Growth of $NaBaCr_2(PO_4)_3$ crystals by high temperature solution method

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Frameworks built with transition metals MO_6 octahedra and $(XO_4)^{n-}$ polyanions (X = phosphorus, chalcogen, silicon, aluminium or some 3d and 5d transition metal) offer the same kind of chemical flexibility that the well-known perovskite and/or spinel-type structures. Fundamental interest in polyanionic frameworks regarding magnetic properties appears quite new. Using $(XO_4)^{n-}$ polyanions as a building element, rather than the more traditional oxo anion, will help to obtain ferroic solids. $NaBa_{1-x}Sr_xCr_2(PO_4)_3$ 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) [1]. In order to investigate the physical properties / nuclear relationship with respect to an external stimulus single crystals of $NaBa_{1-x}Sr_xCr_2(PO_4)_3$ with Langbeinite type structure are needed.
Several Langbeinite type crystals ($P2_13$ space group) have already been obtained by high temperature solution growth in molten phosphate salts but single crystals of $NaBa_{1-x}Sr_xCr_2(PO_4)_3$ have never been obtained by this method [2,3]. In this work we study three systems (Na_2O – $NaBaCr_2(PO_4)_3$ – $NaPO_3$ & RbF – $NaBaCr_2(PO_4)_3$ – $RbPO_3$ & Na_2O – $NaBaCr_2(PO_4)_3$ – WO_3) in order to determine if the crystals of interest can be grown. In all the three systems $NaBaCr_2(PO_4)_3$ crystals have been obtained by spontaneous nucleation but in phosphate fluxes a compositional change occurs during the crystal growth process due to a high evaporation of the solution. In molten tungstate salts no evaporation of the solution is observed but tiny crystals belonging to a secondary phase (Cr_2WO_6) have been obtained (Fig. 1).

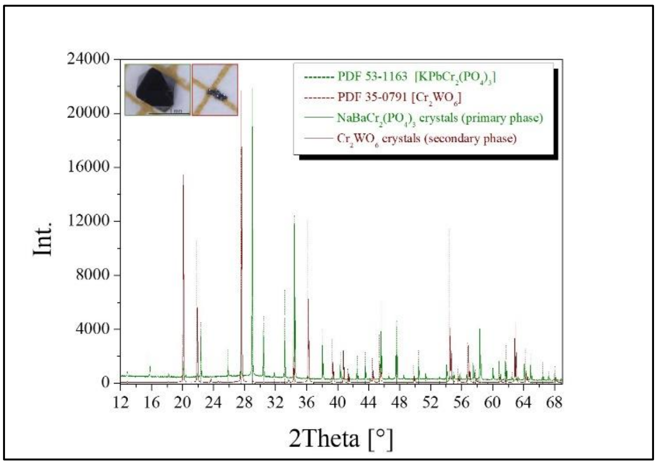

Figure 1. Powder x-ray diffraction of the crystals obtained by spontaneous nucleation from a high temperature solution of the chemical the system Na_2O – $NaBaCr_2(PO_4)_3$ – WO_3. A picture of one $NaBaCr_2(PO_4)_3$ crystal (left hand side) and several Cr_2WO_6 crystals (right hand side) are shown in the inset.

Solutions with different compositions of the system Na_2O – $NaBaCr_2(PO_4)_3$ – WO_3 are under study in order to determine the compositional zone where only $NaBaCr_2(PO_4)_3$ crystals are stable.

[1] Souiwa K et al. Synthesis and characterization of the phosphates $Na_{1+x}Mg_{1+x}Cr_{2-x}(PO_4)_3$ (x = 0; 0.2) and $NaZnCr_2(PO_4)_3$ with the α-$CrPO_4$ structure**.** J Alloys Compd. 2015;627:153-160.
[2] Carvajal JJ et al. Growth and structural characterization of $Rb_2Ti_{1.01}Er_{0.99}(PO_4)_3$. Chem. Mater. 2003;15:204-211.
[3] Peña A et al. Yb:Ta:$RbTiOPO_4$, a new strategy to further increase the lanthanide concentration in crystals of the $KTiOPO_4$. Chem. Mater. 2007;19:4069-4076.