EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: XRD study of multilayered graphene oxides in liquid amines	**Experiment number**: HC/3238
Beamline:	**Date of experiment**: from: 2017.11.08 to: 2017.11.10	**Date of report**: 2018-01-31
Shifts:	**Local contact(s)**: Mashikoane Wilson Mogodi mashikoane-wilson.mogodi@esrf.fr	*Received at ESRF:* ---

Names and affiliations of applicants (* indicates experimentalists):

Korobov Mikhail , Department of Chemistry, Moscow State University, Moscow, Russia

*Rebrikova Anastasiia, Department of Chemistry, Moscow State University, Moscow, Russia

*Talyzin Alexandr, Department of Physics, Umeå University, Sweden

*Jinhua Sun, Department of Physics, Umeå University, Sweden

*Iakunkov Artem, Department of Physics, Umeå University, Sweden

Report: The purpose of project was to make X-ray diffraction study of Graphite Oxide (GO) swelling (intercalation of solvent between graphene oxide layers) in liquid amines. Our goal was to study GO structure in solvent immersed state as a function of temperature and to reveal posisble anomalies/phase transitions connected to insretion/de-insertion of solvent. Graphite oxide synthetised by Brodie's method was loaded into glass capilleries with liquid solvent, sealed and powder XRD was recorded in the temperature range of ~230-480K.

Our experiments have not revealed phase transitions in the systems GO- hexylamine at low temperatures with only minor gradual changes observed, see Figure 1. The change of interplanar distance was negligibly small for GO/ethylenediamine for the whole inetrval of temperature below ambient down to below freezing point of solvent. The data allow to validate structural models proposed earlier for GO in amine solvents. No multilayered intercalation of amines was found in our experiments. That is in contrast with our earlier experiments with GO immersed in liquid large alcohol molecules (1-octanol).[1] Most likely amine molecules attach to certain points of graphene oxide layers and remain in "stand up" orientation within the studied interval of temperatures. Slight variations of inter-layer distance of GO structure are likely connected to small changes in the orientation of amine molecules relative to the GO planes.

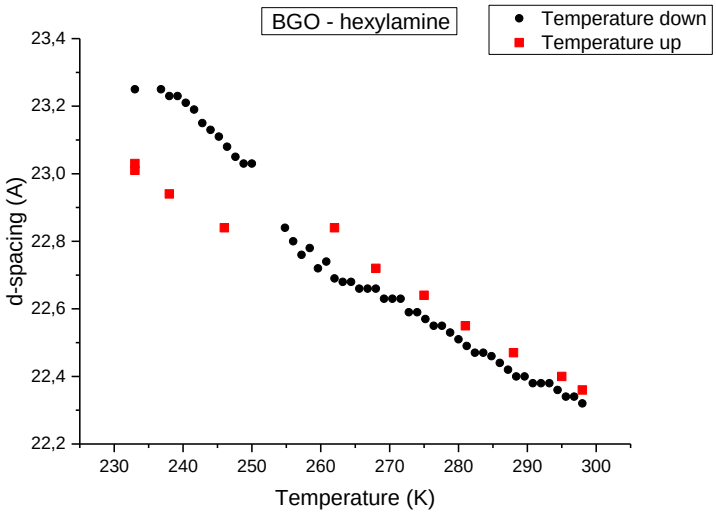

Figure 1. Temperature dependence of d(001), interplanar distance, in the system Brodie's GO – hexylamine recorded in process of cooling and heating from low temperature back to ambient.

Therefore, we performed additional set of experiments aimed on study of GO swelling in several other solvents. Temperature dependent experiments were performed for GO immersed in propanol, butanol, pentanol and hexanol. Phase transition corresponding to insertion of additional solvent layer was found for BGO in propanol, but not for butanol, pentanol and hexanol. It is unclear at the moment why so strong diffrence is observed for swelling in solvenst with rather similar chemical properties. This could be a subject of separate study and publication. Several experiments were performed also with GO immersed in acetonitrile solutions. BGO exhibits phase transition in acetonitrile and this phase transition is found to be modified very strongly in presence of dissolved ions. Concentration dependence of swelling transitions in acetonitrile solutions was never reported before. Finally we made temperature dependent study of GO swelling in sugar alcohols: xylitol and sorbitol. Last two experimenst were performed at temperatures above ambient since both sugar alcohols are solids at room temperatures. The experiments demonstrated swelling of GO in molten xylitol and sorbitol and formation of solid solvate phases with expanded GO lattice when the samples are cooled back to ambient temperature. To our knowledge it is first observeation of GO swelling in sugar alcohols.

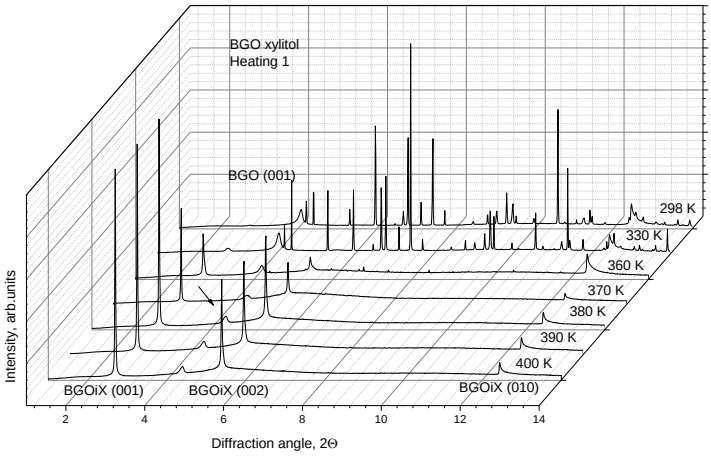

Figure 2. XRD patterns recorded from BGO/xylitol sample in situ in process of heating from room temperature up to 410K (above the melting point). Swelling transition is observed once the xylitol become liquid. This phase also preserved upon cooling back to ambient temperature and bulk xylitol solidification.

The XRD data recorded in the experiments described above are in process of analysis. Modelling of GO/solvent structures is performed at the moment in collaboration with theoreticians from Technical University of Dresden. Experimental XRd data will be then compared with theoretically simulated structures. It is expected that results obtained within HC3238 experimental session will be used in at least two publications.

1. Klechikov, A.; Sun, J. H.; Baburin, I. A.; Seifert, G.; Rebrikova, A. T.; Avramenko, N. V.; Korobov, M. V.; Talyzin, A. V. *Nanoscale* **2017,** 9, (20), 6929-6936.