一种直接混合生成 Al₁₃ 硫酸盐晶体的简易方法

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摘要：将一定量的 Na₂SO₄ 溶液直接加入在 60~80 ℃温度下预处理过的 Al₁₃ 溶液中，然后室温陈化 12 h，可简便快速地制备具有四面体形貌和纤维状形貌的 Al₁₃ 基硫酸盐晶体。所得晶体的 SEM 和 OS 图显示：用本文报道的方法合成的四面体形貌的硫酸盐晶体尺寸大小在 150~200 μm，而通过滴定方法的却只有 15~25 μm；纤维状的硫酸盐晶体的长径尺度分别是>1 000 μm 和 0.5~1 μm。对四面体形貌的 Al₁₃ 基硫酸盐晶体的生长机理进行了初步探讨。

关键词：Al₁₃ 多聚阳离子；SEM；直接混合；四面体结晶
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Facile Synthesis of Crystalline Al₁₃ Sulfates *via* Direct Mixing Route

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Abstract: Uniform tetrahedral and fiber-like crystalline sulfates of $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ polyoxocations were synthesized via a direct mixing and aging route. XRD patterns reveal that tetrahedral and fiber-like crystalline Al₁₃ sulfates are cubic and monoclinic structure, respectively. SEM and Optical Scanning (OS) images show that the size of tetrahedral crystalline Al₁₃ sulfates prepared via a direct mixing way is 150~200 μm, which is almost 10 times larger than that via traditional titration way (15~25 μm). The size of the fiber-like crystalline Al₁₃ sulfates is 0.5~1 μm in diameter and up to 1 000 μm in length. A possible crystal growth mechanism for the tetrahedral crystalline Al₁₃ sulfates is discussed.

Key words: Al₁₃ polyoxocations; SEM; direct mixing route; tetrahedral crystalline

0　Introduction

The $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ polyoxocations (Al₁₃) play an important role in water treatment, catalysis, material science and other fields owing to their diverse purposes. Al₁₃ are the optimum contents in polyaluminum chloride[1,2]. Due to the characteristics of higher positive charge and strong binding ability to aggregates, Al₁₃ were widely used in water purification. Furthermore, Al₁₃ have been used to prepare mesostructured γ-Al₂O₃ materials[3] and a theoretical model for γ-Al₂O₃[4]. They were also used as pillaring agents to synthesize intercalated clay materials[5,6] and as building blocks in combination with other large anions to build porous solid materials[7,8]. Other atoms such as Ga and Ge can substitute the center Al atoms of Al₁₃ to

derive similar polyoxocations[9,10]. In general, Al₁₃ and similar polyoxocations[9~11] can be precipitated in sulfates[9~15], oxalates[13] and nitrates[14,15]. Crystalline sulfates are the common forms due to their applications in separation, purification and speciation analysis of the polyoxocations[16,17].

In recent years, a great deal of work has been carried out on the synthesis of Al₁₃ and its similar polyoxocations, and their relevant salts. Tsuchida et al.[12] and Wang et al.[13] prepared crystalline Al₁₃ sulfates and amorphous oxalates with 7~70 days aging time. Kloprogge et al.[14,15] studied the structure of Al₁₃ sulfates and nitrates by means of Raman Microscopy and near-infrared spectroscopy, but the samples were aged for 42 days. The preparation of Al₁₃ and $[GaO_4 Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ (GaAl₁₂) sulfates after aging for a few days were reported by Parker et al.[9] Colorless tetrahedral crystalline $[GeO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{8+}$ (GeAl₁₂) selenates were synthesized by Lee et al.[10] with one week aging. Relatively long aging time (≥7 day) was required for all synthetic processes of Al₁₃ salts and their analogs reported in literature. So it would be in-

teresting if a facile and effective method could be developed with shorter aging time for preparing Al₁₃ salts and their analogs.

In this paper, we present an efficient direct mixing and aging route for synthesis of the crystalline Al₁₃ sulfates. The crystalline Al₁₃ sulfates with uniform morphologies were obtained after 12 h aging. The salts were characterized by XRD, FTIR, SEM and OS. A possible mechanism on the formation of tetrahedral crystalline Al₁₃ sulfates is also discussed.

1　Experimental

XRD patterns were recorded on a MSAL XD-2 Powder X-ray Diffractometer using Cu Kα radiation of wavelength 0.154 06 nm at 40 kV and 20 mA. FTIR spectra were recorded on a Bruker Equinox 55 Fourier Transform Infrared Spectrometer using KBr pellets. SEM images were taken on a JEOL JSM-T300 and a Philips XL-30 Scanning Electron Microscopy at 10 kV. OS was carried on a Nikon ECLIPSE E600W POL polarizing microscope.

$AlCl_3 \cdot 6H_2O$, NaOH and $Na_2SO_4 \cdot 2H_2O$ were ana-

Table 1　Relevant crystal morphologies under different synthesis conditions

Ways of mixing	No. of samples	Pretreatment temperature of Al₁₃ / ℃	Aging time / h	Ratio of $Al^{3+} : SO_4^{2-}$	Crystal morphology
Direct mixing way	1	0	24	1:3	Fiber-like
	2	30	24	1:3	Irregular crystal
	3	60	12	1:3	Tetrahedral
	4	70	12	1:3	Tetrahedral
	5	80	12	1:3	Tetrahedral
	6	60	12	1:2	Tetrahedral, fiber-like*
	7	60	12	1:1	Fiber-like
	8	60	12	1:0.5	Fiber-like
	9	80	12	1:2	Fiber-like
	10	80	12	1:1	Fiber-like
Titration way	11	0	24	1:3	Irregular precipitates
	12	30	24	1:3	Irregular crystal
	13	60	12	1:3	Tetrahedral
	14	60	72	1:3	Tetrahedral
	15	60	168	1:3	Tetrahedral
	17	60	12	1:1	Tetrahedral
	18	70	12	1:3	Tetrahedral
	19	80	12	1:3	Tetrahedral

* dominant products.

lytical reagents and were used as received.

Al_{13} solution was synthesized in a 100 mL inter-layer glass reactor at 60 ℃. 65 mL of 0.2 mol·L^{-1} of NaOH solution was added dropwise (1.5~2.0 mL·min^{-1}) to 30 mL of 0.2 mol·L^{-1} of $AlCl_3$ solution in the glass reactor with vigorous stirring. The obtained clear solution was continuously stirred for 20 min and then was cooled under ice-bath for about 8~10 h.

A typical synthetic process for the crystalline tetrahedral Al_{13} sulfates was as follows: the prepared Al_{13} solution was firstly cooled in ice-bath for about 10 min, and then heated in 60 ℃ water-bath for 20 min. 30 mL of 0.6 mol·L^{-1} Na_2SO_4 solution at room temperature was directly mixed with a 95 mL pretreated Al_{13} solution (the molar ratio of Al^{3+} to SO_4^{2-} was 3[12]) to form a homogenized mixture. The pellucid mixture was transferred into a 100 mL autoclave. The autoclave was sealed and the solution was aged at room temperature for 12 h. After the reaction was completed, the solid products were separated, and washed with distilled water for several times, and then air dried.

To further understand the crystal growth process of the Al_{13} sulfates, several factors were studied. These factors include the pretreatment temperature of Al_{13} solution, the dosages of Na_2SO_4 solution, the aging time and the ways of reactants addition. A traditional titration way was also employed for comparison. The detailed synthesis conditions and results are given in Table 1.

2 Results and discussion

Fig.1 shows typical XRD patterns of these Al_{13} sulfates prepared in Table 1. (a) in Fig.1 is the XRD patterns for sample No.3~5 and No.13~19 in Table 1, the strong and sharp peaks indicate that they are well crystallized. These peaks at 8.74°, 10.06°, 17.37°, 20.09°, 24.60°, 26.12°, 28.46°, 33.45°, 39.01° and 46.59° (2θ) can be assigned to (111), (200), (222), (004), (224), (333), (600), (444), (800) and (357) lattice planes, respectively. All the peaks can be indexed as tetrahedral crystalline Al_{13} sulfates in a cubic structure. The result is in good agreement with the reference results[9,12,13], and the relevant chemical formula is $Na[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_4·nH_2O$. (b) in Fig.1 exhibits the XRD patterns for sample No.7~10 in Table 1. It is obvious that it is very different from Fig.1a, which reveals that fiber-like Al_{13} sulfates are in a monoclinic structure[12,13], the corresponding chemical formula is $[Al_{13}O_4(OH)_{24}(H_2O)_{11}(OH)][SO_4]_3·nH_2O$, in which each tridecamer (consisting of three Al octahedra) is believed to have lost one proton from the structure existing in the solution. Furthermore, the Keggin structure of the Al_{13} is not destroyed.
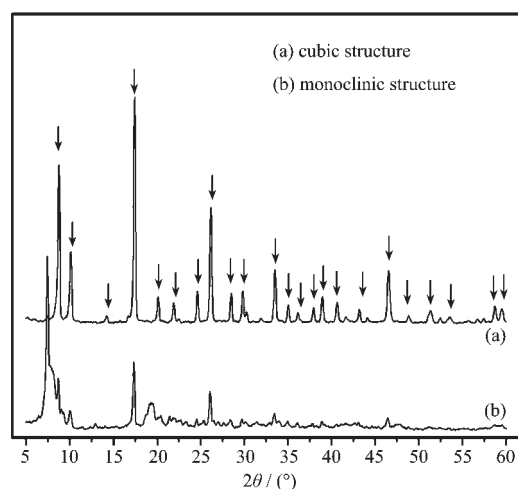
(a) No.3~5 and No.13~19, (b) No. 7~10
Fig.1 XRD patterns of Al_{13} sulfates prepared in Table 1

The IR spectra for all of Al_{13} sulfates are very similar (Fig.2). There are four characteristic peaks of Al_{13} at the range of 400~800 cm^{-1}, that is, 726 cm^{-1} (Al-O)$_{Td}$, 624 cm^{-1} (Al-OH)$_{Oh}$, 555 cm^{-1} (Al-O)$_{Oh}$, 494 cm^{-1} (Al-OH$_2$)$_{Oh}$, respectively, which agrees well with reference values[14,15]. The characteristic bands for SO_4^{2-} anions are also found at 1 113 cm^{-1} (strong flexing vibration of S-O bonds) and 910 cm^{-1}, 990 cm^{-1} (weak bending vibration of S-O bonds), respectively. IR spectra indicate that all of these Al_{13} sulfates hold Keggin structures of Al_{13} and SO_4^{2-} ions.

SEM images of Al_{13} sulfates in Table 1 are shown in Fig.3. The sample No.3 has uniform tetrahedral shape and the size is in the range of 150~200 μm. It has a cubic structure[9,12,13]. The sample No.7 has fiber-like morphology with diameter in the range of 0.5~1 μm and length up to 1 000 μm, respectively. The
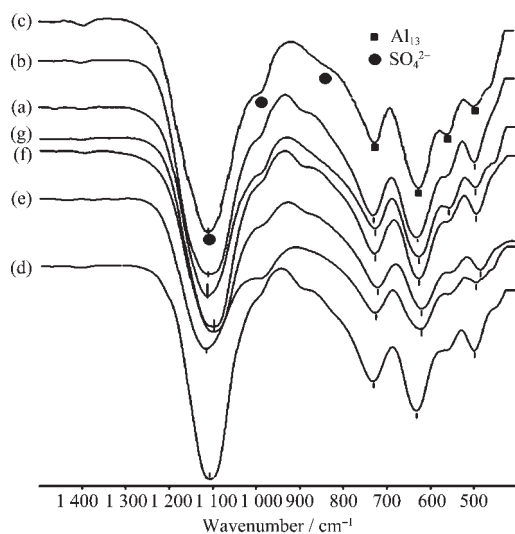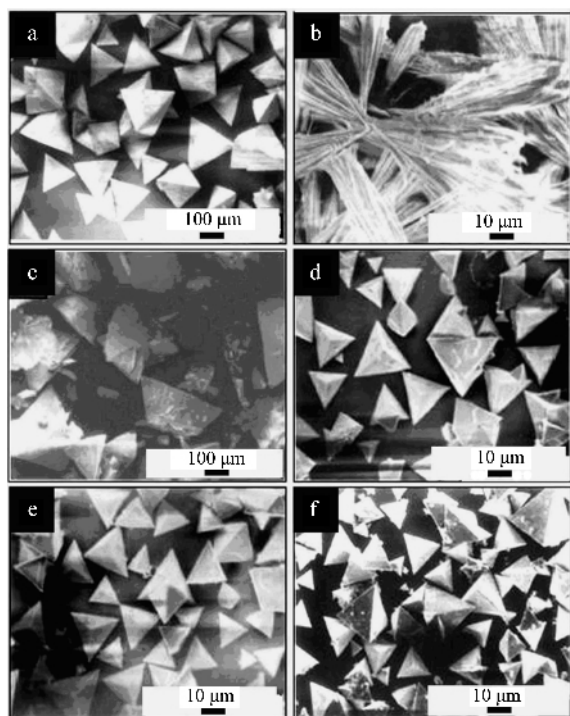
Fig.2　FTIR spectra of Al_{13} sulfates in Table 1,
(a~c) No.1~3; (d~g) No. 11~14

(a) No.3, (b) No. 7, (c) No. 2,
(d) No.13, (e) No.14 and (f) No.15

Fig.3　SEM images of the crystalline Al_{13} sulfates in Table 1

sample No.2 has complex and irregular crystal surface with size up to 200 μm. The sample No.13, No.14 and No.15 have uniform tetrahedral shape and very similar size (15~25 μm). These SEM images show that tetrahedral crystalline Al_{13} sulfates keep identical size when aging time is increased.

A series of experiments for sample No.3 (direct mixing way, 60 ℃ and $n_{Al^{3+}}$:$n_{SO_4^{2-}}$=1:3) with different aging time were carried out to investigate the growth process of the tetrahedral crystalline Al_{13} sulfates. The morphologies of corresponding sulfates were recorded on a Nikon polarizing microscope, as shown in Fig.4. At the first 30 min mixing of reactants, tetrahedral and fiber-like crystalline Al_{13} sulfates are were simultaneously formed (Fig.4, a). When the reaction lasted for 1 h, lots of tetrahedral crystalline Al_{13} sulfates were obtained (Fig.4, b). After 3 h, small sized tetrahedral crystalline Al_{13} sulfates were grew epitaxially (Fig.4, c). After 6 h, tetrahedral crystalline Al_{13} sulfates continuously grew up (Fig.4, d). Well developed, uniform tetrahedral crystalline Al_{13} sulfates were formed after aging for 12 h (Fig.4, e) with an average size of 150~200 μm. Over a longer aging time, the size of tetrahedral crystalline Al_{13} sulfates changed only a little (Fig.4, f). The OS results reveal that tetrahedral crystalline Al13 sulfates grow up little by little in the initial 12 h aging time. It is noteworthy that there are not only tetrahedral crystalline Al_{13} sulfates, but also some trigonal shape Al_{13} sulfates (Fig.4, c, Fig.5, a) in the synthesis process. The XRD pattern of trigonal sulfates indicates that they are in cubic struc-
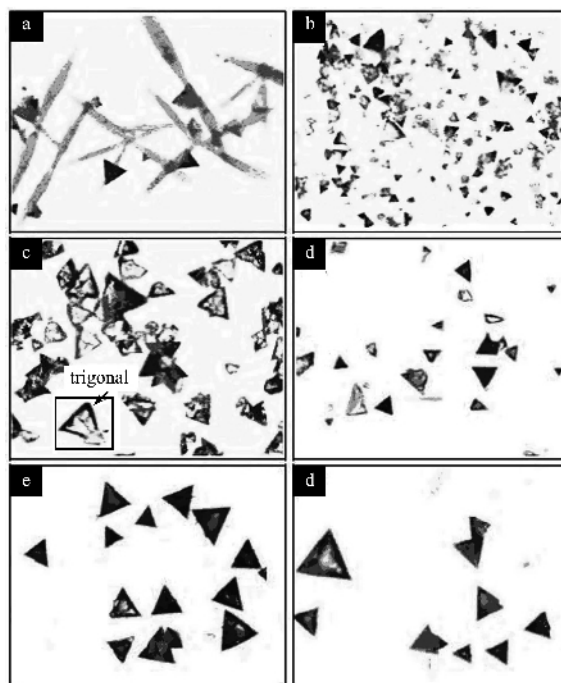
0.5, 1, 3, 6, 12, 24 h from (a) to (f), respectively;
a, b, c, zoomed in 200 times; d, e, f, 100 times

Fig.4　Optical images of sample No.3 with different aging time

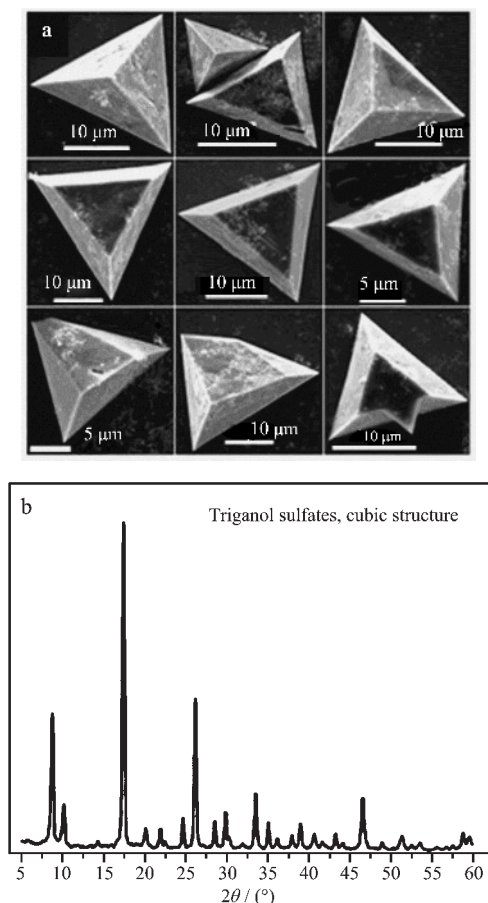ture (Fig.5, b). Therefore, the trigonal sulfates can be regarded as the tetrahedrons with cut off tops.

Fig.5　SEM images (a) and XRD pattern (b) of the trigonal
　　　Al$_{13}$ sulfates via a direct mixing way

The influence factors such as pretreatment temperatureof Al$_{13}$ solution, Na$_2$SO$_4$ dosage, aging time and ways of reactants addition on the growth of crystalline Al$_{13}$ sulfates were investigated in detail. The morphologies were observed in an optical microscope and experimental results at different conditions are given in Table 1.

For direct mixing, when the pretreatment temperature of Al$_{13}$ solution was increased, the morphologies of Al$_{13}$ sulfates were changed from fiber-like to irregular, and then to uniform tetrahedral shapes. The pretreatment temperature can significantly affect the formation of tetrahedral crystalline Al$_{13}$ sulfates. When the molar ratio of Al^{3+}:SO$_4^{2-}$ was changed from 1:3, to 1:2, 1:1 and 1:0.5, respectively, the translations from tetrahedral to fiber-like were observed. Tetrahedral and fiber-like crystalline Al$_{13}$ sulfates were produced

when the molar ratio of Al^{3+}:SO$_4^{2-}$ was 1:2. Even the pretreatment temperature was raised to 80 ℃, there were similar phenomena when increasing the Na$_2$SO$_4$ dosages. The results attest that the dosages of Na$_2$SO$_4$ indeed influence the growth of crystalline Al$_{13}$ sulfates. It is very interesting that the size of crystalline tetrahedral Al$_{13}$ sulfates is changed under diffenent mixing ways. The size of the tetrahedral crystalline Al$_{13}$ sulfates by a direct mixing way is 150~200 μm, whereas it is only 15~25 μm by a titration way, as shown in Fig.3 and Table 1.

There are similar phenomena in a titration way at different Al$_{13}$ solution pretreatment temperature. The results further prove that the pretreatment temperature can influence the growth of sulfates. When the molar ratio of Al^{3+}:SO$_4^{2-}$ is 1:3 and 1:1, there are only tetrahedral Al$_{13}$ sulfates produced in titration way. Hence, the dosages of Na$_2$SO$_4$ do not influence the growth of Al$_{13}$ sulfates in titration way.

As to aging time, when it is less than 12 h, tetrahedral Al$_{13}$ sulfates grow epitaxially (Fig.4). When it is more than 12 h, even up to 168 h, the tetrahedral crystalline Al$_{13}$ sulfates obtained have almost identical sizes (Fig.3, e, f).

In a word, pretreatment temperature for Al$_{13}$ solution and Na$_2$SO$_4$ dosages remarkably affect the morphologies of crystalline Al$_{13}$ sulfates, mixing ways affect the size of tetrahedral crystalline Al$_{13}$ sulfates.

Based on the experimental results and crystal growth unit model of anionic coordination polyhedron[18~20], a possible crystal growth mechanism for tetrahedral crystalline Al$_{13}$ sulfates is suggested. (a) and (b) in Fig.6 show the Keggin structure of Al$_{13}$ [4,7]. The Keggin polyoxocations usually combine with their counter ions, SO$_4^{2-}$ anions, in their trimer directions [Al$_3$O$_{13}$][7]. The interactions between them include electrostatic bonding and hydrogen bonding. Larger sized Al$_{13}$[SO$_4$]$^{4-}$ anions are then formed (Fig.6, d~f), which can be regarded as crystal growth units. The Al$_{13}$[SO$_4$]$^{4-}$ units are self-assembled into some more larger sized units, nAl$_{13}$[SO$_4$]$^{4-}$, which are combined with Na$^+$ cations. Each Na$^+$ ion coordinates with four Al$_{13}$[SO$_4$]$^{4-}$ anions to form tetrahedral coordinated anions, Na(Al$_{13}$[SO$_4$]$_4$)$_4^{3-}$

(Fig.6, h) and each Al$_{13}$[SO$_4$]$^{4-}$ anion coordinates with four Na$^+$ ions (Fig.6, i) according to ion coordination theory. In succession, many nAl$_{13}$[SO$_4$]$^{4-}$ units combine each other to form tetrahedral Al$_{13}$ sulfate crystal seeds and the crystal seeds grow epitaxilly to produce macroscopical tetrahedral crystalline sulfates (Fig.6, k). (j) in Fig.6 shows the model of Al$_{13}$[SO$_4$]$^{4-}$ units building in the plane direction. In fact, we have obtained trigonal crystalline Al$_{13}$ sulfates and tetrahedral Al$_{13}$ sulfates (Fig.4 and Fig.5).
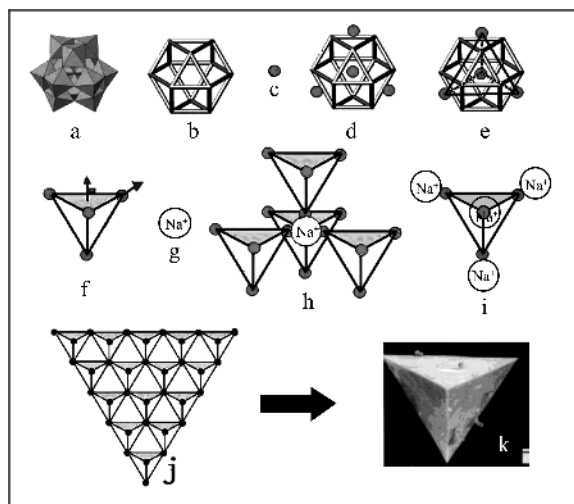

Fig.6　Possible crystal growth mechanism for tetrahedral crystalline Al$_{13}$ sulfates (c, SO$_4^{2-}$ anions)

On all accounts, the crystal growth process of tetrahedral crystalline Al$_{13}$ sulfates undergo three steps: the primary Al$_{13}$ combines with SO$_4^{2-}$ ions to form the secondary Al$_{13}$[SO$_4$]$^{4-}$ anions, which are the crystal growth units. Secondly, many Al$_{13}$[SO$_4$]$^{4-}$ units self-assemble into larger units, nAl$_{13}$[SO$_4$]$^{4-}$, which are combined with Na$^+$. Finally, larger units build into the tetrahedral crystalline Al$_{13}$ sulfates.

Using this possible crystal growth mechanism for tetrahedral crystalline Al$_{13}$ sulfates and general principle about crystal growth, it is easy to explain why the size of tetrahedral Al$_{13}$ sulfates is larger via a direct mixing way than that by a titration way.

According to general principle of crystal growth, the number of crystal seeds, homogeneous nucleation, transport processes and the degree of supersaturation are main factors to dominate the dynamics of crystal growth process. Supersaturation solution could be obtained by lower solution temperature. Fig.7 presents a classical phase diagram of a two-component system for a solute with a positive temperature coefficient of solubility $dC_0/dT > 0$. The diagram can be divided into three zones, namely, stable zone, metastable zone, and labile zone. In these zones, the metastable zone is very important because crystal growth from solution generally occurred within this zone. The width of the metastable zone is correlative with the nature of starting materials and reaction conditions such as stirring, impurity, temperature, and so on.
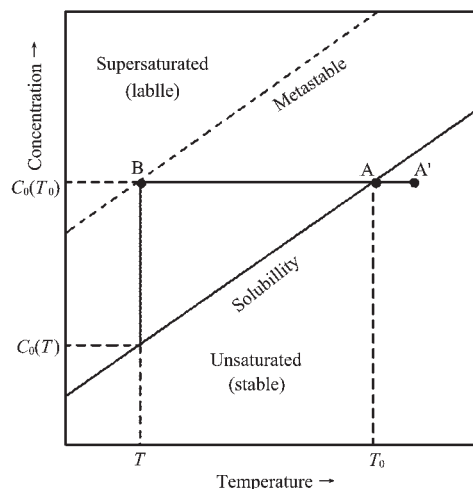

Fig.7　Phase diagram for a binary system solid-liquid in ref.[21]

In the direct mixing process, when two reactants are directly mixed and shaked to homogeneous about 1 min, a pellucid mixture was obtained and it could keep pellucid for 10~20 min. During the pellucid period, Al$_{13}$ were combined with SO$_4^{2-}$ to form Al$_{13}$[SO$_4$]$^{4-}$ units and larger units, the pellucid state corresponds to the metastable zone. Increasing the aging time, the temperature of the mixture becomes lower, and the state of mixture is changed from labile region into metastable zone. Crystal seeds are spontaneously produced. In fact, tetrahedral and fiber-like Al$_{13}$ sulfates are formed after mixing the reactants for 30 min. And then the formed Al$_{13}$[SO$_4$]$^{4-}$ units and larger units are efficiently and directly surrounded on tetrahedral crystal seeds, and tetrahedral crystals grow epitaxially. On the other hand, fiber-like sulfates are then gradu-

ally disappeared, because monoclinic Al_{13} sulfates can be converted into tetrahedral crystalline Al_{13} sulfates via Gibbs process[13].

As to a titration way, the situation is completely different. When Na_2SO_4 solution is slowly added into Al_{13} solution with vigorous stirring, white precipitates are immediately formed, which can be seen as some small crystal seeds. The results show that the mixture is within labile zone at the beginning, not in metastable zone. The added Na_2SO_4 is dispersed and adsorbed on all these crystal seeds, not on some special crystal seeds. So there are only small tetrahedral crystals by this way.

Hence, direct mixing way and higher pretreatment temperature are the main reasons with which tetrahedral crystalline Al_{13} sulfates can be grown bigger than that via a titration way. The Na_2SO_4 dosages mainly affect the reaction environments and the sulfate crystal morphologies.

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