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Liquid crystal mixtures show great glass-forming properties (in quest for ever better material for top performance LC displays)

The liquid crystals used in displays nowadays are usually in a nematic phase, i.e. a liquid-like state of almost parallel oriented molecules. However, there is another liquid crystal phase which has a chance to be used in displays in the future, and it is the chiral smectic C_A^* phase with a high tilt angle of molecules. The liquid crystal mixture denoted as W-1000, known already for a broad stability range of the smectic C_A^* phase, has been recently proven not to crystallize (we do not want the LCD material to go crystal) but to retain its liquid-like character. It undergoes the vitrification even at very slow cooling, making it a good material to obtain easily the smectic C_A^* glass. The crystal phase of W-1000 does not form on cooling. Moreover, cold crystallization, observed often during heating of previously vitrified substances, does not occur for the investigated mixture, therefore low temperatures do not destroy the liquid crystal state and the alignment of molecules. The same properties are reported for the W-356 mixture, which is a new derivative of W-1000.

Liquid crystal is one of possible intermediate states between a crystal and liquid. The molecules in a liquid crystal have an ability to flow and at the same time their arrangement is ordered in some manner. In the smectic liquid crystals, the molecules form layers. In the simplest smectics, the layer order is of a quasi-long-range type, while within these layers the molecules can move as in a liquid. The basis of how liquid crystal displays (LCDs) work is the susceptibility of liquid crystals to the external electric field. If a suitable liquid crystal is placed between crossed polarizers, one can control the arrangement of molecules by the electric field to enable or disable the transmission of light through the polarizers. Most of currently used LCDs are based on a nematic phase. However, there is a certain type of a smectic phase, namely the smectic C_A^* phase (SmC_A^*), which in proper conditions shows the antiferroelectric properties, i.e. the tristable switching of molecules caused by external electric field. Moreover, by the application of the SmC_A^* phase with a tilt angle close to 45° (named the orthoconic SmC_A^* phase) it is possible to obtain easily the perfect dark state of a display.

Substances used in the LCD technology should stay in the liquid crystalline state in the broad temperature range covering also the room temperature because in a crystal phase the switching of molecules by electric field does not occur anymore. The liquid crystals used in LCDs are always mixtures. The melting point of a crystal phase is lower in mixtures than in the pure compounds, therefore it is easier to obtain the wider stability range of a liquid crystal state in the former. The liquid crystal orthoconic mixture named W-1000, prepared in the Military University of Technology in Warsaw, is an eutectic mixture of two chiral fluorinated compounds. W-1000 and its modifications are known for the remarkably wide temperature range of the SmC_A^* phase with a high tilt angle of molecules.

„The properties of the W-1000 mixture down to −23°C have been extensively studied in recent years. My goal was to check what happens at lower temperatures, especially to investigate the glass transition of the SmC_A^* phase. I was sure that W-1000 exhibits the SmC_A^* glass because in my PhD Thesis one of its components had been proven to have the same property", says Dr.

Aleksandra Deptuch from the Institute of Nuclear Physics, Polish Academy of Sciences. *"We applied a few complementary methods. Polarizing optical microscopy, differential scanning calorimetry and broadband dielectric spectroscopy measurements were carried out in my Institute, while the X-ray diffraction and electro-optic measurements were done in the M. Smoluchowski Institute of Physics of Jagiellonian University. Additionally, the density functional theory calculations were performed at the Prometheus cluster in the Academic Computer Centre Cyfronet AGH. Together with W-1000, we investigated its new modification W-356, also prepared in the Military University of Technology. The results of this teamwork have been published recently in Physical Review E."*

As it was presumed, both W-1000 and W-356 show the SmC_A^* glass. Their vitrification occurs at −44°C and −41°C, respectively. W-356 shows slightly different electro-optic and structural properties than W-1000 but their behaviour in the vitrified state is similar. The X-ray diffraction was applied to determine the smectic layer spacing and the extent of the short-range order (i.e. the correlation length) within the smectic layers. It was shown that the short-range order freezes in the vitrified SmC_A^* phase, as the correlation length is constant below the glass transition temperature. Meanwhile, the layer order still evolves in the SmC_A^* glass: the layer spacing decreases slowly with decreasing temperature and the distribution of electron density in a direction perpendicular to the smectic layers deviates more and more from a simple sinusoidal wave. The broadband dielectric spectroscopy results indicate that the molecular dynamics in both mixtures do not differ significantly. The fragility index is 79 for W-1000 and 73 for W-356, which is an intermediate value (experimental fragilities are in the 16-200 range). The mentioned fragility index is not related to the mechanical properties and it describes the temperature dependence of one of characteristic relaxation times. Glassformers with lower fragility index are expected to have less tendency to crystallization.

"Originally, my plan was to examine also the kinetics of cold crystallization of W-1000 and W-356 mixtures. It is a common feature of glass-forming materials that they do not crystallize on cooling but their crystal phase is formed during heating above the glass transition temperature. However, in W-1000 and W-356 we did not observe any signs of crystallization even upon slow heating", says Dr. Deptuch. *"Actually, it is a better result than I expected because it means that the crystallization of these mixtures would be unlikely to be triggered by accidental lowering of the temperature a hypothetical display works in. In the vitrified smectic phase, the switching of molecules is absent as well, however, after re-heating above the glass transition temperature, the situation in the sample is the same as before cooling, therefore a display is not damaged. Meanwhile, if the crystal phase was formed, it would destroy the proper alignment of molecules in the smectic phase and even after melting of a crystal, a display would probably not work properly anymore."*

Finally, the W-1000 and W-356 samples used in the XRD measurements were kept in the room temperature afterwards. About ten weeks later, their XRD patterns were collected again. Both samples were still in the SmC_A^* phase, without the signs of crystallization. It confirms that W-1000 is a good basis for future mixtures used in LCDs. The vitrification of the SmC_A^* phase is a separate subject which requires further investigation. The structural changes observed for both mixtures below and above the glass transition should be studied also for other mixtures and pure compounds to check whether the observed behaviour is universal. The SmC_A^* glass has anisotropic optical properties due to partial order of molecules and for some applications other than LCDs, the smectic materials with a higher vitrification temperature than W-1000 may be required, to obtain the SmC_A^* glass at the room temperature. It gives perspectives for further tests of new modifications of W-1000.

The Henryk Niewodniczański Institute of Nuclear Physics (IFJ PAN) is currently one of the largest research institutes of the Polish Academy of Sciences. A wide range of research carried out at IFJ PAN covers basic and applied studies, from particle physics and astrophysics, through hadron physics, high-, medium-, and low-energy nuclear physics, condensed matter physics (including materials engineering), to various applications of nuclear physics in interdisciplinary research, covering medical physics, dosimetry, radiation and environmental biology, environmental protection, and other related disciplines. The average yearly publication output of IFJ PAN includes over 600 scientific papers in high-impact international journals. Each year the Institute hosts about 20 international and national scientific conferences. One of the most important facilities of the Institute is the Cyclotron Centre Bronowice (CCB), which is an infrastructure unique in Central Europe, serving as a clinical and research centre in the field of medical and nuclear physics. In addition, IFJ PAN runs four accredited research and measurement laboratories. IFJ PAN is a member of the Marian Smoluchowski Kraków

Research Consortium: "Matter-Energy-Future", which in the years 2012-2017 enjoyed the status of the Leading National Research Centre (KNOW) in physics. In 2017, the European Commission granted the Institute the HR Excellence in Research award. The Institute holds A+ Category (the highest scientific category in Poland) in the field of sciences and engineering.

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SCIENTIFIC PUBLICATIONS:

"Comparative study of electrooptic, dielectric, and structural properties of two glassforming antiferroelectric mixtures with a high tilt angle"
A. Deptuch, S. Lalik, M. Jasiurkowska-Delaporte, E. Juszyńska-Gałązka, A. Drzewicz, M. Urbańska, M. Marzec
Physical Review E 2022, 105, 024705
DOI: https://doi.org/10.1103/PhysRevE.105.024705

LINKS:

http://www.ifj.edu.pl/
The website of the Institute of Nuclear Physics, Polish Academy of Sciences.

http://press.ifj.edu.pl/
Press releases of the Institute of Nuclear Physics, Polish Academy of Sciences.

IMAGES:

W-1000_XRD.jpg **HR:** https://press.ifj.edu.pl/en/news/2022/06/02/IFJ220602b_fot01_en.jpg
XRD results for the W-1000 mixture. Upper panel: diffraction patterns of W-1000 in the vitrified SmC_A^* phase in −123°C and in the SmC_A^* phase after 10-weeks-long storage in the room temperature. The schematic structure of the SmC_A^* phase is presented. The tilt of molecules is in the opposite direction in neighbour layers. Within layers, only the short-range order, like in liquids, is present. Bottom panel: smectic layer spacing and correlation length of the short-range order vs. temperature determined from the XRD patterns of W-1000. Note the change in temperature dependence of both parameters at the glass transition temperature, indicated by the vertical dashed line. (Source: IFJ PAN)