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# Mullite interaction with bismuth oxide from minerals and sol–gel processes

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**Abstract**

Mullite compounds with bismuth oxide in the $SiO_2$–$Al_2O_3$–$Bi_2O_3$ ternary system were synthesized from TEOS $(C_2H_5O)_4Si$, aluminum nitrate $Al(NO_3)_3{\cdot}9H_2O$ and bismuth nitrate $Bi(NO_3)_3$. Thermal and structural transformations were studied at temperatures ranging from 1000 to 1400 °C. The coexistence of $Al_4Bi_2O_9$ and $Bi_4Si_3O_{12}$ phases at temperatures up to 1000 °C was observed in compositions containing 5–31 mol% $Bi_2O_3$. Mullite is observed at temperature higher than 1000 °C in composition not exceeding 5 mol% of $Bi_2O_3$. Corundum coexist with a liquid above 1000 °C in all compositions containing more than 5 mol% $Bi_2O_3$. The liquid temperature is slightly above 1000 °C for all compositions. A tentative pseudo-binary diagram mullite-$Bi_2O_3$ is proposed. A similar system was studied with silico-aluminate compositions containing kaolinite and muscovite minerals. The occurrence of a liquid when $Bi_2O_3$ is added highly favors the mullite growth at temperature below 1200 °C. It is favored by local concentrations at interfaces of a transient liquid phase, which enhance the mobility of species.


*Keywords:* Ceramics; Chemical synthesis; Phase equilibria

## 1. Introduction

Mullite is an important high-technology ceramics for high temperature applications [1]. The addition of cations in the reaction mixture of mullite allows the improvement of the physical properties of sintered materials. $Ca^{2+}$ or $Ba^{2+}$ can be added [2], but the addition of $Bi^{3+}$ appears to be a promising way for mullite formation in compositions. It was also observed the effects of some oxides ($SnO_2$, $SbO_2$) in the phase formation and the microstructural evolution of mullite ceramics [3]. In general, $Bi_2O_3$ doping have a much better effects on densification than $SnO_2$ and $Sb_2O_3$, whereas the latter is an effective additive to decrease the temperature of mullite phase formation in diphasic gels [4]. The addition of other oxides which form a solid solution with mullite such as $Fe_2O_3$ or $TiO_2$ induces the increase of both the unit cell volume and of the crystallite size when they are added in large proportion (up to 10 mol%). In the case of $Fe_2O_3$, it leads to the decrease of the crystallization temperature (∼200 °C). Simultaneously the crystal morphology is also changed from parallelepipedic to acicular [5].

In mullite ceramics, some additives were considered to reduce the viscosity of the $SiO_2$-rich liquid phase, favoring a higher mobility of the diffusing species. The dissolution of $Al_2O_3$ species into the $SiO_2$-rich liquid phase controls the rate of the mullite formation [6]. Also, the aluminum compounds might act as nuclei for the crystallization of mullite crystal and the mullite formation temperature is significantly decreased.

The aim of the study is to determine the phase formation against temperature, from mullite-bismuth oxide compounds, which are synthesized using diphasic gels. The role of existing liquid phases is observed in the case of mullite crystallization in muscovite-kaolinite compounds.

## 2. Experimental

Mullite powders are usually prepared by methods such as co-precipitation using salts [2], sol–gel [2–7] and spray pyrolysis [8–10]. In this study, mullite compositions were synthesized with sol–gels using TEOS $(C_2H_5O)_4Si$, aluminum nitrate $Al(NO_3)_3{\cdot}9H_2O$ and bismuth nitrate $Bi(NO_3)_3$. Aluminum nitrate and bismuth nitrate were dissolved in aqueous solution

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Table 1
Compositions of mullite compounds.

| Sample | Stoichiometry | $Bi_2O_3$ (mol%) |
|---|---|---|
| 1 | $3Al_2O_3{\cdot}2SiO_2$ | 0 |
| 2 | $3Al_2O_3{\cdot}2(Si_{0.84}Bi_{0.16})\ O_2)$ | 2.69 |
| 3 | $3(Al_{1.8}Bi_{0.2})O_3{\cdot}2SiO_2$ | 4.0 |
| 4 | $3Al_2O_3{\cdot}2(Si_{0.7}Bi_{0.3})O_2)$ | 5.15 |
| 5 | $2Al_2O_3{\cdot}1.2SiO_2{\cdot}0.11Bi_2O_3$ | 3.40 |
| 6 | $2Al_2O_3{\cdot}1.2SiO_2{\cdot}0.54Bi_2O_3$ | 14.34 |
| 7 | $2Al_2O_3{\cdot}1.2SiO_2{\cdot}1.44Bi_2O_3$ | 30.88 |

of nitrite acid. TEOS was diluted in ethanol. Solutions were subsequently mixed at 60 °C and become gel after 4 days. Gels were dried at 110 °C for 24 h. In Table 1 the stoichiometry of used compounds are presented and reported in the ternary diagram $SiO_2$–$Al_2O_3$–$Bi_2O_3$ in Fig. 1 [11–13]. All compositions are along and beside the pseudo-binary mullite-bismuth oxide.

X-ray diffractions were performed with a D5000 (Bruker) and pattern refinements were obtained by the Rietveld method, using the FullProf software [14]. The thermal behavior of gels after calcinations at different temperatures up to 1100 °C was studied by DTA (Setsys, SETARAM) under air atmosphere at a constant heating rate of 10 °C $min^{-1}$. Curve backgrounds were corrected by preliminary experiments with α alumina.

## 3. Results and discussion

### 3.1. DTA study

Differential thermal analysis (DTA) of mullite gel exhibits typical endothermic peaks at 550–650 °C, due to the loss of hydroxyls and an exothermic peak at ∼980 °C related to the crystallization of Al–Si spinel. A second weak exothermic peak at ∼1250 °C corresponds to a secondary mullitization process and cristobalite crystallization [15,16].

DTA of samples containing bismuth (4–7 in Table 1), were performed after heating at 500 °C to preliminary remove all volatile species. The DTA curve of sample 4 in Fig. 2 presents four exothermal peaks at 530, 892, 958 and at 1044 °C.

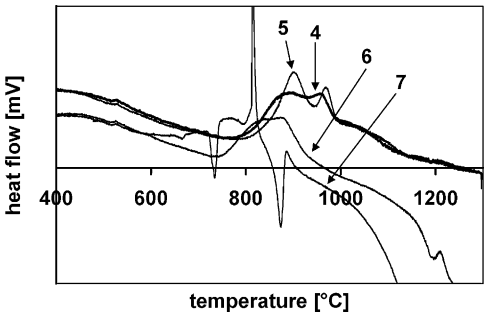


Fig. 2. DTA curve of samples 4–7.

With sample 5, the DTA curve in Fig. 2 indicates four exothermal peaks at 530, 905, 971 °C and one weak peak between 1000 and 1100 °C. DTA curve of sample 4 differs to that of sample 5 in the intensity of the two main exothermic peaks. With sample 5, the crystallization process is slightly more accentuated and occurs at a higher temperature.

The sample 6 in Fig. 2 exhibits three DTA exothermal peaks at 526, 885 and 1210 °C and one small endothermic peak at 730 °C.

In the case of sample containing 7, the DTA curve (Fig. 2) shows two endothermic peaks at 725 and 875 °C and two exothermal peaks at 815 and 1293 °C.

In this sample with the highest bismuth content, some peaks should be related to the transition of monoclinic α-phase to δ-phase (fcc, face central cubic) of bismuth oxide, which occurs at 705–1013 °C. The wide variation of the transition temperature is related to the purity of samples. The melting point of $Bi_2O_3$ is at 840 °C [17].

Whereas pure mullite (sample 1) presents a typical exothermic peak at 980 °C, mullite with more than 2 mol% bismuth exhibit a more complex behavior. The comparison of curves from sample 4 ($3Al_2O_3{\cdot}2(Si_{0.7}Bi_{0.3})\ O_2$) and from sample 5 (3.40 mol% bismuth oxide) shows a significant difference in intensity of the two main peaks. With sample 6 (14.34 mol% bismuth oxide), we observe a smoother variation, in comparison with curve variations of other samples. The weak peaks at 730 and at 885 °C are probably related to the transition of bismuth oxide. In sample 7 (30.88 mol% bismuth), we observe three peaks, which are originated from transitions of bismuth oxide (735, 815 and 875 °C). The high temperature peaks at 1210 °C for mullite with 14.34 mol% Bi and at 1193 °C in mullite with 30.88 mol% Bi are due to the structural transformation of Al–Si spinel to orthorhombic mullite. In general, the curve slope at high temperature increases with the bismuth content.

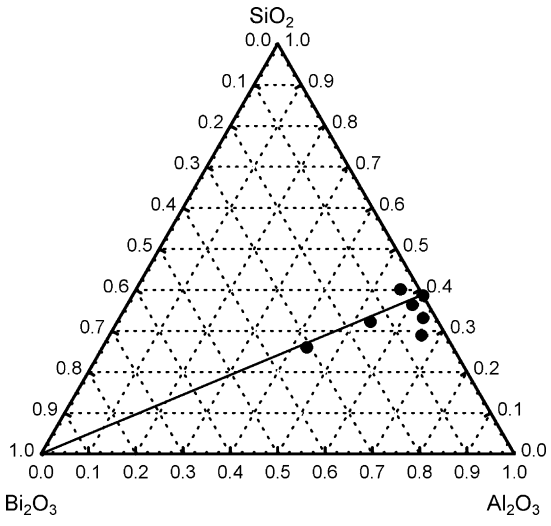


Fig. 1. Compositional area (mol%) in the ternary diagram $SiO_2$–$Al_2O_3$–$Bi_2O_3$.

### 3.2. X-ray experiments

In a first approach, dried gels of samples 1–3 were heated at 1350 °C for 3 h before XRD measurements. The Rietveld method was used to determine the mullite structural characteristics with bismuth additions in initial compositions.

When the bismuth content increases, the orthorhombic mullite structure and the ideal stoichiometry $3Al_2O_3{\cdot}2SiO_2$ are

Table 2
Quenching temperatures of samples 4–7.

| Sample | Temperature |
|---|---|
| 4 | 1000 °C, 1100 °C |
| 5 | 1000 °C, 1100 °C |
| 6 | 1000 °C, 1100 °C, 1250 °C |
| 7 | 770 °C, 845 °C, 930 °C, 1200 °C |

always obtained. But a significant background variation is observed from an increasing content of liquid phase.

For a better understanding of transformations with temperature, X-ray diffractometry was used with heated samples 4–7, at typical temperatures near the onset and end of peaks in DTA curves of Fig. 2. During all thermal cycles, we used a 30 min holding time were followed by a quenching stage to retain a steady state of phases. Temperature values for samples are reported in Table 2.

Patterns of sample 5, containing 3.40 mol% of $Bi_2O_3$ and heated at 1000 and 1100 °C are in Fig. 3. It is seen that only orthorhombic mullite with the stoichiometry $3Al_2O_3{\cdot}2SiO_2$ is identified.

Fig. 4 shows X-ray patterns of sample 4 containing 5.15 mol% of $Bi_2O_3$ ($3Al_2O_3{\cdot}2(Si_{0.7}Bi_{0.3})O_2$) heated at 1000 and 1100 °C. At 1100 °C, peaks from mullite, aluminum bismuth oxide and aluminium bismuth oxide are clearly recognized. Identified phases are orthorhombic mullite $Al_2(Al_{2.8}Si_{1.2})O_{9.54}$ (pattern no. 01-084-1205), cubic bismuth silicon oxide $Bi_{12}Si_{0.87}O_{20}$ (pattern no. 01-084-0090) and aluminium bismuth oxide $Al_4Bi_2O_9$ (pattern no. 00-025-1048). At 1100 °C, peaks from sample 4 indicate that the quantity of aluminum bismuth oxide vanishes and that the relative content of bismuth silicon oxide increases in comparison to that of mullite.

For both patterns the large variation of the background indicate the presence of an amorphous phase or a liquid. Correspondingly, the smooth endothermic variation in the DTA curve of Fig. 2 above 958 °C should be related to the liquid formation.

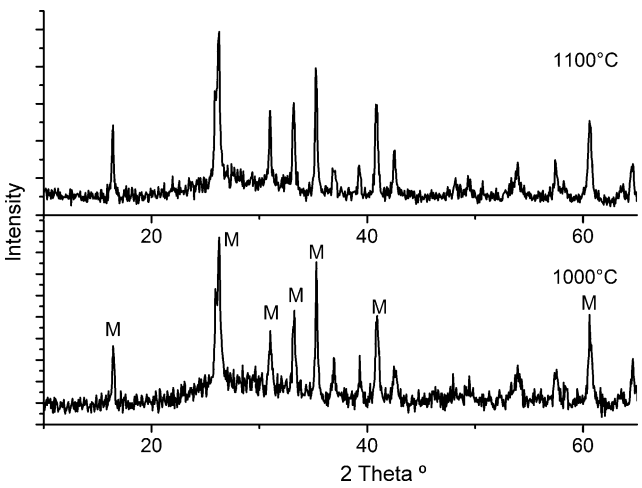


Fig. 3. X-ray patterns of sample 5 heated at 1000 and 1100 °C.

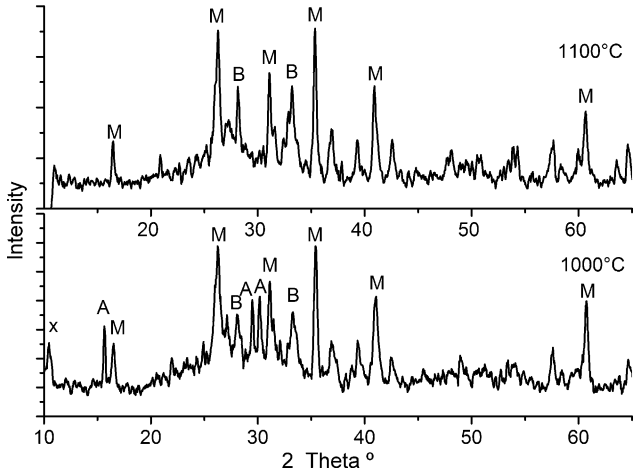


Fig. 4. X-ray diffractogramms for sample 4 ($3Al_2O_3{\cdot}2(Si_{0.7}Bi_{0.3})O_2$) calcined at 1000 and 1100 °C (M, mullite; A, aluminum bismuth oxide; B, bismuth silicon oxide).

In Fig. 5, sample 6 with 14.34 mol% bismuth heated at 1000 °C has peaks from bismuth silicon oxide and aluminum silicon oxide. But a new phase is evidenced with a major peak at 10.44° 2$\theta$. This new phase also occurs in sample 4 at 1000 °C and in all samples containing more than 3 mol%, below 1100 °C. The stoichiometry of this phase is supposed to be similar to an aluminium silicon bismuth oxide, but further work will be necessary to details the structural characteristics. At the 1000 °C temperature, the background variation indicates the occurrence of a liquid, in accordance to the DTA curve, which shows a significant endothermic variation at 885 °C.

At 1100 and 1250 °C, sample 6 show the progressive formation of sharp peaks from a single phase, very similar to corundum (pattern no. 00-010-0173). Structural characteristics of this phase were identified after heating at 1200 °C during 14 h holding time and sampling a single crystal. The obtained structural parameters are the following: system hexagonal (rhomboedric, R-3C or R3C); $a = 4735$ Å; $b = 4735$ Å; $c = 12{,}941$ Å; $\alpha = 90°$; $\beta = 90°$; $\gamma = 120°$. These data are close to that of corundum ($\alpha$-$Al_2O_3$).

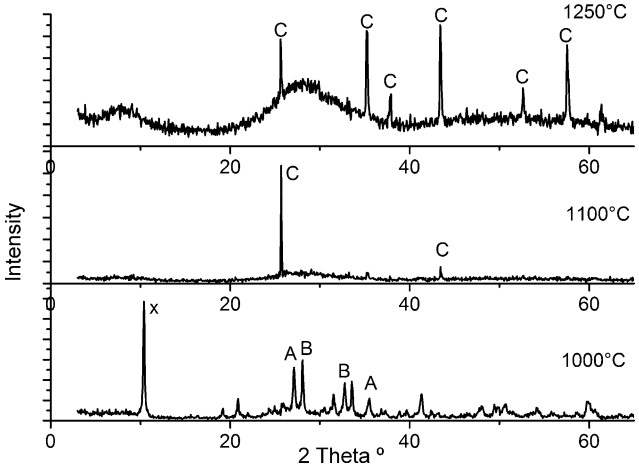


Fig. 5. X-ray patterns of sample 6 mullite with 14.34 mol% $Bi_2O_3$, heated at 1000, 1100 and 1250 °C. C, Corundum.

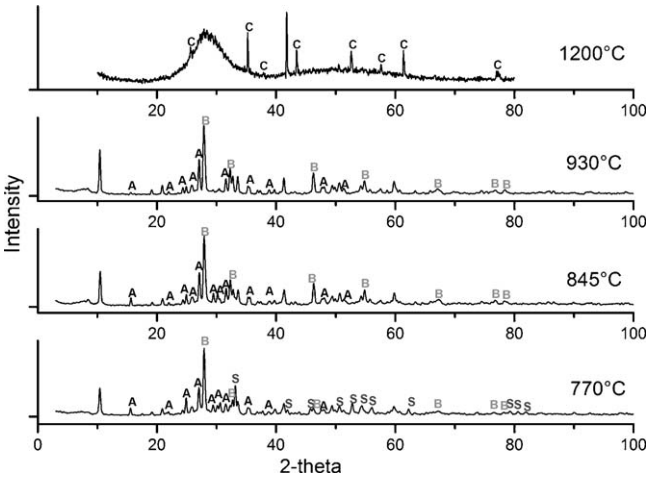


Fig. 6. X-ray patterns of sample 7 mullite with 30.88% $Bi_2O_3$, heated in the 770–1250 °C temperature range (A, aluminum bismuth oxide; B, bismuth silicon oxide; C, corundum; S, sillenite).

For a higher $Bi_2O_3$ content (Fig. 6), sample 7 with 30.88 mol% $Bi_2O_3$ heated at 770 °C has peaks from bismuth silicon oxide, aluminum silicon oxide and bismuth silicate (sillenite $Bi_{12}SiO_{20}$, pattern no. 00-037-085). After heating at 845 and 930 °C, peaks from sillenite vanished and peaks from bismuth silicon oxide and aluminum bismuth oxide are present. At 1200 °C, peaks from the same phase already observed in sample 6, are very similar to those of corundum peaks.

The major peak at 10.44° 2$\theta$, observed at 770, 845 and 930 °C, is similar to that from sample 6. From these experiments, we note the occurrence of a liquid at temperatures above 930 °C, which corresponds to the strong endothermic variation in the DTA curve of Fig. 2.

### 3.3. Three-phases diagram

The literature review reveals the lack of information about the $SiO_2$–$Al_2O_3$–$Bi_2O_3$ ternary system. Only two-phase diagrams are reported: $Al_2O_3$–$SiO_2$ [12], $Al_2O_3$–$Bi_2O_3$ [11], $Bi_2O_3$–$SiO_2$ [13]. The $Al_2O_3$- and $SiO_2$-rich regions of two binary diagrams are in Fig. 7a and b respectively. We observe in the $Al_2O_3$–$BiO_3$ system the presence of the $Al_4Bi_2O_9$ phase which was observed in compositions 6 and 7 containing 20–40 mol% $Bi_2O_3$. Beside, the alumina-rich region indicates a first liquid at 1070 °C. This temperature is very similar to the temperature range for liquid phases detection in compositions 4, 5, 6 and 7 in Figs. 4 and 5. The $Bi_2O_3$–$SiO_2$ system is different as it contains the $Bi_4Si_3O_{12}$ phase, which is different from the $Bi_{12}Si_{0.87}O_{20}$ detected in samples 6 and 7 at 1000 and 1100 °C. But the first liquid appears at the 1020 °C temperature, close to the liquid temperature of our samples.

A tentative pseudo-binary diagram mullite-$Bi_2O_3$ is presented in Fig. 8. The liquid limit is slightly below 1000 °C, for a large $Bi_2O_3$ content. At temperature higher than 1000 °C, mullite is observed up to about 5 mol% of $Bi_2O_3$ and above, corundum coexist with a liquid. Bismuth silicon oxide and aluminum bismuth oxide are transient phases, which temperature stability domain depends on the $Bi_2O_3$ content. The

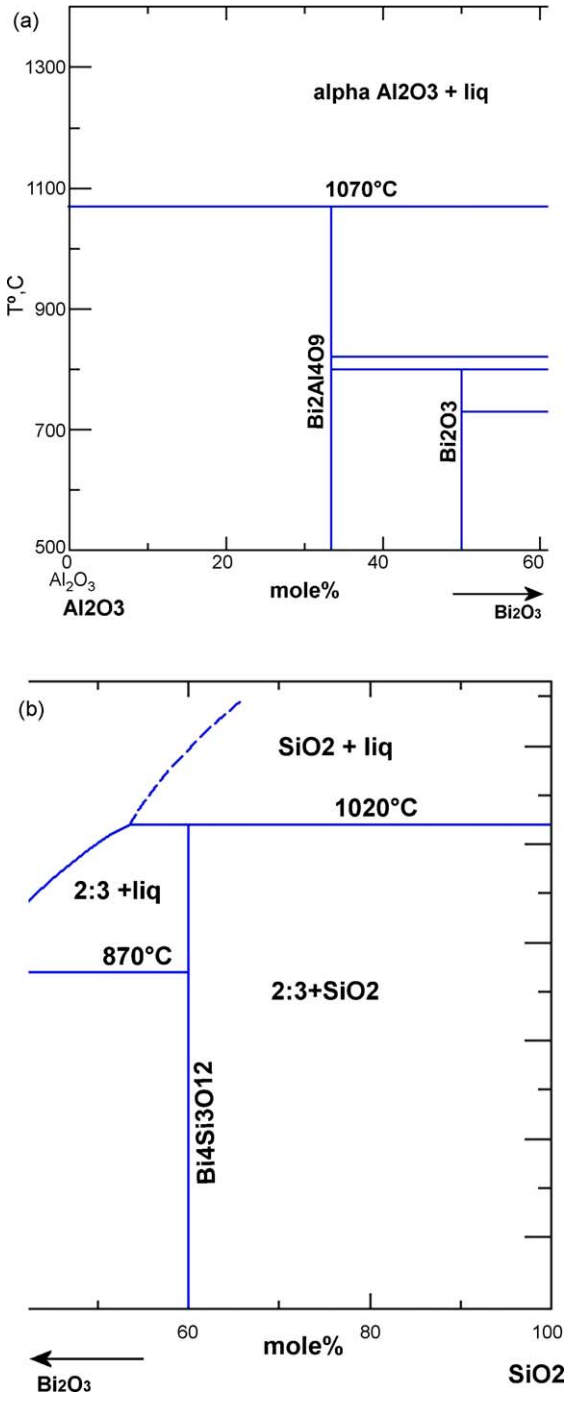


Fig. 7. Binary diagrams in the system $SiO_2$–$Al_2O_3$–$Bi_2O_3$.

sillenite phase is very specific and appears temporarily for higher $Bi_2O_3$ content.

### 3.4. Mullite formation in phyllosilicate mixes

The effect of $Bi_2O_3$ addition on phase formation and microstructural evolution of mullite ceramics from kaolinite-muscovite minerals was investigated. In this material, $Bi_2O_3$ was added as a thin coating onto muscovite flakes before the muscovite-kaolinite mixing, using a bismuth nitrate aqueous

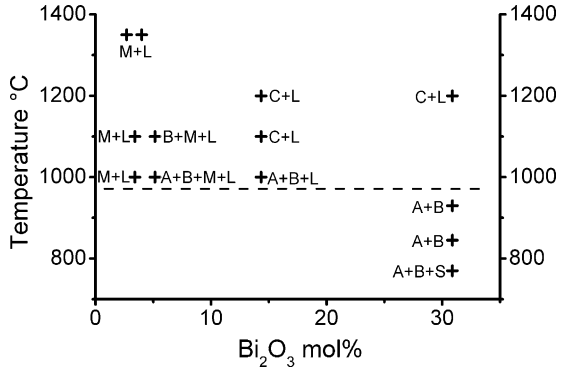


Fig. 8. Projection in the pseudo-binary phase diagram $Bi_2O_3$, mullite; B, bismuth silicon oxide; A, aluminum bismuth oxide; S, sillenite; M, mullite; C, corundum.

solution. The $Bi_2O_3$ to mineral ratio in sintered material is close to 5 mol%, which favors mullite formation during sintering. It indicates that the relative concentration of bismuth oxide to mullite at crystallite interfaces does not exceeds 5 mol%, as it was reported in the pseudo-binary diagram of Fig. 8.

With muscovite-kaolinite compound, SEM observations point to the acceleration of mullitization with the presence of $Bi_2O_3$. In Fig. 9, the surface of muscovite sintered at 1250 °C for 1 h holding time shows large anisotropic mullite grains, which average length attains 30 μm.

In this material, whereas the probable occurrence of crystallized compounds of $Bi_2O_3$ with alumina and silica, no different crystallizations than mullite are found by X-ray. The most interesting point is the significant mullite crystallization and growth at low temperature. $Bi_2O_3$ highly favors the densification during sintering and this effect is attributed to the specific role of a local low-viscosity liquid phase in the systems.

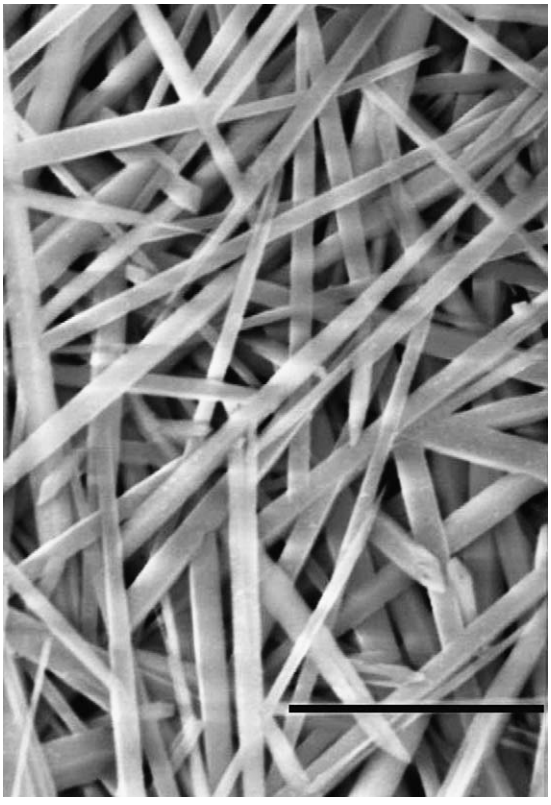

Fig. 9. Microstructure at the muscovite–kaolinite interface when 5 mol% of $Bi_2O_3$ is added. Bar = 20 μm.

## 4. Conclusion

Mullite doped by bismuth was synthesized by a sol–gel process. Effect of $Bi_2O_3$ on phase formation and microstructural evolution of mullite ceramics were investigated by different methods. They all point to the important role of $Bi_2O_3$ on mullite formation. For all studied compositions, a liquid phase appears at temperature close to 1000 °C. At low bismuth content, mullite is crystallized in all mixes above 1000 °C. When bismuth content exceed about 5 mol%, mullite is no longer crystallized and both bismuth silicon oxide, aluminum bismuth oxide, sillenite and corundum are present in variable contents.

In silico-aluminate compositions, the occurrence of a liquid when $Bi_2O_3$ is added highly favors the mullite growth at temperature below 1200 °C. It is favored by local concentrations at interfaces of a transient liquid phase, which enhance the mobility of species.

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