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 (C2H5O)4Si, aluminum nitrate Al(NO 3)3.9H2O and bismuth nitrate Bi(NO3)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 Bi2O3 content, mullite coexists with amorphous silico-aluminate phases, even at high temperature. When the Bi2O3 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 Bi2O3 additions. Above the liquidus, only corundum and a liquid coexist. A tentative mullite-Bi2O3 binary phase diagram is then proposed. These results evidence the Bi2O3 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, Bi2O3.

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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. Ca2+ or Ba2+ can added [2], but the addition of Bi3+ appears to be a promising way for mullite formation in compositions. It was also observed the effects of some oxides (SnO2, SbO2) in the phase formation and the microstructural evolution of mullite ceramics [3]. In general, Bi2O3 doping have a much better effects on densification than SnO2 and Sb2O3, 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 Fe2O3 or TiO2 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 Fe2O3, 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 SiO2-rich liquid phase, favoring a higher mobility of the diffusing species. The dissolution of Al2O3 species into the SiO2-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 (C2H5O)4Si, aluminum nitrate Al(NO3)3.9H2O and bismuth nitrate Bi(NO3)3. Alumina 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 SiO₂-Al₂O₃-Bi₂O₃ in figure 1 [10-12]. All compositions are along and beside the pseudo-binary mullite-bismuth oxide.

<table>
<thead>
<tr>
<th>ref</th>
<th>Stoechiometry</th>
<th>Bi₂O₃ wt% - mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3Al₂O₃ . 2SiO₂</td>
<td>0 – 0</td>
</tr>
<tr>
<td>2</td>
<td>3Al₂O₃ . 2(Si₀.₈₄Bi₀.₁₆)O₂</td>
<td>15- 19</td>
</tr>
<tr>
<td>3</td>
<td>3(Al₁.₈Bi₀.₂)O₃. 2SiO₂</td>
<td>26 - 33</td>
</tr>
<tr>
<td>4</td>
<td>3Al₂O₃ . 2(Si₀.₇Bi₀.₃)O₂</td>
<td>26 - 42</td>
</tr>
<tr>
<td>5</td>
<td>3Al₂O₃ . 2SiO₂ + 5 mol% Bi₂O₃</td>
<td>5.2 – 5</td>
</tr>
<tr>
<td>6</td>
<td>3Al₂O₃ . 2SiO₂ + 20 mol% Bi₂O₃</td>
<td>18 – 20</td>
</tr>
<tr>
<td>7</td>
<td>3Al₂O₃ . 2SiO₂ + 40 mol% Bi₂O₃</td>
<td>30 - 40</td>
</tr>
</tbody>
</table>

**Tab. I**: Compositions of mullite compounds

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.

**Fig. 1**: Compositional area (wt%) in the ternary diagram SiO₂-Al₂O₃-Bi₂O₃

**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 Bi₂O₃ is at 840°C [15].

**Fig. 2**: DTA curve of samples 4, 5, 6 and 7.
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 3Al2O3·2SiO2 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature</th>
</tr>
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<tbody>
<tr>
<td>4</td>
<td>1000°C, 1100°C</td>
</tr>
<tr>
<td>5</td>
<td>1000°C, 1100°C</td>
</tr>
<tr>
<td>6</td>
<td>1000°C, 1100°C, 1250°C</td>
</tr>
<tr>
<td>7</td>
<td>770°C, 845°C, 930°C, 1200°C</td>
</tr>
</tbody>
</table>

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

Patterns of sample 5, containing 5wt% Bi2O3 and heated at 1000°C and 1100°C are in figure 3. It is seen
that only orthorhombic mullite with the stoechiometry 3Al₂O₃ 2SiO₂ is identified. Figure 4 shows X-ray patterns of sample 4 containing 26wt% of Bi₂O₃ (3Al₂O₃ 2(Si₀.7 Bi₀.3)O₂) heated at 1000°C and 1100°C. At 1100°C, peaks from mullite, aluminum bismuth oxide and aluminum bismuth oxide are clearly recognized. Identified phases are orthorhombic mullite Al₂(Al₂.8Si₁.2)O₉.₅₄ (pattern 01-084-1205), cubic bismuth silicon oxide Bi₁₂Si₀.₈₇O₂₀ (pattern 01-084-0090) and aluminum bismuth oxide Al₄Bi₂O₉ (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°2θ. 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; α = 90°; β = 90°; γ = 120°. These data are close to that of corundum (α-Al₂O₃).

Three-phases diagram

A literature review reveals the lack of information about the SiO₂ – Al₂O₃ – Bi₂O₃ ternary system. Only two-phase diagrams are reported: Al₂O₃ – SiO₂ [11], Al₂O₃–Bi₂O₃ [10], Bi₂O₃ – SiO₂ [12]. The Al₂O₃ and SiO₂ rich regions of two binary diagrams are in figure 7a-b respectively. We observe in the Al₂O₃ – SiO₂ system the presence of the Al₂Bi₂O₉ phase which was observed in compositions 6 and 7 containing 20-40mol% Bi₂O₃. 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 Bi₂O₃ – SiO₂ system is different as it contains
the Bi₂Si₃O₈ phase, which is different from the
Bi₂Si₉O₂₄ 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.

Mullite formation in phyllosilicate mixes

The effect of Bi₂O₃ addition on phase formation and
microstructural evolution of mullite ceramics from
kaolinite-muscovite minerals was investigated. In this
material, Bi₂O₃ was added as a thin coating onto
muscovite flakes, before the muscovite-kaolinite
mixing, using a bismuth nitrate aqueous solution. The
Bi₂O₃ 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 Bi₂O₃ in the pseudo
binary diagram of figure 8.

With muscovite-kaolinite compound, SEM
observations point to the acceleration of mullitization
with the presence of Bi₂O₃. In figure 9, the surface of
muscovite sintered at 1250°C for 1 hour holding time
shows large anisotropic mullite grains, which average
length attains 30µm.

In this material, whereas the probable occurrence of
crystallized compounds of Bi₂O₃ with alumina and
silica, no reactions are found by x-ray in sintered
materials. Also, Bi₂O₃ was not detected even for
samples with high Bi₂O₃ addition. The most interesting
point is the significant mullite crystallization and
growth at low temperature. Simultaneously, Bi₂O₃
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 Bi₂O₃ on phase formation and
microstructural evolution of mullite ceramics were
investigated by different methods. They all point to the
important role of Bi₂O₃ 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 Bi₂O₃ 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 Bi₂O₃ 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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References