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Application of Mechanical Activation to the Solid-Phase Synthesis of Beryllium Indialite

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Abstract

The effect of grinding method on the size of particles of the mixture components and on the parameters of the solid-phase synthesis of beryllium indialite from a mixture of dry oxides BeO, MgO, Al_2O_3, SiO_2 is investigated. It is demonstrated that with the use of mechanical activation the formation of intermediate phases starts at a temperature of 1100 °C, while beryllium indialite starts to form at 1200 °C. The content of beryllium indialite in the activated mixture at the moment when the temperature of 1340 °C is achieved is ~90 %, while without mechanical activation it is only ~50 %.

INTRODUCTION

The materials (crystals, ceramics and glass) of the system $RO-BeO-Al_2O_3-SiO_2$ attract permanent attention as the basis of solid-phase lasers, optical glass, high-strength optical glass fibre, insulators, thermoluminescent dosimeters due to the unique combination of valuable physicochemical, spectroscopic and mechanical properties (transparency, low thermal expansion coefficient, high hardness, *etc.*) [for example, [1–4]. It should be stressed that, for example, for the $MgO-Al_2O_3-SiO_2$ system one of the compounds widely used in ceramic industry is cordierite $Mg_2Al_4Si_5O_{18}$. Valuable properties of the cordierite-based ceramics attract the attention of researchers and compel them to carry out intense search for energy-saving methods of its synthesis, including variations of the character of initial components [5].

One of the promising materials of the $BeO-MgO-Al_2O_3-SiO_2$ system is beryllium indialite (BI, the ideal formula: $Mg_2BeAl_2Si_6O_{18}$). This compound is isostructural to the hexagonal beryl $Al_2Be_3Si_6O_{18}$ and indialite $Mg_2Al_4Si_5O_{18}$ [6, 7]; it was synthesized using the solution-melt, melt, solid-phase [8] and hydrothermal [9] procedures. However, in order to obtain practically single-phase cake of beryllium indialite by the solid-phase synthesis, it is necessary to apply high temperature (1340 °C) and long exposure (45–50 h). On the other hand, it is known that mechanical grinding of the mixture for solid-phase synthesis allows one to intensify the interaction processes [10]. This causes a substantial decrease in the synthesis parameters. For rhombic cordierite, which is an isochemical analogue of indialite, mechanical activation of the initial mixture allowed one to decrease by at least 100 °C the temperature at which the intermediate and final products of the synthesis start to form [11]. In doing this, one successes in obtaining a single-phase cake of cordierite as soon as after a 1 h exposure at the synthesis temperature (1400 °C). It is pointed out that the sequence of phase transformations is almost independent of mechanical treatment of the mixture.

It was established previously [8] that a small amount (~35 %) of BI is formed at a temperature of 1220 °C and 288 h exposure during the solid-phase process in a $2MgO \cdot BeO \cdot Al_2O_3 \cdot 6SiO_2$ mixture. The content of BI in the synthesis product reached 90 % only after agglomeration for 180 h at 1340 °C. Optimal conditions for obtaining beryllium indialite from a stoichiometric mixture of oxides (suitable for subsequent crystal growth from the melt) are: heating of the mixture to 1340 °C followed by isothermal exposure at this temperature for 45–50 h. It was shown that the formation of BI is a complex process of stage-by-stage transformation and interaction of the single- and two-component intermediate phases. Cristobalite, spinel, chrysoberyl, enstatite, forsterite are observed as intermediate compounds. In addition to beryllium indialite, the final product of synthesis contained cristobalite.

In the present work we estimate the effect of mechanical activation on the particle size of mixture components and on the parameters of the solid-phase synthesis of BI.

EXPERIMENTAL

The initial mixture was composed of dry, mainly X-ray amorphous oxides: BeO (ch.), Al_2O_3 (ch.), MgO (ch.d.a., contains ~15 % periclase) and SiO_2 (os.ch.) at a ratio of 1 : 1 : 2 : 6, which corresponds to the ideal stoichiometry of BI. Grinding of the mixture was carried out using two procedures. For the first one (composition I), the components were ground manually in ethanol until a visually homogeneous mixture was obtained. This procedure is similar to that used previously in [8]. The size of oxide particles was determined with a supersonic laser analyzer Micro-Sizer-201. For the second procedure (composition II), a mixture of oxides was ground in a ball centrifugal mill Pulverizette-6 (treatment time was 120 min). Mechanical activation of the mixture and determination of particle size were carried out with Analyzette-20 photosedimentograph.

The regime of solid-phase synthesis included simultaneous heating of compositions I and II and their quenching in the air when the temperature of 900, 1000, 1100, 1160, 1200, 1240, 1280, 1300 (after isothermal exposure for 18 h) and 1340 °C (after isothermal exposure for 1 h) was achieved. X-ray phase analysis of the samples was carried out using DRON-3 diffractometer (CuK_α radiation, the rate of counter movement: 1 deg/min).

RESULTS AND DISCUSSION

It was established that different procedures of grinding the initial mixture led to strongly different results (Table 1, Fig. 1). It should be noted that the generalized curve of granulometric composition of composition I was built up on the basis of measuring the diameter of Al_2O_3, MgO and SiO_2 grains taking into account their mass concentration in the mixture. It was decided to neglect the effect of BeO on the type of the curve because the concentration of beryllium in the mixture was only 4.4 mass %.

One can see that the granulometric characteristics of composition I lie within a broad range from several tenths to several hundred micrometers. The range for composition II is very narrow.

The difference in mixture preparation caused substantial differences in the results of the solid-phase synthesis (Fig. 2). One can see that almost all the phases, including the final one (beryllium indialite) and numerous intermediate ones, are formed in composition I at substantially higher temperature than in

TABLE 1

Grinding conditions and granulometric characteristics of mixtures

Parameter	Composition I, hand grinding	Composition II, MA
Grinding time, min	Till visually homogeneous mass	120
d_{50}, μm	54.52	4.43
d_{min}/d_{max}, μm	<0.6/300 and more	<0.6/22
d prevailing, μm	100–150	4–10

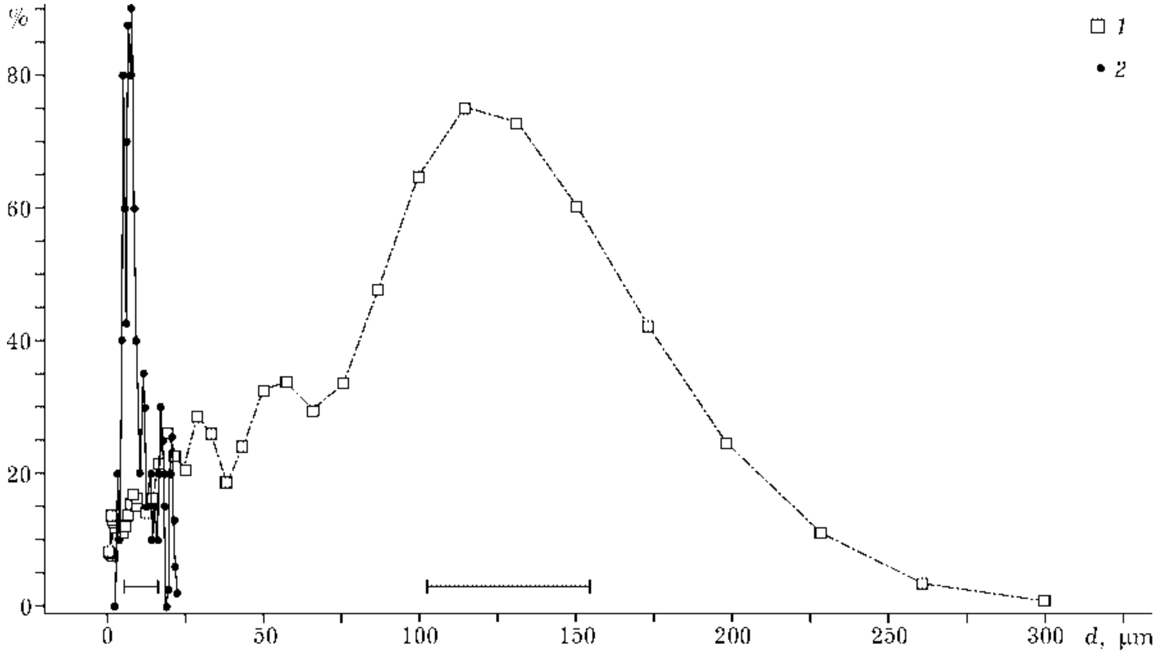

Fig. 1. Granulometric composition of mixtures of compositions I (*1*) and II (*2*). The ranges of predominant particle size values are indicated.

composition II. In addition, the temperature range of crystallization for almost all the phases in composition I is much more narrow than that in composition II. Let us consider in more detail the differences between the compositions investigated. In addition to periclase, additional reflections (presumably quartz) were observed in the X-ray diffraction patterns of the initial mixture of composition II. The phase composition remained practically unchanged in the samples of mixtures I and II after heating to 900 °C. Only the fraction of X-ray amorphous phase had slightly increased in mixture II (due to a decrease in the amount of quartz and initial periclase). When 1000 °C was achieved, bromellite was formed in mixture I (in addition to the initial periclase), while, to the contrary, almost complete transition into the amorphous state occurred in mixture II. The samples synthesized at 1100 °C were substantially different from each other in phase composition. Only single-component crystal phases were present in composition I: periclase, quartz and bromellite. In mixture II, along with the lower intensity of the X-ray diffraction peaks of periclase and quartz and the absence of bromellite, we observed not very intensive but well resolved reflections of two-component compounds: forsterite and enstatite. Heating to 1200 °C resulted in the formation of one more single-component phase (corundum) in mixture I, together with forsterite and enstatite. At the same temperature, the initial periclase was observed to disappear completely in mixture II; in addition to forsterite and enstatite present in the mixture, new phases were formed: beryllium indialite, chrysoberyl, and a compound which we identified as a phase with petalite structure (PPS). The latter phase was previously described [8] as a four-component beryl-containing structural analogue of the PPS of $MgO-Al_2O_3-SiO_2$ system which was close in composition to BI. At 1240 °C, mixture I

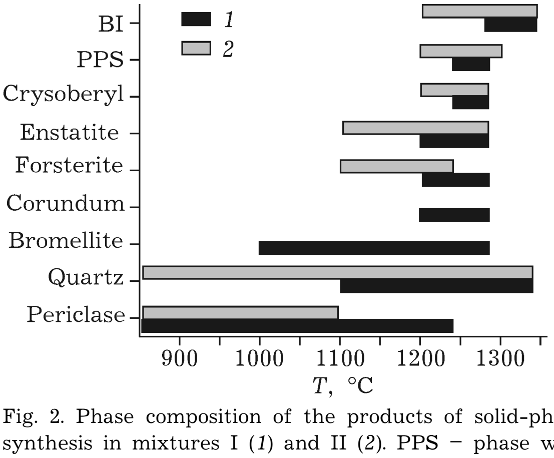

Fig. 2. Phase composition of the products of solid-phase synthesis in mixtures I (*1*) and II (*2*). PPS – phase with petalite structure.

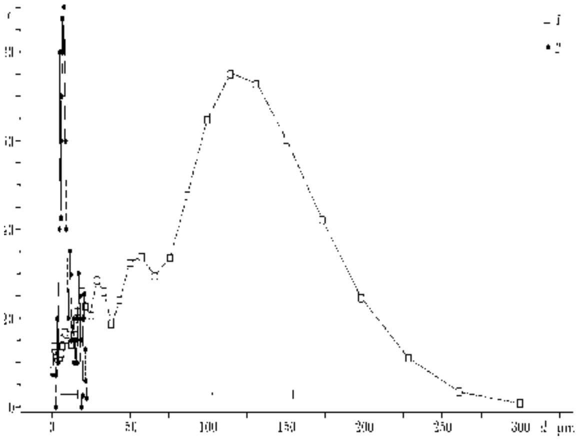

Fig. 3. Dependence of beryllium indialite content on the temperature of solid-phase synthesis for compositions I (*1*) and II (*2*).

was almost free from periclase but contained forsterite, enstatite, corundum, bromellite, cristobalite; chrysoberyl and PPS appeared. Only forsterite disappeared in mixture II at this temperature. A small amount of beryllium indialite was detected in the sample of mixture I only at 1280 °C. At this temperature, the fraction of BI increased to 50 % in mixture II, at the background of a decrease in the amount of intermediate phases (Fig. 3). After exposing a sample of mixture II at 1300 °C, it was observed to contain BI, cristobalite and traces of PPS; enstatite and chrysoberyl disappeared. At 1340 °C, BI (~50 %), tridimite (or a phase with its structure) appeared in mixture I; the amount of cristobalite decreased. At this final temperature, an ingot of composition II was a combination of BI (~90 %) and cristobalite.

So, it was shown that the application of mechanical activation of the mixture causes a substantial decrease in the temperature of the start of formation of BI, and the rate of its crystallization increases. The difference in synchronous intermediate phase composition of mixtures I and II is due to the difference in reaction rates. Possible effect of mechanical activation on the mechanism of formation of beryllium indialite requires additional investigation.

CONCLUSIONS

The following results were obtained with mechanical activation applied to the initial mixture of the composition $BeO : Al_2O_3 : MgO : SiO_2 = 1 : 1 : 2 : 6$.

1. A substantial decrease in the temperature of the start of solid-phase interaction of the components (by 80–100 °C) was achieved.

2. The rate of crystallization of beryllium indialite as a product of solid-phase reactions increases substantially.

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