Mullite interaction with bismuth oxide from minerals and sol-gel processes

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Abstract

The high temperature treatment of kaolinite-muscovite alternate layers doped by bismuth oxide was studied by TGA and DTA, X ray diffraction, and electron microscopy (SEM). Thermal analyses shows that the two main transformation stages are the dehydroxylation of phyllosilicates and the structural reorganization of the whole assembly. During dehydroxylation, a progressive decrease of the structural order of kaolinite and muscovite occurs. It is more significant at temperature above 1000°C and mullite, glass and Al-rich oxides are formed. Mullite exhibits an accentuated acicular morphology along 3 preferential orientations in relation to the remaining structure in the basal $(001)_{musc}$ planes of the former muscovite. With addition of bismuth oxide, SEM observations point to the strong accentuation of mullite growth along the c axis, at the very low temperature of 1050°C. This behavior was studied with various mullite-bismuth oxide compounds at temperatures ranging from 1000°C to 1400°C. Sol-gel processing were performed with TEOS $(C_2H_5O)_4Si$, aluminum nitrate $Al(NO_3)_3.9H_2O$ and bismuth nitrate $Bi(NO_3)_3$. From Rietveld refinements of X ray diffraction patterns it was found that bismuth doesn't form a specific phase with mullite during the mullite nucleation and growth. At low Bi_2O_3 content, mullite coexists with amorphous silico-aluminate phases, even at high temperature. When the Bi_2O_3 content increases above 12mol%, mullite is no longer crystallized. Above 750°C, aluminum bismuth oxide coexists with silicon bismuth oxide. The liquidus temperature is below 1100°C and decreases with Bi_2O_3 additions. Above the liquidus, only corundum and a liquid coexist. A tentative mullite-Bi_2O_3 binary phase diagram is then proposed. These results evidence the Bi_2O_3 role on the early and large mullite growth in kaolinite-muscovite materials. Particularly, a very low quantity of a low viscous phase favor the local mobility of diffusing species and promotes the nucleation and growth of very large mullite crystals. In this way, highly textured and dense ceramics are obtained at low sintering temperature. Thin substrates (<500μm) present specific mechanical behaviors with the deviation of cracks along mullite layers.

Keywords: Muscovite, Kaolinite, Mullite, Bi_2O_3.

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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 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. 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 10mol%). 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 [4].

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 [5]. Also, the aluminum compounds might act as nuclei for 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.

Experimental

Mullite powders are usually prepared by methods such as co-precipitation using salts [2], sol-gel [1,6] and spray pyrolysis [7-9]. In this study, mullite compositions were synthesized with sol-gels using TEOS $(C_2H_5O)_4Si$, aluminum nitrate $Al(NO_3)_3.9H_2O$ and bismuth nitrate $Bi(NO_3)_3$. Aluminum nitrate and bismuth nitrate were dissolved in aqueous solution 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 hour. In table I the stoechiometry of used compounds are presented and reported in the ternary diagram SiO_2-Al_2O_3-Bi_2O_3 in figure 1 [10-12]. All compositions are along and beside the pseudo-binary mullite-bismuth oxide.

ref	Stoechiometry	Bi_2O_3 wt% - mol%
1	$3Al_2O_3 \cdot 2SiO_2$	0 – 0
2	$3Al_2O_3 \cdot 2(Si_{0,84}.Bi_{0,16})\,O_2)$	15- 19
3	$3(Al_{1,8}.Bi_{0,2})O_3 \cdot 2SiO_2$	26 - 33
4	$3Al_2O_3 \cdot 2(Si_{0,7}.Bi_{0,3})\,O_2)$	26 - 42
5	$3Al_2O_3 \cdot 2SiO_2 +$ 5 mol% Bi_2O_3	5.2 – 5
6	$3Al_2O_3 \cdot 2SiO_2 +$ 20 mol% Bi_2O_3	18 – 20
7	$3Al_2O_3 \cdot 2SiO_2 +$ 40 mol% Bi_2O_3	30 - 40

Tab. I : Compositions of mullite compounds
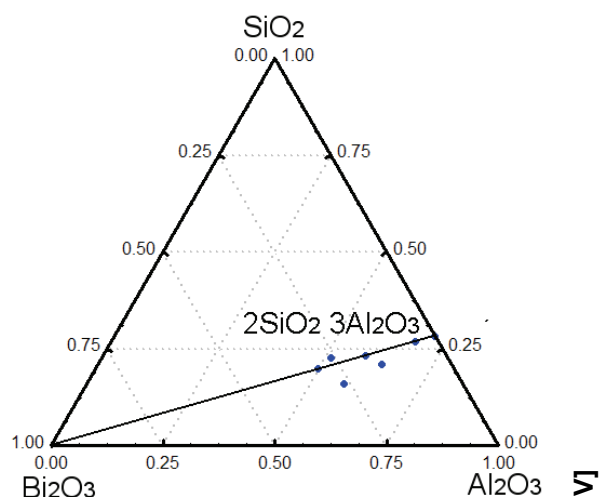
Fig. 1: Compositional area (wt%) in the ternary diagram SiO_2-Al_2O_3-Bi_2O_3

X-ray diffractions were performed with a D5000 (Bruker) and pattern refinements were obtained by the Rietveld method, using the FullProf software. The thermal behavior of gels after calcinations at different temperatures up to 1100°C were 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.

Results and discussion

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 [13,14].

DTA of samples containing bismuth (4, 5, 6 and 7 in table I), were performed after heating at 500°C to preliminary remove all volatile species. The DTA curve of sample 4 in figure 2 presents four exothermal peaks at 530, 892, 958 and at 1044°C.

With sample 5, the DTA curve in figure 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 figure 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 (figure 2) shows two endothermic peaks at 725°C and 875°C and two exothermal peaks at 815°C and 1293°C. In this sample with the highest bismuth content, some peaks should be related to the transition of monoclinic α-phase)→δ (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 [15].
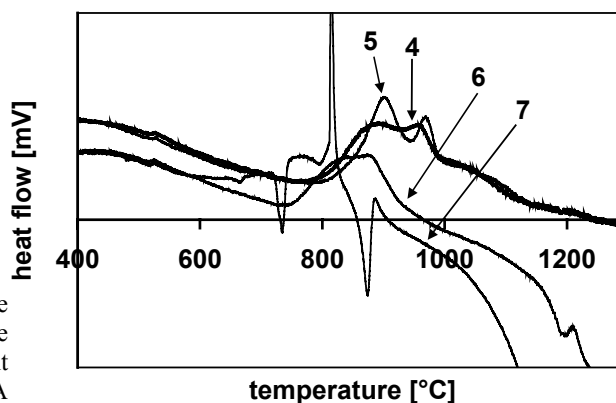

Fig. 2: DTA curve of samples 4, 5, 6 and 7.

Whereas pure mullite (sample 1) presents a typical exothermic peak at 980°C, mullite with more than 5 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 (5mol.% bismuth) shows a significant difference in intensity of the two main peaks. With sample 6 (20 mol.% bismuth), we observe a smoother variation, in comparison with curve variations of other samples. The weak peaks at 730°C and at 885°C are probably related to the transition of

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bismuth oxide. In sample 7 (40 mol.% bismuth), we observe three peaks, which are originated from transitions of bismuth oxide (735°C, 815°C and 875°C). The high temperature peaks at 1210°C for mullite with 20 mol.% Bi and at 1193°C in mullite with 40 mol.% Bi are due to the structural transformation of Al-Si spinel to new phases. In general, the curve slope at high temperature increases with the bismuth content.

X ray experiments

In a first approach, dried gels of samples 1, 2 and 3 were heated at 1350°C for 3 hours before XRD measurements. The Rietveld method was used to determine the mullite structural characteristics with bismuth additions in initial compositions.

In general, the orthorhombic mullite structure and the stoechiometry $3Al_2O_3$ $2SiO_2$ are always obtained. When the bismuth content increases. 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, 5, 6 and 7, at typical temperatures near the onset and end of peaks in DTA curves of figure 2. All thermal cycles with 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 II.

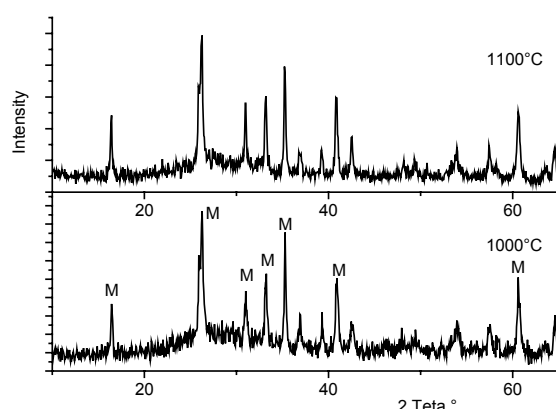| Sample	Temperature
4	1000°C, 1100°C
5	1000°C, 1100°C
6	1000°C, 1100°C, 1250°C
7	770°C, 845°C, 930°C, 1200°C

Tab. II : Quenching temperatures of samples 4, 5, 6, 7

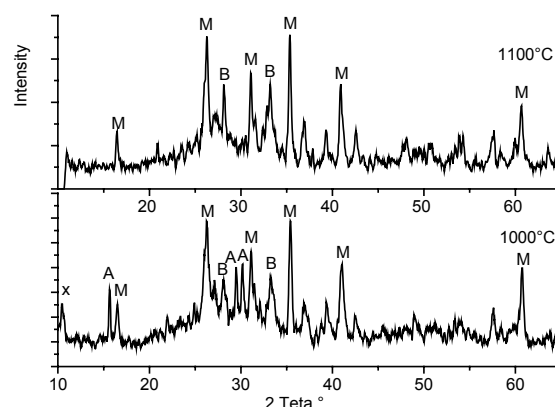Fig. 3 : X-ray patterns of sample 4 heated at 1000°C and 1100°C

Fig. 4 : X-ray diffractogrammes for sample 5 ($3Al_2O_3$. $2(Si_{0,7}.Bi_{0,3}) O_2$) calcined at 1000 and 1100°C ; (M-mullite, A-aluminum bismuth oxide, B-bismuth silicon oxide).
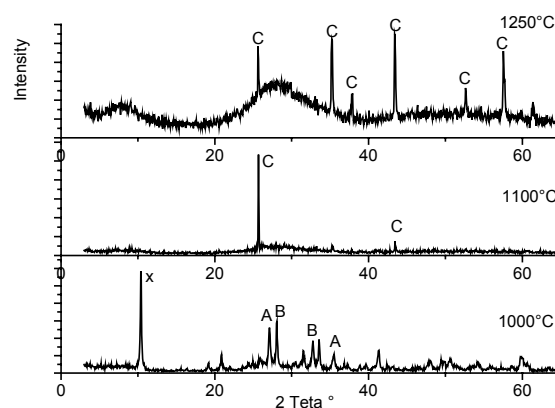
Fig. 5 : X-ray patterns of sample 6 mullite with 18wt.% Bi_2O_3, heated at 1000°C, 1100°C and 1250°C. C: corundum.
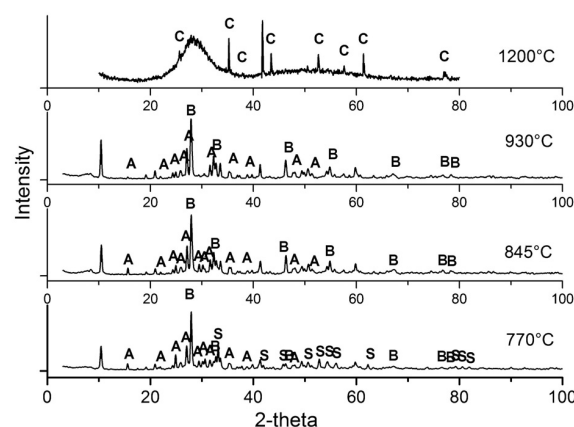
Fig. 6 : X-ray patterns of sample 7 mullite with 40wt.% Bi_2O_3, heated in the 770-1250°C temperature range. C: corundum.

Patterns of sample 5, containing 5wt% of Bi_2O_3 and heated at 1000°C and 1100°C are in figure 3. It is seen

that only orthorhombic mullite with the stoechiometry $3Al_2O_3$ $2SiO_2$ is identified.

Figure 4 shows X-ray patterns of sample 4 containing 26wt% of Bi_2O_3 ($3Al_2O_3 2(Si_{0.7}.Bi_{0.3})O_2$) heated at 1000°C 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 01-084-1205), cubic bismuth silicon oxide $Bi_{12}Si_{0.87}O_{20}$ (pattern 01-084-0090) and aluminium bismuth oxide $Al_4Bi_2O_9$ (pattern 00-025-1048). At 1100°C, peaks from sample 4 indicate that 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 figure 2 above 958°C should be related to the liquid formation.

In figure 5, sample 6 with 18wt.% 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 2teta°. This new phase also occurs in sample 4 at 1000°C and in all samples containing more than 5wt%, below 1100°C. The stoechiometry of this phase is supposed to be similar to a Aluminium Silicon Bismuth oxide, but further work are necessary to precise 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°C and 1250°C, sample 6 show the progressive formation of sharp peaks from a single phase, very similar to corundum (pattern 00-010-0173). Structural characteristics of this phase were identified after heating at 1200°C for 14 hours holding time and sampling a single crystal. The obtained structural parameters are the following: system hexagonal (rhomboedric, R-3C or R3C); a = 4,735 Å; b = 4,735 Å; c = 12,941 Å; $\alpha = 90°$; $\beta = 90°$; $\gamma = 120°$. These data are close to that of corundum (α-Al_2O_3).

For a higher Bi_2O_3 content (figure 6), sample 7 with 30wt% 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 00-037-085). After hating at 845°C 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 corundum peaks.

The major peak at 10.44°2teta is also observed at 770°C, 845°C and 930°C, as in samples 6. It must be precisely identified in a future work. From these experiments, we note the occurrence of a liquid at temperatures above 930°C that corresponds to the strong endothermic variation in the DTA curve of figure 2.
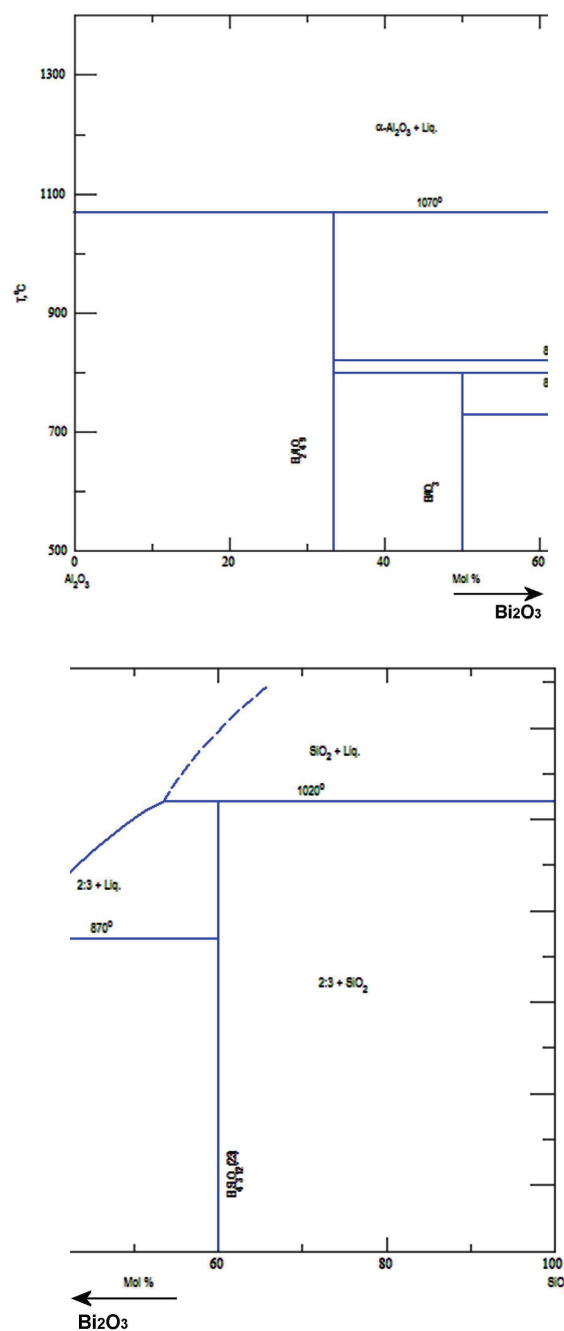

Fig. 7 : binary diagrams in the system $SiO_2 - Al_2O_3 - Bi_2O_3$.

Three-phases diagram

A 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: $Al_2O_3 - SiO_2$ [11], Al_2O_3-Bi_2O_3 [10], $Bi_2O_3 - SiO_2$ [12]. The Al_2O_3 and SiO_2 rich regions of two binary diagrams are in figure 7 a-b respectively. We observe in the $Al_2O_3 - SiO_2$ system the presence of the $Al_4Bi_2O_9$ phase which was observed in compositions 6 and 7 containing 20-40mol% 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 figures 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°C and 1100°C. But the first liquid appears at the 1020°C temperature, close to the liquid temperature of our samples.
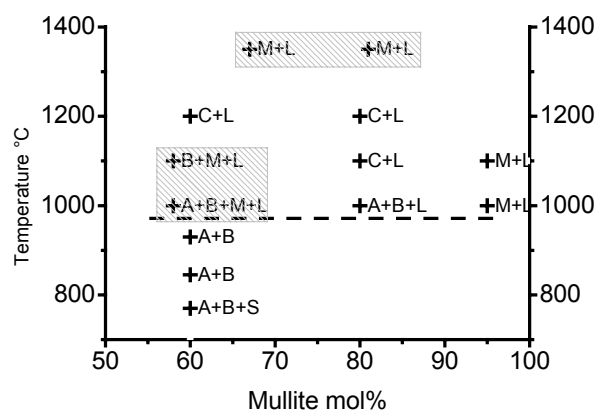

Fig. 8: Phase diagram Bi_2O_3 – mullite; B – Bismuth Silicon Oxide; A – Aluminum Bismuth Oxide; S – Sillenite; M – Mullite; C - Corundum

A tentative pseudo-binary diagram mullite-Bi_2O_3 is presented in figure 8. The liquid limit is slightly below 1000°C, for a large Bi_2O_3 content. Above approximately 1100°C, corundum coexists with the liquid and this behavior is similarly observed in the Al_2O_3-Bi_2O_3 system above 1070°C. For compositions outside the mullite - Bi_2O_3 axis (samples 2,3 and 4) the crystallized phases are different (composition plotted in gray shade in figure 7), but the liquid temperature is not different.
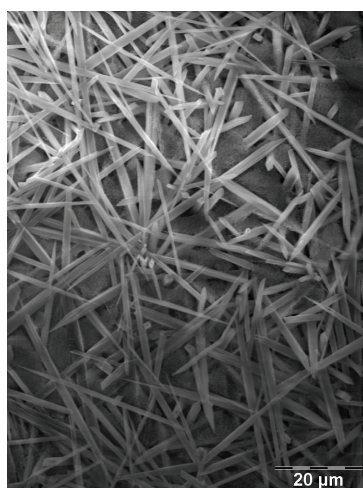

Fig. 9: Microstructure at the Muscovite-kaolinite interface when 1mol% of Bi_2O_3 is added.

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 solution. The Bi_2O_3 to mullite ratio in sintered material is close to 5mol%. But, it can be supposed that a local high concentration of bismuth oxide exist at crystallite interfaces. In these restricted zones, local interactions could be described by the behavior of compounds containing high concentration of Bi_2O_3 in the pseudo binary diagram of figure 8.

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

In this material, whereas the probable occurrence of crystallized compounds of Bi_2O_3 with alumina and silica, no reactions are found by x-ray in sintered materials. Also, Bi_2O_3 was not detected even for samples with high Bi_2O_3 addition. The most interesting point is the significant mullite crystallization and growth at low temperature. Simultaneously, Bi_2O_3 highly favors the sintering densification and this effect is attributed to the specific role of a local low-viscosity liquid phase in the systems.

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. At weak bismuth content, mullite is crystallized in all mixes below 1000°C and above. When bismuth content exceed about 10mol%, mullite is no longer crystallized and both bismuth silicon oxide, aluminum bismuth oxide, sillenite and corundum are present in variable contents. Mullite is detected in sample with high bismuth content at temperature exceeding 1200°C and for compositions beside the mullite Bi_2O_3 axis. For all studied compositions, a liquid phase appears at temperature in the 950-1000°C temperature range.

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.

Acknowledgements

References

1. M. Mizuno, H. Saito: "Preparation of Highly Pure Fine Mullite Powder", J.Am. Ceram. Soc., 72 [3] 377-82, (1989)

2. L.Saadi, R.Moussa: "Synthesis of Mullite Precursors in Molten Salts. Influence of the Molten Alkali Nitrate and Additives", J. Eu. Ceram. Soc., 19, (1999)

3. L.B.Kong, T.S. Zhang: "Some main group oxides mullite phase formation and microstrukture evolution", Journal of Alloys and Compounds, 359, (2003)

4. S. Hong, G.Messing: "Anisotropic Grain Growth in Boria doped Diphasic Mullite Gels", J. Eu. Ceram. Soc., 19, (1999)

5. D.Amutharani, F.D. Gnanam: "Low temperature pressureless sintering of sol-gel derived mullite", Material Science and Enginnering, A264, 254-261, (1999)

6. Chen Y.F., Vilminot S., "Characterization of sol gel mullite powders", Materials Research Bulletin 30, 291-298, (1995)

7. Janackovic D., Janackovic V., "Synthesis of mullite nanostrucured spherical powder by ultrasonic spray pyrolysis", NanoStructured Materials 10, 341-348, (1998)

8. Patil M.M., "Synthesis of bismuth oxide nanoparticles at 100°C", Mater. Letters 59, 2523-252,(2005)

9. Chakraborty A.K., "Aluminosilikate formation in various mixtures of tetra ethyl ortosilicate (TEOS) and aluminum nitrate (ANN)", Thermochimica Acta 427, 109-116 (2005)

10. Speranskaya E.I., Skorikov V.M., "System Al_2O_3 – Bi_2O_3", Inorg. Mater., 6 [7] 1201-1202, (1970)

11. MacDowell J.F., Beall G.H., "System SiO_2-Al_2O_3", J.Am. Ceram. Soc., 52 [1] 17-25, (1969)

12. Kargin Yu. F., Zhereb V.P., "System Bi_2O_3-SiO_2", Russ. J; Inorg. Cehm., 36 [10] 1466-1469, (1991)

13. Chen Z., Zhang L., "Novel Method og adding seeds for preparation of mullite", Jour. of Mat. Proc. Tech. 166, 183-187, (2005)

14. Akshoy K., "DTA study of preheated kaolinite in the mullite formation region", Thermochinica Acta 398, 203-209, (2003)

15. V. Fruth, A.Ianculesca: "Synthesis, structure and properties of doped Bi_2O_3", J. Eu. Ceram. Soc., (2006)