. The coefficients A , B and D are positive and the sign of G is undefined. Note that the factor $A(T_0 - T)$ is positive at low temperatures in agreement with the fact that the order parameter is non-zero above the phase transition.

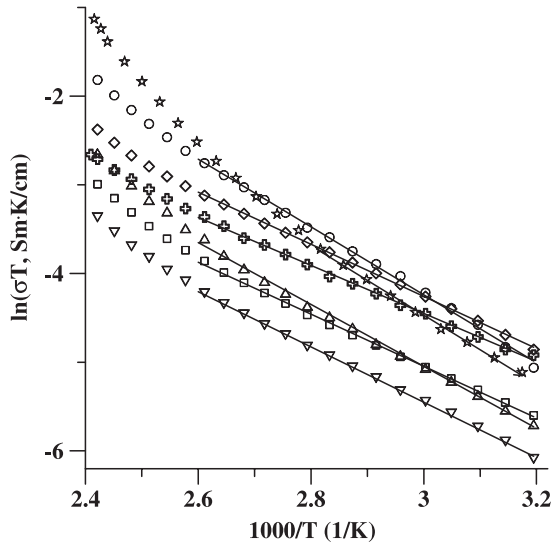


Figure 3. The Arrhenius plots for confined β -AgI. Circles, diamonds, squares, triangles and inverted triangles correspond to the AgI-loaded MCM-41 with pore size 37, 26.1, 24.3, 23.8 and 20.3 Å, respectively. Crosses and stars correspond to SBA-15 filled with AgI and bulk AgI, respectively. Solid lines show linear fits.

From (1) one can get the Euler–Lagrange equation

$$D\nabla^2\eta = A(T_0 - T)\eta + G\eta^2 + B\eta^3 \quad (3)$$

which together with the boundary conditions (2) leads to the boundary value problem for η in the particle. The numerical analysis of this problem (quite similar to that made in [28–30]) shows that the phase transition shifts to higher temperatures for positive δ and for the chosen sign of the factor outside η^2 in the volume integral of equation (1) for any numerical phenomenological coefficients in the Landau model. Therefore, the phenomenological consideration predicts the increase of the superionic phase transition temperature in an ensemble of small particles.

To analyze alterations in the activation mobility of silver ions below the superionic phase transition we drew the Arrhenius plots for conductivity at 1 MHz (figure 3). The conductivity measured at 1 MHz is obviously due to intrapore charge carrier mobility in agreement with the strong increase in conductivity with increasing frequency. Therefore, figure 3 reflects charge mobility in confined AgI particles. The activation enthalpy H_a obtained for the temperature range 310–385 K where the Arrhenius graphs are linear (figure 3, solid lines), implying the usual equation for the conductivity σ

$$\sigma = \frac{\sigma_0}{T} \exp(-H_a/k_B T) \quad (4)$$

(k_B is the Boltzmann constant and σ_0 does not depend on temperature), is listed in table 1 for all samples under study. Its values are strongly reduced compared to bulk single-crystalline samples whose activation enthalpy exceeds 0.8 eV. The reduction of H_a shows that the observed conductivity is mainly related to surface transport [32]. When approaching the phase transition, the slope of the Arrhenius graphs increases, probably due to the increased contribution of the intraparticle

conductivity [23]. Similar behavior was observed for pressed powder AgI (figure 3). The dependence of $\ln(\sigma T)$ on inverse temperature remains linear in the narrower range 310–355 K where $H_a = 0.34$ eV also corresponds to surface conductivity. At elevated temperature the conductivity increases more strongly than in the composite samples due to a comparatively larger contribution of intragrain ionic mobility because of a higher surface-to-volume ratio in confined AgI particles.

Extending the linear fits to zero inverse temperature (0 on the abscissa in figure 3), one can immediately find the value of σ_0 according to equation (4). This allows us to estimate the density n of mobile ions responsible for the conductivity, since σ_0 can be represented as [21]

$$\sigma_0 = \frac{nq^2 l^2 \nu_0}{6k_B}, \quad (5)$$

where q is the charge of mobile ions, l is the jump length, ν_0 is the attempt frequency of mobile ions to overcome the potential barriers and k_B is the Boltzmann constant. For silver ions q is equal to the electron charge; l in AgI is of the order of 2 Å [23]; ν_0 is of the order of the Ag^+ ion oscillation frequency, $\nu_0 \sim 3 \times 10^{12}$ Hz [33]. For bulk pressed AgI $\sigma_0 \cong 1.4 \times 10^3$ Sm K cm⁻¹, which yields $n \sim 4 \times 10^9$ cm⁻³. The obtained value agrees with the surface nature of conductivity near room temperature. Comparing σ_0 for bulk with σ_0 evaluated by extending the linear fits for confined AgI one can find the ratio between the mobile ion density in the bulk and composite samples. It is maximal and equal to about 0.5 for the sample with the 37 Å pore size and lies in between 3 and 15 for other samples. For these estimates the volume of pores was taken to be about half of the total molecular sieve volume [18, 19]. Therefore, these estimates also agree with the surface nature of conductivity in the nanocomposite samples.

In conclusion, conductivity measurements on superionic AgI particles embedded in MCM-41 and SBA-15 molecular sieves revealed a regular increase of the temperature of the superionic phase transition with decreasing pore size. The shift of the phase transition was ascribed to thermodynamic size effects since NMR and dielectric studies confirmed that the structure of confined particles did not change noticeably compared to that of bulk AgI. The ionic conductivity in β -AgI under confinement was also analyzed and shown to be due to silver mobility on the particle surface.

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