

Occurrence of large temperature-activated dipole moments of sulfur clusters in zeolite inclusions

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(Submitted 16 July 1979)

Pis'ma Zh. Eksp. Teor. Fiz. **30**, No. 7, 409–411 (5 October 1979)

A lattice of S_{28} sulfur clusters is obtained in the zeolite cavities NaA. The dielectric constant of the system ϵ' increases with the temperature and reaches a value of ~ 160 , which is much larger than that for the original components, and then decreases sharply. It is assumed that the increase of ϵ' is due to thermal excitation in the clusters of the Jahn-Teller states which produce free dipole moments as a result of interaction with the medium.

PACS numbers: 36.40. + d, 61.70. – r

It is possible to obtain matter in an ultradispersed state by using zeolites as dielectric matrices.⁽¹⁾ Of particular interest are the chalcogens which have a large number of stable and metastable structures.

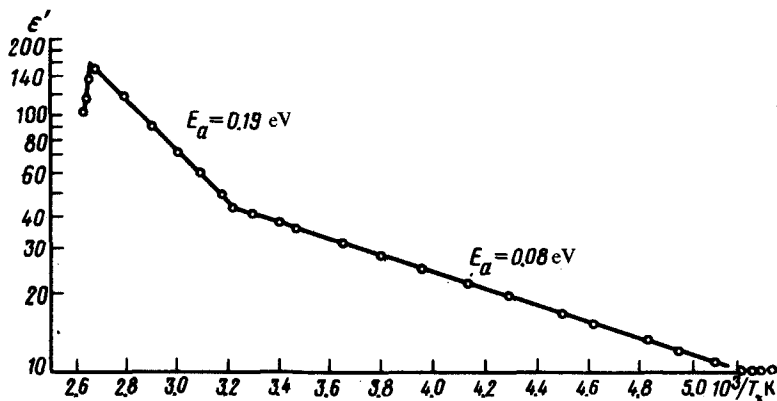


FIG. 1. Temperature dependence of the dielectric constant ϵ' of NaA-S at the frequency $f = 10^3$ Hz for two values of the activation energy E_a .

Sulfur, like other chalcogens, can be introduced into the atomic-diameter cavities in zeolites in two ways: adsorption and pressurized melt. In the first case, distinct molecular structures are formed in the cavities, e.g., two S_8 rings^[2] and a Te_8 ring,^[3] and in the second case, clusters of 23 to 29 atoms containing different stable and unstable molecular fragments are produced.^[4] The NaA zeolite cavities have a diameter of 11.4 Å, and under pressure are filled with 28 sulfur atoms. Each large cavity has a small counterpart with a diameter of 6.6 Å, in which there are four additional sulfur atoms.

In our samples the total number of sulfur atoms in one large and one small cavity, which was determined from the measured sample density, amounted to 32 atoms, which is almost the limiting population of zeolite. Introduction of sulfur from the melt was accomplished at a pressure of 8 kbar and at $T = 700$ K. The zeolite single crystals with sulfur NaA-S were pressed into tablets and then measured in a vacuum and in an inert gas atmosphere using gold contacts.

The concentration of cavities in zeolite is $\sim 5 \times 10^{20}$ cm⁻³ and the total volume of the cavities is $\sim 50\%$ that of the zeolite crystal; thus, the NaA-S system is comprised of two sublattices of equal volume of highly dispersed dielectrics, each of which has a static dielectric constant $\epsilon_{\text{stat}} < 10$. We found, however, that the dielectric constant ϵ' of the Na-S system reaches a value of ~ 160 , which, after conversion to a cluster sulfur by using the composition formulas, is ~ 500 . If the sulfur is replaced by the same amount of water ($\epsilon_{\text{st}} = 81$), the dielectric constant of the system will be only $\epsilon' \sim 20-30$ cm. Thus, the sulfur clusters in zeolite cavities acquire a dipole moment that is several times larger than that of water.

The dependence $\epsilon'(T)$ (Fig. 1) is described well by the activation law $\epsilon' \sim \exp E_a/kT$ with the activation energy $E_a = 0.08$ eV in the temperature region $193 \text{ K} \leq T \leq 313 \text{ K}$ and by the value $E_a = 0.19$ eV for the temperature region $313 \text{ K} \leq T \leq 374 \text{ K}$. At lower temperatures $120 \text{ K} \leq T \leq 193 \text{ K}$, ϵ' is almost independent of temperature. At $T = 374 \text{ K}$ the exponential increase of $\epsilon'(T)$ is followed by a sharp

decrease, at which a temperature hysteresis occurs. Apparently, at $T = 374$ K there is a partial or complete "fusion" of S_{28} clusters, which destroys their structure and their molecular composition. At higher temperatures we could not obtain stable results because of the intense thermal destruction of the sample.

The exponential increase of $\epsilon'(T)$ may be attributed to the thermal activation of the dipole excitations in the sulfur cluster. Such large values of the dielectric constant can apparently be obtained only in the framework of the orientational polarization mechanism. For example, the S_3 and S_4 molecules in several structural modifications may cause such dipole excitations. Earlier, we observed bands in our samples in the optical spectra of sulfur clusters, which correspond to the S_3 and S_4 molecules^[4]; i.e., unstable S_3 and S_4 sulfur states are stabilized in the zeolite cavities. Because these molecules are Jahn-Teller molecules,^[5] it is natural that they may acquire a dipole moment as a result of interaction with the zeolite matrix.

After replacing by means of ion exchange in zeolite some of the Na^+ ions by Li^+ ions, which have a smaller diameter and weaker adsorptive properties, we obtained the decay temperature $\epsilon'(T)$ of $T = 341$ K. The excitation of the dipole moments in the cluster is apparently attributable to the interaction with the adsorption centers, which are ions of alkaline metals situated on the walls of the zeolite cavities.

Thus, in the dielectric matrices with cavities of atomic dimensions, it is possible not only to stabilize metastable materials and to obtain heretofore unknown modifications of materials, but also to use them in certain physical phenomena. The metastability of these states causes them to be highly sensitive to the external effects, which may be useful in the development of materials for electronics.

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