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Low-temperature synthesis of pure $BaAl_2Si_2O_8$ glass–ceramic powder by citrate process

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Abstract

The citrate process was successfully used to prepare a glass–ceramic powder with the stoichiometric composition of $BaAl_2Si_2O_8$ (BAS_2). The solutions of barium and aluminum nitrate, colloidal silica, citric acid, and diethylene glycol were combined and afforded a clear gel on mixing which was further decomposed on heating to an easily handled precursor in a powder form. The characteristics of this dried precursor were analyzed by X-ray powder diffraction (XRD), differential thermal (DTA) and thermal gravimetric (TGA), and thermal mechanical analyses (TMA). An intermediate grinding of the precursor is crucial for the successful synthesis of the hexagonal $BaAl_2Si_2O_8$ directly from the precursor which was crystallized at temperature as low as 850 °C for 4 h calcination.

1. Introduction

Barium aluminosilicate ($BaAl_2Si_2O_8$, BAS_2), a potential matrix materials applied in low temperature co-fired ceramic (LTCC) process, has been extensively investigated owing to its highly refractory property, low thermal expansion, and chemical stability [1–5]. BAS_2 is known as the only ternary compound in BaO–Al_2O_3–SiO_2 system and exists in three different polymorphs: celsian (monoclinic), hexacelsian (hexagonal), and α-hexacelsian (orthorhombic). Among the three, celsian is stable below 1590 °C and hexacelsian is stable from 1590 °C to its melting point (about 1760 °C) [6]. BAS_2 is reported to be synthesized by a variety of processes, including glass–ceramic processing [7], sol–gel processing [1,8–12], and solid-state reaction [13]. However, metastable hexacelsian is always crystallized as the first product irrespective of the process used, due to the sluggishness of the hexacelsian-to-celsian transformation. It is necessary to dope with mineralizers [14] to aid the formation of celsian, which is favorable in view of the prevention of undesired expansion on hexagonal-to-orthorhombic transformation at about 300 °C.

When BAS_2 is used in the LTCC process, the BAS_2 glass precursor is generally produced by melting method in the industry. As the high melting point of BAS_2, the melting process needs to be finished at extremely high temperature. In order to improve the preparation of BAS_2 precursor for LTCC application, soft-chemistry routes have been used to produce celsian glass–ceramic at a lower temperature. So far, the reported wet-chemical syntheses of celsian glass–ceramic powders are mainly by sol–gel methods. Although the sol–gel methods are with advantages in compositional purities and homogeneities for the preparation of a multi-component ceramic powder [15], the metal alkoxide precursors are frequently not cost-effective. Furthermore, the hydrolysis and condensation processes of the

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desired metal alkoxides to a homogeneous system are usually time-consuming. On the other hand, the citrate process does not carry the above-mentioned drawbacks. In a modified Pechini method, metal cations of the desired composition are chelated to the carboxylate groups on molecular level in the solution of citric acids with the proper adjustments of pH values and ligand concentrations. The clear solution is further gelled by the polymerization of an added monomer source, and this provides a steric entrapment effect to ensure the homogeneity in the polymeric networks [16,17]. The citrate process has been used in the low-temperature syntheses of many multi-component oxides [18]. For the synthesis of silicate compounds, there is no proper nitrate salt of silicon to be used. Therefore, the silicon alkoxide is still the reagent used in the citrate process for silicate synthesis in reported literatures [18]. We think colloidal silica with finely divided nanoparticles could be an alternative source for silicon in the citrate process. In this study, we used the citrate process with colloidal silica to synthesize the $BaAl_2Si_2O_8$ precursors followed by studying their thermal and the crystallization behaviors.

2. Experimental procedure

For the citrate process, barium nitrate, aluminum nitrate nona-hydrate, and colloidal silica were used as cation sources. Citric acid monohydrate (CA) and diethylene glycol (DEG) were used as chelating agents and the steric entrapment organic polymers, respectively. Powders of stoichiometric barium aluminosilicate compositions were prepared by the following process, Fig. 1, and its composition was $Ba(NO_3)_2$:$Al(NO_3)_3$: colloidal silica:CA:DEG = 1:2:2:16:20. First, DEG (0.2 mol) and CA (0.16 mol) were dissolved in deionized water until a clear solution was obtained. Barium nitrate, aluminum nitrate, and colloidal silica were dissolved in stoichiometric proportions in deionized water, respectively. The resulted liquid was mixed in a blender for a few minutes, and this was then added to the premixed solution of DEG and CA. The mixed sol was continued to be blended for a few minutes at room temperature. Water was first evaporated by continuous stirring during heating at 100 °C on a hot plate. The resulting gel-type precursors were further dried for several hours at 350 °C. The dried precursors were then dry ground in a ball mill for 10 h using a plastic jar and zirconia balls. After milling, the precursors were fired at various temperatures between 700 °C and 1000 °C at a heating rate of 10 °C/min in air for 4 h.

The ground and fired samples were examined by X-ray powder diffraction (XRD), thermal analysis and thermal mechanical analyzer. XRD measurements were performed using a diffractometer (XRD-6100, Shimadzu) with monochromated Cu Kα radiation and a scan rate of 4° (2θ)/min. The high-temperature attachment (HTK 1200, Anton Paar) was used in in situ experiments. The phase identification of the final products and precursors after firing at various temperatures were carried out. Differential thermal analysis (DTA) and thermogravimetry (TG) of the precursors were carried out in order to study the decomposition and

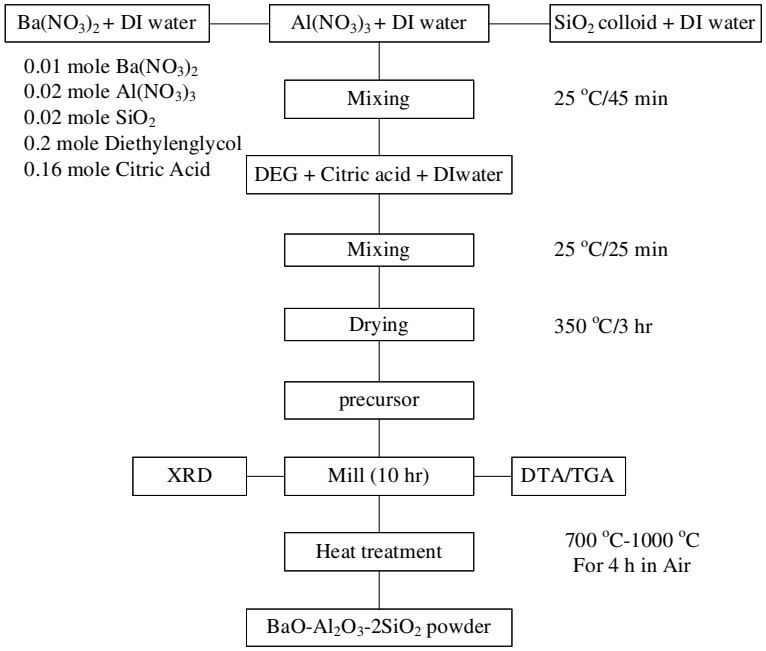

Fig. 1. A flow diagram of barium aluminosilicate gel–glass production route.