Synthesis of nanocrystalline mixed metal fluorides in nonaqueous medium

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Abstract. Synthesis of mixed metal fluorides of the general formula, KMF_3 (M = Mg, Mn, Co, Ni, Cu and Zn), possessing perovskite structure was investigated in non-aqueous medium. The fluorides were characterized by powder X-ray diffraction, FT–IR spectroscopy, thermal analysis, SEM and TEM. Monophasic cubic phases were obtained for the central metal ions such as Mg, Mn, Co, Ni, and Zn and a tetragonally distorted phase was observed for Cu. The usage of non-aqueous medium is advantageous for the bulk synthesis of these fluorides, since it eliminated the generation and handling of the hazardous HF that has usually been encountered during aqueous preparations. The average crystallite size of the fluorides obtained by this approach was estimated to be in the range of 9–30 nm. SEM micrographs of $KZnF_3$ showed cubic morphology of perovskite phases. TEM studies on $KCuF_3$ confirmed the presence of tetragonal distortion. The fluoride content was determined by titrimetry and found to be nearly stoichiometric. Some of these fluorides were found to be thermally stable up to 225°C in air. These fluorides were employed as fluorinating agents in organic fluorination reactions, thereby suggesting their possible utilization for selective fluorination of aliphatic and aromatic hydrofluorocarbons (HFCs) that are industrially relevant.

Keywords. Fluorides; perovskites; nanomaterials; soft synthesis; X-ray diffraction; non-stoichiometry.

1. Introduction

Materials possessing perovskite structure have received enormous attention over the past two decades because of their interesting properties such as high-temperature superconductivity and colossal magnetoresistivity (Rao and Raveau 1995). With the advent of nanoscience and nanotechnology much effort has been devoted to the synthesis of inorganic materials with specific morphologies possessing unique optical and electronic properties (Rao *et al* 2007). There has been an increased interest in the study of simple ternary fluorides with perovskite structures (e.g. $KMgF_3$, $KMnF_3$, $KNiF_3$, $KZnF_3$) because of their interesting structural and physical properties, such as magnetism, photoluminescence and piezoelectricity (Hirakawa *et al* 1960; Knox 1961; Suemune and Ikawa 1964; Holloway and Kestigian 1966; Svensson *et al* 1969; Gesi *et al* 1972; Rose *et al* 1976; Takeuchi *et al* 1979; Yamaguchi *et al* 1999). The synthesis and characterization of fluorometallates which are iso-electronic and iso-structural with their oxide counterparts is the subject of the present investigation. Traditionally complex fluorides are prepared by solid state reaction at high tempera-

ture (>400°C) and high pressure or by high pressure (>100 MPa) hydrothermal technique (Demiamets 1990). A milder hydrothermal synthesis of the complex fluorides at 120–240°C has also been reported (Zhao *et al* 1996, 1997; Xun *et al* 1997, 1998). The major difficulties that are encountered in the synthesis of fluoride perovskites are the choice of the container, the evolution of hydrofluoric acid (HF) and the corrosive nature of the fluorine gas which also may lead to the non-stoichiometry of the products. In the case of $KCuF_3$ prepared from aqueous solutions, replacement of one fluoride ion by one hydroxyl ion resulting in a composition of $KCu(OH)F_2$ has been observed (Machin *et al* 1963; Li *et al* 2000). The oxygen content in the complex fluorides synthesized by solid state reaction was higher than that of the corresponding complex fluorides synthesized by hydrothermal technique (Haendler *et al* 1958). The earliest work on the synthesis of these fluorometallates in non-aqueous medium was carried out by Crocket and Haendler (1960), for the synthesis of NH_4MF_3 (M = Cd, Co, Cu, Mn, Zn, Mg, Fe) in methanol in the year 1958. They extended the same approach for the preparation of KMF_3 and $RbMF_3$ (M = Cd, Co, Cu, Mn, Zn, Fe). Recently, $KMgF_3$ and $KZnF_3$ were prepared in ethylene glycol at 150–180°C using an autoclave (Hua *et al* 2002). Also $KNiF_3$ has been prepared solvothermally at 110°C using ethanol (Zhang *et*

al 2005). Very recently, KZnF$_3$ and KCdF$_3$ crystals were obtained in methanol employing mild solvothermal synthesis (Huang *et al* 2005). While the non-aqueous approach provides an easy means for the synthesis, the solvothermal method required the use of autoclaves. Although many different synthetic routes have been described in the literature for the preparation of these fluorides, there has not been any comprehensive study describing the nature of the products from the non-aqueous medium, their thermal stability and possible applications. During the preparation of our paper, we came across a publication describing microwave assisted metathesis synthesis of these fluorides (Parhi and Manivannan 2008). However, the hazardous fluorine gas evolution may occur in these kinds of reactions. In the present study, we have prepared fluorometallates possessing perovskite structure through soft chemistry or a green synthetic approach by the use of non-aqueous medium which eliminates the use of harsh conditions such as high temperatures and high pressures that were generally employed to obtain these fluorides. Also the preparations through non-aqueous medium resulted in final products with improved stoichiometry. These fluorides were characterized by the powder X-ray diffraction, FTIR spectroscopy, transmission electron microscopy and thermal analysis. For the first time, we have also demonstrated the application of these fluorides in organic fluorination reactions.

2. Experimental

Typically divalent metal chlorides were first dissolved in absolute methanol (HPLC Grade) and added to potassium fluoride in absolute methanol. The molar ratio of potassium fluoride to metal chlorides was kept 3 : 1 in all the preparations. The solid product obtained was filtered, washed with ethanol followed by acetone and air dried. Perkin-Elmer FT–IR spectrometer model 2000 was employed to obtain the absorption spectra of the powder samples using KBr as the dispersal medium. The powder X-ray diffraction patterns were recorded using Bruker D8 Advance Diffractometer employing Cu Kα radiation. The fluoride content of the samples was estimated by titrating against the standardized thorium nitrate solution using sodium alizarin sulphonate as indicator (Cumming and Kay 1956). A Tecnai 20 G2 (FEI make) transmission electron microscope at 200 kV was used to carry out TEM studies. Thermal analysis of the samples was carried out using Shimadzu DTG-60 instrument. The ^{19}F NMR spectrum was recorded using Bruker Toxispin (300 MHz) spectrometer.

3. Results and discussion

We prepared KMF$_3$ (M = Mg, Mn, Co, Ni, Cu and Zn) in aqueous medium following the procedure of Langley

et al (1984). However, from the observation of etching of glass beakers used for the synthesis, we concluded that in the aqueous medium one cannot avoid the generation of hydrofluoric acid. The generation of HF might be one of the main reasons for the non-stoichiometry observed in the total fluoride content and also for the presence of hydroxyl groups in the final products as observed in earlier reports (Haendler *et al* 1958; Crocket and Haendler 1960). We have chosen non-aqueous medium for the synthesis of these ternary fluorides mainly for two reasons viz. safety and to minimize the fluoride content loss during synthesis. In figure 1, we show the powder X-ray diffraction patterns of KMF$_3$ (M = Mn, Co and Mg) prepared via non-aqueous medium. While KMgF$_3$ and
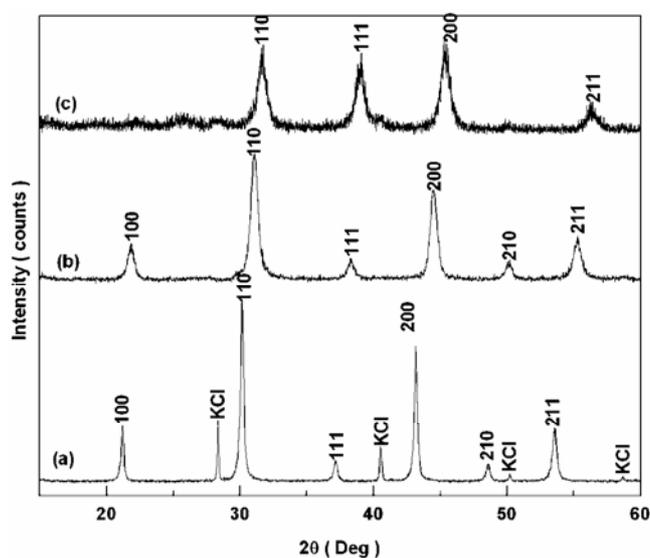

Figure 1. Powder X-ray diffraction patterns of (a) KMnF$_3$, (b) KCoF$_3$ and (c) KMgF$_3$.
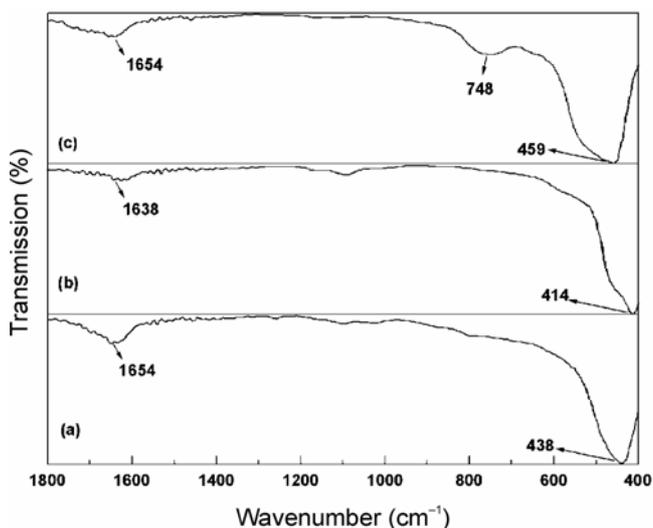

Figure 2. FTIR spectra of (a) KMnF$_3$, (b) KCoF$_3$ and (c) KMgF$_3$.

$KMnF_3$ were white coloured fine powders, $KCoF_3$ was bright pink in colour. We have observed the formation of KCl in our preparations along with the fluoride as reported in the solvothermal approach by Zhang *et al* (2005). The cubic lattice constants of our preparations were 4·186(2), 4·063(5) and 3·997(1) Å for $KMnF_3$, $KCoF_3$ and $KMgF_3$, respectively and they agreed well with the reported values (JCPDS Cards 821334; 712442; 181033). We calculated the average crystallite size from the powder X-ray diffraction patterns of $KMnF_3$, $KCoF_3$ and $KMgF_3$ using Scherrer's formula (Cullity 1978) to be 28, 12 and 17 nm, respectively. In the literature, $KMnF_3$ and $KCoF_3$ prepared by an aqueous approach contained oxy, hydroxyl groups or the hydrates (Wanklyn *et al* 1979). We examined our preparations by FT–IR spectroscopy for the presence of oxy, hydroxyl or hydrates. The FT–IR spectra of $KMnF_3$, $KCoF_3$ and $KMgF_3$ are shown in figure 2. We observed shallow bands in 3430–3450 cm^{-1} region and around 1645 cm^{-1} in all the three cases corresponding to the antisymmetric and symmetric OH stretching and HOH bending modes of lattice water (Nakamoto 1978). In addition to these bands, we observed a strong band between 420 and 430 cm^{-1} and a shoulder at 720 cm^{-1} that could be assigned to M–F stretching (M = Mn, Co and Mg) and phonon modes (Nakagawa *et al* 1967; Young and Perry 1967). The total fluoride content by titration indicated a perfectly stoichiometric compound. This synthetic approach for making bulk fluorides of Mg, Mn and Co may facilitate the study of their luminescent properties by doping of suitable activators (Furetta *et al* 2001).

We prepared $KNiF_3$ and $KZnF_3$ possessing cubic perovskite structure in non-aqueous medium. The SEM micrograph of $KZnF_3$ confirmed the cubic morphology of the powders (figure 3). We focused more on the preparation of $KCuF_3$ using non-aqueous medium for a variety of reasons. Firstly, Cu^{2+} being a Jahn-Teller ion, $KCuF_3$ exists in two poly types with varying stacking disorder (Hutchings *et al* 1969; Towler and Dovesi 1995). Secondly, the presence of hydroxyl groups in place of fluoride ions seriously affects the magnetic properties of bulk $KCuF_3$ (Haendler *et al* 1958). We obtained tetragonal $KCuF_3$ by reacting methanol solutions of $CuCl_2 \cdot 2H_2O$ or $CuBr_2 \cdot 2H_2O$ with KF at room temperature. In figure 4, we show the powder X-ray diffraction patterns of $KCuF_3$ prepared from $CuCl_2 \cdot 2H_2O$ as well as $CuBr_2 \cdot 2H_2O$. It is noteworthy that KBr formed when cupric bromide is used as the copper source, dissolves in methanol with time thereby eliminating the necessity of water washing. In the case of $KCuF_3$, the crystallite size was in the range 9–16 nm. The splitting of highly intense (200) and (112) *hkl* reflections observed in the powder X-ray diffraction pattern of $KCuF_3$ prepared from $CuCl_2 \cdot 2H_2O$ was absent when $CuBr_2 \cdot 2H_2O$ was used as the starting material. The tetragonal lattice parameters for $KCuF_3$ were $a = 4 \cdot 138$ Å, $c = 3 \cdot 945$ Å (prepared from $CuCl_2 \cdot 2H_2O$) and $a = 4 \cdot 120$ Å, $c = 3 \cdot 964$ Å (prepared from $CuBr_2 \cdot 2H_2O$) matched well with the values from literature (JCPDS Cards 730233; 730232). We could not prepare $KCuF_3$ if CuI is used as the starting material. The fluoride content estimation confirmed that the compounds were stoichiometric. These studies suggest that highly reactive organometallic species containing halides might be formed in methanol at room temperature as suggested by earlier theoretical results and experimental studies (Bradley *et al* 1957; Karim *et al* 1997; Faralli *et al* 2007). We strongly believe that this synthetic method can be considered as green as it is a safer chemistry which is energy efficient requiring no harsh conditions. It is important to note that higher members in this series such
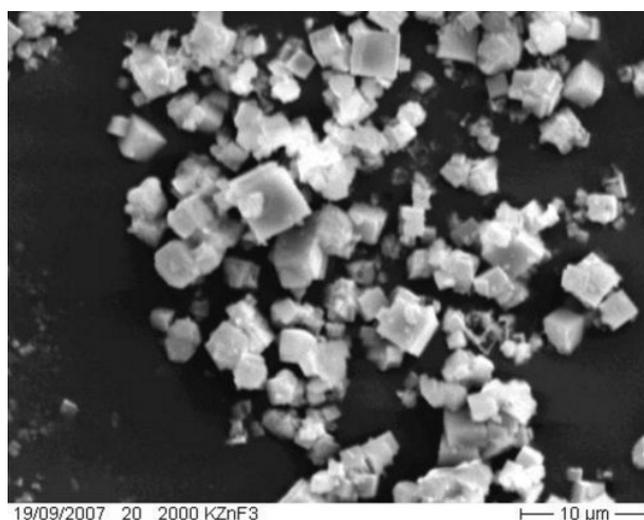

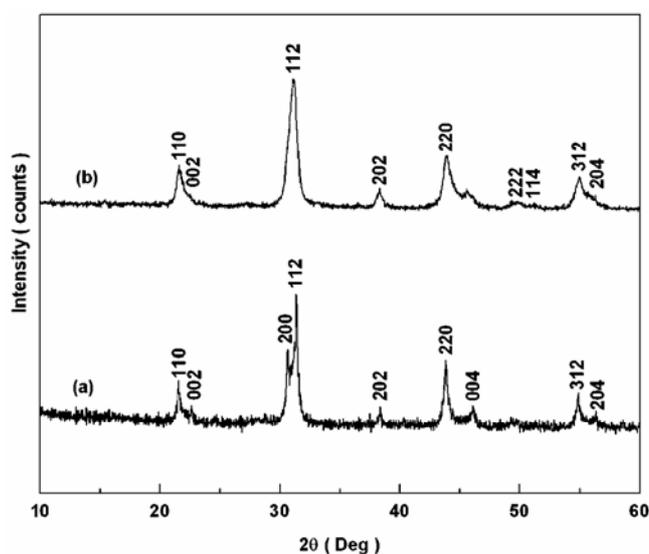**Figure 3.** Scanning electron microscopy image of $KZnF_3$.

Figure 4. Powder X-ray diffraction pattern of $KCuF_3$ prepared via nonaqueous medium using (a) $CuCl_2 \cdot 2H_2O$ and (b) $CuBr_2 \cdot 2H_2O$.

as K_2CuF_4, K_2NiF_4 could not be prepared by this method. In figures 5(a) and (b) we show the electron diffraction and TEM images of $KCuF_3$ confirming the tetragonal unit cell of nano crystallites.

We performed thermogravimetric studies in air of $KCuF_3$ to investigate the thermal stability and nature of decomposition product. From the thermogram shown in figure 6, it appeared that there was no appreciable mass loss till 225°C. After this temperature the mass loss took place gradually and appreciably till 900°C. The total mass loss of 14% suggested that the product obtained at 900°C might correspond to KCuOF; such a compound has not yet been reported in the literature. We could not verify the structure and composition of the left over product at 900°C because of the experimental difficulties associated with heating $KCuF_3$ in macroscale quantities. However, under highly oxidizing conditions such as the $LiNO_3$–KNO_3 eutectic mixture flux, we got the respective divalent metal oxides.

It is well known that alkali metal fluorides have wide applications in the organo fluorine chemistry both as a fluorinating agent as well as a catalyst in various reactions (Yakobson and Akhmetova 1983). We were interested to examine whether the ternary perovskite structure type fluorides could act as fluorinating agent in an organic reaction. Typically, *o*-chloronitrobenzene (3·15 g, 1 mol), $KNiF_3$ (1·74 g, 1·5 mol), DMSO (8·5 ml, 6 mol), benzyltriethylammonium chloride (0·455 g, 0·1 mol) were refluxed at 170°C for ~3 h. The product was filtered and the filtrate was treated with $CHCl_3$–H_2O system several times to extract the fluorinated product in the organic layer. The extracted layer was evaporated under reduced pressure to obtain the final compound. The fluorinated product showed a singlet at $\delta = 118$ ppm in the ^{19}F NMR spectrum. These ternary fluorides were found to be stable up to 225°C in the solid state, but liberate fluorine at 170°C under refluxing in DMSO to yield fluorinated organic product. This observation suggested the use of ternary fluorides for the manufacture of aliphatic and aromatic hydrofluorocarbons (HCFs) where direct and selective conversion of C–H bond to a C–F bond is desirable (Subramanian and Calvarese 2006).
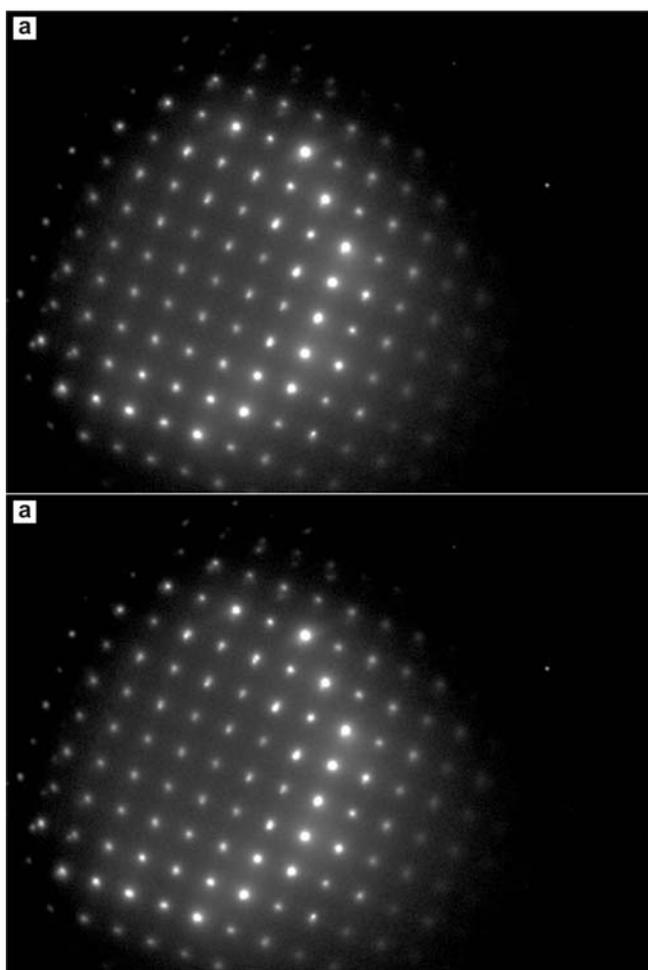
4. Conclusions

In conclusion, nearly stoichiometric fluorides of the general formula, KMF_3 (M = Mg, Mn, Co, Ni, Cu and Zn), possessing perovskite structure were prepared in non-aqueous medium. This reaction eliminates the generation of harmful hydrofluoric acid and is driven by salt (KCl) formation which is harmless. The average crystallite size of the fluorides obtained by this method was in the range 9–30 nm and was thermally stable up to 225°C in air. For the first time, these fluorides have been
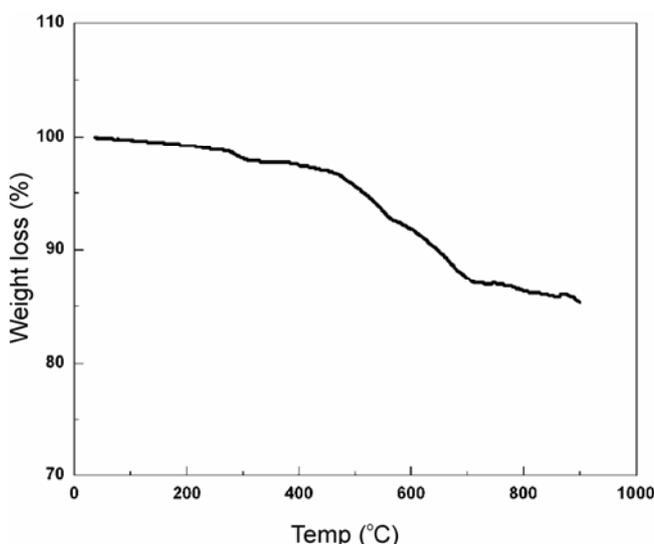

Figure 5. **a**. Electron diffraction pattern of $KCuF_3$ and **b**. transmission electron microscopy image of $KCuF_3$.

Figure 6. Plot of percentage mass lost vs temperature of $KCuF_3$ in air.

demonstrated to be used as fluorinating agents in organic fluorination reactions.

Acknowledgements

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