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Upconversion luminescence properties of Er^{3+}/Yb^{3+} in transparent α-Sialon ceramics

Bin Li [a], Bhupendra Joshi [a,*], Yuwaraj K. Kshetri [a], Rajesh Adhikari [a], R. Narro-Gracia [b], Soo Wohn Lee [a]

[a] Research Center for Eco Multi-Functional Nano Material, Sun Moon University, Chungnam 336-708, Republic of Korea
[b] Centro de Investigaciones en Optica, A.P. 1-948, Leon, Gto. 37150, Mexico

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ABSTRACT

Er^{3+} stabilized transparent α-Sialon ceramics with upconversion (UC) luminescence properties were fabricated for the first time by hot press sintering method. The fabricated samples show better transparency as well as UC luminescence properties. Moreover, the effect of Yb_2O_3 as a sensitizer on UC properties was analyzed in Er-α-Sialon system. The change in Sialon phases and crystal structure were analyzed by X-ray diffraction. The chemical compositions and morphology of grains and intergranular phase were analyzed by EDS and Transmission Electron Microscopy, respectively. The UC emissions were observed around 527, 547 and 670 nm corresponding to the $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ transitions, respectively when excited by 980 nm continuous wave (CW) laser diode. UC process in Er^{3+} is found to be two photon processes. Intense green UC luminescence was observed with Er^{3+} and low amount of Yb^{3+} addition but higher amount of Yb^{3+} addition shows higher UC luminescence in red region. The transparency was higher in higher Er_2O_3 and low Yb_2O_3 content Sialon that was around 60% in visible light region. The chromaticity was also calculated for different samples and high color purity above 90% was obtained for green and yellow emissions. The mechanical properties were also investigated in this study.

1. Introduction

α-Sialon is the solid solution of α-Si_3N_4. During the formation of α-Sialon, Si–N is not only replaced by Al–O, but also is substituted by Al–N, whereas it would form imbalance of electric charge which needs cations to make the charge compensation. The cations usually are Li^+, Mg^{2+}, Ca^{2+} and most rare earth ions [1]. Sialon has been utilized into area of high-temperature structural ceramics in the past decades because of its excellent mechanical properties, thermal stability and oxidation resistance [2]. In recent years, α-Sialon ceramics, which show their potential application in the field of optics, have attracted considerable interest. Various cations doped translucent and transparent α-Sialon ceramics had been fabricated and studied [3–9], but few fabricated α-Sialon ceramics showed high transmittance in the range of visible light wavelength as well as in the range of near infrared wavelength.

According to computation, the band gap of α-Sialon ceramics is larger than 5.0 eV [10]. Due to its large band gap, α-Sialon ceramics can be made transparent by controlling the microstructure. Besides, the reduction of glassy phase in grain boundaries by transient liquid phase sintering would also contribute to transparency [3]. Engineering of upconversion (UC) material attracts a great deal of concern due to their potential applications including optical devices, data storage, biomedical applications and photovoltaics [11]. UC materials are rare earth doped compounds, in particular, glassy materials. However, due to their poor chemical stability and mechanical properties, these materials have limited industrial applications. Therefore, other advanced UC materials are yet to be investigated. Sialon ceramics, in particular is one of the promising host materials due to excellent chemical, mechanical and optical properties. In addition, host materials with low phonon energies and minimal impurities are desired in order to effectively generate phosphorescence. The transparent α-Sialon ceramics, which have low phonon energy, can accommodate rare earth cations, thus making them promising host materials for UC phosphors. Moreover, these materials can be utilized in lighting and display technology fields [12].

In the present work, α-Sialon ceramics doped with different amount of Er_2O_3 and Yb_2O_3 were investigated in order to achieve a good combination of the mechanical properties, transparency and UC properties.

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[*] Corresponding author at: GRL B121, Natural Science Building, Sun Moon University, Tanjeong Myeon, Asan si, Chungnam 336-708, Republic of Korea. Tel.: +82 41 530 2882; fax: +82 41 530 2840.
E-mail address: joshibhupen@gmail.com (B. Joshi).

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2. Experimental

The composition investigated here was designed according to the formula $Me_{m/v}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ [1]. Three main compositions with Er_2O_3 were made with $m = n = 0.9$, $m = n = 1$ and $m = n = 1.1$ for samples denoted as SAE09 (9.03 wt% Er_2O_3), SAE10 (10 wt% Er_2O_3) and SAE11 (10.92 wt% Er_2O_3), respectively. For comparative study, 0.5, 1 and 8 wt% Yb_2O_3 were co-doped in Sialon with $m = n = 1.1$ and the samples as prepared were named as SAEY05 (10.5 wt% Er_2O_3 and 0.5 wt% Yb_2O_3), SAEY1 (10 wt% Er_2O_3 and 1 wt% Yb_2O_3) and SAEY8 (3 wt% Er_2O_3 and 8 wt% Yb_2O_3), respectively for our convenience. The starting powders used for the composition were α-Si_3N_4 (SN-E10, UBE Co., Japan), Al_2O_3 (High purity chemicals Co. Ltd., Japan), AlN (Grade F, Tokuyama Corp., Japan), Er_2O_3 (High purity chemicals Co. Ltd., Japan) and Yb_2O_3 (High purity chemicals Co. Ltd., Japan). The mixed powders were put into the polyethylene bottle with high purity Si_3N_4 balls in absolute ethanol and milled for 24 h. After the milling, the mixed slurry was dried at 40 °C in a rotary evaporator and then put into drying oven at 80 °C for 8 h. The obtained powder was dry milled with Si_3N_4 balls for 12 h. Then the powder was sieved through a 150 μm aperture sieve.

15 g of sieved powder was packed into the graphite mould with an inner diameter of 50 mm to make about 2 mm thick sample and transferred into a hot pressing graphite-element furnace (MVHP, Monocerapia Co. Ltd., Korea). Samples were sintered at 1900 °C for 2 h in nitrogen environment with a pressure of 30 MPa. The heating rate was firstly 20 °C/min from room temperature to 1050 °C and then 10 °C/min to 1900 °C. The cooling rate was 10 °C/min from 1900 °C to 1050 °C, then naturally to room temperature in the furnace.

The bulk densities of specimens were measured according to Archimedes principle. The phases of crystalline Sialon ceramics were characterized by X-ray diffractometer (XRD, Cu Kα, RIGAKU D/MAX 2200HR diffractometer, Japan). Hardness and fracture toughness were measured by Zwick 3212 hardness tester. The indentation of specimens was performed under 98 N loads for 15 s on mirror polished surface. The microstructure were detailed by SEM (SNE-3000, SEC, Co. Ltd., Korea) and 400 kV TEM (JEM-4010, JEOL, Co. Ltd., Japan). The optical transmittance from 200 nm to 1100 nm was measured by spectrophotometer (MECASYS Optizen2120). The UC emission spectra of specimen excited with 980 nm IR light and supplied by 100–200 mW of a Continuous Wave Laser Diode were obtained on the PC-controlled SP-2357 spectrograph (Acton Research). The emitted signal was detected and collected by the photomultiplier tube R955 (Hamamatsu).

3. Results and discussion

3.1. XRD and microstructure analysis

The phases were studied from XRD pattern analysis as shown in Fig. 1. Both Er^{3+} and Yb^{3+} ions contribute to stabilize α-Sialon completely. Main phase appeared as α-Sialon in higher rare earth cations doped samples. But in sample SAE09, low concentration of rare earth oxide caused lacking of liquid phase to enhance the formation of α-Sialon through diffusion of cations in grains from liquid phase, therefore a little amount of β-Sialon phase was formed. The volume percentage of α-Sialon is given in Table 1. As the amount of rare earth oxide additions increased, more cations were utilized to form α-Sialon during the sintering. Thus higher volume percentage of α-Sialon was observed in higher amount of rare earth oxide doped α-Sialon ceramics. The result shows that the amount of rare earth oxide is crucial to control the liquid phase and phase transformation.

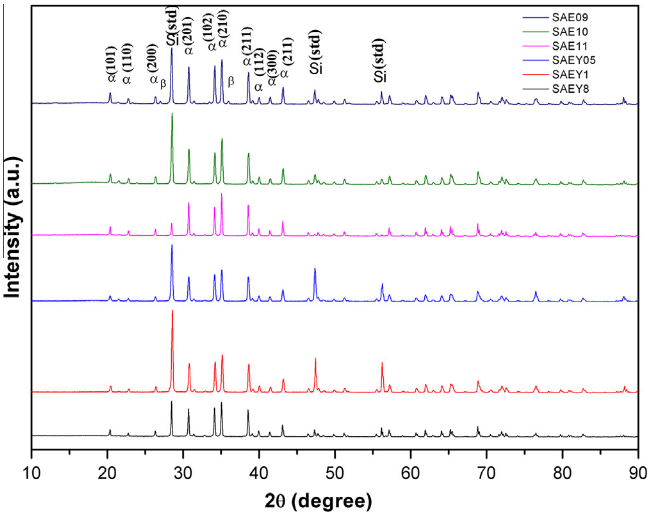

Fig. 1. XRD patterns of Sialon with different compositions.

Table 1
Phase composition and cell parameters of sintered Sialon ceramics.

Sample	Phase composition (vol%)		α-Sialon		β-Sialon	
	α	β	a (Å)	c (Å)	a (Å)	c (Å)
SAE09	91.04	8.96	7.8121	5.6938	7.6308	2.9268
SAE10	95.17	4.83	7.8194	5.6954	–	–
SAE11	96.71	3.29	7.8185	5.7019	–	–
SAEY05	94.48	5.52	7.8065	5.6626	–	–
SAEY1	94.80	5.20	7.8231	5.6954	–	–
SAEY8	96.44	3.56	7.8089	5.6500	–	–

The SEM of fracture surface morphologies of α-Sialon ceramics were observed as in Fig. 2. As shown, the grains of samples with Er_2O_3 are all isometric, which are the most common α-Sialon grains morphology. Compared with other samples, the fracture surface of SAE09 shows larger grains as shown in Fig. 2. Additionally, most grain showed equiaxed morphology, which is consistent with most transgranular fractures and few intergranular fractures that were observed by SEM.

The equiaxed polyhedral grains with thin grain boundaries, which are good for transparency, were observed in both samples SAE11 and SAEY8 by TEM as shown in Figs. 3 and 4, respectively. The EDS analysis of sample SAE11 at point 2 shows that the grain of α-Sialon was stabilized by Er^{3+} as shown in Fig. 3. The α-Sialon phase was confirmed by EDS as higher amount of Si was observed along with Al, N, O and Er elements and also by diffraction pattern DP2 as shown in Fig. 3. The EDS analysis and diffraction pattern DP1 of point 1 in Fig. 3 reveals AlN polytypoid as Al concentration was higher than other elements. The diffusion of Er^{3+} cation was also confirmed in AlN polytypoid by EDS. Higher Er^{3+} concentration observed at triple junction at point 3 suggests that the most of the Er^{3+} cations remained in intergranular oxynitride glassy phase. The fabricated Sialon ceramics is not single phase polycrystalline but other phases also exist due to the addition of different additives. Even though, there exist other phases, the fabricated Sialon ceramics are transparent. As revealed by EDS, the existence of Er^{3+} cation in other phases may contribute to UC luminescence. Herein, it is difficult to observe the UC luminescence of AlN polytypoid grains and intergranular glassy phase because they exist as a minor phase.

In Fig. 4, for the sample SAEY8, which was co-doped with Yb_2O_3 along Er_2O_3, the α-Sialon grain consists of Yb^{3+} ions while Er^{3+} was located in triple junctions and grain boundaries. This is because of the α-Sialon structure which has two sites in the unit cell that only