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Preparation and second harmonic generation of $Ba_2TiSi_2O_8$ films

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Abstract

The synthesis and characterization of the $Ba_2TiSi_2O_8$ films are described. The $Ba_2TiSi_2O_8$ crystal was obtained after heat treatment at above 630 °C of a sol–gel derived glassy material which has a chemical composition (mole ratio) 2BaO, TiO_2, $2SiO_2$, and then the $Ba_2TiSi_2O_8$ films were formed from the hydration of $CaO–P_2O_5$ glass powders. Heat treatment conditions and crystallization of the synthesized materials were studied by DSC-TG, XRD, and FT-IR. Second order nonlinear optical property has been verified by second harmonic generation test at 1064 nm. These results showed that the hydration process has a potential in rendering shape-comfortable optical materials.

Keywords: SHG; $Ba_2TiSi_2O_8$ film; Sol–gel; Hydration; Fresnoite

1. Introduction

To explore alternatives to nonlinear optical single crystals that are typically more difficult to prepare, processing, and have limited adaptability, transparent glass-ceramics have been studied extensively, especially those of nonlinear optical glass-ceramics containing nano- or micro-sized crystals with high ionic and electronic polarizabilities [1–3]. One of these glass-ceramics, fresnoite glass-ceramics has attracted considerable attention due to its second order nonlinearity as well as permanent optical nonlinearity [4–8]. However, the chemical compositions of transparent glass-ceramics examined in the previous studies were limited, and the preparation of the glasses having a composition close to $Ba_2TiSi_2O_8$ stoichiometry by conventional melt quenching process was difficult because the glasses have high melting and heat treatment temperature of above 1500 °C, 820 °C respectively. These glasses also show high devitrification tendency and have poor glass forming ability.

Sol–gel process is an alternative and a unique method for preparing glasses at low temperature. However, sol–gel derived fresnoite crystals have been seldom reported because of difficulties in obtaining pore and cracks free samples. Sol–gel derived fresnoite films on Si substrates were reported by Dai et al. while even and completely crystallized films were difficult to obtain [9]. In this work, we introduce a technique that combines sol–gel and hydration of calcium phosphate glass to synthesize fresnoite crystal dispersed films. Firstly, the glassy material was prepared by sol–gel process and its thermal property and the effect of heat treatment on crystallinity were investigated by DSC-TG, XRD and FT-IR. In the subsequent experiments, $Ba_2TiSi_2O_8$ crystals dispersed film was fabricated from hydration of calcium phosphate glass at room temperature and its transparency and nonlinear optical property (SHG) were investigated.

2. Experimental procedure

The precursors used to prepare $2BaO–TiO_2–2SiO_2$ (mole ratio) material were barium acetate (DAEJUNG CHEMICALS & METALS CO. LTD, purity >97.5%), titanium butoxide (Dupont product Sigma-Aldrich, purity >97%), and tetraethyl orthosilicate (ACROS ORGANICS, purity >98%). All these reagents were dissolved into ethanol and acetic glacial, and then mixed to get final solution. Fig. 1 shows the flow chart for $Ba_2TiSi_2O_8$ preparation. After drying, the morphology was observed with an Optical Microscope. Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were performed with a heating rate of 10 °C/min in air (TG 8110,

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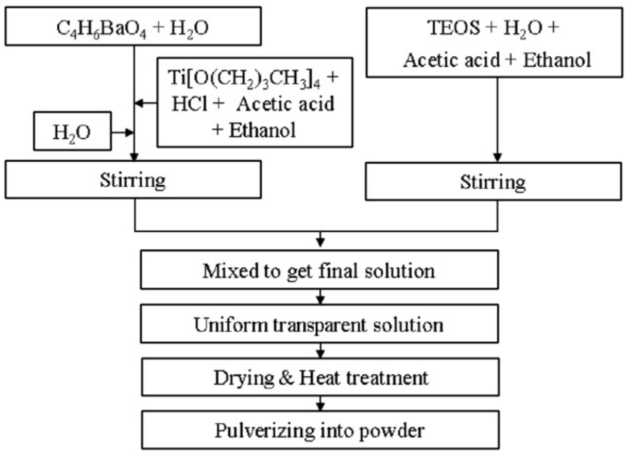

Fig. 1. Flow chart for preparation of $Ba_2TiSi_2O_8$ powders by sol–gel process.

Rigaku). The vibration characteristics and crystallization of synthetic material were determined by Fourier transform infrared (FT-IR, FTS-3000MX, Bio-rad) with computer aid system and X-ray diffractometer (XRD) at room temperature.

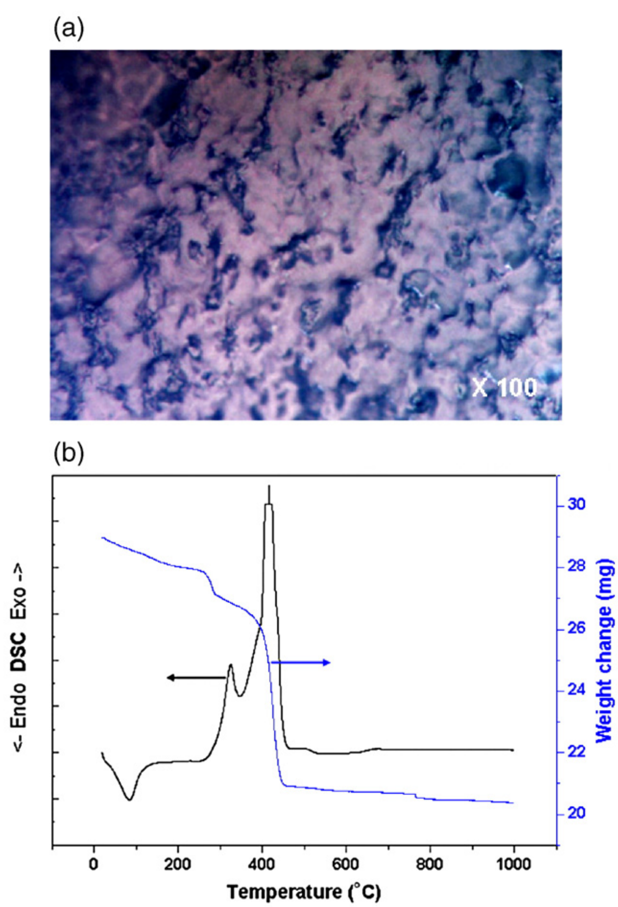

Fig. 2. Surface micrograph (a) and thermal analysis result (b) for synthesized material. (a) Surface morphology of synthesized materials after drying at 60 °C for 12 h, (b) DSC-TGA curve for synthesized material with a heating rate of 10 °C/min in air.

To prepare $Ba_2TiSi_2O_8$ film we used hydration of calcium phosphate glass, $CaO–P_2O_5$ prepared with $CaCO_3$ (Junsei, purity >98.5%) and H_3PO_4 (Duksan Chemical, purity >85%) in a Pt crucible at 1300 °C for 0.5 h. After quenching on a carbon plate, this glass was pulverized using an alumina mortar and then mixed with distilled water and $Ba_2TiSi_2O_8$ powder. This mixture was placed on plastic Petri dish up to 4 weeks to allow hydration. The container is covered using vinyl tape for prevention from excessive drying. $Ba_2TiSi_2O_8$ crystal dispersed films were fabricated from hydration of calcium phosphate glass at room temperature and their second harmonic generation (SHG) and transparency were subsequently investigated.

3. Results and discussion

3.1. Synthetic of $Ba_2TiSi_2O_8$ crystal

After aging and drying, the uniform transparent solution converted to rigid gel state which was still transparent in visible range. Fig. 2(a) shows the surface morphology of the synthesized material. The size of this sample was in the range of below 5 mm × 5 mm after drying at

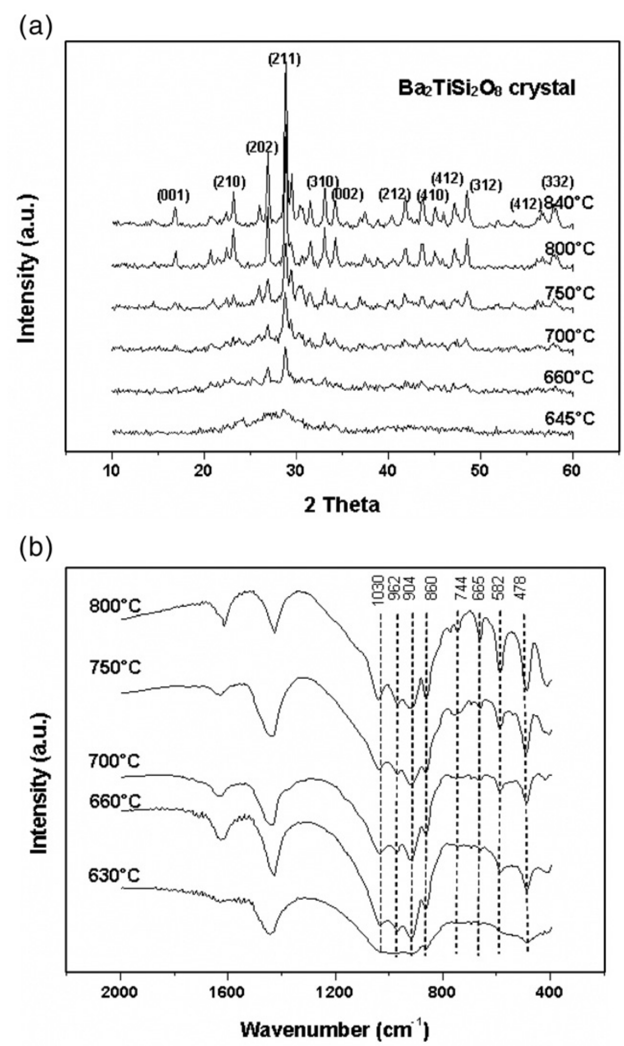

Fig. 3. Comparisons of XRD patterns (a) and FT-IR spectra (b) of the synthesized materials at various heat treatment temperature.