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Czochraski growth, defect analysis and refractive index of $Ba_2TiGe_2O_8$ crystal with excellent optical nonlinearities

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ABSTRACT

$Ba_2TiGe_2O_8$ (BTG) shows excellent second-order nonlinearity and electro-optical effects. However, it is difficult to grow a perfect BTG single crystal, and the accurate refractive indexes of this crystal are unavailable at present. In this paper, a sizeable single BTG crystal with high quality was grown by Czochraski (CZ) method. SEM and EDS analyses of crystal defect indicate that the volatilization of GeO_2 and the obvious supercooling feature of BTG melt were the main inducements of inclusion defects. The accurate refractive indexes were measured by the self-collimating method. The birefringence and SHG results show that the angle phase matching of SHG at 1064 nm hardly be achieved in this crystal. Nevertheless, the effective frequency-doubled laser output may be achieved by using the technique of *periodic polarization* reversal for quasi phase matching. In view of the high optical transmittance and the huge nonlinear optical coefficients, BTG crystal may be a good candidate material for nonlinear optical devices and electro-optical devices.

1. Introduction

As the further research of nonlinear optics and the emergence of new materials, the nonlinear optical crystal have been widely used in laser communications, integrated circuits, image processing and other civilian and military fields [1–8]. So searching a new nonlinear optical crystal is a hot topic of current research in the field of optical material.

$Ba_2TiGe_2O_8$ (BTG) crystal has an orthorhombic and non-centrosymmetric crystal structure with Cmm2 space group, which is similar to that of fresnoite ($Ba_2TiSi_2O_8$) [9,10]. In this crystal structure, TiO_6 octahedrons are connected by GeO_2 tetrahedron and Ge_2O_7 double tetrahedron, and Ba^{2+} ion is filled in the interspace between two TiO_6 octahedrons. Because Ba^{2+} ion has a large radius, the TiO_6 octahedron is extruded seriously and then yields a large deformation, and even become a square-pyramidal TiO_5 structure formed with four long Ti–O bonds and one short Ti–O bond. Such special configuration makes TiO_5 have a great microscopic polarization that can induce a strong microscopic nonlinear optical effect. In addition, the TiO_6 octahedrons in BTG crystal are arranged orderly along the ⟨100⟩ and ⟨010⟩ direction, which is helpful for accumulating the microscopic nonlinear optical effect and thus forming a strong macroscopic nonlinear optical effect in BTG crystal. Moreover, BTG crystal has a stable polarity along the ⟨001⟩ direction, and thus shows many prominent features, such as ferroelastic, piezoelectric and pyroelectric properties [11–13].

In 1976, a sizeable single crystal of BTG with the dimensions of $8 \times 8 \times 15\ mm^3$ was grown by Drafall and Spear [14], and its piezoelectric property was also reported. However, the as-grown crystal has a poor quality, containing many inclusions and cracks. In recent years, many research results show that the crystallized glass containing $Ba_2TiGe_2O_8$ or $Ba_2TiSi_2O_8$ microcrystal has excellent second-order optical nonlinearity [15–18]. Moreover, after an accurate heat treatment process, the second-order nonlinear optical susceptibility d_{33} of $Ba_2TiGe_2O_8$ crystallized glass could reach 24 pm/V [19], comparable to d_{22} and d_{31} susceptibilities of $LiNbO_3$ [15]. So far, there are few reports concerning the nonlinear optical properties of BTG single crystal and the information of refractive indexes. In this paper, the crystal growth, defect analysis, crystal hardness, nonlinear optical property, and the accurate refractive indexes of BTG crystal are reported.

2. Experiments

The polycrystalline materials used for the crystal growth were synthesized by the solid-state reaction method from the raw

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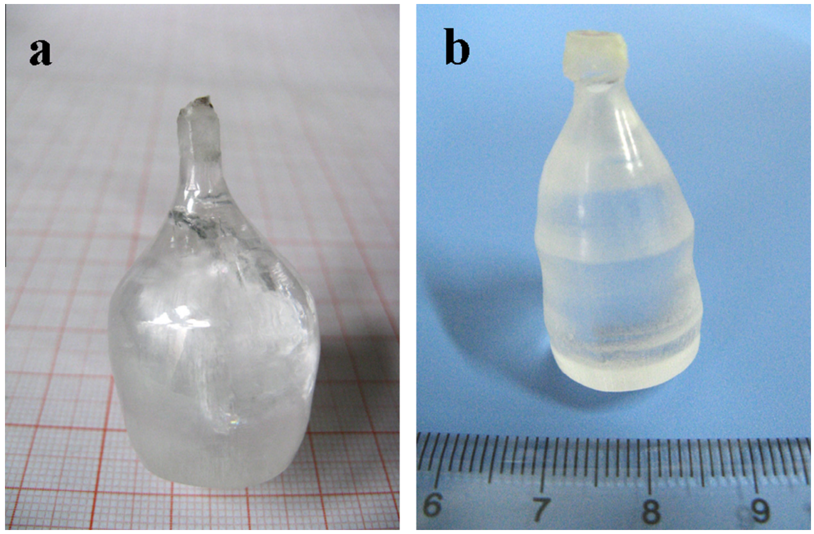

Fig. 1. Photos of as-grown BTG crystals grown by the Czochralski method. (a) BTG-1 crystal grown from the stoichiometric polycrystalline material, (b) BTG-2 crystal grown from the polycrystalline material with 2 at.% excess of GeO_2.

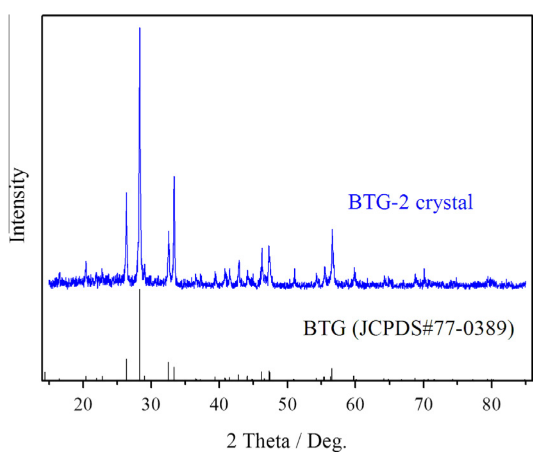

Fig. 2. XRD powder patterns of as-grown BTG-2 crystal.

materials of TiO_2, $BaCO_3$ (A.R.) and GeO_2 (A.R.). The raw material of TiO_2 was obtained from the hydrolysis of tetrabutyl titanate (99.99%). The raw materials were ground evenly and then put in an Al_2O_3 crucible to react at 900 °C for 12 h in an air atmosphere. To ensure complete reaction, the synthesized polycrystalline materials were reground again and pressed into tablets, and then sintered for 12 h at 950 °C. By using the same process, the polycrystalline materials were sintered again at 980 °C.

BTG crystals were grown by the Czochralski method in a radio-frequency furnace with N_2 atmosphere. BTG polycrystalline materials were melt in a platinum crucible with the diameter of 50 mm and the depth of 30 mm, and then crystal was grown with the pulling rate of 1.05 mm/h and the rotating velocity of 10 r/min. After crystallization, the crystal was pulled out of the melt and slowly cooled down to room temperature within 30 h in order to prevent it from cracking. By this method, two BTG crystals were grown and marked as BTG-1 and BTG-2, respectively. BTG-1 crystal was grown from the stoichiometric polycrystalline materials, while

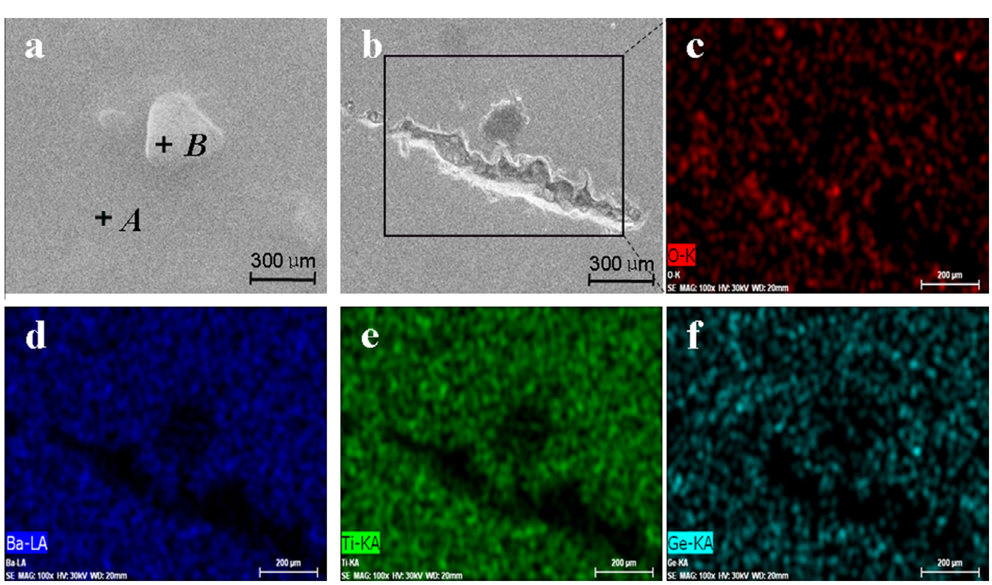

Fig. 3. SEM image of inclusion defect (a), SEM image (b) and surface scanning of EDS images (c–f) of microcrack defect in BTG-1 crystal.