CHEMCOMM
Communication
www.rsc.org/chemcomm

Organic template-directed crystallization of the complex fluoride NH_4MnF_3 with perovskite structure

Lehui Lu, Haishui Wang, Hongjie Zhang* and Shiquan Xi*

Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China. E-mail: xisq@public.cc.jl.cn

Received (in Cambridge, UK) 21st March 2001, Accepted 14th June 2001
First published as an Advance Article on the web 5th July 2001

(100)-oriented NH_4MnF_3 perovskite with different morphologies have been obtained *in situ via* an organic template; experimental results can be rationalized in terms of electrostatic interactions and lattice matching between the organic template and the ions undergoing nucleation.

Recently, complex fluorides with perovskite structure have been extensively studied because of their interesting structures and particular physical properties such as magnetic, piezoelectric characteristics and photoluminescence behavior.[1–4] However, traditional preparation methods, to a great degree, have limited such studies on their properties since many exploitable properties are often related to the structure, size, morphology and orientation of inorganic materials. Such conventional preparation methods often fail to generate consistent results with respect to the control over the structure, size, morphology and orientation. Thus it is important to develop new synthetic strategies. A recent advance in this field involves the use of organic templates (Langmuir or SAM monolayers) for orientation nucleation of inorganic crystals.[5–7] One of the advantages of this method is that the crystal structure, size, morphology and orientation can be readily controlled *via* selection of the template and experimental conditions at room temperature. In this communication, the behenic acid (BA) monolayer template-directed room-temperature crystallization of NH_4MnF_3 is studied.

The experimental procedure was similar to that described elsewhere.[6] Throughout the experiment, the temperature was maintained at room temperature. Briefly, subphases **1** and **2** were prepared by mixing NH_4F (A.R.) and $Mn(NO_3)_2$ (A.R.) solutions. The concentrations of F^- ions in subphases **1** and **2** were 0.71 and 1.065 mol L^{-1} and that of Mn^{2+} ions were 0.355 and 0.533 mol L^{-1}, respectively. The monolayer template was prepared by spreading a measured quality of behenic acid (1 mg mL^{-1} in chloroform) over the surface of the subphase. After the evaporation of chloroform, the monolayer was compressed to the targeted pressure (28 mN m^{-1}) and the crystals formed under the monolayer transferred onto glass or wafer silicon substrates *via* a down stroke for further characterization. The aging time between the spreading and transferring was 55 and 45 min for subphases **1** and **2**, respectively. Crystals grown in the absence of monolayer were collected on a glass substrate placed at the bottom of the trough allowing a collection time of 5 h. The experiment of controlled crystallization under the BA monolayer was performed using a KSV 5000 instrument (Finland). The morphology of crystals formed under the monolayer were examined by scanning electron microscopy (SEM; JXA-840). The crystal faces of the samples were measured by X-ray diffraction (XRD; D/max2000, Rigaku, Cu-Kα). Elemental analysis of the samples was performed by energy dispersive X-ray analysis (EDXA).

In the absence of the monolayer, the majority of crystals were located at the bottom of the trough as a result of sedimentation. The crystals are obviously irregular in shape and the corresponding XRD pattern of crystals showed several groups of diffraction peaks roughly consistent with the reflections of cubic NH_4MnF_3 [Fig. 1A(a)] indicative of poor crystal quality.

In the presence of the monolayer, crystallization exclusively occurred at the monolayer–solution interface. Fig. 1B shows the typical morphology of crystals grown under the BA monolayer template over subphase **1**. As is evident from Fig. 1B, the crystals formed under the BA monolayer exhibit a square morphology and have a rather homogeneous size distribution with an average grain size of 6 μm. The corresponding XRD pattern of the crystals shows two sharp and strong diffraction lines at 2θ 20.90 and 42.56° [Fig. 1A(b)]. These diffraction lines correspond to the (100) and (200) reflections for cubic NH_4MnF_3 with perovskite structure indicating that the crystals are (100)-oriented. The high quality and uniformity of the crystals is evidenced by the sharp and strong (*n*00) reflections. Moreover, by comparison with the XRD pattern of the standard sample, we find that the crystals formed under the monolayer template are pure and no other impurity peaks were present. Interestingly, changing the concentration of the supersaturated solution has a marked effect on the morphology of crystal growns under the BA monolayer. For subphase solution **2**, the crystals grown under the BA monolayer exhibit a needle-like morphology (Fig. 2B) while in the XRD pattern (Fig. 2A), two sharp and strong diffraction lines together with a weak line appear at 2θ 20.90, 42.56 and 66.00°, which are assigned to the (100), (200), and (300) reflections, respectively, of cubic NH_4MnF_3 with perovskite structure.

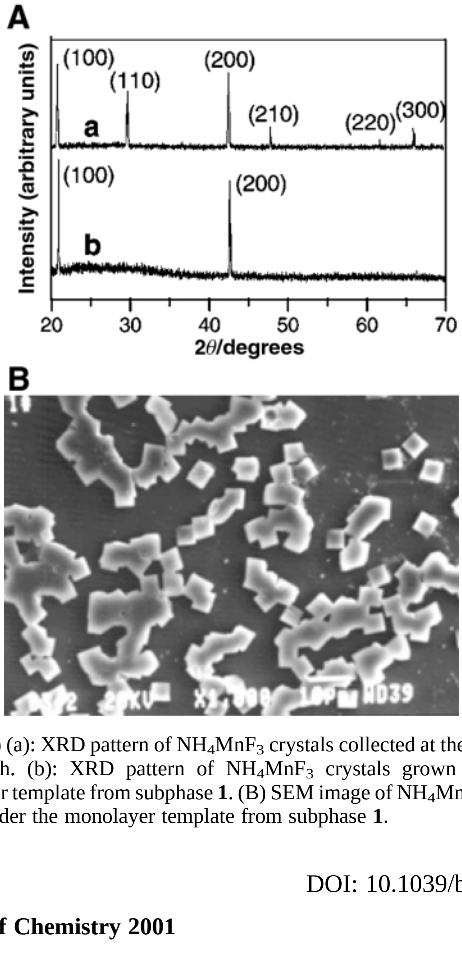

Fig. 1 (A) (a): XRD pattern of NH_4MnF_3 crystals collected at the bottom of the trough. (b): XRD pattern of NH_4MnF_3 crystals grown under the monolayer template from subphase **1**. (B) SEM image of NH_4MnF_3 crystals grown under the monolayer template from subphase **1**.

DOI: 10.1039/b102642a

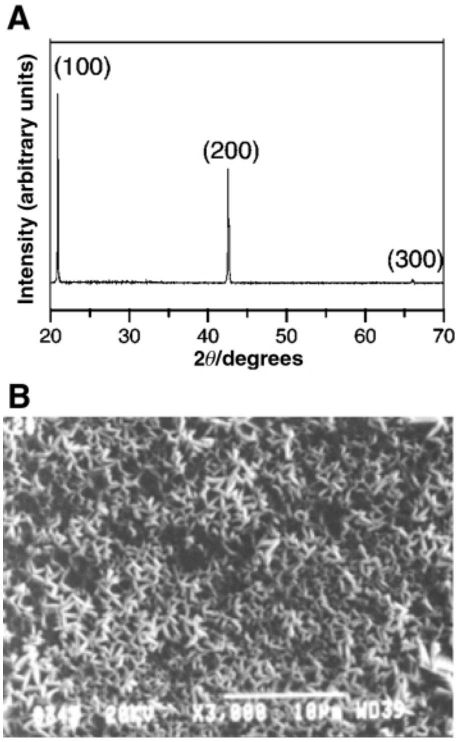

Fig. 2 (A) XRD pattern and (B) SEM image of NH_4MnF_3 crystals grown under the monolayer template from subphase **2**.

In addition, elemental analysis of crystals grown *via* the monolayer template was performed by EDXA. The EDXA patterns showed the presence of N, F, Mn, O and C peaks, which also further confirmed the XRD result. The C and O peaks originate from the BA monolayer indicating that the NH_4MnF_3 crystals are attached to the monolayer.

What aspects of the (100) face of NH_4MnF_3 crystal could be simulated by the interactions between the monolayer template and the crystal? According to an AFM study[8] on the compressed BA monolayer over the solution containing Mn^{2+} ions, the BA monolayer adopts rectangular packing with unit cell dimensions of 0.46 × 0.87 nm. We can compare the structure of the BA monolayer with the two-dimensional packing of Mn atoms in different crystal faces of cubic NH_4MnF_3 by simulation techniques. It is found that the superimposition of a rectangular lattice of the monolayer template on the (100) face of the NH_4MnF_3 crystal provides a good lattice matching. A comparison of the Mn–Mn distance (0.424 nm) along the (010) direction in the (100) crystal face with the monolayer lattice $\boldsymbol{a}$ (0.46 nm) reveals a misfit of 8%. Moreover, the interatomic Mn–Mn distance (0.424 nm) in the (001) direction of the (100) crystal face is approximately 0.5 times the monolayer lattice $\boldsymbol{b}$ (0.87 nm) with a misfit of only 2% (Fig. 3). However, such lattice matching does not exist with other crystal faces of NH_4MnF_3. Thus the rectangular packing arrangement of the monolayer generates a template similar to the (100) face of NH_4MnF_3 crystal which directs crystallization of NH_4MnF_3 along the (100) face.

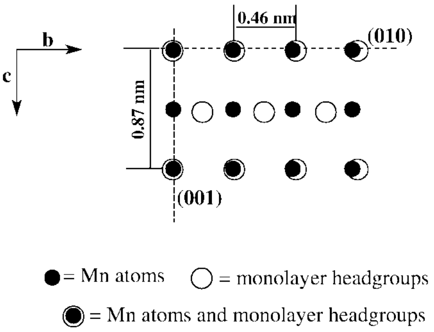

Fig. 3 Schematic two-dimensional representation of the proposed overlap between the monolayer template and Mn atoms in the (100) face of NH_4MnF_3 crystals.

The dependence of crystal morphology on the concentration of supersaturated solution can be explained as follows. A previous study[9] showed that the concentration/ionic strength of the reagents and the extent of nuclei–ion binding influence the structure and the morphology of the crystals grown under the monolayer. In the present study, the variation of the concentration of supersaturated solution results in a change of ionic strength and the extent of nuclei–ion binding, *i.e.* the Stern and boundary layers under the monolayer by electrostatic interactions. As a result, NH_4MnF_3 crystals with different morphologies were obtained under the BA monolayer.

A more detailed mechanism will be investigated further.

In summary, (100)-oriented NH_4MnF_3 perovskite crystals with different morphologies were prepared *via* a monolayer template at room temperature. The solution conditions, the electrostatic interactions and lattice matching between the organic template and ions undergoing nucleation are important factors for control over the morphology, size, and orientation of crystals. Compared with traditional methods, the organic template technique appears advantageous in terms of lower synthesis temperature, high purity, and providing controllable morphology and orientation of crystals.

This work was supported by the National Natural Science Foundation of China.

Notes and references

1 M. A. Laguna, M. L. Sanjuan, V. M. Orera, J. Rubin, E. Palacios, M. C. Pique, J. Bartolome and J. F. Berar, *J Phys: Condens. Matter.*, 1993, **5**, 283.
2 C. Zhao, S. Feng, R. Xu, C. Shi and J. Ni, *Chem. Commun.*, 1997, 945.
3 O. Pilla, P. T. C. Freire and V. Lemos, *Phys. Rev. B.*, 1997, **52**, 177.
4 M. Eibschutz, *Phys. Lett. A*, 1969, 409.
5 A. L. Litvin, S. Valiyaveettil, D. L. Kaplan and S. Mann, *Adv. Mater.*, 1997, **9**, 124.
6 L. Lu, H. Cui, W. Li, H. Zhang and S. Xi, *Chem. Mater.*, 2001, **13**, 325.
7 H. Q. Shi, W. B. Tsai and B. D. Ratner, *Nature*, 1999, **96**, 9933.
8 R. Wiswanathan, J. A. Zasadzinski and D. K. Schwartz, *Science*, 1993, **261**, 449.
9 S. Mann, D. D. Archibald, J. M. Didymus, T. Douglas, B. R. Heywood, F. C. Meldrum and N. J. Reeves, *Science*, 1993, **261**, 1286.