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Reactivity of aluminum sulfate and silica in molten alkali-metal sulfates in order to prepare mullite

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Abstract

With the aim of preparing mullite, reactions between aluminum sulfate and silica in appropriate proportions and molten sulfate media M_2SO_4 (M = Na and/or K) were performed at different temperatures. The powders obtained were characterized by XRD, FT-IR, SEM and TEM. The reactivity was the same in Na_2SO_4 and $(K,Na)_2SO_4$ media. The best results in terms of yield (98.3%) and weight of mullite produced (95%) were obtained in Na_2SO_4 at 950 °C. The mullite phase exhibits an acicular morphology ($75 \times 0.75\,\mu m$) and a specific surface area close to $20\,m^2/g$. In K_2SO_4 medium, a potassium alumino silicate is formed as well as mullite.

Keywords: Mullite; Molten salts; Sulfates; Synthesis

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1. Introduction

In the binary system Al_2O_3–SiO_2 at atmospheric pressure, mullite $3Al_2O_3{\cdot}2SiO_2$ is the only stable alumino-silicate.[1] Mullite ceramics exhibit important properties:[2] high thermal resistance (incongruent melting at $1890 \pm 10\,°C$), low thermal expansion coefficient ($\alpha = 3.9 \times 10^{-6}\,°C^{-1}$), excellent creep resistance ($\varepsilon > 10^{-10}\,s^{-1}$ at 1200 °C), great bending strength (360–370 MPa).

Since the beginning of the 1990s, the strong increase in the number of papers dealing with mullite synthesis indicates that considerable effort has been devoted to processing and microstructure control of mullite. Though it requires very high temperatures and often gives powders of heterogeneous morphology, the ceramic method is still used[3–7] for reasons of simplicity. Other methods providing better control of the morphology have been developed such as chemical vapor deposition which leads directly to mullite,[8] or sol–gel,[9–11] or hydrothermal synthesis[12] which produce mullite precursors.

When molten, the oxo-salts of alkali-metals (nitrites, nitrates, carbonates, sulfates, etc.) are ionic liquids characterized by solvent properties stronger than those of aqueous media because of their higher melting point.[13] Thus, they enable chemical reactions producing fine oxide powders with specific properties.[14,15] It is well known that, for the synthesis of mixed oxides from mixtures of the corresponding simple oxides, the addition of a molten flux (e.g. addition of Li_2SO_4/K_2SO_4 eutectic for the reaction $MgO + Fe_2O_3 \rightarrow MgFe_2O_4$) decreases the reaction temperature a few hundred degrees and accelerates the kinetics of mixed oxide formation. The flux does not participate directly in the chemical reaction, but weakly dissolves the chemical reagents, shifting the equilibrium a until complete transformation with precipitation of the reaction product.

In the reaction of transition metal salts with molten media made up of alkali-metal and oxo-anion salts, the oxo-anion is involved in the chemical reaction as a Lux-Flood base, i.e. a donor of oxygen anions O^{2-}, whereas the transition metal cation reacts as a Lux-Flood acid, i.e. an acceptor of O^{2-} ions.[16] Thus, various simple or mixed oxides, characterized by high specific surface areas and excellent homogeneity of chemical composition, have been prepared

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by reaction at 450 °C of transition metal salts with molten alkali-metal nitrates: x mol% Y_2O_3–ZrO_2 ($0 \leq x \leq 8$),[17] alumina–zirconia dispersions,[18] TiO_2 anatase,[19] CeO_2,[20] 3 mol% Y_2O_3–HfO_2,[21] $PbTiO_3$.[22]

The molten salts method has been scarcely used for the preparation of mullite. Saadi et al. prepared mullite precursors by reaction, in nitrate media at 450 °C for 2 h, of aluminum sulfate and amorphous silica.[23–25] By annealing the precursors, mullite appears around 1200 °C, but it is necessary to heat up to 1600 °C to achieve the transformation and to get pure mullite.

Hashimoto et al. synthesized acicular mullite particles by reaction, at 1100 °C for 3 h, of aluminum sulfate, silica and potassium sulfate.[26]

The present paper is concerned with the investigation of mullite synthesis by reaction of aluminum sulfate and silica precursors with various alkali-metal sulfate media, at temperatures ranging from 900 to 1150 °C.

2. Experimental

2.1. Chemical reagents

The starting materials were anhydrous aluminum sulfate (obtained by calcinations of reagent grade $Al_2(SO_4)_3 \cdot 18H_2O$ (Aldrich) at 300 °C for 2 h) and an amorphous silica gel (Kieselgel Merck). The reaction media used were anhydrous reagent grade Na_2SO_4 (mp = 897 °C) and K_2SO_4 (mp = 1069 °C) and the eutectic mixture 80 mol% Na_2SO_4–20 mol% K_2SO_4 (mp = 830 °C).

2.2. Synthesis procedure

Aluminum and silicon sources in appropriate proportions and an excess of alkali-metal sulfate(s), in regard to the stoichiometry of the reaction, were intimately mixed. Then, the mixture was poured in an alumina crucible and heated in a muffle furnace at different temperatures for various times. At the end of the treatment, the furnace was cooled to room temperature and the water-insoluble oxide powder formed was recovered by filtration, after washing away the excess of salts, and dried at 120 °C overnight.

The reaction temperatures were 900, 950 and 1000 °C for Na_2SO_4 and eutectic $(Na,K)_2SO_4$ media and 950, 1100 and 1150 °C for K_2SO_4 medium. The heating rate was 150 °C/h and the temperatures were maintained for 4 or 6 h.

2.3. Powder characterization

The products were characterized by X-ray diffraction (Siemens D501 diffractometer for powders, $\lambda \text{CuK}\alpha = 1.5418$ Å), infrared spectroscopy (FT-IR, Perkin Elmer 1760), scanning and transmission electron microscopies (SEM Jeol JSM 6400 provided with energy dispersion (X-EDS), TEM Jeol 2010) and size distribution analysis by laser deviation (Malvern Mastersizer 2000s). The percentages of crystallized phases were calculated from the relative intensities of the strongest peak characteristic of each phase, according the formula used by Saadi et al.:[24] $x\,(\%) = 100(I_x^{\text{int}}/\sum I^{\text{int}})$, where $\sum I^{\text{int}}$ is the sum of the relative intensities of all the crystallized phases present in the sample (semi-quantitative analysis).

3. Results

The reactivity of the aluminum and silicon sources was first studied for Na_2SO_4 and eutectic mixture $(K,Na)_2SO_4$, and finally for K_2SO_4.

3.1. Reactivity with Na_2SO_4 and $(Na_{0.8},K_{0.2})_2SO_4$

The investigation focused on the influence of the following parameters:

- mol% of X_2SO_4 (X = Na and/or K): $100X_2SO_4/(X_2SO_4 + Al_2(SO_4)_3 + SiO_2)$
- molar ratio Al_2O_3/SiO_2 and dwell time
- reaction temperature

3.1.1. Effect of the mol% of the alkali-metal sulfates on the reaction yield

For this study, reactions were carried out at 950 °C with an alumina/silica ratio in the range 0.9–2.0 and mol% of alkali-metal sulfate(s) of about 50 and 80.

In the results gathered in Table 1, the reaction yield is the ratio mass of the oxides obtained × 100/initial mass of SiO_2 + mass of Al_2O_3 equivalent to the initial mass of $Al_2(SO_4)_3$. The results revealed unambiguously that, for the two dwell times, the factor influencing the yield most was the mol% of alkali-metal sulfate(s) in the reaction medium. Indeed, for a mol% close to 50, the yields ranged from 80 to 95%, whereas for a mol% close to 80, the yields did not exceed 65%. In the following, only 50 mol% will be considered.

No appreciable differences were noted between the values obtained in sodium sulfate and in sodium potassium eutectic media. The increase of dwell time from 4 to 6 h had no influence.

3.1.2. Effect of the molar ratio alumina/silica and of dwell time on the proportion of mullite in the powders obtained

Reactions were also performed at 950 °C with Al_2O_3/SiO_2 molar ratios varying from 0.9 to 2.0.

Whatever the dwell time or the nature of the molten medium, the highest proportion of mullite was obtained for the lowest Al_2O_3/SiO_2 ratio (0.9) which corresponds to an excess of silica in the reaction medium when compared to the proportions in mullite $3Al_2O_3 \cdot 2SiO_2$ (Table 2). XRD patterns of the powders obtained (Fig. 1) revealed that the

Table 1
Influence of the molar content of alkali-metal sulfate(s) on the reaction yield for various values of the Al_2O_3/SiO_2 molar ratio at 950 °C, for 4 and 6 h

Al_2O_3/SiO_2	Na_2SO_4				$(Na,K)_2SO_4$			
	Molar content	Yield	Molar content	Yield	Molar content	Yield	Molar content	Yield
4 h								
0.9	48	88	82	63	49	92	88	62
1.5	55	82	81	61	54	90	89	46
2.0	53	94	80	54	53	85	88	54
6 h								
0.9	65	88	82	65	48	89	88	62
1.5	54	85	78	62	53	87	88	49
2.0	53	93	80	58	54	98	87	54

Table 2
Influence of the Al_2O_3/SiO_2 molar ratio on the molar proportion of mullite in samples obtained at 950 °C with dwell time of 4 and 6 h

Al_2O_3/SiO_2	Na_2SO_4 (molar%)	M (mol%)	A (mol%)	$(Na,K)_2SO_4$ (molar%)	M (mol%)	A (mol%)
4 h						
0.9	48	86	14	49	85	15
1.5	55	80	20	54	77	23
2.0	53	64	35	53	66	34
6 h						
0.9	65	90	10	48	80	20
1.5	54	75	25	53	66	34
2.0	53	66	34	54	62	38

M: mullite; A: Al_2O_3.

proportion of mullite is slightly higher for the 6 h dwell time than for the 4 h dwell time. For the ratio 1.5 (i.e. the same proportions as in mullite), the effect of the dwell time seemed to be opposite. In the presence of an excess of alumina (ratio = 2) the dwell time had almost no influence.

3.1.3. *Effect of the reaction temperature*

From reactions carried out at 900, 950 and 1000 °C with dwell times of 6 h and an Al_2O_3/SiO_2 ratio of 0.9 (Table 3), it was noticed, on the one hand, that sodium sulfate molten medium led to higher contents of mullite than the sodium–potassium eutectic one and, on the other hand, that the best compromise for obtaining both a high yield and significant mullite content is to set the reaction temperature at 950 °C.

In the XRD data, only the crystallized phases, mullite and alumina, were considered. But, when both XRD data and chemical analysis were taken into account, it was shown that amorphous silica was also present in the reaction products. The sample exhibiting the best results, in terms of mullite content and yield, was prepared at 950 °C for 6 h with an Al_2O_3/SiO_2 ratio of 0.9 and a Na_2SO_4 molar content of 50%. It was characterized by XRD and the following weight a contents were obtained according to the formula of Saadi et al.[24] mullite 93.15%, α-alumina 1.64% and amorphous silica 5.21%.

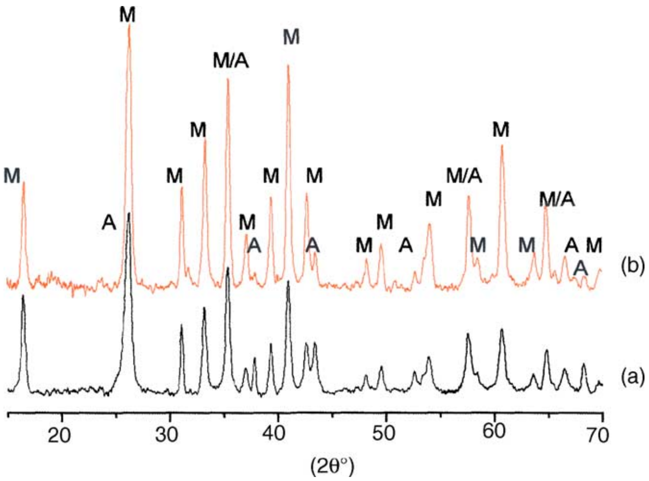

Fig. 1. Influence of dwell time on the XRD pattern of mullite samples prepared at 950 °C with Al_2O_3/SiO_2 = 0.9 and Na_2SO_4 (mol%) = 50, with reaction times of 4 h (a) and 6 h (b).

3.2. *Reactivity with K_2SO_4*

The reactivity of aluminum sulfate and silica in K_2SO_4 was investigated by performing reactions at three temperatures, 950, 1100 and 1150 °C with Al_2O_3/SiO_2 = 0.9 and K_2SO_4 (mol%) = 50. Even though the first temperature is below the melting point of K_2SO_4, the appearance of the reaction mixture after cooling showed undoubtedly that melting occurred during the reaction.

Whatever the reaction temperature and dwell time, the results showed that, like in Na_2SO_4 and eutectic media, the

Table 3
Influence of reaction temperature on the yield and molar proportions of crystallized phases, mullite and alumina, for reactions carried out at 950 °C for 6 h in Na_2SO_4 and eutectic 0.8 Na_2SO_4–0.2 K_2SO_4

	900 °C			950 °C			1000 °C		
	Yield (%)	M (%mol)	A (%mol)	Yield (%)	M (%mol)	A (%mol)	Yield (%)	M (%mol)	A (%mol)
Na_2SO_4	75	90	10	88	90	10	90	85	15
0.8 Na_2SO_4–0.2 K_2SO_4	72	87	13	89	80	20	91	60	40

M: mullite; A: Al_2O_3.

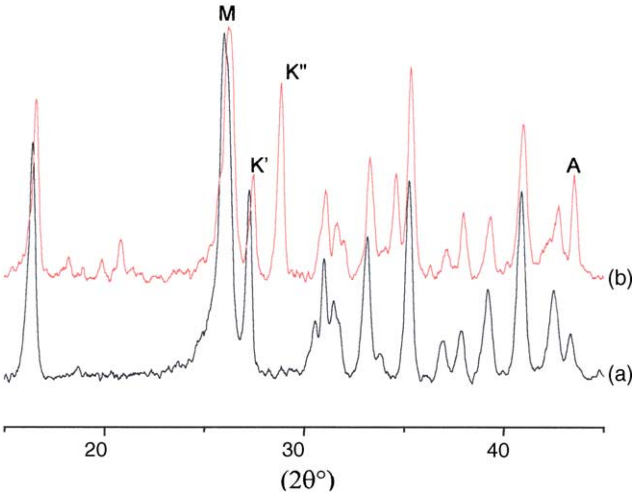

Fig. 2. Influence of the temperature on the XRD pattern of mullite samples prepared in molten K_2SO_4 at 950 °C (a) and 1100 °C (b) for 6 h. M is mullite, A is alumina, K′ is $KAlSi_2O_6$ and K″ is $KAlSiO_4$.

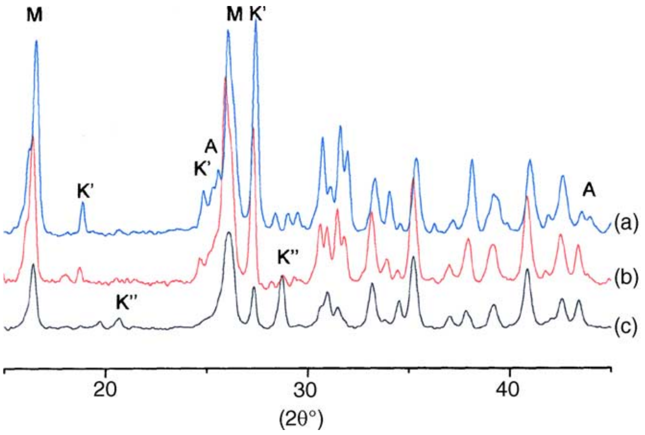

Fig. 3. Influence of dwell time on the phase composition of samples prepared in K_2SO_4 at 1100 °C for 1 h (a), 3 h (b) and 6 h (c).

mullite was obtained in the presence of a varying or less proportion of alumina. But, unlike the reactions in the previous media, the formation of two potassium alumino-silicates, $KAlSi_2O_6$ (K′, JCPDS file 81-2221) and $KAlSiO_4$ (K″, JCPDS file 48-1028) was observed by XRD (Fig. 2). The proportion of mullite decreased significantly when the temperature and the dwell time increased (Table 4). Simultaneously the proportion of alumina increased. The K′ phase was already formed in reactions carried out at 950 °C and the K″ phase did not appear. The proportion of K′ increased as that of mullite decreased. For reactions at 1100 and 1150 °C, the proportion of K′ decreased as that of K″ increased. K′ seemed to be formed quickly and to be progressively transformed into K″ as the dwell time increased as shown for samples prepared at 1100 °C (Fig. 3).

3.3. Characterization of the sample showing the best results

The best sample, i.e. the mullite powder prepared at 950 °C for 6 h with $Al_2O_3/SiO_2 = 0.9$ and Na_2SO_4 (mol%) = 50, was characterized.

3.3.1. Infrared spectroscopy

The attribution of bands and shoulders, detected in the FT-IR spectrum of the powder recorded in transmitance (Fig. 4), as previously reported[8,27] (Table 5), corroborates the presence of mullite, α-alumina and amorphous silica.

3.3.2. Electron microscopy

Powders were characterized by SEM and TEM. The SEM micrographs (Fig. 5a) revealed the presence of three kinds of particles: acicular ones (Fig. 5b), large rather plate-like

Table 4
Influence of dwell time and reaction temperature in the composition of the products obtained by reaction in K_2SO_4

Temperature (°C)	Dwell time 3 h				Dwell time 6 h			
	M (%mol)	A (%mol)	K′ (mol%)	K″ (mol%)	M (%mol)	A (%mol)	K′ (mol%)	K″ (mol%)
950	75	6	19		61	7	32	
1100	53	8	39		43	13	24	20
1150	45	9	30	16	40	15	16	29

M: mullite; A: Al_2O_3; K′: $KAlSi_2O_6$; K″: $KAlSiO_4$.

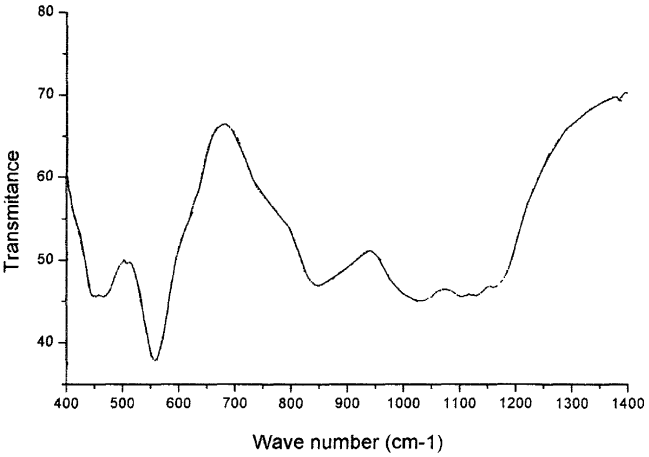

Fig. 4. FT-IR spectrum of mullite powder prepared at 950 °C for 6 h with $Al_2O_3/SiO_2 = 0.9$ and Na_2SO_4 (mol%) = 50.

crystals (Fig. 5c) and clusters of smaller angular crystals (Fig. 5d).

From TEM (Fig. 6) and X-EDS investigations (Table 6), the three kinds of particles were identified, respectively, as mullite, alumina and silica.

As previously said, the dwell time had almost no effect on the proportion of mullite or on the yield, but influenced the morphology of the mullite particles: rods for 4 h (Fig. 7a) and needles for 6 h (Fig. 7b). The transformation cannot be attributed to a decrease in the size of the rods (indeed the opposite effect would be expected as the dwell time increased) but to splitting of rods leading to bundles of needles (Figs. 5b and 7b).

Table 5
Attribution of FT-IR bands for a sample obtained at 950 °C for 6 h in molten Na_2SO_4

Wave number (cm^{-1})	Attribution
450	α-Alumina
460	Silica
557	Mullite
590	Mullite
600	α-Alumina
640	α-Alumina
730	Mullite
820	Mullite
1030	Silica
1090	Silica
1120	Mullite
1175	Mullite

Table 6
X-EDS analysis: atom% of Al and Si in each kind of particle

Element	Needles	Large plates	Small crystals
Al	27.89	63.51	2.47
Si	9.68	0.01	28.41

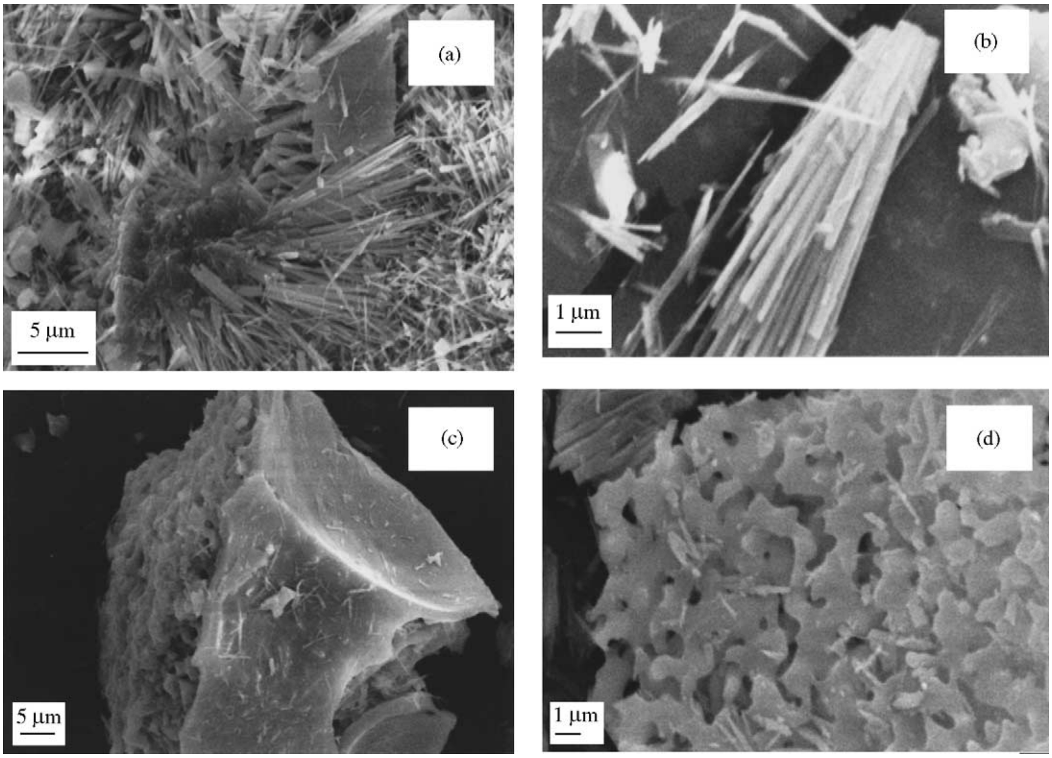

Fig. 5. SEM micrographs of mullite powder prepared at 950 °C for 6 h with $Al_2O_3/SiO_2 = 0.9$ and Na_2SO_4 (mol%) = 50. General view (a), area rich in mullite (b), area rich in a Al_2O_3 (c) and area rich in amorphous SiO_2 (d).

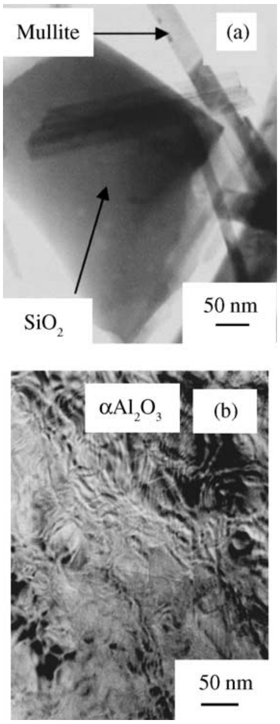

Fig. 6. TEM micrographs of mullite powder prepared at 950 °C for 6 h, with $Al_2O_3/SiO_2 = 0.9$ and Na_2SO_4 (mol%) = 50. Area showing a large crystal of SiO_2 and some mullite needles (a), area rich in a Al_2O_3 (b).

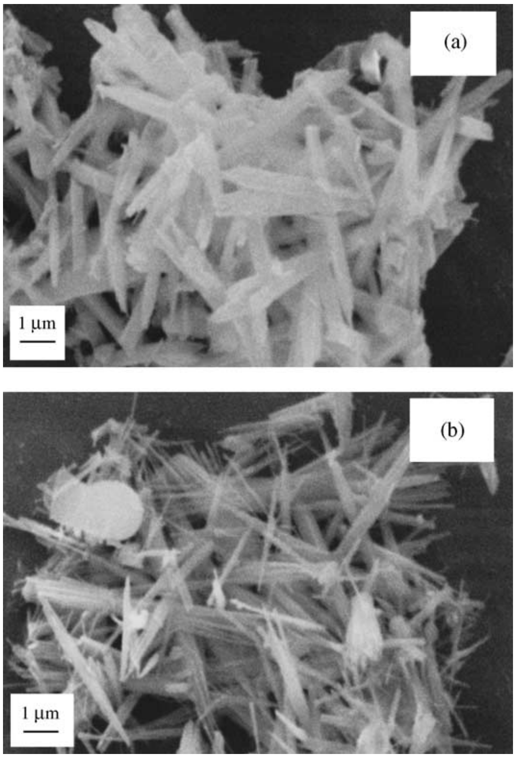

Fig. 7. Influence of dwell time on the size of mullite needles: 4 h (a) and 6 h (b).

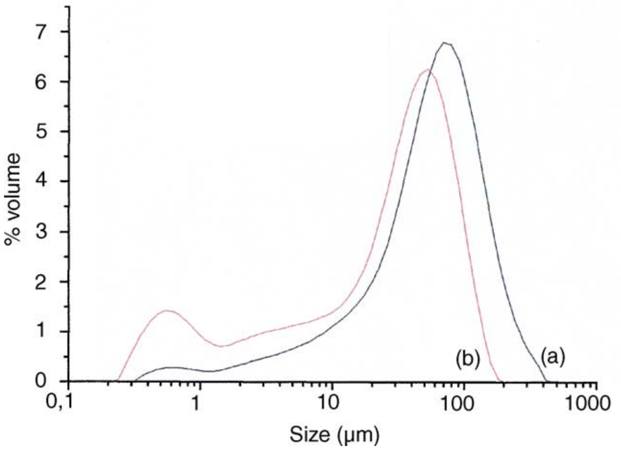

Fig. 8. Size distribution curve of mullite powder prepared at 950 °C for 6 h with $Al_2O_3/SiO_2 = 0.9$ and Na_2SO_4 (mol%) = 50. Without ultra-sonication (a), with ultra-sonication for 5 min (b).

3.3.3. Granulometric analysis

The size distribution curves showed a bimodal distribution centered around 70–80 and 0.6–0.7 μm (Fig. 8, curve a). Ultra-sonication for 5 min increased the proportion of small particles and shifted the signal representative of the other population toward sizes centered around 45–55 μm (Fig. 8, curve b). The submicronic population is then probably composed of mullite needles. As for the other population, it can be representative of agglomerates of mullite needles (Fig. 7b), alumina particles (Fig. 5c) or silica (Fig. 5d).

3.3.4. Elimination of minor phases

According to Katsuki,[28] mullite is insoluble in basic media. Our experiments corroborated that mullite is not soluble in 3 M NaOH and showed that it is not soluble in 3 M HCl either. So, in order to eliminate α-Al_2O_3 and amorphous SiO_2 in mullite samples, heating under reflux for 3 h was tested. Alumina, could not be eliminated by heating in 3 M HCl. On the contrary, amorphous silica was dissolved by boiling in 3 M NaOH, then cooling and leaving the mullite and alumina suspension under stirring for 9 h. Chemical analysis of the non-dissolved powder, after filtration and washings, gave the following molar contents: mullite 98.3%, alumina 1.7%.

4. Discussion

Generally, mullite formation depends mainly upon the crystalline form of the starting materials.[29,30]

So as to get a better insight into the mechanism of formation of mullite in molten alkali-metal sulfate(s), reactions with each of the two starting materials were carried out in molten Na_2SO_4 at 950 °C for 6 h. Aluminum sulfate led first to γ-Al_2O_3, which then transformed in α-Al_2O_3, whereas amorphous silica crystallized into cristobalite. The presence of alkali-metal cations, even in very low amounts, is likely to considerably decrease the crystallization temperature of silica[31] and to increase the temperature of the phase transformation of γ- to α-alumina.[32]

The α-alumina obtained and cristobalite were intimately mixed in the proportion $3Al_2O_3/2SiO_2$ and reacted first in the solid state at 1500 °C (heating rate 150 °C/h, dwell time 2 h) and second at 950 °C for 6 h in the presence of a molten Na_2SO_4 flux. The formation of mullite was never observed. It did not occur either in the reaction of α-alumina and amorphous silica with molten Na_2SO_4 which led only to the crystallization of silica. Therefore, it was clearly demonstrated that silica, either amorphous or crystallized, does not react with α-alumina to form mullite.

In contrast, the formation of mullite and α-alumina occurred when mixtures of aluminum sulfate and silica, either amorphous or crystallized, reacted with molten Na_2SO_4 or a eutectic mixture $(Na_{0.8},K_{0.2})_2SO_4$. Consequently, it was concluded that mullite is formed by the reaction of silica with γ-alumina. The proportion of mullite was significantly higher when amorphous silica was involved; this can be easy understood if it is accepted, in agreement with Saito et al.[33], that the transformation γ- to α-alumina is slower in the presence of amorphous silica than in the presence of cristobalite. In fact, in the reactions of aluminum sulfate and silica with molten Na_2SO_4 or eutectic $(Na_{0.8},K_{0.2})_2SO_4$, the formation of mullite via $3\gamma Al_2O_3 + 2SiO_2 \rightarrow 3Al_2O_3 \cdot 2SiO_2$ and the polymorphic transformation γ- to α-Al_2O_3 are in competition. Indeed, it is usual to obtain a higher proportion in mullite for an initial Al_2O_3/SiO_2 ratio of 0.9 where the silica content is above that of mullite, than for an initial ratio of 2.0 where the silica content is below that of mullite. In regard to α-alumina, the proportion of mullite was always very significant which shows that the reaction kinetics of γ-alumina with silica are much faster than those of the polymorphic transformation γ- to α-alumina. Therefore, the reaction of aluminum sulfate and silica towards molten sodium sulfate or eutectic sodium sulfate–potassium sulfate at 900–950 °C promotes the formation of mullite.

5. Conclusion

Mullite can be prepared in significant proportions and with a satisfactory yield, by reaction at 950 °C for 6 h of anhydrous aluminum sulfate and silica in molten Na_2SO_4 or eutectic $(Na_{0.8},K_{0.2})_2SO_4$. Amorphous silica and α-alumina are present beside mullite in the reaction products. The silica is eliminated by treatment with 3 M NaOH. The alumina cannot be eliminated. Its presence comes from competition between formation of mullite by reaction of γ-alumina and silica and the polymorphic transformation γ- to α-alumina. Reactions carried out with optimized parameters led to a powder containing 98.7 wt.% of mullite and 1.3% of α-Al_2O_3; it is characterized by an acicular morphology and a specific surface area close to 20 m^2/g.

When the reactions were performed in the same conditions, but replacing Na_2SO_4 or eutectic mixture by K_2SO_4 alone, a third crystallized phase was always present beside mullite and α-alumina.

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