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Experiment report: SC-728

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This experiment allowed us to study order within lamellar phase $H_3Sb_3P_2O_{14}$, $HSbP_2O_8$ as well as of the laponite clays. It should be noted that we used residual time to study the organizational ordering of another mineral phase: KNb_2PS_{10}, that self-assemble into nanotube and for which an hexagonal ordering could be described. A total of four publications came out of this experiment:

1) « *Swollen Liquid-Crystalline Lamellar Phase Based on Extended Solid-Like Sheets.* » J.-C. P. Gabriel, F. Camerel, B. J. Lemaire, H. Desvaux, P. Davidson, P. Batail, ***Nature*** **413**, 504-508, 2001

   Abstract :Here we describe a lyotropic liquid-crystalline lamellar phase comprising an aqueous dispersion of planar solid-like sheets in which all the atoms involved in a layer are covalently bonded. The spacing of these phosphatoantimonate single layers can be increased 100-fold, resulting in one-dimensional structures whose periodicity can be tuned from 1.5 to 225 nanometres. These highly organized materials can be mechanically or magnetically aligned over large pH and temperature ranges, and this property can be used to measure residual dipolar couplings for the structure determination of biomolecules by liquid-state NMR.We also expect that our approach will result in the discovery of other classes of mineral lyotropic lamellar phases.

2) « *Solvent-induced Folding of the Mineral Chains* $^{1}_{\infty}[Nb_2PS_{10}]^-$ *into Nanotubes.* » Franck Camerel, Jean-Christophe P. Gabriel, Patrick Davidson, Marc Schmutz, Thaddée Gulik-Krzywicki, Bruno Lemaire, Claudie Bourgaux, Patrick Batail, **Nano Letters** , **2**(4) 403-407, 2002.

   Abstract: This paper reports the synthesis of a new one-dimensional phase, $NaNb_2PS_{10}$, which is found to be soluble in polar organic solvents such as N-methylformamide (NMF) or dimethylformamide (DMF). Small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) studies have revealed that these covalent polymer coils fold into unprecedented single wall monodispersed nanotubules in NMF (external diameter 10 nm; wall thickness) 1.6 nm; length from 10 nm to over one micrometer). Cooperative weak bonds involving the hydrogen bond donor/acceptor ability of the primary amide solvent at the organic-inorganic interface are likely to assemble the flexible, charged covalent mineral polymer and indeed stabilize the nanotubule wall.

3) *« The measurement by SAXS of the nematic order parameter of laponite gels »* B. J. Lemaire, P. Panine, J.C.P. Gabriel and P. Davidson, ***Europhysic Letters***, **59**(1), 55–61. 2002.

   Abstract: We performed small-angle X-ray scattering (SAXS) experiments on oriented samples of laponite clay gels obtained by slow evaporation. The SAXS patterns are clearly anisotropic, which demonstrates the existence of nematic-like orientational correlations of the laponite disc-like particles. The iso-intensity lines of the SAXS patterns are elliptical and roughly homothetic over the

whole scattering vector range examined in this experiment. The value of the nematic order parameter, S = 0.55 ± 0.05, derived from the SAXS patterns is comparable to that of usual liquid crystals. This large value proves the importance of orientational correlations in these gels at concentrations higher than 0.02 g · cm−3, even in the absence of shear.

4) « *Combined SAXS-rheology studies of liquid-crystalline colloidal suspensions of mineral moieties*.» F. Camerel, J.-C. P. Gabriel, P. Panine, P. Davidson, ***Langmuir*** **19**(24); 10028-10035, 2003

Abstract: This article describes simultaneous rheological and small-angle X-ray scattering (SAXS) studies of complex fluids, using a modified rheometer that allows in situ synchrotron SAXS measurements. We investigated the behavior under shear stress of lamellar liquid-crystalline suspensions, recently reported, comprised of covalent mineral sheets ofH3Sb3P2O14 in water, that form sols and gels. Two original nematic mineral suspensions of HSbP2O8 disklike and H4Nb6O17 rodlike nanoparticles were also examined. We correlate both the existence of a yield stress and a strong decrease in viscosity (shear-thinning behavior) with textural changes easily detected by SAXS. The exact nature of the phase (nematic or lamellar) does notseemto affect suchphenomenaas long as there is orientational order. Moreover, strongly flow-birefringent and shear-thinning isotropic suspensions of anisotropic nanoparticles displayed very anisotropic SAXS patterns under shear.