Facile fluoride-mediated syntheses of layered (Al/Fe)-JDF-L1 materials featuring macromorphological square-sheet structures

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This study aims to prepare the Jilin-Davy-Faraday, Layered solid no.1 (JDF-L1) type of layered materials and to elucidate the role of fluoride mineralizing agents in inducing crystal orientation growth featuring lamellar textures. The layered zeotypes synthesized by fluoride routes were characterized by several techniques, viz. X-ray diffraction, fourier transform infrared spectroscopy, field emission scanning electron microscopy, ²⁷Al and ²⁹Si magic angle spinning-nuclear magnetic resonance, etc. The JDF-L1 crystals were shown to crystallize in the uniform habit of square-sheet structures when the fluoride synthesis systems adopted a lower initial alkalinity and reduced crystallization temperatures. This method facilitated both the isostructural incorporation of tetrahedral [AlO₄]⁻ or [FeO₄]⁻ for unique SiO₄ units and also allowed the orientation growth of lamellar Al(Fe)-JDF-L1 crystals. Isomorphous substitution of trivalent Al or Fe was likely to perturb the JDF-L1 structure and hence caused the orthogonal multiplication of smaller lamellar subindividuals onto the basal crystal surfaces.

Key-words : Layered JDF-L1, F⁻-mediated synthesis, Heteroatom substitution, Oriented growth, Lamellar texture, Orthogonal multiplication

1. Introduction

According to the foundations laid in hydrothermal chemistry of zeolites, the discovery of new families of zeolite analogues (zeotypes) has considerably broadened the scope of zeolitic catalysis from formerly acid-catalyzed reactions, viz. hydrocarbon cracking, isomerisation, and alkylation, to special oxidation as commercially exemplified by olefin epoxidation. More attractive is recently the subtle fabrication of high-capacity lithium ion battery anodes, a conceptual development by using layered titanosilicate-derived nanosheets as a template-like precursor.

Particular attention has been focused on the development of novel synthesis routes and structural modification of zeotypes of possessing non-tetrahedral framework Ti atoms, which may result in potential application to where conventional titanosilicate zeolites have proved unsuit ed. Some promising advances in this study and understanding of these zeotypes should come from the effective synthesis and structural resolution of layered titanosilicate JDF-L1 (Na₄Ti₂Si₈O₂₂·4H₂O, viz. Jilin-Davy-Faraday, Layered solid no.1), a structural counterpart of AM-1 (or NTS) with the chemically equivalent compositions. JDF-L1 has shown to be an exclusive synthetic non-centrosymmetric, tetragonal layered solid, which contains [Ti₂Si₈O₂₂]₄⁻ layers along the a axis, featuring five-member rings in the crystallographic bc or ac plane built up of four SiO₄ tetrahedra and one TiO₅ square pyramid, along with six-member rings in the ab plane built up of four SiO₄ tetrahedra and two TiO₅ units, and the interlayer space is filled with H₂O and Na⁺ countercations. Occurrence of the five-coordinated titanium (IV) is an influential event in material chemistry due to the less ligand-saturation compared with the octahedral Ti atoms known in microporous titania and other crystalline titanosilicates. Such structural character makes JDF-L1 a compelling layered material for potential application in oxidation catalysis, radioactive cation adsorption, and small molecular sieving through fabrication of composite membranes. Although many other following studies with respect to JDF-L1 materials, the fluoride synthesis directing to morphological control remains to be a challenge for layered JDF-L1 and the related structural analogues thereof
The seeded syntheses of the JDF-L1 have been proved to require appropriate titanium contents in high alkaline media in which the layered JDF-L1 would normally crystallize in aggregation state.\(^{22}\) In the light of successful media in which the layered JDF-L1 would normally crystallize, the orthogonally branching phenomena of smaller lamellar subindividuals are observed to arise from the basal crystal surfaces of the substituted zeotypes.

2. Experimental

2.1 Material synthesis

The fluoride-mediated hydrothermal synthesis of lamellar titanosilicate JDF-L1 and heterosubstituted samples was conducted at lower temperatures for a limited period, according to initial gel compositions and pH values in Table 1. In a typical procedure for the preparation of ferro-titansilicates (Fe-JDF-L1s), the starting mixture was prepared by adding the aqueous solutions of iron nitrate ([Fe(NO\(_3\)_3·9H\(_2\)O, 98.5 wt %]) and titanium sulphate ([Ti(SO\(_4\))\(_2\), 96 wt %] to the alkaline solution prepared by mixing sodium silicate solution (28 wt % SiO\(_2\), 8.2 wt % Na\(_2\)O), NaOH (96 wt %), and KF·2H\(_2\)O (99 wt %), in that order. The resulting gel, after ageing at the adjusted pH around 10.0, was statically crystallized at 200 °C for 72 h in Teflon-lined autoclaves. The solid products were filtered and washed repeatedly with deionized water (pH 8.0) and dried at 110 °C overnight. The same procedures except for varying pH were applied to the synthesis of alumino-titansilicates (Al-JDF-L1s) using an alternative alumina source (NaAlO\(_2\), Al\(_2\)O\(_3\) 41.0 wt %). More details on syntheses of lamellar JDF-L1 crystals and the Al-JDF-L1 aggregates can be seen in previous studies.\(^{26)-28}\)

2.2 Physicochemical characterization

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku D/max-2400 diffractometer with Cu K\(_{\alpha}\) radiation (\(\lambda = 0.15418 \text{ nm} \)) in the 2\(\theta\) range of 5–60° (step 0.02° and counting time 3 s). Phase identification and cell parameters were performed using an indexing program of MID jade 6.5.

Field emission scanning electron microscopy (FE-SEM, JEOL JSM-7500F made in Japan, accelerating voltage 2 kV and beam current 10 µA) was used to image crystal morphology while the multiple energy dispersive X-ray (EDX) technique adopted in this study helped us achieve...
data on atomic composition upon elaborately selected areas on large crystals. Fourier transform infrared spectroscopy (FTIR) was carried out in the 400–1400 cm⁻¹ region on a Spectrum GX spectrometer equipped with an infrared DTGS detector with 4 cm⁻¹ resolution.

Solid-state ²⁷A¹ and ²⁹Si magic angle spinning-nuclear magnetic resonance (MAS-NMR) spectra were recorded on a Bruker MSL 400P spectrometer at 104.26 and 79.49 MHz, respectively. Clearly, ²⁹Si MAS-NMR spectra were recorded with 50° pulses, 40 s recycle delays and spinning rates of 5–5.5 kHz. Chemical shifts for ²⁹Si NMR spectra are quoted in ppm from tetramethylsilane. ²⁷A¹ MAS-NMR spectra were acquired with a very short radio-frequency pulse (0.6 μs equivalent to 10°), 0.5 s recycle delays and spinning rates of 14–15 kHz. Chemical shifts for ²⁷A¹ NMR spectra are quoted in ppm from Al(H₂O)₆³⁺.

3. Results and discussion

3.1 Fluoride-mediated synthesis of JDF-L1 and Al(Fe)-JDF-L1

3.1.1 XRD crystal phase identical to layered JDF-L1

By drawing upon the fluoride-mediated wet gel route from similar starting materials, all the typical samples with various Al(Fe)/Ti ratios (Table 1) were synthesized in the absence of organic templates. Following the XRD results illustrated in Fig. 1, this experimental approach of fluoride synthesis allows for the facile preparation of well crystalline (Al/Fe)-JDF-L1 samples and, especially, can afford the layered crystals of preferential growth along [001] and [010] directions. No crystalline phases are directly related to the occurrence of sodium-rich Al/Fe-silicate species in Al-JDF-L1 and Fe-JDF-L1 and the approaches to use fluoride ions as a mineralizing agent have been proved highly available to suppress crystallization of undesired phases for lamellar JDF-L1 and Al(Fe)-JDF-L1 syntheses. In addition, Al or Fe substitution in JDF-L1 framework leads to a slight right-shift (Δ2θ = 0.06 or 0.08°) of the typical [001] reflection compared to one of lamellar JDF-L1 sample. More details on XRD refinement fits can be seen in Fig. A1.

However, the introduction of either Al or Fe precursor into the hydrothermal system of lamellar JDF-L1 leads to a significant decrease in relative crystallinity (I_{rel,XRD}) of resulting materials as compared to lamellar JDF-L1. Note that the Fe-JDF-L1 samples [Fig. 1(a)] crystallized more completely than the corresponding Al-JDF-L1 samples [Fig. 1(b)], albeit the identical Al/Ti and Fe/Ti ratios in individual initial gels. In short, the reduction of crystallinity in value relies largely on the increased Al(Fe)/Ti ratios in solid products rather than in nominal initial gels. The devil is factually in the detail, i.e. the relatively low framework Fe/Ti ratios. The exception further proves the rule that it seems more difficult to incorporate Fe into framework sites.

3.1.2 Crystal composition and cell dimensions

The data of chemical compositions and crystal parameters are shown in Table 2. Upon indexable XRD reflections, these materials obtained by fluoride routes are shown to crystallize in the more suitable tetragonal space group of highest symmetry, P4̂212 (No. 90), with unit cell parameters exhibiting slight distortions compared with the layered JDF-L1 values. For all substituted samples, the (Na + K)/Ti ratios increase with Al(Fe)/Ti ratios and the ratios are apparently larger than the normal ratio formulated by Na₄Ti₂Si₈O₂₂·4H₂O. Although closely related, the atomic K/Na ratios are not constant, which seem higher for Al-JDF-L1s than for corresponding Fe-JDF-L1s. However, their atomic ratios of T/Ti (T = Si, Al and Fe) are quite close to the composition of lamellar titanosilicate JDF-L1. In line with this, the materials of Al-

![Fig. 1. Powder XRD patterns for lamellar titanosilicate JDF-L1 and two series of isostructural analogues with different framework compositions: (a) Al-JDF-L1s (Al/Ti = 0–0.41) and (b) Fe-JDF-L1s (Fe/Ti = 0–0.35).]
JDF-L1 and Fe-JDF-L1 are evaluated to have reached an Al or Fe atom fraction of at least 6.7 or 4.8% in respect to Si in lamellar JDF-L1 crystals. Accordingly, the heteroatom introduction is to have a major impact on the increase in total charge-balancing cations, and the tetrahedral \[\text{AlO}_4^-\] or \[\text{FeO}_4^-\] units are more likely to occur in JDF-L1 framework considering the charge compensation effects.

Incorporation of Fe has been proved to remain more difficult than for Al atoms, resulting in obvious distinction in XRD crystallinity, heteroatom contents, and hence in interesting crystal morphologies to be seen. As it stands, the attributes in chemical affinity and bond length differ for silica and can help interpret the difference observed in crystal growth between the two series. Incorporation of heteroatoms into JDF-L1 framework indeed causes the tetragonal lattice dilation of Al-JDF-L1 and Fe-JDF-L1 with respect to those determined for lamellar JDF-L1, both of which are scrutinized to change in the equivalent \(a/b\) axes and in the \(c\) axis, particularly for high Al/Ti and Fe/Ti ratios. Similar unit-cell expansions have been observed on ETAS-10 and ZSM-5 due to framework Al incorporation. Therefore, these phenomena are themselves subject to limitations as a whole. The compositional variety at atomic level during crystal growth can lead to changes in cell dimension and even in crystal morphology (see Fig. 2).

### 3.2 Morphological variations induced by heteroatoms

The heteroatom substitution of JDF-L1 zeotype has induced certain morphological variations of products and the observations by FE-SEM allow the further understanding of the influence of framework compositions on crystal growth habits to be discerned. The FE-SEM micrographs in Fig. 2 show the morphological differences among lamellar JDF-L1 and Al(Fe)-JDF-L1 samples with various Al(Fe)/Ti ratios. In Figs. 2(a) and 2(b), the tetragonal lamellar JDF-L1 displays the characteristics of disaggregating large lamellar crystals with square-sheet structure in three-dimensions of ca. 15 x 15 x 1.5 \(\mu\text{m}^2\). Following from observations in Figs. 2(c)–2(f), there seems no textural difference in two-dimensional orientation between the differently compositional Al(Fe)-JDF-L1s and typically lamellar JDF-L1. Similarly, the two sets of Al(Fe)-JDF-L1s also represent the similar orientation of much larger single crystals grown predominantly in the [001] and [010] directions, giving rise of nearly uniform square sheets in size of ca. 21.6 x 21.6 \(\mu\text{m}\) for Al-JDF-L1 and ca. 24.9 x 24.9 \(\mu\text{m}\) for Fe-JDF-L1.

However, strictly different from lamellar JDF-L1 crystals is that there appears to be a periodic rise of new sub-sheets from the parental basal planes, one typical phenomenon of orthogonally branching multiplications of smaller subindivudials. The distinct characteristics in a novel habit of orthogonally spiral growth can be observed especially on Al(Fe)-JDF-L1 crystals having low Al(Fe)/Ti ratios [Figs. 2(c) and 2(e)]. It is explicit that they are identified to hold a single crystal character. Highlighted here are the deliberations upon Al or Fe incorporation that might induce the orthogonally spiral re-growth of Al(Fe)-JDF-L1 crystallites. As demonstrated in Figs. 2(a)–2(f), the extent to which Al(Fe)-JDF-L1 crystals enabled the orthogonal propagation behaviour has been identified to be associated with the Al(Fe)/Ti increases, especially in cases of the higher levels used. Elucidations on the characteristic features of lamellar structures have been complemented each other by data from SEM and XRD analyses for this type of layered materials.

### 3.3 FTIR and NMR spectra

FTIR spectra of various samples are diagrammatized in Fig. 3. Samples of Al-JDF-L1 and Fe-JDF-L1 with different compositions represent framework-vibration infrared spectra similar to those of layered JDF-L1 and the synthesized lamellar JDF-L1. However, symmetric stretching bands (773 and 778 cm\(^{-1}\)) occur on the spectra of Al-JDF-L1 and Fe-JDF-L1 frameworks, respectively. At this point, the important shoulder peak at 876 cm\(^{-1}\) can be attributed to the oriented short Ti–O bond in the mere titanosilicate JDF-L1 structure. Thus, the appearance of the two vibrations is likely to be significant for substantiating the incorporation of Al and Fe into JDF-L1 framework, considering that they should be closely related to this proximal shoulder peak observed also on the lamellar JDF-L1.

Particularly, the asymmetric stretching vibrations of Si–O–Si(Ti) linkages in JDF-L1 structure show slight redshifts, for example, from 981 to 974 cm\(^{-1}\) and from 1086 to 1048 cm\(^{-1}\). The red-shifts observed are suggested to disclose the local lattice perturbation by heteroatom incor-

### Table 2. Crystal compositions and crystallographic parameters of JDF-L1 and Al(Fe)-JDF-L1 zeotypes

| Sample          | Crystal atomic ratios by EDX (mol/mol)\(^a\) | Tetragonal cell dimensions\(^b\) |  |
|-----------------|---------------------------------------------|---------------------------------|--|
| Lamellar JDF-L1 | K/Na 0.08 Na+K)/Ti 2.09 Si/Ti 4.70 Al/Ti 0.2 | Tetragonal cell dimensions |  |
| Al-JDF-L1@0.18 | 0.17 2.23 4.35 0.18 — 0.20 — | 7.425(5) 10.779(2) |  |
| Al-JDF-L1@0.20 | 0.21 2.28 4.31 0.20 — 0.20 — | 7.428(7) 10.782(6) |  |
| Al-JDF-L1@0.41 | 0.26 2.39 4.20 0.41 — 0.41 — | 7.432(1) 10.783(4) |  |
| Fe-JDF-L1@0.14 | 0.13 2.19 4.44 — 0.14 | 7.410(8) 10.747(3) |  |
| Fe-JDF-L1@0.19 | 0.16 2.24 4.40 — 0.19 | 7.418(1) 10.757(9) |  |
| Fe-JDF-L1@0.35 | 0.19 2.32 4.38 — 0.35 | 7.425(8) 10.762(1) |  |

\(^a\) Nominal atomic ratios refer to the average of every 10 parallel EDX measurements.

\(^b\) Space group: \(P4_2\).
This spectroscopic phenomenon might proceed from partial introduction of longer Al-O and Fe-O bond distances than the corresponding Si-O bond distance since the vibration frequency reduces with increasing bond strengths. No change at ca. 670 cm\(^{-1}\) is identified for symmetric stretching vibrations of SiO\(_4\) units, indicating that the stretching vibrations of [AlO\(_4\)]\(^{-}\) or [FeO\(_4\)]\(^{-}\) tetrahedra are coupled with ones of major SiO\(_4\) units rather than exceptional others. Solid-state \(^{29}\)Si MAS-NMR spectra of various samples with JDF-L1 structure are shown in Fig. 4. Pure JDF-L1 structure has been well known to have uniquely equivalent SiO\(_4\) tetrahedra in coordination environments, four of them build up each of [TiO-Si\(_4\)]\(^4\) units to form continuous sheets, and accordingly, the \(^{29}\)Si MAS-NMR spectrum displays a single peak at -107.4 ppm to the uniform Si(3Si,1Ti) location. Whilst the less shoulder peak observed at ca. -115.4 ppm shows the resonance to Si(4Si,0Ti) relating to amorphous SiO\(_2\) in the entities. Solid-state \(^{29}\)Si MAS-NMR spectra of the series of Al-JDF-L1 samples are composed of the primary resonance at -107.4 ppm in common with the Si site suggested and the newly observed ones at -101.4 and at -105.8 ppm to slightly diverse Si(2Si,1A1,1Ti) environments which to rely on an
increased framework Al/Ti ratio. Fe-JDF-L1 with low Fe/Ti ratio exhibits differently intensive resonances at \(-90.8\) and \(-111.2\) ppm, which can be attributed analogously to two Si sites of the types of Si(2Si,1Fe,1Ti) and Si(3Si,1Ti), respectively. Note that Fe-JDF-L1 differs from the referenced JDF-L1 in NMR values to the primary Si sites because of special spin coupling effects between the existing metal cations.38)

To probe into whether the heteroatom incorporation could have induced such local lattice distortion, \(^{27}\)Al MAS-NMR spectra of Al-JDF-L1 samples were correlated with the framework Al/Ti ratios in a range of 0.18–0.41. As can be seen in Fig. 5, only one NMR resonance at 50.3 ppm can be assigned to tetrahedral \([\text{AlO}_4]^-\) sites whereas no resonance at 0.00 ppm is observed to correlate with six-coordinated extra-framework Al species. However, the single resonance at 50.3 ppm is broadened by increasing Al contents, corresponding to the different extents of spiral growth of crystallites. Therefore, crystal growth in altering habits correlates with the level of lattice perturbation resulting from incorporation of trivalent Al, Fe heteroatoms and the results on composition and NMR studies clearly substantiate the isomorphous substitution of \([\text{AlO}_4]^-\) or \([\text{FeO}_4]^-\) for tetrahedral SiO\(_4\) sites in JDF-L1 framework.

3.4 Isomorphous substitution of Al or Fe heteroatoms

In view of the above spectroscopic observations, one of major issues on Al(Fe)-JDF-L1 synthesis is to explain the crystallographic positions of heteroatom substitution to take place. As demonstrated (Fig. 6) by Ferdov et al.,11) all of Ti and Si atoms are in their general positions, respectively, while each of SiO\(_4\) tetrahedra in JDF-L1 framework keeps connection to one of TiO\(_5\) units to construct five-member rings which are the secondary building units of the \([\text{Ti}_2\text{Si}_8\text{O}_{22}]^{4-}\) layers.5,10) Such connections (see also Fig. A2) have explained the equivalent SiO\(_4\) tetrahedra in tetrahedral \([\text{TiO}·\text{O}_3(\text{SiO}_3)_4]\) locations, viz. only one type of crystallographic positions for Si instead of topologically different occupancies.

On the other hand, it seems rather impossible to incorporate the trivalent cations into five-coordinated Ti(IV) sites in the form of TiO\(_3\) square pyramids. These results, coupled with XRD, FTIR, NMR and compositional analyses, suggest the co-occurrence of normal Si–O–Si(Ti) and Si–O–Al(Fe) but also unexpected Ti–O–Al(Fe) linkages, considering the isomorphous substitution of heteroatoms for Si in \([\text{TiO}_2\text{Si}_2\text{O}_5]^-\) layers.31) Although it is not clear at present to what extent allowance has been made for the latter, there seems no reason to reject the alternative possibility of Al or Fe substitution in those...
zeotypes, since some of which are likely to behave very differently from classical zeolite structures.

3.5 Inducing role of F$^-$ ions in crystal orientation growth

The further important point concerns the influence of various synthesis methods on the orientation effect of JDF-L1 crystal growth resulting in a limited variety of crystal morphologies. Materials of this type generally require severe hydrothermal conditions (e.g. high alkalinity and temperatures up to 230°C to achieve better mineralization. However, the use of fluoride routes associated with lower pH 9.0–10.5 and temperature 200°C (Table 1) should have a huge impact on the growth mechanism of JDF-L1 crystals. As demonstrated by Figs. 7 and 2, the direct consequence of these improvements is the morphological changes of (Al/Fe)-JDF-L1 crystals from spatially oriented crystal plates [Figs. 7(a) and 7(b)] into uniformly sized square sheets [Figs. 7(c) and 7(d)], whereas such results began to appear which were not achievable by pure hydroxide routes.

Upon fluoride synthesis mechanisms, relevant explanations for the phenomena observed can be provided as follows: F$^-$ mineralizing power is less than OH$^-$, nucleation rates may be reduced by the low solubility and effective supersaturations so that larger crystals are formed; formation of certain fluoride species in low-pH systems facilitates the structural incorporation of heteroatoms where the precursor species would be precipitated in conventional base systems. The Al-JDF-L1 relating to Fig. 7(b) is another type of comparable aggregates consisting of larger lamellar crystals. For preparation of this sample, mention should be made of the exceptional conditions, i.e. crystallization at 190°C (for 120 h) in a fluoride-containing but strong alkaline (pH ca. 11.5) system. In this high-pH case, the F$^-$ mineralizing capability to mobilize reaction components and the better performance of complexation with trivalent cations would be moderated by a higher concentration of OH$^-$ ions under the given conditions. It is the main reason that the disoriented overgrowth of lamellar crystals occurred in the run product except for the lower temperature that was compensated by extending the crystallization duration.

For Al(Fe)-JDF-L1 samples, the further variations in crystal orientation and morphology were illustrated in Fig. 7(d) and also Figs. 2(c)–2(f). In contrast to the hydroxide route, the isomorphous substitution of heteroatoms upon fluoride synthesis results in the gradual formation of less lamellar crystallites onto the basal crystal surfaces, which depends on framework Al(Fe)/Ti ratios. It is clear that Al or Fe incorporation brings the internal stresses in framework and eventually results in non-crystallographic branching of smaller secondary subindividuals atop, taking account of periodic stress relaxations to keep a structural long-range ordering nature. The extents to deviate from two-dimensional structures were found to rely essentially on increasing framework Al(Fe)/Ti ratios. Herein, the inducing effects of stress relaxation, coupled with fluoride promotion, might enable the periodic re-growth of even more crystallites in similar orthogonally spiral habits.

In summary, the preferential formation of large lamellar crystals should be ascribed to fluoride-induced competitions between the nucleation and growth processes subjected to the low alkalinity and temperature. The key

Fig. 7. Comparison of FE-SEM micrographs between traditional OH$^-$- and F$^-$-mediated zeotypes: (a) aggregated JDF-L1; (b) Al-JDF-L1 by a high-pH fluoride route; (c) lamellar JDF-L1 and (d) Al-JDF-L1@0.20 both by a low-pH fluoride route.
issues for the fluoride route are to adopt the low temperature and alkaline conditions to induce crystal growth in the uniformly lamellar habit. In addition, the above observations on a new type of crystal branching may provide a potential chance of swelling/self-pillaring manipulations to achieve a structural variety of layered zeotypes-based materials.

4. Conclusions

The fluoride–mediated approaches were investigated for the alternative synthesis of lamellar JDF-L1 and its structural analogues [Al(Fe)-JDF-L1s] in the absence of any organic compounds. These materials typical of lamellar JDF-L1 single crystals are identified to crystallize in the more symmetrically tetragonal space group, $P4_{2}12$, together with slight distortions of cell dimensions. No constant atomic K/Na ratio can be seen for all well crystalline samples. The use of fluoride synthesis systems with a lower alkalinity (pH 9.0–10.5) and crystallization temperature (200 °C) leads to the JDF-L1 orientation growth in the uniform habit of lamellar structures and facilitates the framework incorporation of $[\text{AlO}_{4}]^{1-}$ or $[\text{FeO}_{4}]^{1-}$ for SiO$_4$ tetrahedra. Isomorphous substitution of trivalent Al or Fe is likely to perturb the JDF-L1 structure and hence causes orthogonally spiral multiplications of smaller lamellar subindividuals onto the basal crystal surfaces. Finally, the key issues by fluoride route are to adopt the combination of low temperature and alkalinity for controlling crystal morphologies in the synthesis of these crystalline layered materials.

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