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Preparation and Characterization of Nd^{3+}:ZnO-B_2O_3-Al_2O_3-SiO_2 Transparent Glass-Ceramics

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Nd^{3+}-doped transparent ZnO-Al_2O_3-B_2O_3-SiO_2 glass ceramics was prepared by controlled crystallization of melt-quenched glass. The glass-ceramics sample is characterized by DSC, XRD, SEM and photoluminescence spectra. We discussed the crystalline phase of glass-ceramic composition, crystal structure, microstructure morphology and the relationship of the heat-treatment to the optical transmittance and absorption lines, The fluorescence spectra of the glass-ceramics samples were studied and results showed that the neodymium ion doped glass-ceramics samples in the range of 850-1400 nm emission intensity is higher than the neodymium doped glass samples and glass to glass-ceramic conversion of the fluorescence properties of the neodymium ion enhance and different heat treatment. The fluorescence spectra were compared to identify the variation between the heat treatment temperature and the emission intensity.

Key Words: ZnO-B_2O_3-Al_2O_3-SiO_2, Glass-ceramic, Nd^{3+}-doped.

INTRODUCTION

Glass-ceramics were discovered by Stookey[1], glass-ceramics are polycrystalline ceramic materials consisting of at least one crystalline phase or a vitreous of phase[2], prepared by the controlled nucleation and crystallization of precursor glass, where the amount of residual glassy phase is usually less than 50 %. The precursor glass is melted, quenched and shape-processed and then is thermally converted into a composite material formed by a crystalline phase dispersed within a precursor glass. The basis of controlled internal crystallization lies in efficient nucleation often enabled by a little amount of a nucleating agent, it allows the development of fine, randomly oriented grains, in a ceramic generally without voids, micro-cracks, or other porosity[3-7]. Various oxides such as TiO_2, ZrO_2, are generally added as nucleating agents in the base glass composition. During controlled heat treatment, nuclei are formed and different crystalline phases are grown in the glass depending on the heat treatment. Glass-ceramics has some good characteristics, such as uniform, transparency, good chemical stability and isotropic, *etc.*, it easily to make all sorts of sizes and shapes of products such as fiber special-shaped products and big size products. It can be doped high concentrations of rare earth activator ions and is good host materials for preparation of optical materials The 4*f* electronic structure of rare earths making its good fluorescence properties, such as pure, luminous chromaticity, physico-chemical properties stable and higher conversion efficiency characteristic[8,9]. ZnO-B_2O_3-Al_2O_3-SiO_2 glass-ceramics is one of the commonest and also the most extensively used glass material, mainly applied to building, automobile, adornment, lighting, photoeleetricity, *etc*. and the raw materials is cheaper, preparation technology is mature, so the study of rare earth ions in ZnO-B_2O_3-Al_2O_3-SiO_2 glass-ceramics is important and practical application meaning. The aim of this study is to compare the photoluminescence spectra of Nd^{3+} in ZnO-B_2O_3-Al_2O_3-SiO_2 glass-ceramics and glasses, as is a foundation of further research on glass-ceramic laser materials.

EXPERIMENTAL

Preparation: Analytical grade SiO_2, Al_2O_3, ZnO, KOH, H_3BO_3, TiO_2, ZrO_2 and Sb_2O_3 are used as the starting materials for the precursor glass preparation. The composition of glass is given in Table-1. TiO_2 and ZrO_2 are used as nucleating agent s and Sb_2O_3 is used as the clarifier. The introduction of K_2O in the glass composition modifies thermo-physical properties, including reduction in viscosity, increase in thermal expansion. And Nd_2O_3 was used to introduce Nd^{3+} ions, which would radiate light after being excited.

The raw materials were homogenized in a planetary ball mill. The batch was melted in a carborundum crucible at 1300 ºC for 1 h in the $MoSi_2$ electrical resistance-heating furnace having a PID temperature controller. The melt was then poured on a stainless steel plate at room temperature and

TABLE-1
COMPOSITIONS OF THE $ZnO-B_2O_3-Al_2O_3-SiO_2$ GLASS BATCH

Element	Batch composition mol (%)	Starting materials
B	4.5	H_3BO_3
Al	14.6	Al_2O_3
Si	21.9	SiO_2
O	54.5	H_3BO_3, Al_2O_3, SiO_2
Zn	2.0	ZnO
K	1.5	KOH
Zr	0.4	ZrO_2
Ti	0.4	TiO_2
Sb	0.2	Sb_2O_3
Nd	0.1	Nd_2O_3

samples obtained subsequently were annealed at 500 ºC for 2 h and allowed to cool to room temperature at a rate of 8 ºC/min to relieve internal stress. Finally, light purple, transparent, bubble-free glasses were obtained. The glass-ceramic samples of 10 mm × 10 mm × 1 mm were cut and polished before optical measurements were made.

Characterization: The nucleation and crystallization temperatures of the glass were determined by differential thermal analysis (Pyris-Diamond, Perkin-Elmer). The DTA curve was recorded over 30-1000 ºC at a heating rate of 10 ºC/min.The commercial X-ray powder diffraction system (D/max 2500V, Rigatu, Japan) with CuK_α radiation (1.54056 Å) was used for identification of crystalline phases. Each pattern was scanned from $2\theta = 5$-50º at the rate of 4 º/min. The resulting glass-ceramics were investigated by UV-VIS-NIR scanning spectrophotometer (UV-3101PC, Shimadzu, Japan). Prior to optical spectrometry measurements, the specimens were cut into blocks and polished to 10 mm × 10 mm × 1 mm. The photoluminescence (PL) spectra of samples were studied at room temperature using a fluorescence spectrometer under Ar ion laser excitation (PL9000, BIO-RAD, UK).

RESULTS AND DISCUSSION

The DSC curve taken on the ZBAS precursor glass is shown in Fig. 1. Two events can be observed: (1) a change of the slope line, corresponding to the T_g range; (2) two exothermal peaks associated with crystallization. The DSC curve is characterized by a unobvious endothermic peak at 572-648 ºC and the endothermic base line shift at 572 ºC gives the beginning of glass transition temperature T_g. The highest points of the two exothermic peaks locate at 741 and 798 ºC, respectively, there might exist a crystal transformation around 798 ºC to be testified by XRD measurements. To obtain glass-ceramics with a large number of crystal nuclei, heat treatments were performed at temperatures near to the maximum nucleation and growing rates, 580, 600 ºC were chosen as the nucleation temperatures and it has been verified that the nucleation at 600 ºC is the most advisable. As the maximum crystal growth occurs at temperatures near to the second exothermic peak, so 650, 700, 740 and 780 ºC were chosen as the crystallization temperatures.

XRD patterns for some specimens of present investigations are shown in Fig. 2. Experimental results show that heat treatments at 650-780 ºC lead to the formation of crystals. All the peaks were analyzed with JCPDS files. The diffraction peaks attributable to $ZnAl_2O_4$ and Al_4BO_9 are marked by open

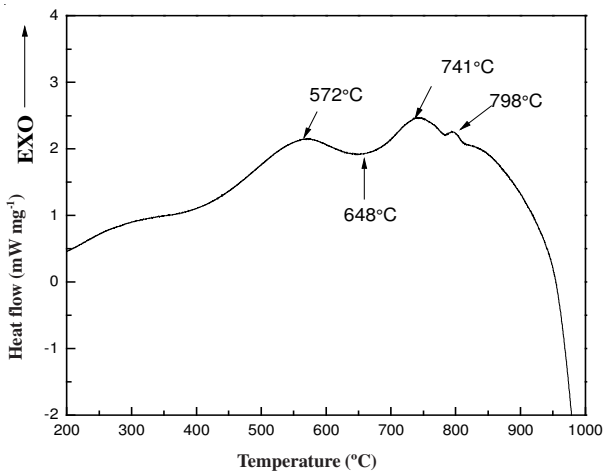

Fig. 1. DSC curve of precursor glass

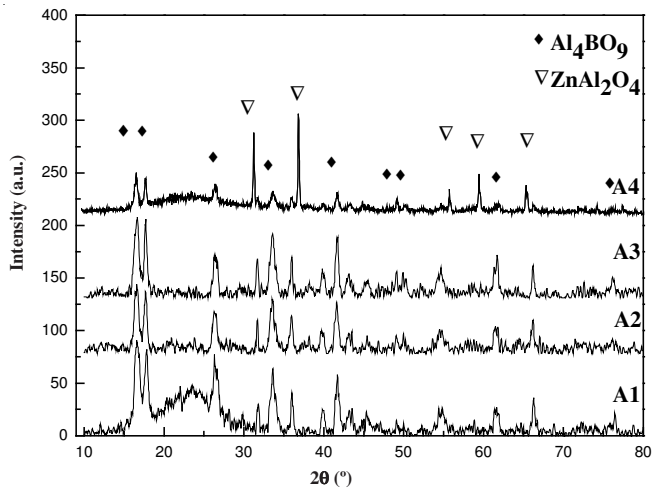

Fig. 2. XRD patterns of glass-ceramics under different heat treatment processes

TABLE-2
HEAT-TREATMENT PROCESSES AND CRYSTAL PHASES

Samples No.	Temp. (ºC) × time (h) for nucleation	Temp. (ºC) × time (h) for crystallization	Main crystal phase	Minor crystal phase
A_1	600 × 2	650 × 1	Al_4BO_9	$ZnAl_2O_4$
A_2	600 × 2	700 × 1	Al_4BO_9	$ZnAl_2O_4$
A_3	600 × 2	740 × 1	Al_4BO_9	$ZnAl_2O_4$
A_4	600 × 2	780 × 1	$ZnAl_2O_4$	Al_4BO_9

circles and observed for all of the heat treated specimens. It is noted that the intensity of gahnite $ZnAl_2O_4$ crystalline phase becomes larger with the increase of heat treatment temperature duration. It is clear that $ZnAl_2O_4$ also precipitates in the heat treated specimens when the temperature is above 780 ºC, the diffraction peaks attributable to $ZnAl_2O_4$ are signed by open squires.

SEM: SEM has been used to study the glass-ceramics morphology, the grain size and distribution in the residual precursor glass. Glass-ceramics A3 is composed of crystallites of 50 nm in size as shown in Fig. 3, which can also explains its transparency even when high crystallized. These small crystallites are generally in clusters conglomerated. The sample A 1 has smaller grain size, nearly 20 nm for their shorter creaming duration.

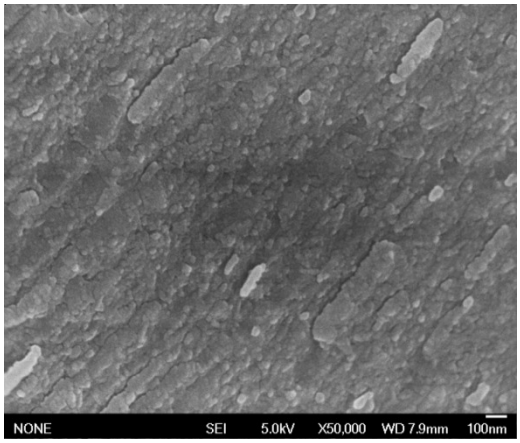

Fig. 3. SEM micrograph of specimens A3

The transmission spectra of glass-ceramics and precursor glass are shown in Fig. 4 from Fig. 4, there exist six absorption peaks around 523, 582, 658, 744, 802 and 870 nm corresponding to the electron transitions $^4I_{9/2} \rightarrow {}^4G_{7/2}$, $^4I_{9/2} \rightarrow {}^4H_{11/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^4I_{9/2} \rightarrow {}^4F_{13/2}$ of neodymium ion and the main absorption concentrates at 582 nm. The absorption intensity of glass is lower than that of glass-ceramics, which is explained as above. The glass-ceramic has a sharp absorption of light when pumped by the mercury-xenon lamp or diode laser.

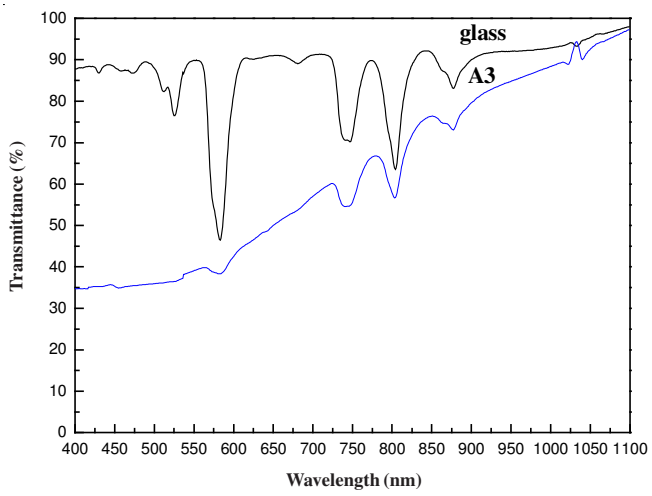

Fig. 4. UV-VIS-NIR spectroscopy for glass and glass-ceramics: A3

Photoluminescence analysis: From Fig. 5, there exists four main emission peaks in photoluminescence spectra around 892, 1057, 1107 and 1333 nm and the emission light intensity of precursor glass is little higher than that of glass-ceramics. These transitions correspond to $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$. The sharp emission peak is around 1064 nm and the lasing of glass-ceramics materials can be achieved. From the combination of Fig. 5, one can observe that the glass-ceramics has stronger emission than the glass, although the former has weaker absorption than the later, which is contributed to the surrounding conditions difference of neodymium ion in the two materials. In glass, the ground energy level electrons, absorbing the photons, transit to the pumping energy level and most of the excited atoms are transferred by fast radiation less transitions into the ground energy level, in this process the energy lost by electron is transferred to the lattice, the main energy is absorbed by the phonons, so the emission light intensity is weakened. But in glass-ceramics, the energy loss caused by phonons is lower than that in glass, because of the lower phonon energy, so the high light emission intensity can be obtained. From the photoluminescence line shape, the widths broadened in homogeneously are caused by random distribution of static crystalline fields acting on the neodymium ions. The line shape of glass-ceramics is much better than that of precursor glass.

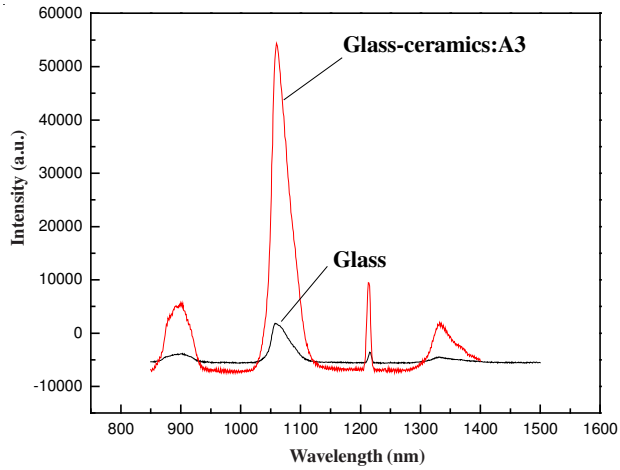

Fig. 5. Fluorescence spectra of Nd^{3+} ions in glass and glass-ceramics: A3

Conclusion

The $ZnO\text{-}B_2O_3\text{-}Al_2O_3\text{-}SiO_2$ transparent glass-ceramic are formed by the melting and quenching technique. The transmittance and photoluminescence of glass and glass-ceramics are measured. The glass-ceramics has a lower transmittance than that of precursor glass, contributed to the electron configuration difference of materials. The main light absorptions are around 582, 744 and 802 nm and the main emission are around 892 and 1333 nm. The lasing at 1064 nm can be achieved if pumped by mercury-xenon or diode laser. The glass-ceramics has weaker absorption and stronger emission than those of oxide precursor, which indicates that the $ZnO\text{-}B_2O_3\text{-}Al_2O_3\text{-}SiO_2$ glass-ceramics is a more prospective precursor for transparent glass-ceramic laser material, which will have a lot of work to do.

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