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Electrical characterization of iodine species formed inside the one-dimensional nanochannels of microporous aluminophosphate $\text{AlPO}_4\text{-5}$ single crystal

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ABSTRACT

I/AFI nanocomposites have been prepared by infiltration of the one-dimensional nanochannels of AFI zeolite-like microporous aluminophosphate ($\text{AlPO}_4\text{-5}$) host matrix with iodine guest substance. Direct current flowing through I/AFI microcrystals has been measured along (I_{\parallel}) and across (I_{\perp}) the \bar{c} -axis of the single crystal in the temperature range of 20-120°C. In contrast with the monotone temperature dependence $I_{\perp}(T)$, the $I_{\parallel}(T)$ curve demonstrates the distinct peculiarity at ~70°C which is due to the phase transition of iodine species from the chain structures to molecular iodine.

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KEYWORDS

Nanostructures;
Nano porous materials;
Electronic transport;
Phase transitions.

INTRODUCTION

Zeolites^[1,2] and zeolite-like regular microporous crystalline solids can be successfully used as host matrices to design wide variety of unique nanocomposite

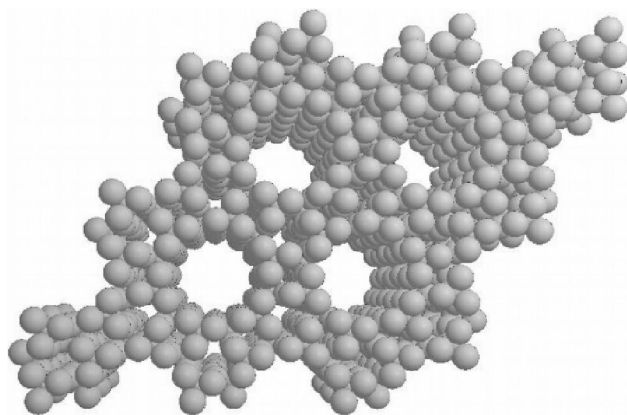


Figure 1 : Structural model of zeolite-like microporous aluminophosphate type AFI ($\text{AlPO}_4\text{-5}$). Large spheres represent oxygen atoms

materials by infiltrating their voids and channels with guest substances^[3,4], e.g. iodine species, which were primarily studied by spectroscopic methods^[5-16]. AFI aluminophosphates ($\text{AlPO}_4\text{-5}$ or SAPO-5) are very convenient for infiltration of their microporous structure with guest substances because the concentration of aluminum atoms in their lattice is equal to that of phosphorus atoms, and therefore their one-dimensional channels are free from exchangeable cations^[17,18]. These parallel channels with the inner diameter 0.73 nm are oriented along the \bar{c} -axis of the crystal (Figure 1).

EXPERIMENTAL

In this work, AFI crystals have been prepared by the hydrothermal synthesis^[19,20] in a stainless-steel autoclave at 190÷210°C during 10-24 hours, starting with the gel of the molar composition $1\text{Al}(\text{OH})_3 \cdot 1\text{H}_3\text{PO}_4 \cdot 0.75(\text{C}_2\text{H}_5)_3\text{N} \cdot 500\text{H}_2\text{O}$. To remove the organic tem-

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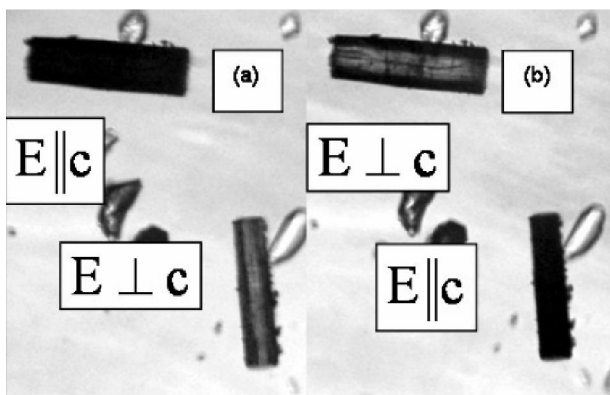


Figure 2 : The images of I/AFI single crystals in transmitted light under polarized optical microscope with two perpendicular directions of incident polarization.

plate and water molecules, AFI crystals have been annealed in air at 580°C for 11 h and under vacuum at 465°C for 2-12 h. To incorporate iodine species into AFI channels, vapour phase adsorption at 500°C for 6 h has been used. The variation of the iodine vapour pressure during this preparation process results in the variation of the iodine concentration in the I/AFI nanocomposite, as well as of the sample colour. The latter varied from light brown (for low-loaded crystals) to dark brown (for heavy-loaded samples). The images of I/AFI single crystals under polarized optical microscope (Figure 2) clearly demonstrate large anisotropy of their optical absorption. This pronounced optical anisotropy should be considered as an important argument for the formation of iodine chains inside AFI channels.

In order to study electrical properties of individual microscopic zeolite single crystals and zeolite-based nanocomposite samples ($\sim(20\div 100)\mu\text{m}$ in size), different types of measuring cells have been proposed by Markov et al.^[21] In our work, we have fixed the microscopic I/AFI single crystal along or across its \bar{c} -axis on quartz substrate between two push indium contacts

RESULTS AND DISCUSSION

The current-voltage characteristics $I(U)$ of the samples under study are linear only at low voltages ($U < 10\text{V}$). At high voltages the power law $I = CU^m$ takes place, where $m \approx 1.5$. This behaviour is similar to that of the pure zeolite-like microporous aluminophosphates AFI^[18,20]. However, the electronic current in I/AFI nanocomposites is about 10^2 times higher than the ionic

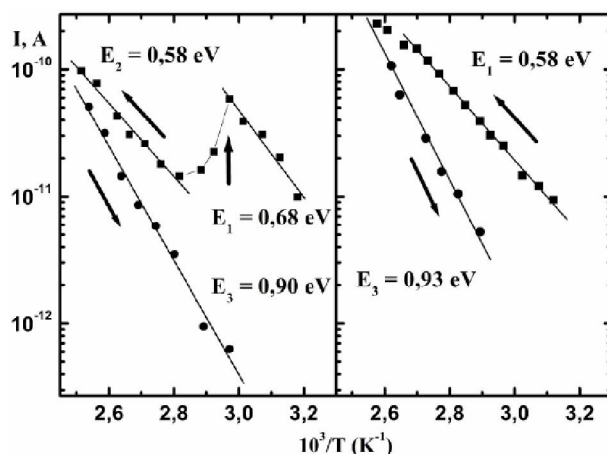


Figure 3 : Arrhenius temperature dependences of the direct current flowing through I/AFI composite along ($I_{||}$, left panel) and across (I_{\perp} , right panel) the \bar{c} -axis of the single crystal. Inclined arrows indicate heating and cooling of the sample (heating or cooling rate was about 1.5 K/min). Vertical arrow corresponds to the temperature of phase transition ($t_0 \approx 70^\circ\text{C}$) current in initial AFI hosts (without guest substances) under the same applied voltage.

Temperature dependences of the direct current flowing through I/AFI composite along,

$I_{||} = f\left(\frac{10^3}{T}\right)$ and across $I_{\perp} = f\left(\frac{10^3}{T}\right)$ the \bar{c} -axis of the single crystal are plotted in figure 3.

The corresponding values of the activation energy calculated from these Arrhenius plots are also shown in the figure. When the temperature of the I/AFI composite increases from $\sim 310\text{K}$ to $\sim 340\text{K}$, the value of activation energy seems to be in a good consistency with the value $\frac{E_g}{2}$, where $E_g \approx 1.25\text{eV}$ is the semiconductor band gap for the bulk iodine. The most striking feature of the Arrhenius plots is the pronounced peculiarity at $t_0 \approx 70^\circ\text{C}$ which could be observed when the temperature increases slowly and the current flows through I/AFI composite along the iodine chains. We suppose that this peculiarity is due to the iodine first-order phase transition from the chain structures to the molecular species, which was found recently at 71.3°C by means of optical characterization and phase dynamics of the iodine species in iodine@AFI composite system^[9,10]. The possible mechanism of the charge transport in I/AFI composite at $t > t_0$ is the tunnelling of electrons between iodine molecular species. One could expect, that the melting of iodine chain (aligned with the \bar{c} -axis of the

AFI single crystal) to molecular iodine vapour has no noticeable effect on the direct current which flows across the \bar{c} - axis (probably, also due to the tunnelling process). Actually, our experimental results confirm this expectation (Figure 3, right panel). Moreover, this phase transition does not occur during cooling of the “hot” I/AFI composite, infilled with disordered iodine molecular vapour phase, resulting in the enhanced value of the activation energy (Figure 3). After few days the ordered iodine molecular wires in I/AFI composite become partially reconstructed, and the phase transition at $\sim 70^\circ\text{C}$ during heating could be observed again.

CONCLUSIONS

In summary, we have prepared iodine species in the regular system of parallel nanochannels of AFI zeolite-like aluminophosphate ($\text{AlPO}_4\text{-5}$) microporous host matrix. Direct-current electrical measurements prove the occurrence of the phase transition of iodine species from the chain structures to molecular iodine near $\sim 70^\circ\text{C}$.

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