NÉEL INSTITUTE Grenoble

Topic for Master 2 internship – Academic year 2022-2023

Phase diagram determination and growth of Langbeinite type crystals by high temperature solution growth

General Scope:

It has already been demonstrated that a large variety of synthetic langbeinites, based on the structure of $K_2Mg_2(SO_4)_3$, can be stabilized with room temperature non-centrosymmetric structures . Chemically speaking, fully substituting both sulfate $SO4^{2-}$ for phosphate $PO4^{3-}$ group and diamagnetic Mg^{2+} ions for paramagnetic Cr^{3+} cations is possible only if a mixed counter cation (Na^+A^{2+}) is introduced on the potassium site. $NaBa_{1-x}Sr_xCr_2(PO_4)_3$ solids, ceramics, with x=0 and 1 were recently reported to show intriguing physical properties (hysteric magneto capacitance signal when x=0 and a parallel magnetic long range ordering when x=1). During this internship we aim to grow single crystals $NaBa_{1-x}Sr_xCr_2(PO_4)_3$, from high temperature solutions, because obtaining single crystals is mandatory to investigate the physical properties/nuclear structure relationships with respect to an external stimulus. This work is developed in the frame of a collaboration project which main goal is the search of multiferroics solids based on polyanionic framworks.

Research topic and facilities available:

Before beginning the growth of crystals of Langbeinite family, ($Na_{1-x}Cu_{1+x}Cr_{2-x}(PO_4)_3$, $NaBa_{1-x}Sr_xCr_2(PO_4)_3$), that are of interest for ANR MultiPhos project, phase diagrams should be determined in order to find the chemical composition allowing to grow and stabilize the phases sought for its exotic magnetic properties. After this step, small crystals will be grown by spontaneous nucleation from high temperature solutions and the ones showing better magnetic properties will then be grown by Top Seeded Solution Growth-Slow Cooling (TSSG-SC) process.

We have already obtained $Rb_2Ti_2(PO_4)_3$ Langbeinite type phase by high temperature solution growth in molten phosphate salts ($Rb_6P_4O_{13}$ self flux) at temperatures close to 1000°C. As $M_6P_4O_{13}$ fluxes have already been used to dissolve refractory oxides such as TiO_2 (Tm = 1843 °C) leading to homogeneous growth solutions, they will be used during this internship. Considering that the growth of crystals with Langbeinite phase and adequate stoichiometry may require a perfect homogenization of solutions containing SrO (Tm = 2531°C), Cr_2O_3 (Tm = 2435 °C) and BaO (Tm = 1923 °C) and also growth temperatures higher than 1100 °C, a Nabertherm muffle furnace with working temperatures up to 1400 °C, available at Institut Néel, will be necessary. Moreover, in order to decrease the homogenization temperature of the solution, a molten phosphate-molybdate (or tungstate) salt could be used. These molten salts have been already used to grow $K_2Fe(MO_4)(PO_4)_2$, $K_2Sc(MoO_4)(PO_4)_2$ and $K_2Sc(WO_4)(PO_4)_2$; three langbeinite-related compounds.

Chemical reagents, muffle furnaces, powder X-ray diffractometers and Raman Spectrometer are available to the realization of this internship.

Possible collaboration and networking: CRISMAT (Caen, France), ICMCB (Bordeaux, France)

Possible extension as a PhD: Possible in the frame of the ANR project MultiPhos..

Required skills: Strong interest in materials science and experimental work is needed. Skills in crystal growth will be appreciate.

Starting date: February/March 2023

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