



# Mechano-chemical synthesis $K_2MF_6$ ( $M = Mn, Ni$ ) by cation-exchange reaction at room temperature

Pooja Rawat, Rajamani Nagarajan \*

Materials Chemistry Group, Department of Chemistry, University of Delhi, Delhi, 110 007, India

## ARTICLE INFO

### Article history:

Received 27 October 2017

Received in revised form

5 December 2017

Accepted 10 December 2017

Available online 11 December 2017

### Keywords:

Mechanochemical

$K_2PtCl_6$

Double perovskite

Red phosphor

## ABSTRACT

In order to establish the power of mechanochemistry to produce industrially important phosphors, synthesis of  $K_2MnF_6$  has been attempted by the successive grinding reactions of manganese (II) acetate with ammonium fluoride and potassium fluoride. The progress of reaction was followed by ex-situ characterization after periodic intervals of time. Cubic symmetry of  $K_2MnF_6$  was evident from its powder X-ray diffraction pattern which was refined successfully in cubic space group ( $Fm-3m$ ) with  $a = 8.4658(20)$  Å. Stretching and bending vibration modes of  $MnF_6^{2-}$  octahedral units appeared at 740 and 482  $cm^{-1}$  in the fourier transformed infrared spectrum. Bands at 405 and 652  $cm^{-1}$  appeared in the Raman spectrum and they were finger-print positions of cubic  $K_2MnF_6$ . Other than the ligand to metal charge transfer transition at 242 nm, transitions from  $^4A_{2g}$  to  $^4T_{1g}$ ,  $^4T_{2g}$  and  $^2T_{2g}$  of  $Mn^{4+}$ -ion appeared at 352, 429, 474 and 569 nm in the UV–visible diffuse reflectance spectrum of the sample. Red emission due to  $Mn^{4+}$  was observed in the photoluminescence spectrum with a decay time of 0.22 ms. Following the success in forming cubic  $K_2MnF_6$ , this approach has been extended to synthesize cubic  $K_2NiF_6$  at room temperature. All these results confirmed the susceptibility of acetate salts of transition metals belonging to first-row of the periodic table to facile fluorination at room temperature aided by mechanical forces.

© 2017 Elsevier Masson SAS. All rights reserved.

## 1. Introduction

Attempts to popularize mechanochemical synthesis are on the rise as it has enormous potential to discover newer solids or molecules by altering the reaction landscapes [1,2]. It is quite economical in terms of energy and does not require an intricate set-up to execute it. Mostly, mechanochemical reactions are faster than conventional ceramic methods. They are environmentally benign, single-step and conducted in one pot. Alloy formations, phase transformation, co-crystal formation and generating metal organic frameworks are some of the typical examples wherein mechanochemical reactions have been explored [3–10]. There exists limited exploration of such mechanochemical reactions for the synthesis of metal fluorides and mixed metal fluorides [11–14]. Recently, this approach has also been used for the synthesis of mixed halide compounds such as  $SrFCl$  and for the generation of rare earth doped materials [15–17]. It is highly relevant to synthesize mixed metal

fluorides by mechano-chemical methods as safer alternatives are absolutely necessary avoiding the use hazardous and highly corrosive fluorine gas or HF [18]. Though solvothermal or hydrothermal synthesis can take care of some of these issues, there is no control over the composition and purity of final product as they are prepared under non-equilibrium conditions. Lu et al. [11], have demonstrated the formation of  $A_3GaF_6$  ( $A = Li, Na, K$  and  $NH_4$ ) by the mechanochemical milling of metal fluorides. Two other reports followed this publication in which mechanochemical synthesis was employed and provided some important conclusions [11–13]. Ammonium fluoride has been found to become part of structure in addition to its role as fluorinating agent when reacted mechanochemically with aluminium hydroxyl acetate [13]. Though fluoro perovskites of  $AMF_3$  ( $A = K, Rb; M = Co, Cu, Mg$ ) type and  $A_2MF_4$  are readily obtained by the mechanochemical reaction between the fluoride salts of constituent metal ions, the two-dimensional structure is found to be only kinetically stable transforming ultimately to three dimensional perovskite  $AMF_3$  [12]. The key role, played by starting materials to influence the nature of final products in metal fluoride synthesis, has been adequately demonstrated both by wet-chemical synthesis and by mechanochemical reactions

\* Corresponding author.

E-mail addresses: [poojarwatchemistry@gmail.com](mailto:poojarwatchemistry@gmail.com) (P. Rawat), [rnagarajan@chemistry.du.ac.in](mailto:rnagarajan@chemistry.du.ac.in) (R. Nagarajan).

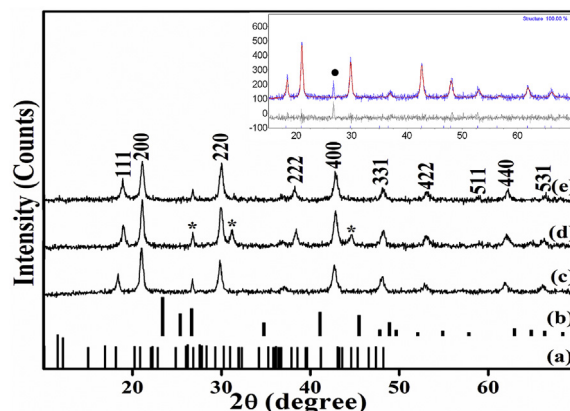
[19–21]. The recent research report on the realization of highly crystalline  $\alpha$  and  $\beta$  polymorphs of  $\text{PbF}_2$  mechanochemically reinforced the susceptibility of metal acetates to undergo facile fluorination to yield crystalline lattices under the influence of mechanical forces [14]. With this scientific background and realizing the importance of  $\text{Mn}^{4+}$  as red phosphor together with the complexity of reported synthetic methods of preparing  $\text{K}_2\text{MnF}_6$ , its synthesis has been attempted mechanochemically [22–29]. In order to reduce reaction time employing an agate pestle and mortar, first the manganese (II) acetate was reacted with ammonium fluoride followed by cation exchange reaction with KF. The same approach has been extended to oxidize  $\text{Ni}^{2+}$  to  $\text{Ni}^{4+}$  to prepare  $\text{K}_2\text{NiF}_6$ . The results reported in this paper will be quite useful to industrial chemists for the bulk synthesis of these important phosphors.

## 2. Experimental

$\text{NH}_4\text{F}$  (Thomas Baker, 95.00%),  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (Alfa Aesar, 99.00%),  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (Spectrochem, 99.00%) and KF (Central Drug House, 99.9%) were used as purchased. 0.2228 g (6.02 mmol) of  $\text{NH}_4\text{F}$  was ground with 0.2456 g (1.00 mmol) of  $\text{Mn}(\text{OAc})_2$  in an agate pestle and mortar for varying durations. 0.0581 g (2.00 mmol) of KF was added to the product from the above reaction and ground further for 3 h. The same method was again performed by grinding 0.2226 g (6.01 mmol) of  $\text{NH}_4\text{F}$  with 0.2489 g (1.00 mmol) of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  in an agate pestle and mortar for varying durations. 0.0581 g (2.00 mmol) of KF was added to the product from the above reaction and ground for varying durations. Powder X-ray diffraction (PXRD) patterns of solid samples were collected using a high resolution X'Pert PANalytical diffractometer, equipped with an Xe proportional detector employing  $\text{Cu K}_\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). They were obtained with a scan rate of 4.5 s per step and step size of  $0.04^\circ$  at  $25^\circ \text{C}$ . The instrument was calibrated using Si standard externally. Using this data, Rietveld refinement was carried out using TOPAS 3 software [30]. Fourier transformed infrared (FT-IR) spectra of the samples were collected using Perkin-Elmer FT-IR spectrometer model 2000 employing KBr as dispersal medium. Raman spectrum was collected using a Renishaw spectrometer via a microscope system using diode laser ( $\lambda = 785 \text{ nm}$ ). Diffuse reflectance spectra of the samples were collected on Perkin-Elmer UV–visible spectrophotometer Lambda-35 attached with an integrating sphere and using  $\text{BaSO}_4$  as the reference. The photoluminescence (PL) spectroscopy measurements of samples in solid form were carried out on Horiba Jobin Yvon Fluorolog-modular spectrofluorometer at room temperature employing CW xenon lamp source. For time resolved emission, a mechanical chopper (12 Hz), a lock-in amplifier and a monochromator (Acton SP 2300) coupled to a photomultiplier tube (PMT) and digital storage oscilloscopes were used.

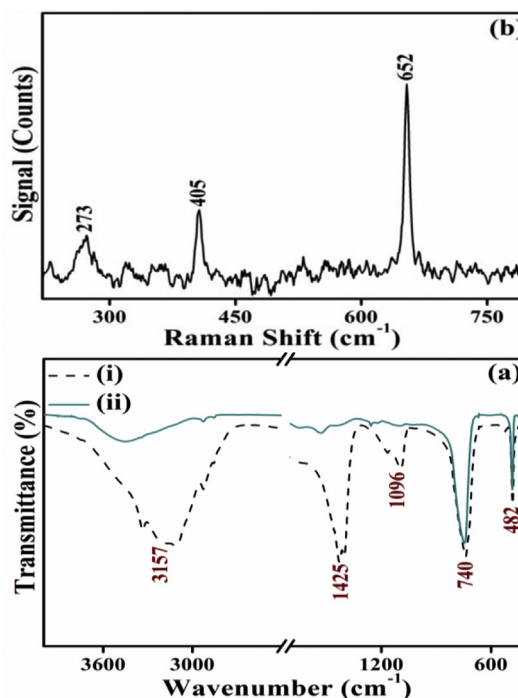
## 3. Results and discussion

When ammonium fluoride was ground with manganese (II) acetate for 1 h, a liquid phase appeared suggesting a chemical reaction between the two. On continuing the grinding process for two more hours, the liquid transformed to a solid. At this stage, the grinding was stopped and the solid was subjected to powder X-ray characterized. The PXRD pattern of the product was completely different from both the reactants (Fig. 1). It did not resemble with any entry of ammonium and manganese containing fluorides compositions or with precursor used ( $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{F}$ ) listed in JCPDS data base (Fig. 1). However, all the reflections could be indexed in a cubic unit cell with  $a = 8.4829 (29) \text{ \AA}$ . Five bands at 3157, 1425, 1096, 740 and  $482 \text{ cm}^{-1}$  were present for this sample in



**Fig. 1.** (a) JCPDS data of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ , (b)  $\text{NH}_4\text{F}$ , (c) PXRD pattern of the product from the mechanochemical reaction of  $\text{NH}_4\text{F}$  and  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ , (d) product from further grinding of (c) with 2 mmol of KF for 3 h and (e) for 5 h. Rietveld refinement of PXRD pattern of (e) is shown in the inset where in observed, calculated (profile matching) and difference profiles are represented as blue, red and grey lines, respectively. Bragg positions are marked as blue vertical lines. Reflection marked with "\*" and "●" are due to KF and unidentified impurity, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

its FT-IR spectrum (Fig. 2(a)). While bands at 740 and  $482 \text{ cm}^{-1}$  were attributed to arise from stretching and bending vibrations of  $\text{MF}_6^{2-}$  units of  $\text{A}_2\text{MF}_6$ , respectively, N-H stretching and bending vibration modes appeared at 3157 and  $1425 \text{ cm}^{-1}$ , respectively. Surface adsorbed carbonate during FT-IR measurements manifested at  $1096 \text{ cm}^{-1}$ . Further grinding this powder with 2 mmol of KF for 3 h, observed reflections in PXRD pattern moved towards higher two-theta values along with few reflections due to unreacted KF (Fig. 1(d)). Extending the grinding process for two more hours, led



**Fig. 2.** (a) FT-IR spectra of the product from the mechanochemical reaction of  $\text{NH}_4\text{F}$  and  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (i) (represented as dotted line) and product from further grinding with 2 mmol of KF for 5 h (ii) (represented as solid line), (b) Raman spectrum of KF with the mechanochemical product of  $\text{NH}_4\text{F}$ :  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ .

Download English Version:

<https://daneshyari.com/en/article/7914593>

Download Persian Version:

<https://daneshyari.com/article/7914593>

[Daneshyari.com](https://daneshyari.com)