

Synthesis of Mullite Precursors in Molten Salts. Influence of the Molten Alkali Nitrate and Additives

L. Saadi,^{a*} R. Moussa,^a A. Samdi^a and A. Mosset^b

^aEquipe Microstructure et Physicochimie des Matériaux, Faculté des Sciences Aïn Chock, BP 5366, Maârif, Casablanca, Morocco

^bCEMES-CNRS, 29 rue J. Marvig, 31055 Toulouse, France

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Abstract

Silica gel and aluminium salt, in the stoichiometric ratio for mullite ($Al/Si=3$), have been used to prepare the mullite precursor by reaction in molten alkali nitrates at 450°C. The influence of the nitrate ($NaNO_3$, KNO_3 or mixture $NaNO_3-KNO_3$) and the additives (Ca^{2+} , Ba^{2+} , Bi^{3+}) on the phase transformations has been followed between 1000 and 1400°C. It appears that molten $NaNO_3$ favours the crystallization of cristobalite and $\alpha-Al_2O_3$ whereas KNO_3 inhibits the formation of silica and mullite. The mixture $NaNO_3-KNO_3$ seems to be the best choice. Addition of foreign cations improves the mullite formation and favours the synthesis of $\theta-Al_2O_3$, especially in the case of Bi^{3+} . But the crystallization temperature of mullite is not changed.

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1 Introduction

Recently, several research papers on mullite have shown that particular additives introduced during the sintering of mullite-based ceramics improve the physical properties of the materials.^{1–3} However, few studies on the effect of these additives during the preparation of the mullite precursor, have been published.^{4–8} Some oxides which can form a solid solution with mullite such as Fe_2O_3 or TiO_2 ,^{4,5} induce an increase of the unit cell volume and of the crystallite size when they are added in notable proportion (10 and 3%, respectively). The addition

of Fe_2O_3 leads to an important decrease (200°C) of the crystallization temperature of the mullite and changes the morphology;^{6–8} the crystal form changes from parallelepipedic to acicular. The calcium oxide CaO , despite its low solubility in mullite improves the formation of mullite and induces a considerable increase of the grain size.^{9,10} Addition of cations such as Ca^{2+} , Ba^{2+} and Be^{2+} gives the same improvement and allows the mullite crystallization at lower temperatures (1200°C) by reaction of corundum and cristobalite.¹¹

In this paper, the mullite precursors is prepared by the molten salt method. The influence of the molten nitrate and of the additives (Ca^{2+} , Ba^{2+} , Bi^{3+}) on the phase transformations is followed in the temperature range 1000–1400°C.

2 Experimental

Starting products were silica gel (Prolabo) and aluminum sulfate $Al_2(SO_4)_3 \cdot 18H_2O$ (Prolabo). This aluminum salt was chosen as a result of a previous study concerning the influence of the Al salt on the mullite formation.¹² The two products, in the stoichiometric ratio $Al/Si=3$, were carefully mixed with a large excess of alkali nitrate, heated in air to 150°C (heating rate: 150°C/h⁻¹) and kept at this temperature during 30 min. Then the temperature was increased to 450°C and maintained during 2 h. The so-obtained precursor was separated from the nitrate by several aqueous washings and filtrations and finally dried in air at 110°C for 12 h. The chemical analysis shows that the residual content of Na or K does not exceed 1.5%.¹² The powders prepared in molten $NaNO_3$, KNO_3 and $NaNO_3-KNO_3$ are abbreviated as SSNa, SSK and SSNaK, respectively.

*To whom correspondence should be addressed

The role of the additives (Ca^{2+} , Ba^{2+} , Bi^{3+}) was studied in the case of the SSNaK powders. These cations were introduced as chlorides with a mass percentage of 3%.

Precursors were submitted to a pretreatment at 800°C during 2 h in order to eliminate sulfate and chloride anions. Then, the samples were calcined in air during 2 h at temperatures in the range 1000 – 1400°C (heating rate: $10^\circ\text{C}/\text{min}^{-1}$).

Products of reaction were identified by X-ray powder diffraction (Seifert XRD3000 diffractometer— $\text{CuK}\alpha$ radiation—graphite monochromator—divergence slit) and comparison to the JCPDS files. A semi-quantitative analysis of the crystalline phases was done from peak intensities by calculation of the relative intensity of the main peak in each phase using the formula:

$$I_{X'} = I_X / (I_c + I_m + I_\alpha + I_\theta)$$

where $I_{X'}$ is the relative intensity of the main peak of the phase X , I_X , I_c , I_m , I_α and I_θ the measured intensities of the main peak for phase X , cristobalite, mullite, corundum and $\theta\text{-Al}_2\text{O}_3$, respectively.

Infrared studies were carried out on Nicolet 205 fourier transform spectrometer by the KBr pellet technique.

3 Results and Discussion

3.1 Influence of the alkali nitrate

Table 1 and Fig. 1 gather the results obtained for the precursors prepared in the three different molten nitrates.

In each case, the powders prepared at 450°C are amorphous. The influence of the alkali nitrate only appears after the thermal treatment. The SSK powders, prepared in KNO_3 , are ill-crystallized up to 1200°C . However, $\theta\text{-Al}_2\text{O}_3$ is present at 1200°C . $\alpha\text{-Al}_2\text{O}_3$ begins to form at 1300°C and is the only product at 1400°C . For the SSNa powders, $\alpha\text{-Al}_2\text{O}_3$ appears at 1100°C in mixture with $\theta\text{-Al}_2\text{O}_3$. Mullite begins to crystallize at 1300°C and constitutes a third of the mixture prepared at 1400°C . In the equimolar nitrate mixture (SSNaK powders), the prepared precursor presents a behaviour similar to

Table 1. Crystalline phases observed in the temperature range 1000 – 1400°C depending on the alkali nitrate ($\theta = \theta\text{-Al}_2\text{O}_3$, $\gamma = \gamma\text{-Al}_2\text{O}_3$, $\alpha = \alpha\text{-Al}_2\text{O}_3$, C = cristobalite, M = mullite)

$T(^\circ\text{C})$	SSNa	SSK	SSNaK
1000	γ or θ	γ or θ	γ or θ
1100	$\theta + \alpha$	θ	θ
1200	$\theta + \alpha$	θ	$\theta + \text{M}$
1300	$\theta + \alpha + \text{C} + \text{M}$	$\theta + \alpha$	$\theta + \alpha + \text{M}$
1400	α (63.9) C (4.4) M (31.7)	α	α (60.1) M (39.9)

the one observed for the SSNa powders. There is no cristobalite in the final product and the mullite forms 40% of the mixture.

Thus, it is quite obvious that the alkali cations present a strong influence on the thermal behaviour of the mullite precursor. When the potassium ion is the only cation, it inhibits the formation of mullite at 1400°C . On the contrary, the highest percentage of mullite is obtained with the mixture of potassium and sodium. This effect can tentatively be correlated to the with the mixture of

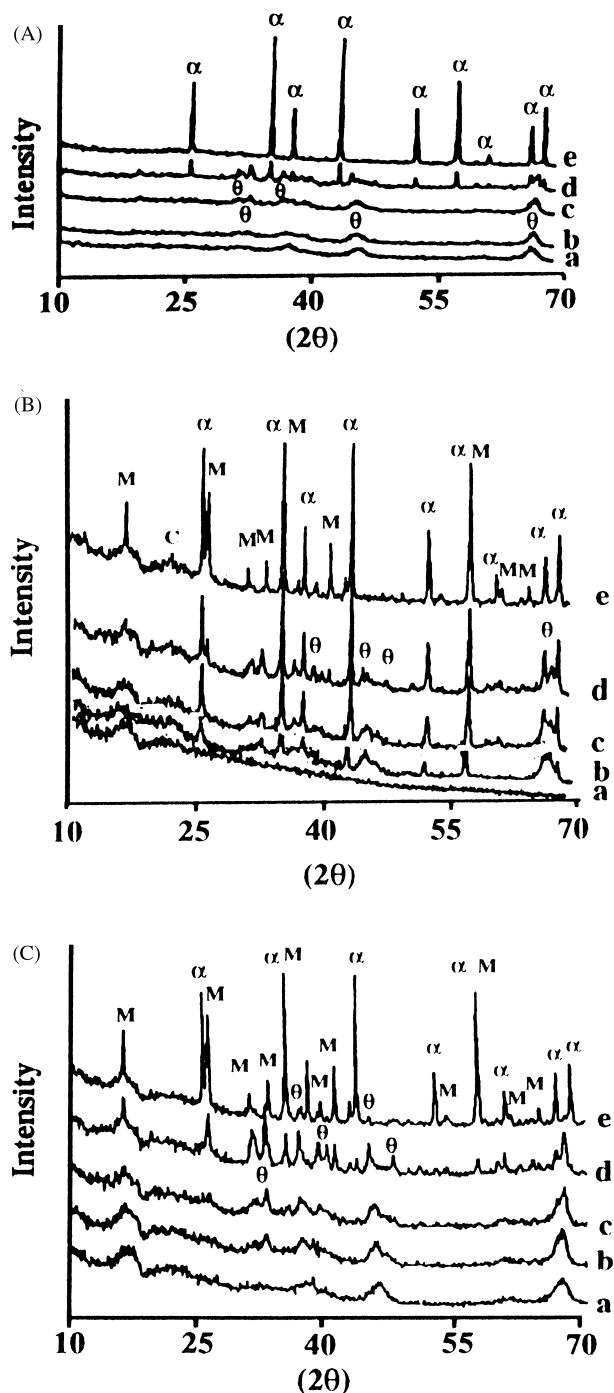


Fig. 1. XRD patterns of the samples (A) SSK, (B) SSNa and (C) SSNaK calcined at (a) 1000°C , (b) 1100°C , (c) 1200°C , (d) 1300°C and (e) 1400°C (M = mullite, C = cristobalite, $\theta = \theta\text{-Al}_2\text{O}_3$, $\alpha = \alpha\text{-Al}_2\text{O}_3$).

potassium and sodium. This effect can tentatively be correlated to the melting temperature of the nitrate medium. The binary phase diagram $\text{NaNO}_3\text{-KNO}_3$ gives 370°C for pure NaNO_3 , 335°C for pure KNO_3 and a minimum of 221°C for the equimolar mixture.¹³ It seems that the proportion of precursor which transforms into mullite at 1400°C increases when the melting point of the nitrate medium decreases. The same conclusion was already drawn for the effect of the molten alkali medium on the physical properties of Y-ZrO_2 .¹⁴

3.2 Influence of the additives

The effect of added cations was studied in the case of the SSNaK samples. Figure 2 shows the XRD patterns for samples containing Ca^{2+} , Ba^{2+} , Bi^{3+} and calcined at temperatures between 1000 and 1400°C .

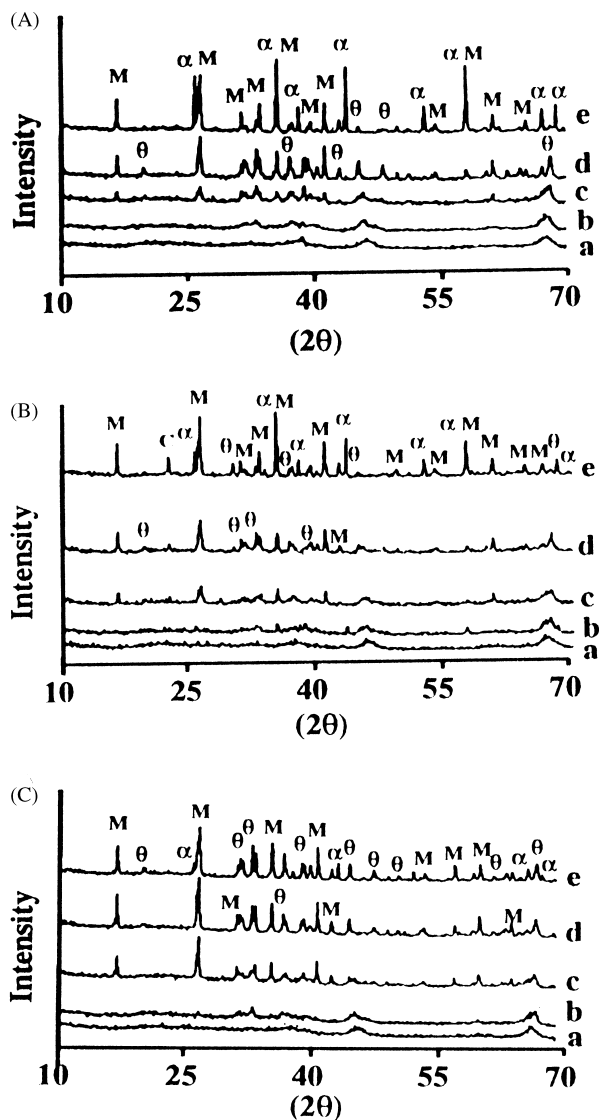


Fig. 2. XRD patterns of SSNaK samples containing (A) Ca^{2+} , (B) Ba^{2+} , (C) Bi^{3+} and calcined at (a) 1000°C , (b) 1100°C , (c) 1200°C , (d) 1300°C and (e) 1400°C (M = mullite, C = cristobalite, θ = $\theta\text{-Al}_2\text{O}_3$, α = $\alpha\text{-Al}_2\text{O}_3$).

From these patterns, it is quite obvious that the added cation has a strong influence on the phase transformations. Indeed, the calcination at 1400°C of the SSNaK precursor free from additives results in a mixture of mullite and corundum which is the major phase. When the cations are added, the mullite becomes the major phase and $\theta\text{-Al}_2\text{O}_3$ is stabilized at the expense of corundum. This last compound begins to crystallize only at 1400°C . On the contrary, the addition of such cations has no effect on the temperature of mullite crystallization which remains 1200°C . Wahl *et al.*¹⁰ report a decrease of the temperature of mullite formation from cristobalite and corundum where Ca^{2+} or Bi^{3+} is added. But the temperature decreases from 1500 to 1200°C , i.e. a final temperature identical to the one observed in the present study.

The residual vitreous phase, constituted mainly with amorphous SiO_2 , is put in obviousness by analysis by infrared spectroscopy, undertaken on the totality of samples calcined. Figure 3 shows the case of precursors calcined to 1400°C (bands to 1100 , 470 cm^{-1}).

The three cations have not exactly the same effect. Crystallization of amorphous silica in cristobalite is only observed for Ba^{2+} . The ratio $\theta/\alpha\text{-Al}_2\text{O}_3$ is approximately the same for Ba^{2+} and Ca^{2+} but very different for Bi^{3+} as shown in Table 2. In this last case, the ratio is inverted. But the main effect of the additives is the increase of the mullite proportion. The three cations present the same influence but Bi^{3+} seems to be the best one as it favours the crystallization of mullite and $\theta\text{-Al}_2\text{O}_3$, but not significantly: the precision of the XRD analysis is known to be rather low. This metastable

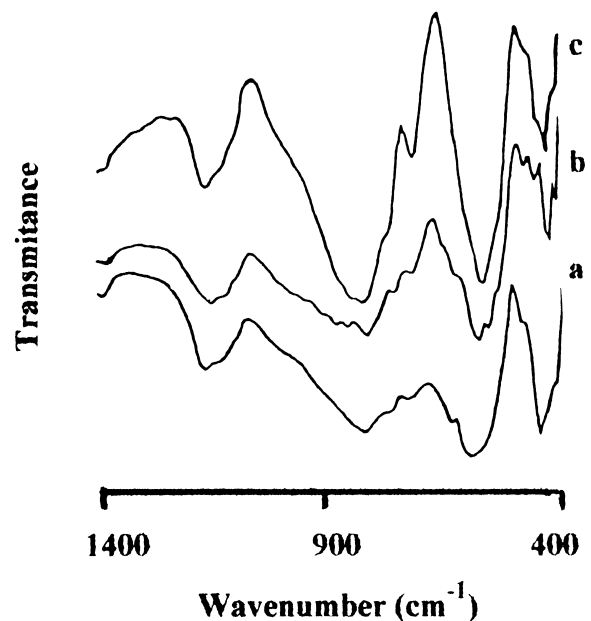


Fig. 3. Infrared spectra of SSNaK sample containing (a) Ca^{2+} , (b) Ba^{2+} , (c) Bi^{3+} and calcined at 1400°C .

Table 2. Relative intensities of the main peak for each crystalline phase in the SSNaK powders calcined at 1400°C with or without additives

Samples	Mullite	α -Al ₂ O ₃	α -Al ₂ O ₃	Cristobalite
SSNaK	39.9	0.0	60.1	0.0
SNNaK + BiC ₃	52.6	31.8	15.6	0.0
SSNaK + BaCl ₂	46.6	8.7	44.7	0.0
SSNaK + CaCl ₂	47.4	9.8	30.4	12.4

phase (θ -Al₂O₃) is at the origin of the mullite formation by reaction with amorphous silica.^{15,16}

4 Conclusions

The formation of mullite has been studied by reaction of silica gel and aluminum sulfate in a molten nitrate medium. The choice of the nitrate is important. KNO₃ completely inhibits the mullite formation at 1400°C; α -Al₂O₃ is the only crystalline phase. NaNO₃ is a better choice for the mullite formation but the amorphous silica partly crystallizes into cristobalite. The best molten medium seems to be an equilar mixture of NaNO₃–KNO₃. In this case, a mixture of α -Al₂O₃ and mullite is obtained with the highest percentage of mullite.

Addition of cations, Ca²⁺, Ba²⁺, Bi³⁺, in the reaction mixture allows to increase notably the percentage of mullite which becomes the major phase at 1400°C. Bi³⁺ appears to be the best choice for the mullite formation. However, the crystallization temperature of mullite remains equal to 1200°C.

References

1. Kapuri, N., Rai, K. N. and Upadhyaya, G. S., Sintering of mullite-based particulate composites containing ZrO₂. *J. Mater. Sci.*, 1996, **31**, 1481–1487.

2. Descamps, P., Sakaguchi, S., Poorteman, M. and Cambier, F., High temperature characterization of reaction sintered mullite–zirconia composites. *J. Am. Ceram. Soc.*, 1991, **74**, 2476–2481.
3. Richards, E. A., Goodbarake, C. J. and Sowman, H. G., Reaction and microstructure development in mullite. *J. Am. Ceram. Soc.*, 1990, **73**, 2404–2410.
4. Schneider, H., Thermal expansion of mullite. *J. Am. Ceram. Soc.*, 1990, **73**, 2073–2078.
5. Baudin, C., and Moya, J. S., Influence of titanium dioxide on the sintering and microstructural evolution of mullite. *J. Am. Ceram. Soc.*, 1984, **C-137–C138**.
6. McGee, T. D. and Wirkus, C. D., Mullitization of aluminosilicate gels. *Bull. Am. Ceram. Soc.*, 1972, **51**, 577.
7. Murthy, M. K. and Hummel, F. A., X-ray study of solid solution of TiO₂, Fe₂O₃ and Cr₂O₃ in mullite. *J. Am. Ceram. Soc.*, 1960, **43**, 267–273.
8. Pulhinge, D. D. R., Contribution à l'étude du frittage-réaction de céramiques à base mullite. Ph.D. thesis, University of Limoges, France, 1986.
9. Johnson, S. M. and Pask, J. A., Role of impurities of mullite from kaolinite and Al₂O₃–SiO₂ mixture. *Bull. Am. Ceram. Soc.*, 1982, **61**, 838–841.
10. Wahl, F. M., Grim, R. E. and Graf, R. B., Phase transformation in silica alumina mixtures as examined by continuous X-ray diffraction. *Am. Miner.*, 1961, **46**, 1064–1069.
11. Budnikov, P. P., Keshishyan, T. N. and Volkova, A. V., Effect of small additions on mullite formation at low temperatures. *Silikaty Okisly Khim. Vys. Temp.*, 1963, 233–243.
12. Saadi, L., Moussa, R., Samdi, A. and Mosset, A., Synthesis of mullite precursors in molten salts: influence of the aluminum source of salt. *Key Eng. Mat.*, 1997, **132–136**, 228–231.
13. Cook, L. P. and McMurrie, H. F., *Phase Diagrams for Ceramists*, Vol. VII. American Ceramic Society, Westerville, OH, 1989, p. 36.
14. Jebrouni, M., Elaboration de zircons et de dispersions alumine–zircone par réaction dans les sels fondus et caractérisation. Ph.D. thesis, University of Lyon, France, 1990.
15. Pach, L., Iratni, A., Hrabe, Z. and Komarneni, S., Sintering and crystallization of mullite in diphasic gels. *J. Mater. Sci.*, 1996, **30**, 5490–5496.
16. Wei, W. C. and Halloran, J. W., Transformation kinetics of diphasic aluminosilicate gels. *J. Mater. Sci.*, 1988, **71**, 581–590.