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FELLOWSHIP FINAL REPORT

Molten Salt Synthesis and Characterization of (Oxo)-(Fluoro)-Aluminates for Electrochemical and Electronic/Photonic Applications

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REPORT INFO

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ABSTRACT

The primary aim of this Le Studium project was a thorough physico-chemical analysis and structural characterization of key phases and compounds of high-temperature fluoride melt/solid interphases. This knowledge is then used for a targeted synthesis and preparation of different compounds and materials (including their physicochemical characterization), based on oxo-fluoro-aluminates of alkali metals.

1- Introduction

Fluoro-, oxo-, and oxo-fluoro-aluminates with monovalent cations are considered as new materials with the potential to have high ionic conductivity and interesting optical properties [1-2]. These properties are related to the crystal structure and its changes by anionic substitution. Crystalline systems with oxygen partially replaced by fluorine have the ability to introduce defects into the structure and thus modify materials' properties, which can directly lead to an increase in the functionality of the material. The existence of these compounds and materials has been recently confirmed. In the case of alkali metal oxo-fluoro-aluminates, the potassium and the rubidium forms were prepared (with the characterization of their structure) [2-4, 5]. Our laboratories' research on the synthesis and characterization of oxo-fluoro-aluminates at the solid/melt interface led to the first preparation and characterization of the compound's rubidium form.

The structure of oxo-fluoro-aluminates is built up of oxygen-connected (AlO_3F) tetrahedra, where three oxygen atoms and one fluorine atom are bonded to the aluminum atom. Two AlO_3F tetrahedra, joined by a common oxygen corner, constitute the basic building unit $[Al_2O_5F_2]$ of $[Al_2O_3F_2]$ layers and K^+ cations are mobile between the layers. Such tetrahedrally coordinated structure of potassium and rubidium oxo-fluoro-aluminates is unique and unusual since aluminum fluorine compounds almost exclusively crystallize into the octahedral form [5].

Much less attention has been focused on new materials with a larger alkali-metal cation, like rubidium or cesium. In this area, only a limited number of rubidium ion conducting solid electrolytes have been reported to this date. It is

clear that the valence and ionic radius have an important effect on the structure and the properties of these compounds. The size of the alkali metal cations plays also a primary role in the formation and stability of oxo-fluoro-aluminates at the interface of the fluoride melt/solid (glass) phase [6]. The rubidium oxo- and oxo-fluoro-aluminate structures are more favorable as the cation size and cation charge increase. Therefore, such electrolytes could have considerable scientific and technological importance. Recently, $Rb_2Al_2O_3F_2$ was synthesized and characterized in our laboratories with very interesting ionic conducting properties [5]. Another very promising field of the possible application of these materials is their use as a base matrix for various dopants, which may in the end increase the functionality of the material (e.g., rare earth metal dopants, etc.).

The size and the role of the cations is also a key factor for an understanding of the transport properties of these materials, as solid conductors. Understanding the unusually high transport ability of alkali metal ions requires a more rigorous characterization of the phases and their systems and subsystems where these phases and compounds arise and exist. The problem is that the information about the related phase diagrams is rather limited, likewise the thermal stability/meta-stability of all compounds wherein (see works [4-5]). All alkali metal oxo-, fluoro-, and oxo-fluoro-aluminates are included in the binary $MF-Al_2O_3$ system, and this system could be considered as a subsystem of a wider reciprocal system, $MF-AlF_3-Al_2O_3-M_2O$ (M = alkali metal). These complex systems can be further subdivided into several sub-systems for their use in the syntheses. The most interesting of them are:

i) Simple binary systems $MF-AlF_3$ and $M_2O-Al_2O_3$. In simple binary $MF-AlF_3$ systems (M = alkali metals), a dozen fluoroaluminate complexes exist, known as elpasolite and cryolite-type minerals. They all have the ordered double perovskite structure, based on (AlF_6) octahedra which might be discrete units or joined in chains, sheets, frameworks, and other groupings [7]. The second binary system contains the known beta alumina group of oxides. They are characterized by structures of alternating closely-packed spinel blocks and loosely-packed layers. These layers are called conduction planes, containing mobile alkali metal ions. There are two distinct crystal structures in this group, β- and β"-alumina, which differ in chemical stoichiometry, stacking sequence of oxygen ions across the conducting plane.

ii) quasi binary part of the larger systems $MF-AlF_3-Al_2O_3$. This system is also interesting from an industrial point of view of aluminum metallurgy, as the $NaF-AlF_3-Al_2O_3$ system is used as an electrolyte in the electrolytic production of primary metallic aluminum [8].

iii) diagonal of the larger system $MF-Al_2O_3$. These systems are being studied as effective catalysts for various esterification processes [9].

Even from this short introduction, it is quite clear, that these inorganic aluminium fluorides, oxides, and oxyfluorides can have significant importance in the development of many new technologies and materials from even rather (i) classic metal production (Li-, Na-, and K-hexafluoroaluminates – cryolites – well known from its use as a solvent in the Hall-Héroult process of extracting Al from Al_2O_3 electrochemically); to (ii) advanced energy production/storage applications (Na-containing aluminum fluorides with a large variety of transition metal combinations as cathode materials for Sodium-ion batteries– NIBs [10], and β-, and β"-aluminas as solid fast-ion conductors with excellent thermal stability) [11]; (iii) photonic and electronic applications [12] (alkali metal cryolites are commonly used as new Mn^{4+} activated fluorides for white light emitting diodes – WLED) [13]; (iv) catalysts (systems $MF-Al_2O_3$, where M = K, Rb, Cs) [9], etc. Therefore, a better knowledge of the

correlation between the structure and the relevant physical properties of these systems is critically important. A thorough understanding and characterization of these complex reciprocal systems, including their high-temperature melts, metastable phases, glass phases, and nonstoichiometric compounds could be vitally important for many areas of industrial R&D.

2- Results and discussion

The primary aim of the submitted project was a thorough and comprehensive physico-chemical analysis and the structural and phase characterization of the key phases and compounds of the high temperature interface fluoride melt/solid phase. This knowledge base was then planned to be used for a targeted synthesis and preparation of previously unknown compounds and materials, based on oxo-fluoro-aluminates of alkali metals (or the identification of new interesting synthesis routes of already known compounds of that group). The project's primary objectives were originally divided into the following steps, which were also considered as partial aims of the project/steps in the research plan.

1. Characterization of multicomponent systems $MF{-}NF_3{-}N_2O_3{-}M_2O$ (M = alkali metal, N = Nd, Y, Al, Sc) and their binary subsystems, using different thermal analysis methods.

1a) The phase equilibria of molten systems of Na_3AlF_6 – NdF_3 and (Na_3AlF_6 – NdF_3)eut – Nd_2O_3 have been for the first time analyzed. Both investigated mixtures seem to form similar systems with one invariant/eutectic point. The coordinates of the eutectic point in the case of the Na_3AlF_6 – NdF_3 system were found to be at approximately 49 mol % of NdF_3 and 905 °C. The coordinates of the invariant point in (Na_3AlF_6 – NdF_3)eut – Nd_2O_3 system are ca. 46 mol % Nd_2O_3 and 733 °C.

1b) The phase equilibria and the phase diagram of molten systems of Na_3AlF_6 – Y_2O_3 have been for the first time investigated with the identification of the related phase fields. The shape of the liquidus line of the phase diagram indicates the existence of one inflection point and relatively low eutectic temperature.

1c) Thermal analysis of the system $CsF{-}Al_2O_3$ was used for the construction of the part of the phase diagram of the system $CsF{-}Al_2O_3$. The classification of each phase transition as a function of temperature and composition was carried out.

2. Preparation of the samples using container-less aerodynamic levitation melting (ADL). Use of quenching techniques to prepare undercooled samples. Ex-post spectral and diffraction analysis of the solidified mixtures.

2a) ADL technique was used for the preparation of the undercooled samples of the following systems: (LiF – CaF_2)eut – NdF_3, (LiF – NaF)eut – NdF_3, (NaF – CaF_2)eut – NdF_3, and (LiF – MgF_2)eut – NdF_3. The concentration range of the NdF_3 in these systems was 0 – 20 mole %. The samples prepared by ADL were subsequently analyzed at room temperature by XRD, MAS NMR, and SEM EDX microscopy.

2b) ADL technique was used for the preparation of the undercooled samples of the following systems Na_3AlF_6 – NdF_3 and (Na_3AlF_6 – NdF_3)eut – Nd_2O_3. The concentration range of the NdF_3 / Nd_2O_3 in these systems was 0 – 50 mole %. The samples prepared by ADL were subsequently analyzed at room temperature by XRD, MAS NMR, and SEM EDX microscopy.

3. A structural characterization of compounds and phases, formed in the analyzed systems, that have not been identified and/or characterized so far (including utilization of new synthesis techniques/routes). Synthesis of new compounds by ADL, and by other techniques as well as by "classical" methods of synthesis (direct synthesis in molten state, pro-longed synthesis in solid state, synthesis at high-temperature and high-pressure).

3a) Utilization of molten fluoride media (molten cryolite – alumina mixture and $CsF{-}Al_2O_3$) as a new synthesis route for the

preparation of different oxide ceramic materials (including doped oxides). XRD and MAS NMR were after synthesis used for the characterization of newly formed phases and compounds in the reaction mixture.

3b) A high temperature analysis of the particular phase fields in CsF-Al_2O_3 system was performed at the following temperatures: 720, 750, and 800 °C.

3c) High energy milling was used for the preparation of sodium oxo-fluoride compounds (initial mixture of NaF and Al_2O_3 in molar ratio 2/1). A high temperature XRD was after the milling procedure used for the high temperature treatment and the phase evolution monitoring/recording.

4. Application of in-situ methods for the characterization of measured systems (LINKAM imaging visual analysis, high-temperature NMR spectroscopy in molten state, high-temperature MAS NMR spectroscopy in solid or solid/liquid state, high-temperature XRD analysis) combined with analytical methods in solid state (MAS NMR, powder XRD analysis). Identification of the chemical nature of possible complex species, presented in molten state, as well as complex compounds, present in crystallization fields.

4a) High temperature RAMAN spectroscopy coupled with the LINKAM furnace was used to record the RAMAN spectra as a function of temperature in the following systems: (LiF – CaF_2)eut – NdF_3, (LiF – NaF)eut – NdF_3, (NaF – CaF_2)eut – NdF_3, and (LiF – MgF_2)eut – NdF_3. The concentration range of the NdF_3 in these systems was 0 – 20 mole %.

4b) MAS NMR spectroscopy and synchrotron powder diffraction data were used to identify cesium oxo-fluoro-aluminate species in the CsF−Al_2O_3 system.

3- Perspectives of future collaborations with the host laboratory

We can draw the conclusion that there are many opportunities for the continuation of mutual cooperation given the already extensive collaboration between the host laboratory (CEMHTI CNRS) and the institute of the Le Studium fellow (IIC SAS), including the experimental data gathered during the fellowship. There are two key categories for the future perspectives in this regard. The first area is the continuation of already previously established collaboration in the fields of molten salt chemistry related to the structural analysis of molten electrolytes for the electrowinning of different metals (Al, Sc, rare earth elements, etc.). A new area of possible cooperation is the field opened during the fellowship related to the new molten fluoride synthesis of functional oxide materials.

4- Articles published in the framework of the fellowship

1) M Korenko, D Krishnan, F Šimko, B Kubíková, A Rakhmatullin, E Véron, M Allix, "The Molten Na_3AlF_6–NdF_3–Nd_2O_3 electrolyte for the Neodymium Electrowinning: Phase Equilibria, Electrical Conductivity, XRD, and MAS NMR", Submitted for the conference 2023 Joint Symposium on Molten Salts (MS12), Kyoto, Japan.

2) M Korenko, "Research Article Theatrum Chymicum: A Brief Pre – History of Chemistry", (2023) Foundations of Chemistry. Springer. Submitted.

3) A Rakhmatullin, F Šimko, D Zanghi, Z Netriová, IB Polovov, R Bakirov, KV Maksimtsev, C Bessada, and M Korenko, "Structural Correlation and Chemistry of Molten Eutectic NaF–ScF_3 with Dissolved Metal Aluminium; TG/DTA, NMR and Molecular Dynamics Simulations", (2023) Rare Metals. Springer. Submitted.

4) D Krishnan, M Korenko, F Šimko, B Kubíková, A Rakhmatullin, "Thermal Analysis and Phase Equilibria of the Molten System Na_3AlF_6–NdF_3–Nd_2O_3", (2023) JOM. Springer. Under review.

5) F Šimko, A Rakhmatullin, G King, M Allix, Z Netriová, C Bessada, D Krishnan and M Korenko, “Cesium Oxo-Fluoro-Aluminates in the $CsF-Al_2O_3$ System: Synthesis and Structural Characterization”, (2023) Inorganic Chemistry. ACS. Submitted.

6) M Ambrová, M Korenko, L Szatmáry, “Influence of the Sulphur Species on the Current Efficiency and Carbon Consumption of Aluminium Electrowinning in Molten Cryolite Electrolytes“, (2023) Metallurgical and Materials Transactions B. Springer. Accepted.

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