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Low temperature synthesis and characterization of Na–*M*–(O)–F phases with *M*=Ti, V

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ABSTRACT

$Na_5Ti_3O_3F_{11}$ was prepared by the microwave assisted method, and presents a chiolite related structure with cell parameters $a=10.5016(5)$, $b=10.4025(5)$, and $c=10.2911(5)$ Å and *Cmca* (no. 64) space group. From solvothermal synthesis at 100 °C the cryolite $Na_{3-\delta}VO_{1-\delta}F_{5+\delta}$ was prepared, which crystallizes in the monoclinic system with $a=5.5403(2)$, $b=5.6804(2)$, $c=7.9523(2)$ Å, $\beta=90.032(7)^\circ$ cell parameters and $P2_1/n$ (no. 14) space group. Under similar synthesis conditions but with higher HF concentration the chiolite-type phase $Na_{5-\delta}V_3F_{14}$ was achieved, which exhibits $a=10.5482(2)$, $b=10.4887(1)$ and $c=10.3243(1)$ Å cell parameters and $Cmc2_1$ (no. 36) space group. A single crystal also having the chiolite structure was synthesized at 200 °C which exhibits tetragonal symmetry ($a=7.380(3)$ and $c=10.381(11)$ Å and space group $P4_22_12$ (no. 94)). Bond valence sum indicates that it contains V^{4+} and therefore can be formulated as $Na_5V_3O_3F_{11}$.

1. Introduction

The chiolite mineral $Na_5Al_3F_{14}$ was first reported by Brosset [1] and fully characterized by Jacobini [2]. Its crystal structure has a tetragonal symmetry with space group *P4/mnc* ($Z=2$) and consists of layers formed by corner-linked octahedra where one of every four octahedra is replaced by a sodium ion. One-third of the MX_6 octahedra share four corners with two-thirds of the MX_6 octahedra that are rotated 45° with respect to the former. Such layers are stacked along the (0 0 1) direction and displaced one respect to the other by half the (1 1 0) diagonal. Additional sodium ions are accommodated in the interlayer space. The chiolite structural type is adopted by a variety of fluorides, oxides and oxyfluorides with general formula $A_5M_3X_{14}$ ($X=O_iF_{14-i}$, $i=0\ldots14$) and presents rich diversity in composition (e.g. $Na_5Fe_2CoF_{14}$, $K_5In_3F_{14}$, $Ag_5W_3O_9F_5$, $Ca_5Te_3O_{14}$ or $NaNd_4Sb_3O_{14}$). [3–5] Indeed, phases with *M* in different oxidation states are formed depending on the nature of the *A* cations and the O/F ratio. Nonetheless, the majority of studies have focused on *A*=Na, K and *M*=Al, Ti, V, Fe, Co, W [3,6–9] amongst which $Na_5Fe_3F_{14}$ and $Na_5W_3O_9F_5$ have received most attention because of their ferromagnetic and ferroelectric properties [10,11].

Most of the compounds exhibiting chiolite-type structures have been synthesized via solid state reaction at high temperature. While oxides $Sr_5U_3O_{14}$, [11] $BaSr_4U_3O_{14}$, [11] and $Ca_5Te_3O_{14}$ [5] have been prepared in either platinum or alumina crucibles in air, in the case of fluorine containing compounds the reactions are usually carried out in a gold sealed tube which allows the control of the phase composition (e.g. $Na_5Fe_3F_{14}$ was prepared [3] starting from NaF and FeF_3 in a sealed-Au tube at 650–700 °C). Single crystals have been grown from melts (e.g. $K_5V_3F_{14}$ under N_2/H_2 flow [7]). Nonetheless, very few reports exist on the use of alternative synthesis routes with the exception of the preparation of $Na_5Al_3F_{14}$ by sol–gel reaction with HF at room temperature, [12] or the more recent preparation of $K_5V_3F_{14}$ and $K_5In_3F_{14}$ [4] using a solvothermal route at temperatures around 200 °C, but in these cases phase purity was difficult to attain. A cryolite type compound is sometimes obtained as a secondary phase, as in the case of the ball milling of NaF and amorphous AlF_3 in order to obtain $Na_5Al_3F_{14}$ [13]. This structural type exhibits an open crystal framework consisting of AlF_6 octahedra surrounded by sodium ions occupying one-half of the octahedral sites, and is an special case of the elpasolite structure ($ABB'X_6$) which is an ordered perovskite that contains two types of anionic groups (BX_6, $B'X_6$) alternated along the 4-fold axes. Therefore, cryolites are described with the general formula $A_3BB'F_6$ where *A* and *B* are chemically equivalent atoms. The hydrothermal synthesis of Na_3VF_6 cryolite has for instance been reported from NaF, V_2O_3 and HF [14]. Similarly, the cryolite-related α-Li_3FeF_6 phase has been

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obtained from aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$, HF and Li_2CO_3 at 50–60 °C [15].

Inspired by such preliminary results and in view of the achievement of other oxyfluorides with softer synthetic routes ($(NH_4)TiOF_3$, [16] $Ag_3MoO_3F_3$ and $Ag_3VO_2F_4$ [17] and $NaMnMoO_3F_3 \cdot H_2O$ [18]), we decided to attempt the preparation of chiolites using similar procedures. Being interested in compounds containing transition metals which can exhibit different oxidation states and hence display potential redox activity to be used as battery electrode materials, [15,19–22] we selected the Na–Ti–O–F and the Na–V–O–F systems as primary objectives. In the first case, Vedrine et al. [23,24] reported the preparation of brown single crystals with $Na_5Ti_3F_{14}$ composition from NaF and TiF_3 in a chloride flux ($NaCl/ZnCl_2$). These were found to exhibit the $P4_2/n$ space group with cell parameters $a=7.497$ and $c=10.287$ Å. Later on, $Na_5Ti_3O_3F_{11}$ was prepared from NaF and $TiOF_2$ treated at ca. 650 °C for 15 h inside a sealed gold tube [6,25]. A monoclinic cell was proposed with $a=7.399$, $b=10.247$, $c=7.399$ Å and $\beta=90.86°$ with a phase transition to a tetragonal structure taking place upon heating to ca. 490 °C. For the case of vanadium, only a dark green $Na_5V_3F_{14}$ compound has been previously reported ($a=7.33$, $c=10.36$ Å [3]) obtained from NaF and VF_3 at 700 °C inside a gold tube sealed under argon which exhibits ferrimagnetic behavior with $T_c=21$ K, a value quite similar to that reported for $K_5V_3F_{14}$ (18 K). [3] Herein we report the synthesis and characterization of a titanium-chiolite $Na_5Ti_3O_3F_{11}$ precipitated via a microwave assisted route and novel vanadium-chiolite and cryolite type phases obtained by a solvothermal route.

2. Experimental section

2.1. Materials

Hydrofluoric acid (40 wt% in H_2O, > 99.99%), vanadium (V) oxide (99.6%), sodium nitrate (99.0%), sodium fluoride (99.0%), sodium acetate trihydrate (99.9%), boric acid (99.5%), hexafluorotitanic acid (60 wt% in H_2O, 99.9%) and ethylene glycol (anhydrous, 99.8%) were all purchased from Sigma-Aldrich and used without further purification.

Hydrofluoric acid and hexafluorotitanic acid are highly corrosive and irritating. Their use requires extreme caution and must be handled with protective clothing. Specialized treatment is required in case of contact with HF [26,27].

2.2. Synthesis

$Na_5Ti_3O_3F_{11}$ was obtained by a microwave-assisted route. 6.0 g (21.6×10^{-3} mol) of H_2TiF_6 (60 wt% in H_2O) were dissolved in a saturated aqueous solution of sodium acetate prepared at room temperature in a 100 mL PTFE beaker and heated in a domestic microwave oven (LG Intellowave, 2.45 GHz) at 800 W power for 20 s. This procedure was repeated several times (total reaction time 3 min) with intermediate 2-min resting periods to limit the temperature increase. Due to the high MW absorbing capacity of the used precursors, no susceptor to provide indirect heating was necessary. The white solid formed was centrifuged and washed several times with water and dried in air at 60 °C.

Solvothermal synthesis were carried out at 100 °C following a similar protocol to that reported by Aldous et al. [28] The cryolite-type phase $Na_{3-\delta}VO_{1-\delta}F_{5+\delta}$ was prepared by dissolving 0.170 g of $NaNO_3$ (2×10^{-3} mol) and 0.182 g of V_2O_5 (1×10^{-3} mol) in 0.5 mL of HF and 10 mL of ethylene glycol, which was used as reducing agent. After cooling to room temperature, the product was washed several times with ethanol and dried in air at 60 °C.

The chiolite $Na_{5-\delta}V_3F_{14}$ was synthesized 0.364 g (2×10^{-3} mol) of V_2O_5 were dissolved in 10 mL HF (40 wt%). The dissolution was kept under stirring for ca. 5 min and first 10 mL of ethylene glycol (reducing agent) and further 0.567 g (6.7×10^{-3} mol) $NaNO_3$ were added. The reaction was carried out in a closed polypropylene container heated at 100 °C for 24 h. The solid was decanted from the solution, washed repeatedly with ethanol and dried in air at 60 °C. A larger batch suitable for neutron diffraction experiments was prepared by doubling the precursor amounts. Synchrotron data revealed the presence of tiny amounts of VF_4 (PDF # 19-1409).

Also, attempts were made to grow single crystals at higher reaction temperatures starting from 0.738 g (9×10^{-3} mol) of $NaNO_3$ with 0.815 g (4.5×10^{-3} mol) of V_2O_5 dissolved in 1.2 mL of HF (40 wt%) and 10 mL of water to which 25 mL of ethylene glycol. The synthesis was carried out in a 50 mL autoclave at 210 °C for 48 h. After cooling to room temperature, the product was washed several times with ethanol and dried at 60 °C. Inspection under the optical microscope allowed detecting that the sample consisted of a mixture of light blue small crystals and yellowish larger ones in similar amounts. The latter were micrometric in size and thus, crystal of $0.48 \times 0.42 \times 0.30$ mm^3 size was selected in order to determine its crystal structure.

2.3. Characterization

The chemical composition of the as prepared solids was analyzed through a combination of techniques. 40 mg of each sample were digested in a mixture of HNO_3 (Baker Instra), H_2O_2 (Merck Suprapur) and HF (Scharlau) inside a closed Teflon reactor in a microwave furnace at 220 °C. Titanium and vanadium contents on the resulting solutions were determined by ICP–OES using a Perkin Elmer Optima 3200 RL spectrometer, while sodium contents were analyzed by ICP–MS using a Perkin Elmer Elan 6000 spectrometer. The presence/absence of structural water molecules was ascertained by IR spectroscopy on a Perkin Elmer FT-IR Spectrum One system with a Universal Attenuated Transmission Reflectance (UATR) accessory and a DiComp™ crystal composed of a diamond ATR with a ZnSe focusing element. Finally, the oxygen to fluorine ratio was roughly estimated through energy dispersive X-ray spectrometry (EDX) using a on field-emission gun scanning electron microscope (SEM) (Quanta 200 ESEM FEG FEI). Transmission electron microscopy (TEM) and electron diffraction (ED) were performed on a JEOL 1210 transmission electron microscope operating at 120 kV and equipped with a Gathan sample holder allowing $\pm 60°$ x and $\pm 30°$ y tilting. Preparation of the samples involved dispersing the powder in heptane (anhydrous, 99%) and depositing a droplet of the dispersion on a holey carbon coated copper grid.

Powder X-ray diffraction (XRD) on as prepared samples has been carried out using a Siemens D-5000 diffractometer (Cu$K\alpha$ radiation) in the range $2\theta=5$–$70°$ width a 2θ step size of 0.02°. Further measurements were carried out using synchrotron X-ray (SXRPD) and neutron powder diffraction (NPD). NPD pattern at RT was measured at D2B beamline of Institut Laue Langevin (Grenoble, France) [29] in high flux mode ($\lambda=1.594$ Å) and Debye Scherrer geometry using ca. 2 g of sample placed inside a ~8 mm diameter vanadium sample-holder. SXRPD patterns were measured at the MSPD beamline of the ALBA synchrotron (Cerdanyola del Vallès, Spain) using Mythen detector. The sample was introduced in a borosilicate glass capillar (0.7 mm in diameter) which was rotated during data collection. The wavelength used was $\lambda=0.620041$ Å. FullProf_suite [30] programs were used for Rietveld refinements.

Single crystal XRD was carried out using an Enraf-Nonius CAD4 diffractometer producing graphite monochromated Mo$K\alpha$ radiation ($\lambda=0.71073$ Å). The crystal was mounted at the tip of a glass fibre. After the random search of 25 reflections indexation was carried out. Intensity data were collected in the ω–2θ scan mode and corrected for Lorenz and polarization effects. Solving structure factor phases was performed with SIR2004 [3], and the full matrix refinement with SHELXL97 [31].