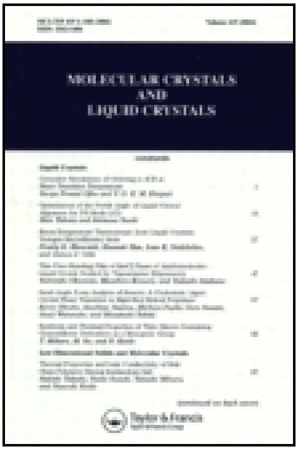

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Liquid Crystal Structures in a Vitreous Acetates of Alkali Metals

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Liquid Crystal Structures in a Vitreous Acetates of Alkali Metals

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The transformation of anhydrous melt glasses of alkali metals acetates in nematic and smectic LC-mesophases have been studied. A change of electric conductivity of samples over the phase transformation has been observed. Textures corresponding to the nematic and smectic mesophases were revealed with the use of polarizing microscopy. It was studied the influence of external pulse unidirectional electric field at the mesophases formation. The role of LC-state as the fundamental energetic level over the going from the melt to the crystalline phase is discussed.

Keywords: liquid crystal; vitreous metal acetate; electric field; conductivity; texture; polarizing microscopy

Introduction

Even two decades ago [1] it was apparent obvious, that the liquid crystals existed only as organic compounds. The discovery of liquid crystalline mesophases in complex compounds [2] and in ionic salts [3] showed that the natural occurrence of LC-state phenomenon in much more wide than it was thought to be formerly. For example, the problem of LC-state in the glass formation was discussed in [4].

In our previous paper [5] mesophases states of glassy lithium acetates were described. Vitreous lithium acetate at a slow heating (a rate is no more, than 0,1 K/min) can go to the mesophases registered by polarizing microphotography. The textures of these mesophases are like those referred to [5]. But, the acetate lithium on being heated quickly yields spontaneously crystals near the vitrifying points. The X-ray scattering of smectic vitreous salts has been seen. It was observed that stratified structure of the smectic mesophases causes series of reflections, coinciding with some peaks which correspond to LiAc crystals. But the reflections of higher order are not accompanied by the Bragg reflections of samples because of absence of translational order in a direction perpendicular to the plane of smectic layers. In this paper we consider formation of the mesophases in Li, K, Cs glassy acetates and the influence of the unidirectional pulsed electric field on this process.

Experimental

Alkali metal acetates were synthesized from pure alkali carboxylic salts and pure acetic acid, they were purified by the recrystallization from dilute acetic acid water solution. The anhydrous salts were prepared by heating at 393-413K with silica gel.

Vitreous samples were prepared by supercooling of melts of corresponding salts, which were placed between two glass plates.

The pulsed unidirectional electric field of 700 Hz and 2kV was applied to the cell, containing the glassy acetate of alkali metal. Figure 1 shows a scheme of this electric field generator.

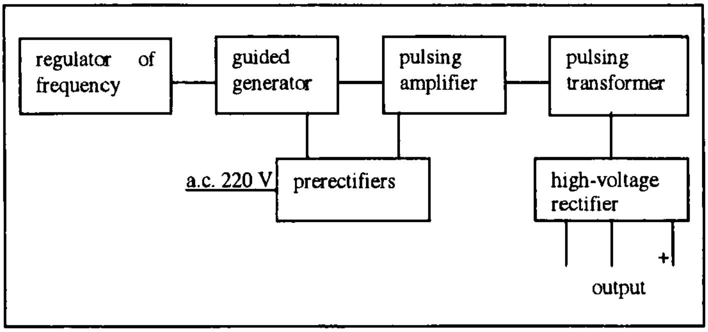


Figure1. Simplified scheme of high-voltage pulsing generator

The study of the textures formation and the influence of the electric field on this process was carried out using the polarizing microscope (crossed nicoles). The conductivity of the samples was measured in the external electric field in a direction perpendicular to the sample plane.

Results and discussion

The phase behavior of the alkali acetates Li, K, Cs in vitreous state were studied by polarizing optical microscopy as well as simultaneously the measurements have been made of temperature dependence of the conductivity for the glassy samples. Figures 2 and 3 samples of the alkali acetates. It can be seen in these figures, that there is a maximum at the curves for K and Cs acetates at 383 and 365K, accordingly. Observing with using of the polarizing microscopy reveals the formation of unique smectic mesophase (S) under these temperatures.

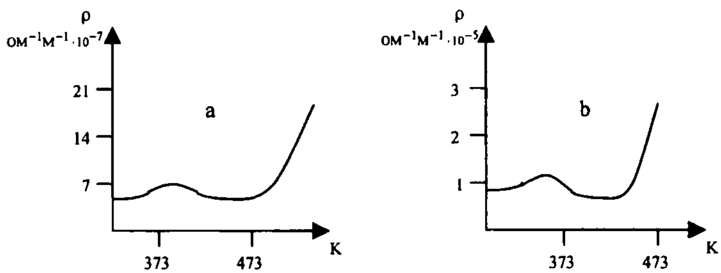


Figure 2. Conductivity vs. temperature: a - KAc, b – CsAc.

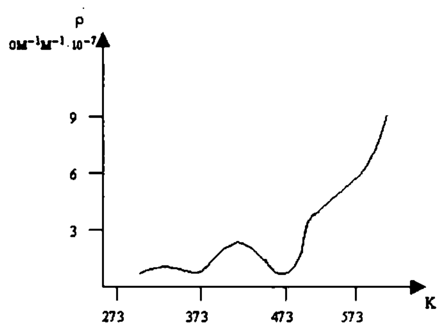


Figure 3. Conductivity vs. temperature of glassy LiAc.

These results correlate well with the report [6], that only one mesophase can be formed of ionic compounds. Metastable structures of the smectic acetates are rather tolerant under constant condition. The sample of acetate potassium has been retaining its texture (S) on keeping over P_2O_5 at a room temperature for three years.

The formation of mesophases for the K, Cs acetates under the action of external electric field does not bring into existence another structures, The formation of mesophases for the K, Cs acetates under the action of external electric field does not bring into existence another structures, but regulates the current smectic structure over the whole sample (see Figure 4).

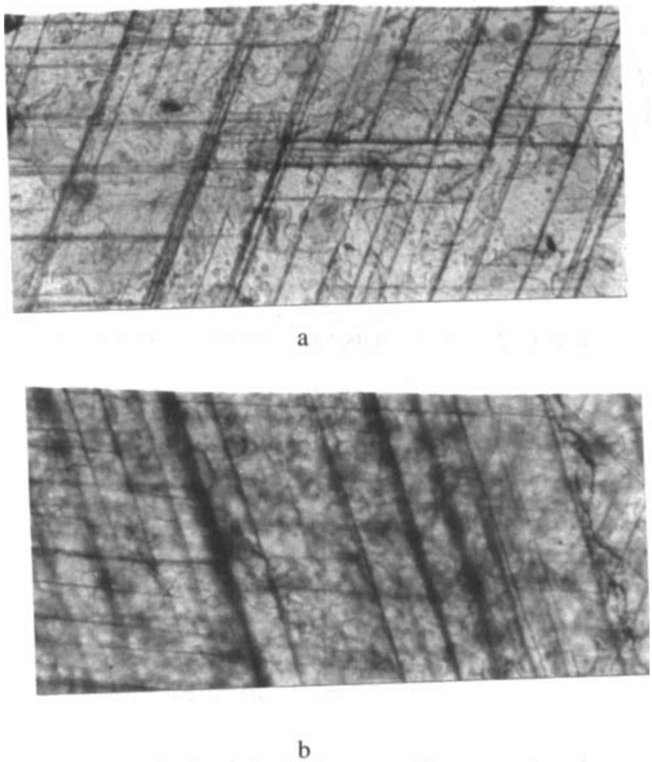
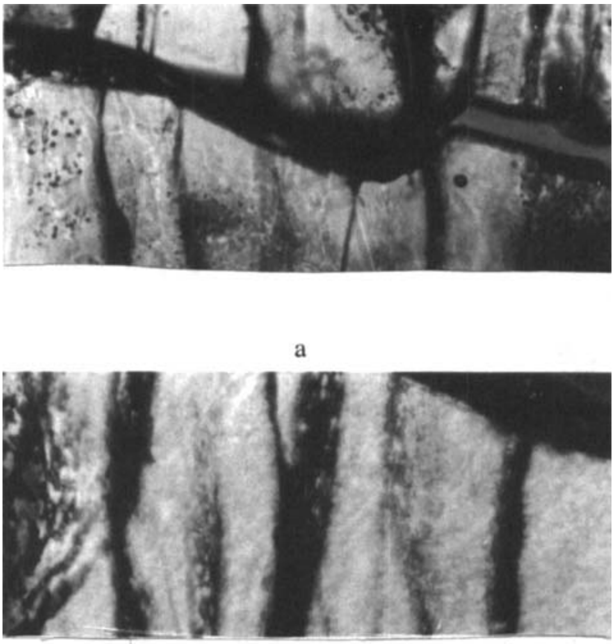


Figure 4. The vitreous KAc in smectic phase; a – field is absent, b - under the action of electric field.
See Color Plate XL at the back of this issue.

Mesophase transformation of vitreous LiAc are more complicated. Three maxima of the curve for the temperature dependence of the conductivity (see Figure 3) conform to a nematic and two smectic transformations. In this case the dynamic of phase transformation is found to be unusual. The imposition of the electric field results in an important ordering (regulation) of the smectic phase (see Figure 5).



a

b

Figure 5. LiAc, smectic phase, 393K; a – field is absent, b - under the action of electric field. See Color Plate XLI at the back of this issue

But at the every temperature , the conductivity of the LiAc layer is more with the electric field present, than without it. The shutdown of the field followed by the relaxation of the ionic structures and decreasing of the conductivity. The described phenomenon were explained with quantum – chemical calculations for LiAc associates according the program HYPERCHEM. The calculation showed that in the case of LiAc the condition for the minimum of the system energy demand of the asymmetric packing of the cation relative to the anions axis. If the external electric field is imposed, electrostatic forces turn round the ionic pairs breaking the balance configuration of the system. In this case the conductivity of the layer as well as the melting temperature of the glassy sample decrease (by 20-25K). The formation of mesophase structures in solid alkali acetates provides an experimental example of negative entropy production over the glass transition, which had been theoretically examined in [7]. On the other hand, it provides a possibility of realizing the mesophase LC-structures for many ionic systems by back transferring within the bounds of the vitreous state, in the direction of the glass transition temperature.

The fact that metastable mesophases at heating of vitreous samples can be formed, is explained by the defrosting (freezing out) of rotary states without translation mobility of the ions. In this case, the possibility exists of the system relaxation with decreasing in its energy at the sacrifice of the glass LC-structuring.

Conclusion

The results of the study leave room for producing, with the use of external electric field, materials with properties of Langmuir – Blodgett films, since the accepted structure of these films and of the liquid – crystalline ionic mesophases are identical.

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