Electrical and optical properties of iodide nanoparticles embedded into zeolite porous matrices

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Abstract. Experimental study of the iodine nanoparticles effect on the optical and electrical properties of zeolite-based matrix nanocomposite materials has been carried out. Phase transitions in the nanocomposites under study have been found.

1. Introduction

Zeolites are well-known regular porous crystalline solids, which are usually referred to as molecular sieves in chemistry and chemical physics [1, 2]. On the other hand, one can use these dielectrics as host matrices to design wide variety of unique nanocomposite materials by infiltrating their voids with guest substances [3, 4]. The guest nanoparticle systems in host zeolite matrices are characterized by low dimensions (~1 nm), regular shapes and arrangements of guest species and their high concentration (~5×10²⁰ cm⁻³). These advantages are due to the crystalline structure of zeolites containing identical cages and channels of molecular dimensions regularly located in their framework.

In the last decades different porous dielectric host matrices filled with iodine guest species were studied by optic and electric methods [5-7].

In this work, we have studied some optical, electrical and thermoelectrical properties of nanocomposite materials prepared by infiltration of cages and channels of synthetic type A zeolite and zeolite-like AFI (AlPO₄ – 5) porous host matrices with iodine guest substance from vapour phase.

2. Structure of zeolites and zeolite-like crystals under study

Zeolite frameworks are constructed by the linking TO₄ tetrahedra (usually T = Si, Al) with shared oxygen atoms [1, 2]. Cages and channels of their open structures are regularly arranged and contain exchangeable alkali or alkaline-earth cations, compensating the negative electrical charge of alumina tetrahedra [AlO₄]⁻ in their framework, as well as water molecules. Both cations and water molecules move freely inside the zeolite. Water can be reversibly removed when the temperature increases during dehydration process, while zeolite porous structure itself usually remains stable up to high temperatures. The general chemical formula of these crystalline aluminosilicates is given by [1, 2]

\[ Me \times [Al \times Si_y O_{2(y+x)}] \times H_2 O \]
where $Me^{n+}$ is a cation. The $Si$-to-$Al$ ratio $R = y/x$ depends upon the type of zeolite and the method of its synthesis.

The ideal framework of zeolite NaA $Na_{12}[Al_1Si_1O_4]·27H_2O$ contains supercages and sodalite cages with inner diameters of 1.14 nm and 0.66 nm, respectively (figure 1).

Ideal unit cell framework formula of $AlPO_4·5$ aluminophosphate is $Al_{12}P_{12}O_{48}$.

This zeolite-like matrix is very convenient for infiltration of its nanoporous structure with guest substances because the concentration of aluminium atoms in its lattice is equal to that of phosphorus atoms, and therefore its one-dimensional channels are free from exchangeable cations. These parallel channels with the inner diameter 0.73 nm are oriented along the crystal $c$-axis (figure 2).

Figure 1. Framework of zeolite NaA [4].

Figure 2. Structural model of zeolite-like aluminophosphate type AFI [4]. Large spheres represent oxygen atoms.

3. Experimental procedure

To prepare I/A or I/AFI nanocomposites, incorporation of iodine species into voids and channels of type A zeolite or AFI zeolite-like matrices during iodine vapour phase adsorption at 580-770 K for 6-12 h has been used.

The diffuse reflectance spectra $R_d = f(\hbar\omega)$ of the powdered samples were determined by the standard method in the photon energy $E = \hbar\omega$ spectral range from 1.05 to 5.65 eV. Magnesium oxide served as a reference sample. The measured reflectance spectra $R_d(\hbar\omega)$ were converted into the values of the Gurevič – Kubelka – Munk function, which describes the optical absorption of the sample in relative units [8, 9]:

$$F(R_d) = \frac{(1-R_d)^2}{2R_d}.$$  

Alternating-current (AC) conductivity of pressed pellets prepared from zeolite powder and KBr at the pressure of 100 MPa was measured at the frequency of 1 kHz with graphite electrodes. However, this method gives no possibility to avoid disturbing effects of grain boundaries and interfaces, arising from the sample polycrystallinity. Therefore, in order to study electrical properties of individual microscopic zeolite single crystals and zeolite-based nanocomposite samples (~20-100 microns in size), different types of direct-current (DC) measuring cells have been proposed by Markov et al. [4, 10, 11]. Using these cells in our work, we have fixed the microscopic I/A or I/AFI single crystals on quartz substrates between two push indium contacts. Thermal electromotive force of small samples was measured by pulse method proposed in [11-13].
4. Results and discussion
In contrast with the pronounced optical anisotropy of I/AFI nanocomposites [5, 12, 14] in transmitted light with two perpendicular directions of incident polarization, we did not find any light absorption anisotropy of I/NaA single crystals under polarized optical microscope. This difference is obviously due to formation of quasi one-dimensional iodine chains observed in [5, 14] inside AFI parallel channels and isotropic distribution of iodine species inside three-dimensional system of cages and channels of zeolite type A nanoporous host matrix.

The calculated optical absorption spectra of the NaA initial zeolite, bulk iodine, and I/NaA nanocomposite are depicted in figure 3. It can be seen from curve 1 that the zeolite host matrix is transparent in the studied spectral range. The absorption edge of the massive iodine is observed at 1.26 eV (curve 2). This agrees with the electronic band gap of the bulk crystalline iodine (1.25 eV). However, the absorption spectrum of the I/NaA nanocomposite (curve 3) is shifted toward the ultraviolet range and demonstrates three absorption bands near 2.70, 3.44 and 4.13 eV. These maxima correlate with three lines in the absorption spectrum of molecular iodine, as well as with the absorption spectra of iodine species in I/AFI sample measured in [14].

The current-voltage characteristics $I = f(U)$ of the samples under study are linear at low voltages ($U < 10V$). At high voltages the power law $I = CU^m$ takes place, where $m > 1$. This behaviour is typical for zeolites and zeolite-based nanocomposites [4, 11]. Temperature dependences of the direct current flowing through I/AFI composite along and across the $c$ - axis of the single crystal are plotted in figure 4.

The most striking feature of the Arrhenius plots is the pronounced peculiarity at $T \approx 343K$ (vertical arrow in figure 4, left panel), which could be observed when the temperature increases slowly (~2 K/min) and the current flows through I/AFI composite along the iodine chains. One can suppose that this peculiarity is due to the iodine phase transition from the chain structures to the molecular species, which was found at this temperature by means of optical characterization and phase dynamics of the iodine species in I/AFI composite system [5, 14].

The possible mechanism of the charge transport in I/AFI composite at $T > 343$ K is the tunnelling of electrons between iodine molecular species. Obviously, the melting of iodine chain (aligned with the $c$ - axis of the AFI single crystal) to molecular iodine has no noticeable effect on the direct current which flows (probably, also due to the tunnelling process) across the $c$ - axis (figure 4, right panel).

Moreover, the phase transition under consideration does not occur during cooling of the “hot” I/AFI composite, filled with disordered iodine molecular vapour phase, resulting in the enhanced value of the activation energy (figure 4). After few days the ordered iodine molecular wires in I/AFI composite become partially reconstructed, and the phase transition at $T \approx 343K$ during heating could be observed again.

Our measurements of thermoelectric current flowing through I/AFI nanocomposite agree with electronic mechanism of charge transport at $T < 343$ K, because Seebeck coefficient $S$ of this material at 300 K is negative: $S_{I/AFI} \approx -1 \frac{\mu V}{K}$ in contrast to that of bulk iodine, where $S_I \approx +1 \frac{mV}{K}$ (typical value for p-type semiconductor).

One can expect more effective electronic charge transport in three-dimensional interconnected channel system filled with iodine species forming I/NaA nanocomposite. Indeed, Seebeck coefficient of I/NaA composite is still negative, but its absolute value is about 10 times larger, than that of I/AFI material.

At the same time, the electronic currents in I/NaA and I/AFI nanocomposites at room temperature are about 10-100 times higher than the ionic currents in initial hydrated NaA and AFI hosts (without iodine guest substance) under the same applied voltage.

On the other hand, the melting of iodine chains to molecular iodine has smaller effect on the DC or AC electric current flowing through I/NaA nanocomposite material with isotropic distribution of iodine species in comparison with the pronounced decrease of electronic conductivity due to the phase transition.
**Figure 3.** Graphs of Gurevich–Kubelka–Munk functions extracted from the diffuse reflectance spectra for the (1) NaA zeolite, (2) bulk iodine, and (3) I/NaA nanocomposite.

**Figure 4.** Arrhenius temperature dependences of the direct current flowing under constant applied voltage through I/AFI composite along (left panel) and across (right panel) parallel channels of the single crystal. Inclined arrows indicate heating and cooling of the sample. Vertical arrow indicates the temperature of iodine chains to molecular iodine phase transition.
transition in iodine chains located in the quasi-one-dimensional channels of AFI matrix. That can be clearly seen from figure 5.

**Figure 5.** Temperature dependences of (1) DC conductivity of I/AFI single crystal, (2) DC conductivity of I/NaA single crystal, (3) DC conductivity of I/NaA+KBr pressed pellet, (4) AC conductivity of I/NaA+KBr pressed pellet. Vertical arrow indicates the temperature of iodine chains to molecular iodine phase transition.

In contrast with the iodine phase transition in I/AFI quasi-one-dimensional system which takes place only during heating of the sample (figure 4), one can observe iodine chains reconstruction in I/NaA nanocomposite during its cooling (figure 6) – probably, due to rather fast diffusion of iodine molecules through three-dimensional interconnected channel system of zeolite type A matrix.
We have prepared also I/KA and I/LiA nanocomposites by infiltration of three-dimensional systems of cages and channels of KA and LiA zeolite matrices, respectively, with iodine. According to our experiments, electric properties of I/KA nanocomposites are quite similar to those of I/NaA material, demonstrating phase transition in iodine subsystem at $T \approx 343 \text{K}$. We suppose that after the break of iodine chains at $T > 343 \text{K}$ the charge transport in I/NaA and I/KA composites becomes predominantly ionic.

The conductivity of I/LiA composite containing small Li$^+$ cations with high drift mobility under applied electric field is probably ionic in the entire temperature region under study: Arrhenius temperature dependence with almost the same activation energy is observed for LiA and I/LiA samples (figure 7).

Here, one cannot see any phase transition in iodine subsystem at $T \approx 343 \text{K}$; instead of it, considerable conductivity enhancement occurs at $T \approx 313 \text{K}$ during heating; some hysteresis takes place during cooling process (figure 7). It should be noted that the conductivity of bulk crystalline LiI is not very high due to rather low concentration of Schottky defects. On the other hand, one can increase this conductivity when infiltrates lithium iodide guest substance into porous alumina host dielectric matrix [15]. We suppose that the dramatic change of I/LiA electric conductivity near $T \approx 313 \text{K}$ (figure 7) may be due to “superionic” phase transition, resulting in remarkable change of unoccupied cation positions number in this complex “host-guest” system.

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