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Original Article

Optical and thermo-mechanical properties of fine-grained transparent yttria ceramics fabricated by hot-press sintering for infrared window applications

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ABSTRACT

In this work, highly transparent yttria ceramics Φ = 55 mm in size were fabricated by a hot-pressing method with 1 at.% ZrO_2 or 12 at.% La_2O_3 as a sintering additive. For a 4-mm-thick specimen doped with ZrO_2, the in-line transmittance reaches 71.1% at 400 nm and 80.9% at 1100 nm, and the transmittance of the La_2O_3-doped specimen is comparable to that of the ZrO_2-doped specimen. By means of the relatively low sintering temperature of 1600 °C, the present samples exhibited very fine microstructures (< 2 μm), giving rise to excellent mechanical strength levels (~200 MPa). With regard to the 1 at.% ZrO_2-doped specimen, the combination of high strength and high thermal conductivity (~10 W/m K) substantially improved parameters related to the thermal shock resistance. The results of this study indicate that the hot-pressed transparent yttria ceramic doped with 1 at.% ZrO_2 is optically, mechanically, and thermally suitable for high-temperature IR window applications.

1. Introduction

Transparent polycrystalline yttria ceramics have long been known as among the most important optical window materials due to their high theoretical transmittance, outstanding refractoriness, and superior chemical stability [1]. Furthermore, compared to other transparent materials such as sapphire, AlON and spinel materials, yttria exhibits a broader range of transparency (0.2–8 μm) and much lower emissivity as well as a smaller absorption coefficient in the infrared (IR) region [2,3]. Therefore, these characteristics make yttria an outstanding candidate as an IR window material.

As early as the 1980s, GTE researchers successfully developed highly transparent La-doped yttria ceramics through a controlled transient-solid second-phase sintering method [4]. Meanwhile, Raytheon exploited undoped transparent yttria ceramic materials by vacuum pre-sintering combined with a post-hot-isostatic pressing (HIP) treatment [5]. Subsequently, based on the two promising products by GTE and Raytheon, a series of studies of the mechanical, thermal, and optical properties was carried out in order to improve the applications of transparent yttria ceramics in aerospace and military equipment (e.g., high-temperature IR windows and missile domes). Generally, both products by the two companies possess outstanding transparency in the IR and visible regions as well as moderate mechanical strength as a result of their relatively large grain sizes (i.e., 50–100 and ~150 μm for the products of GTE and Raytheon, respectively) owing to their very high sintering temperatures (i.e., 2170 and 1900 °C correspondingly) [4–6]. However, the undoped transparent yttria ceramic materials of Raytheon featuring higher thermal conductivity, showed better thermal shock resistance due to the additive-free composition [7,8]. In addition to the optical transmittance, the mechanical strength and thermal shock resistance are the most important properties of window materials for aerospace and military applications. In order to evaluate the mechanical strength of the transparent yttria ceramic materials, various testing methods, such as the uniaxial flexure of bars (three-point or four-point methods) or the biaxial flexure of disks (the ring-on-ring approach or the pin-on-three-balls method) were employed by different researchers [7–9]. Although the testing methods may have some effects on the mechanical strength, the data are generally comparable. It is known that yttria typically exhibits much lower mechanical properties in nature compared to many other transparent ceramic materials [10]. Additionally, the large grain sizes referred to above can deteriorate the strength of yttria ceramic materials further. Therefore, among transparent window materials, the mechanical strength capabilities of yttria (< 165 MPa) ceramics are considerably lower than these of sapphire (700 MPa), AlON (300 MPa), spinel (200 MPa), and silicon (70–340 MPa) [11]. According to available literature, the thermal shock resistance of transparent yttria ceramic materials is usually pre-estimated by the Hasselman mild thermal shock figure of merit using Eq.

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(1) [7,9],

$$R' = S(1-\nu)k/\alpha E, \quad (1)$$

where S is the strength, ν is Poisson's ratio, k is the thermal conductivity, α is the expansion coefficient, and E is Young's modulus. Among all of these parameters, Poisson's ratio, the expansion coefficient, and Young's modulus are intrinsic and nearly constant. However, the strength and thermal conductivity are strongly dependent on the microstructure and composition. Shibata et al. proved that fine-grained (3 μm) yttria samples without sintering additives exhibit much better thermal shock resistance (i.e., 1.37) compared to coarse-grained (~100 μm) pure samples (i.e., 0.57 by Shibata et al. and 0.94 by GET) and lanthanum-doped samples (i.e., ~0.6 by Raytheon) [7,9,11]. Unfortunately, the optical transmittance of the fine-grained pure yttria ceramic sample reported by Shibata et al. is not good enough for use, as it is nearly opaque in the visible range.

Meanwhile, in recent years, studies of transparent yttria ceramics have mainly focused on lasers and new processing methods [1,12–15], whereas investigations of high-temperature IR window applications are much less common. Previously, our group successfully developed a facile hot-pressing approach by which to fabricate highly transparent yttria ceramics, which is enabled simply by wrapping the samples with tantalum foil for the prevention of carbon contamination from the graphite mold. The hot-pressing temperature of 1600 °C is significantly lower compared to typical pressureless sintering temperatures (e.g., 1800 °C) of transparent yttria ceramics. Therefore, it can be expected that strengthened mechanical properties with fine microstructures (~1 μm in grain size) can be achieved by this new method [16,17]. In the present work, the authors demonstrated the fabrication of highly transparent yttria ceramic samples of a relatively large size (55 mm in diameter) by the hot-pressing process. Moreover, the mechanical and thermal properties of the samples were studied in detail with respect to high-temperature IR window applications.

2. Experimental procedure

Commercially available Y_2O_3 (99.99%, Rare Metallic Co. Ltd., Japan), $ZrO(CH_2COO)_2$ (98%, High-Purity Chemicals, Japan) and La_2O_3 (99.99%, Sigma-Aldrich, USA) powders were used as raw materials. According to the optimal compositions as determined in previous studies, 1 at.% ZrO_2 was introduced into the ZrO_2-doped sample, and 12 at.% La_2O_3 was added to the La_2O_3-doped sample [16,17]. The mixed powders were then milled with ZrO_2 balls in anhydrous alcohol (99.9%, Samchun, Korea) for 24 h. After ball-milling, the slurry was dried by a rotary evaporator at 80 °C (D_{50} of the milled and dried raw powder was 0.97 μm). The dried powder mixtures were ground and sieved though a 150-mesh sieve and then calcined at 1100 °C for 4 h to remove any organic components completely. The calcined powder mixtures were dry-pressed at 5 MPa into 55 mm round disks (about 22 mm in thickness) in a steel mold and then cold-isostatically pressed (CIP) at 20 MPa to enhance the green strength. The green bodies were pre-sintered in air at 1400 °C for 6 h. Subsequently, the pre-sintered bodies were hot-pressed with tantalum foil wrapping at 1600℃ for 12 h at a pressure of 20 MPa under a vacuum of about 9×10^{-3} Pa. After the long-term hot-pressing process, both the ZrO_2-doped and La_2O_3-doped samples showed grayness as a result of partial reduction in a vacuum atmosphere. Therefore, the samples were annealed at 1200 °C for 10 h in air for decoloration. In order to improve the transmittance of the annealed samples further, a hot-isostatic pressing (HIP) post-treatment at 1450 °C for 5 h under an Ar gas pressure of 180 MPa was applied to the samples.

Phase identification was conducted via an X-ray diffraction (XRD, D/Max 2500, Rigaku, Japan) analysis using Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 100 mA. A step size of 0.01° was used with a scan speed of 6°/min. The ceramic samples were pulverized into powders before the XRD analysis. Microstructural analyses were carried out using a scanning electron microscope (SEM, JSM-6700F, JEOL, Japan) and a transmission electron microscope (TEM, JEM-2100F, JEOL, Japan) equipped with an energy dispersive spectrometer (EDS, INCA Energy, Oxford Instruments, UK). The polished surface was thermally etched at 1400 °C for 2 h in air before the SEM observations, and the foils for the TEM analyses were prepared by a focused ion beam (FIB) treatment. The optical transmittance was measured by a UV-VIS-NIR spectrophotometer (Cary 5000, Varian, USA). The average grain sizes were examined by the line-intercept method using Eq. (2),

$$G = 1.56L, \quad (2)$$

where G is the average grain size and L is the average intercept length [15].

The flexure strengths were measured by the three-point bending method using machined ceramic bars (3 mm × 4 mm × 36 mm; five bars were prepared for each sample) on a universal tester (Instron 1195, Instron, USA). The thermal conductivity was calculated using Eq. (3),

$$k = \alpha \cdot \rho \cdot c_p, \quad (3)$$

where k is the thermal conductivity, α is the thermal diffusivity, ρ is the density, and c_p is the heat capacity. The thermal diffusivity and heat capacity were measured by the laser flash method using a laser flash analyzer (LFA 467 HyperFlash NETZSCH, Germany), and the densities of the samples were measured by the Archimedes method using distilled water. The samples were machined to 15 mm × 15 mm × 2 mm in size and were coated with platinum and graphite before the measurement. The thermal shock resistance of the samples was evaluated using the Hasselman mild thermal shock figure of merit according to Eq. (1), as mentioned above. The Schlieren image of the 1 at.% Zr-doped sample after annealing and HIPing was taken by an assembled facility, the major components include a 120 W LED lightsource with a 1000 μm pinhole (Cyclops I, KOMI, Korea), and a digital camera (Phantom VEO4K, Vision Research, USA). All measurements were conducted at room temperature.

3. Results and discussion

Fig. 1 presents XRD patterns of the two annealed samples doped with 1 at.% ZrO_2 and 12 at.% La_2O_3, respectively. It was found that both samples consist of the single cubic-yttria phase (JCPDS Card No. 41-1105; see the lower inset in Fig. 1) without impurity phases, which is in agreement with the results of our previous studies [16,17]. Additionally, the diffraction peaks of the La_2O_3-doped sample (see the

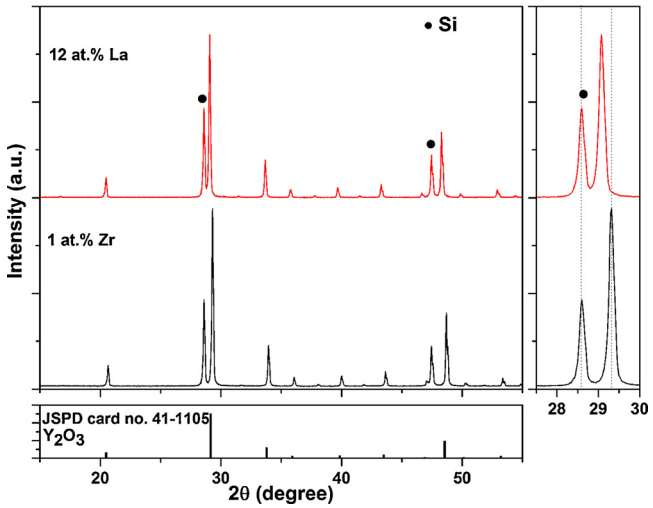

Fig. 1. XRD patterns of the annealed samples doped with 1 at.% ZrO_2 and 12 at.% La_2O_3.