Formation of Crystal Structure in Dielectric BaAl$_2$Si$_2$O$_8$-Based Materials Depending on Preparation Conditions

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Crystal structure formation of BaAl$_2$Si$_2$O$_8$ known as polymorphic compound is investigated in present work depending on conditions of preparation. Characteristics of ceramics have been studied for different modifications of crystal structure. Additional technological operations (grinding with following heat treatment) have been found to result in polymorphic transformation. Dielectric properties of BaAl$_2$Si$_2$O$_8$ ceramics have been studied for hexagonal, monoclinic crystal structure modifications as well as for that based on phase mixture. It has been shown that the sintering of ceramic material based on the monoclinic crystal structure modification of BaAl$_2$Si$_2$O$_8$ takes place in temperature diapason of 1300–1350°C. Sintering of material with the hexagonal crystal structure modification occurs in temperature diapason of 1450–1500°C. Ceramics materials based on compound BaAl$_2$Si$_2$O$_8$ are found to have low porosity, high $Q$-factor and dielectric characteristics, allowing use of these ceramic materials for production of resonators and other microwave equipments.

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1. Introduction

The system BaO-Al$_2$O$_3$–SiO$_2$ arouses a great interest from the point of view of the refractory silicate materials synthesis and production of technical ceramics. This system can be used for obtaining high frequency celsian ceramics and other materials for special purposes [1].

Compound BaAl$_2$Si$_2$O$_8$ has a set of polymorphic transitions crystallizing in monoclinic, hexagonal and orthorhombic structures [2–4]. Physical properties of celsian are determined by the crystal composition. So, the compound with monoclinic structure is thermodynamically stable in the temperature range 20–1520°C [5], whereas the hexagonal celsian phase is stable up to 1700°C [1].

Weak point of hexacelsian is low resistance to thermal shock due to structural transition from α- to β-hexagonal modification in the temperature range 280–320°C [6]. Monoclinic form has no polymorph transitions.

Present work aim is to study polymorphic transformations of dielectric material based on BaAl$_2$Si$_2$O$_8$ compound depending on preparation conditions.

2. Experimental

To synthesize ceramic BaAl$_2$Si$_2$O$_8$ with hexagonal and monoclinic structures we used two different technological approaches.

In the 1st case, the samples with hexagonal modification of crystal structure have been synthesized using two-stage technology. On the first stage, BaAl$_2$Si$_2$O$_8$ powders were synthesized from mixture of oxides BaCO$_3$, Al$_2$O$_3$, SiO$_2$ taken in ratio 1:1:2. The synthesis was performed in air in alundum crucibles by solid state reaction method at temperatures (1350–1450)°C during 6 h.

In the 2nd approach, to obtain the ceramic samples with monoclinic modification of crystalline structure we have performed additionally the following operations. Firstly, after synthesis and the following milling with planetary mill during 30–60 min, the compacted tablets were subjected to heat treatment at 1100–1350°C during 2–4 h. Then the obtained material was ground thoroughly again in planetary mill during 30–60 min, a binding component was added, pressed as tablets, and annealed in electrical furnaces in air at temperatures (1250–1350)°C during 2–4 h.

To study structures and properties we used X-ray diffraction (XRD) phase analysis (DRON 4), electron microscopy (LEO 1455VP), automated system for microstructure analysis on the base of metallographic microscope (Olympus GX 4) with program facility AutoScan 005, measurements of dielectric parameters at the frequency 1 MHz.
3. Results and discussion

X-ray diffraction phase analysis after synthesis of BaAl$_2$Si$_2$O$_8$ samples using the 1st technological scheme have shown only hexagonal modification of crystal structure (monoclinic modification was recorded only at the level of background (see Fig. 1)).

XRD phase analysis after synthesis of BaAl$_2$Si$_2$O$_8$ samples using the 2nd technological approach have shown a mixture of monoclinic and hexagonal modification of crystal structure, see Fig. 2, that exhibits a polymorphic transformation.

The optic microscopy of the etched single-phase BaAl$_2$Si$_2$O$_8$ ceramic samples has shown that the samples with a monoclinic atomic structure exhibit a pronounced granular microstructure with faceted crystallites of different shape and sizes from 1 to 5 $\mu$m (Fig. 3a). At the same time, the samples of hexagonal modification of crystalline structure does not display any grains (Fig. 3b).

The last dependence for the samples with hexagonal modification of crystalline structure at room temperature displays the presence of structural $\alpha$-$\beta$ transition, when cooling, from hexagonal ($\alpha$) to monoclinic ($\beta$) modifications in the temperature range 280–320$^\circ$C. The position of this transition in temperature scale is consistent with the results of differential thermal analysis (DTA) in [7] which was close to 312$^\circ$C. Let us note that for monoclinic form we did not observe any polymorph transitions.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Hexagonal $\alpha$-modification</th>
<th>Monoclinic $\beta$-modification</th>
</tr>
</thead>
<tbody>
<tr>
<td>porosity [%]</td>
<td>5.61</td>
<td>6.45</td>
</tr>
<tr>
<td>relative dielectric constant, $\varepsilon$</td>
<td>$6.5 \pm 0.2$</td>
<td>$6.3 \pm 0.2$</td>
</tr>
<tr>
<td>dielectric loss tangent, $\tan \delta$</td>
<td>not more than 0.0005</td>
<td>not more than 0.0005</td>
</tr>
<tr>
<td>thermal dielectric permittivity factor, $TK \varepsilon \times 10^{-6}$ [1/°C]</td>
<td>$10^6$</td>
<td>$10^6$</td>
</tr>
</tbody>
</table>
4. Conclusion

The compound BaAl$_2$Si$_2$O$_8$ was found to be crystallized in hexagonal α-modification after synthesis by the first technological approach. In order to obtain monoclinic β-modification of the ceramics, which is preferable for practical aims, we perform additional technological operations including some additional remillings and heat treatments. After such a procedure, the polymorph monotropic transformation takes place.

Therefore, changing the preparation conditions one can obtain ceramic materials with the prescribed crystal structure.

References