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Thermally stimulated relaxation processes in two-component solid films of nitrogen-ethanol

Abstract. Experimental study of relaxation processes in solid solutions of nitrogen-ethanol observed in the process of raising the temperature of the film is carried out. Our previous studies have found that the state of the film is not stable. The increase of cry matrix temperature leads to changes in the vibrational spectrum of ethanol. This article focuses on determining the effect of ethanol concentration in the nitrogen matrix on the investigated relaxation processes. Measurements were carried out in a temperature range from 12 to 40K, the pressure in the vacuum chamber was less than 5×10^{-8} Torr. The concentration of ethanol in nitrogen was varied in the range from 0.5% to 3%. Conclusions are made based on the analysis of thermo grams and said that increase the concentration of ethanol in nitrogen leads to the beginning of the relaxation processes at lower temperatures. This is explained by the presence in nitrogen cryomatrix of ethanol polyaggregates with larger size.

Key words: cryomatrix, polyaggregate, hydrogen bond, polymorphic, cry condensate.

Introduction

Development of nanoscience and nanotechnology has led researchers to two fundamentally different approaches to the preparation of nanoparticles and objects – so-called "top-down" and "bottom-up" technologies, i.e. or by destroying macro objects to obtain nanoscale structures ("top-down"), or assembly of nano-objects directly from atoms and molecules ("bottom-up"). The method of cry matrix isolation refers to one of the most effective methods of nanosystems formation "from below" allowing forming nanosystems with predetermined properties consciously and purposefully. [1-3]. The basis of this method is the process of co-condensation of matrix gas with metal vapors or other substances in much smaller proportions with the concentration of the matrix. Reactivity of components is limited by low temperature of the substrate and thus thin film is formed consisting of a matrix with embedded active elements, which at a given temperature does not come into contact with the adjacent elements and to the matrix. In the last two

decades, researchers in different fields of physics, chemistry and biology have come to use the method of cry matrix isolation from mainly analytical to a more technological using. This is due to obtaining of the valuable information about the properties of atoms, clusters and other particles from using the inert matrices and ultra-low temperatures.

The main problem with the implementation of the cry matrix isolation method is to find the relation between the matrix and the active substance, at which the process of cry chemical polymerization reaction of matrix begins at a lower temperature than the temperature of overcome the activation barrier at the beginning of self-organization process between nano-objects. Thus for manipulating of components imbedded in a matrix also raises the question in choosing a matrix having a wide range of controllable properties. Depending on the task it is possible to use the most stable matrix for further studies under normal temperatures. Thus, the properties of the object formed during condensation are determined by the matrix properties of the studied substance and the concentration ratio between them. This article is

devoted to the study of the influence of ethanol concentration in nitrogen matrix on thermally stimulated relaxation processes in the samples.

Results and discussion

The measurements were performed on a modified installation described in detail in [4]. The main objective of experimental studies is to determine the characteristics of the reactivity of ethanol polyaggregates, which are included in a nitrogen matrix. The ethanol concentration in the nitrogen matrix was varied in the range of 0.5-10%, cryocondensate thickness was also varied depending on the concentration. It is assumed that the reactivity of ethanol clusters might depend on their concentration in a nitrogen matrix.

Figure 1 shows the vibration spectra of ethanol in a nitrogen matrix in the range of ethanol monomers vibrations characteristic frequencies (1259 cm^{-1}). The ethanol concentration in a nitrogen matrix is 1%.

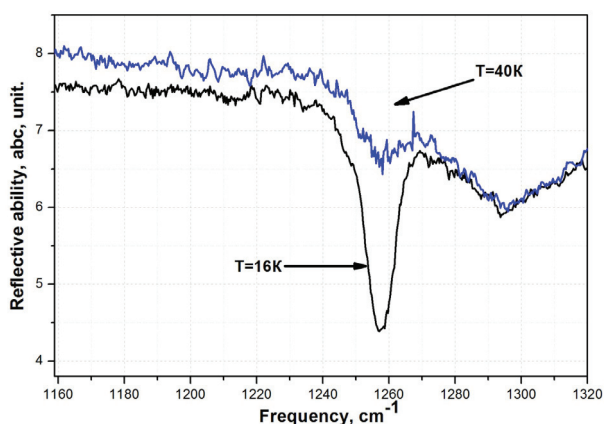


Figure 1 – The vibrational spectra of ethanol in nitrogen matrix in the range of monomers vibration characteristic frequencies (1259 cm^{-1}).

The figure clearly shows the change in the amplitude of the signal of IR radiation in the frequency range 1259 cm^{-1} , which in our opinion is a characteristic feature of monomers self-organizing to larger units (clusters). The state of ethanol clusters can be judged by observing the change in the absorption amplitude at a given frequency during the samples heating.

Figure 2 shows the warming on the (1259 cm^{-1}) frequency of characteristic vibrations of ethanol monomers in nitrogen matrix at various concentrations. For comparison, the data for pure

ethanol film (lower curve) are given. As can be seen, depending on the concentration of ethanol in nitrogen the changes in the amplitude at the observed frequency are varied. In our opinion, these differences are due to size effects of monomers, frozen in nitrogen matrix.

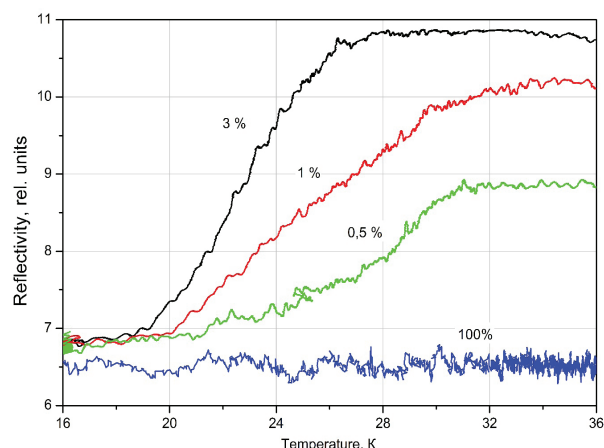


Figure 2 – The registration of IR radiation at a frequency of 1259 cm^{-1} characteristic fluctuations of ethanol monomers in a nitrogen matrix.

For the ethanol concentration of (0.5%) change in the amplitude of infrared radiation at (1259 cm^{-1}) ethanol monomers characteristic frequency occurs at higher temperatures, which can be explained by the fact that the distances between the nearest neighbors of immobilized ethanol are large enough for the self-organization processes. Noticeable change in the IR spectrometer signal is occurring only when a certain temperature is reached or certain activation energy of molecules is received.

For the concentration of (1-3%), under these conditions the process of ethanol molecular self-organization is the most active. It is also possible at insignificant distances between the nearest frozen ethanol molecules. A slight change in the temperature of the matrix-isolated cry condensates film of ethanol leads to the receiving of the molecules required activation energy, which self-organize in larger clusters subsequently.

Figure 3 shows the warming on the frequency (1259 cm^{-1}) of characteristic vibrations of ethanol monomers in nitrogen matrix at large ethanol concentrations. As can be seen, the higher concentration of ethanol in nitrogen leads to the lower temperature at which the relaxation processes start in the two-component films.

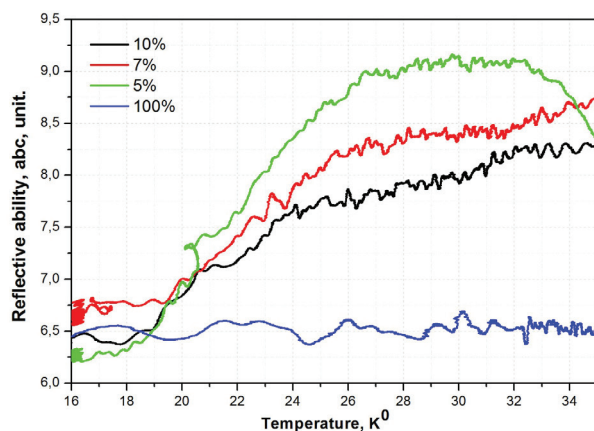


Figure 3 – Registration of infrared radiation at 1259 cm^{-1} frequency of ethanol monomers characteristic fluctuations in the matrix of nitrogen at the indicated concentrations.

Thus, the presence of the absorption band at the frequency 1259 cm^{-1} means that there are ethanol dimers or monomers in the system. Change of the considered absorption amplitude means the

occurring of union process of ethanol monomers and dimers to larger units, with active participation in this process by hydrogen bonding interaction.

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