Preparation and characterization of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped $\text{Na}_2\text{O}-\text{Nb}_2\text{O}_5-\text{SiO}_2$ transparent glass-ceramics

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$\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped transparent niobosilicate glass-ceramics with main crystalline phase NaNbO_3 were prepared by crystallization of glass. The heat treatment temperature, crystalline phase composition, microstructure, optical transmittance and up conversion luminescence of the samples were investigated using differential scanning calorimetry, X-ray diffraction, scanning electron microscopy, Ultraviolet-Visible-Near Infrared spectrophotometer and fluorescence spectrometer. The results show that the optimum crystallization temperature is 700°C , the optimal heat treatment time is 2 h and the transmittance of the sample in the near infrared region at 850 nm is up to 79% under the condition of $\text{Yb}^{3+}/\text{Er}^{3+}$ molar ratio of 7.5:1. The influence of different $\text{Yb}^{3+}/\text{Er}^{3+}$ doping concentration on the luminescent properties of glass-ceramics and the up-conversion luminescence mechanism was discussed. It was found that the luminescence intensity was the highest when the $\text{Yb}^{3+}/\text{Er}^{3+}$ doping molar ratio was 7.5:1.

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Key-words : Glass-ceramics, NaNbO_3 , Erbium, Ytterbium, Up-conversion luminescence

[Received March 7, 2017; Accepted June 22, 2017]

The glass-ceramics is a polycrystalline solid material obtained by heat-treating the matrix glass.^{1),2)} The material has both microcrystalline phase and glass phase, so it has both the easy processing of glass and has a high luminous efficiency of crystal, the glass-ceramics can be used as solid laser material, up-conversion luminescent material and optical storage material.³⁾⁻⁷⁾ In the up-conversion luminescence, Er^{3+} is an important and active ion which has been researched the most in recent years. It can absorb two or more photons to achieve up-conversion luminescence because of the long-lived intermediate state energy level, the emission wavelength can be green or red light in the visible region due to the rich 4f energy level structure.⁸⁾⁻¹⁰⁾ It is common to co-doped Yb^{3+} with larger absorption cross-section as the sensitizer to enhance the up-conversion efficiency of the material because of Er^{3+} ion have a small absorption cross section at the wavelength of 980 nm. Substrate materials have a large effect on the up-conversion luminescence efficiency. Matrix materials suitable for up-conversion luminescent should have smaller phonon energies, if the phonon energy of the host is high, the excited state energy level of the excited ions is associated with the lattice vibrations (phonon), the probability of the activation of non-radiative transition back to the ground state will increase, resulting in a significant decrease in the efficiency of up-conversion luminescence.¹¹⁾⁻¹⁵⁾

Sodium niobate is a chemically stable perovskite type composite oxide with low phonon energy and excellent optical and mechanical properties.¹⁶⁾⁻²⁴⁾ Transparent glass-ceramics containing nanocrystalline NaNbO_3 were obtained by M. M. Layton and

Andrew Heczog and the structure of the glass-ceramic were studied.²⁵⁾ P. Kongputon and A. Niyompan reported that crystallization in $\text{Na}_2\text{O}-\text{Nb}_2\text{O}_5-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass-ceramics system with partial replacement of SnO_2 for Al_2O_3 and dielectric properties were investigated.²⁶⁾ In recent years, investigations of sodium niobate powders have attracted much attention due to their excellent luminescence and structure properties. NaNbO_3 -based up-conversion phosphor with Yb^{3+} , Er^{3+} , and Al^{3+} was prepared by H. Naruke and T. Yamase.²⁷⁾ A. F. Pereira, K. U. Kumar and W. F. Silva reported Thulium/Ytterbium co-doped sodium niobate (NaNbO_3) colloidal nanocrystals by the Pechini sol-gel method as three-photon-excited luminescent nanothermometers.²⁸⁾ Tôru Kyômen, Sayaka Hasuko, Minoru Hanaya and Hiroshi Takashima reported oxide inorganic electroluminescent device in which thin films of Pr-doped NaNbO_3 phosphor and Sb-doped SnO_2 transparent conductor are alternately stacked was prepared by sol-gel and spin-coating methods.²⁹⁾ Until now, there are many studies on dielectric properties of the NaNbO_3 glass ceramics and optical performance of the NaNbO_3 phosphor. But the up-conversion optical performance of transparent glass-ceramics containing nanocrystalline NaNbO_3 has not been studied.

In the paper, $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped niobium silicate glass ceramics were prepared by crystallization of glass method. The heat treatment temperature, composition, microstructure, optical transmittance and optical properties of samples were studied. The effects of the doping concentration of Er^{3+} and Yb^{3+} on the luminescent properties and the up-conversion luminescence mechanism were also discussed.

The glass with composition of $50\text{SiO}_2-15\text{Nb}_2\text{O}_5-25\text{Na}_2\text{O}-10\text{K}_2\text{O}-0.2\text{Er}_2\text{O}_3-1.5\text{Yb}_2\text{O}_3$ (mol %) was prepared using Metal oxide powders by melt-quench technique. The purity of Er_2O_3

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and Yb_2O_3 is 99.99%, and the other raw materials is 99.90%. The raw material was mixed thoroughly in an agate mortar and melted in a platinum crucible in the silicon-molybdenum furnace. First of all, the electric furnace was heated to 1100°C for 1 h, which helps the decomposition of carbonates and gas escape. The furnace was heated up to 1450°C for 2 h in the air with intermittent stirring for homogenization of the glass melt, the melt was transferred into a mold and followed by annealing at 450°C for 2 h to remove the internal stresses in the glass, and then slowly cooled down to the room temperature. The glass is designated as matrix glass. A portion of the glass samples were ground to a powder for DSC testing, and the remaining glass samples were crystallized in a different heat treatment regime to obtain the transparent glass-ceramic sample. The glass-ceramic samples were cut into small pieces with the size of $10\text{ mm} \times 10\text{ mm} \times 3\text{ mm}$ and optically polished for performing the various tests.

The SDT2960 thermal analyser was used to analyze the crystallization temperature of the glass samples at a heating rate of $10^\circ\text{C}/\text{min}$; the temperature range was room temperature to 1200°C . X-ray diffraction (XRD) pattern was recorded using Rigaku D/max 2500V with the anchor scan parameters wavelength $\text{Cu K}\alpha$ equal $1.5406 \times 10^{-9}\text{ nm}$ at 300 K, having a source power of 40 kV and 30 mA, for identifying the developed crystalline phases of the heat-treated glass-ceramics. The samples were characterized by Carl Zeiss XL-30 scanning electron microscopy. The fourier transform infrared transmittance spectra of the glass and glass-ceramics were recorded using a Vertex 70 FTIR spectrometer by Bruker corporation with KBr disc method. The samples were ground to a powder and then thoroughly mixed with dry KBr powder to pressed into thin slices, the FTIR with KBr blanks as a reference were recorded. The transmittance of the samples were measured with Shimadzu UV-Vis-NIR spectrophotometer. The fluorescence spectrum of the samples were recorded using PL9000 fluorescence spectrometer from the BIO-RAD company in the wavelength range from 500 to 700 nm with a scan rate of $1200\text{ nm}/\text{min}$ and step length of 0.2 nm .

Figure 1 is DSC curve of the substrate glass rising from room temperature to 1200°C at a heating rate of $10^\circ\text{C}/\text{min}$. DSC curve can be used to analyze the substrate glass transition temperature and crystallization temperature, and then determine the best heat treatment system. The glass transition temperature (T_g) has been estimated from the point of intersection of the tangents drawn at the slope change is 519°C . There are two exothermic peaks at 603 and 731°C . The matrix glass heat treatment system was determined combined with the experiment as given in **Table 1**.

Fig. 1. DSC curve of the initial glass.

Figure 2 shows the XRD patterns of the glass-ceramic samples (D_1 – D_4) heat-treated under different conditions. It was found that all of the diffraction peaks were consistent with the standard diffraction peak of NaNbO_3 on the Joint Committee for Powder Diffraction Standards (JCPDS) card, and the crystals were NaNbO_3 (33-1270) in the glass-ceramics. We can find that the crystal type of the samples did not change, the diffraction peak intensity gradually increased, and the number of crystals increased with the treatment time prolonged by comparing the XRD curves of samples D_1 , D_2 , D_3 and D_4 in Fig. 2.

Figure 3 shows the scanning electron micrographs of the glass-ceramic samples D_1 – D_4 . The sample D_1 was heat-treated at 700°C for 1 h started to appear round grains, the number of grains is small, and the degree of crystallization is low. The average crystallite size is about 80 nm. After the heat treatment time was extended from 1.5 h to 2 h, grain size increases with the increase of heat treatment time, the average size of D_2 and D_3 are about 110 nm and 150 nm. The grain shape from the circle into a hexagonal, evenly distributed in the matrix glass. The grain size of sample D_4 after heat treatment at 700°C for 2.5 h, resulting in the appearance of a larger crystals and reunion phenomenon, larger degree of crystallization compared with other samples. The grain size is about 190 nm in the D_4 . It is clearly observed that the gradual increase in the grain size and the crystallinity of the heat-treated samples with the increase of the heat-treatment time. This is due to the fact that the relatively large size grains are surrounded by a number of smaller size grain, resulting in a large number of polygonal grains (grain edges which is defined as the number of grains with different orientations in contact with each other), these polygonal grains gradually engulfed the surrounding small grains in the subsequent growth process, and the grain size difference becomes large. The grain size increases with the disappearance of a small part of the original grains.³⁰⁾ The precipitated phase of the system constantly depletes the dopant component of the matrix glass in the process of grain growth. The energy of the

Table 1. Glass heat treatment system

Samples	Nucleation temperature /time	Crystallization temperature /time
D_1	$600^\circ\text{C}/2\text{ h}$	$700^\circ\text{C}/1\text{ h}$
D_2	$600^\circ\text{C}/2\text{ h}$	$700^\circ\text{C}/1.5\text{ h}$
D_3	$600^\circ\text{C}/2\text{ h}$	$700^\circ\text{C}/2\text{ h}$
D_4	$600^\circ\text{C}/2\text{ h}$	$700^\circ\text{C}/2.5\text{ h}$

Fig. 2. X-ray diffraction patterns of glass ceramics samples under different heat treatment processes.

Fig. 3. SEM micrographs of glass-ceramic specimen.

Fig. 4. FT-IR spectroscopy of glass and transparent glass-ceramics.

crystalline phase of the $\text{Na}_2\text{O-Nb}_2\text{O}_5$ system becomes weaker as the crystal grows, and the final crystallization region is formed.³¹⁾

The FTIR absorption spectroscopy of the matrix glass and samples heat-treated in the wavenumber range $400\text{--}1350\text{ cm}^{-1}$ are shown in Fig. 4. Four major absorption bands were observed in the infrared absorption spectra of the matrix glass. The absorption band at 453 cm^{-1} as a result of the bending vibrations of Si–O–Si. The band at 708 cm^{-1} is caused by the Nb–O bond stretching vibration in the NbO_6 octahedra. The symmetrical stretching of O–Si–O vibration corresponds to the absorption band at 803 cm^{-1} . A broad and strong absorption band centered at 1020 cm^{-1} as a result of the asymmetric stretching of Si–O vibration in the SiO_4 tetrahedra. The matrix glass has good stability by three-dimensional network composition of NbO_6 octahedra and SiO_4 tetrahedra. From the absorption spectroscopy of glass-ceramic samples D1 and D4, it is seen that the Nb–O stretching vibration appeared at 660 cm^{-1} , possibly due to lattice vibrations. The absorption band intensity becomes stronger with the increase

Fig. 5. UV-vis-NIR spectroscopy for samples.

of heat treatment time. It is known that the Nb–O bonds of NbO_6 octahedra is a lattice former of NaNbO_3 in the Si–O bonds containing SiO_4 tetrahedral network. The sodium ions play the role of charge compensators of excess negative charge at Nb^{5+} cations.^{32),33)}

Figure 5 shows the transmittance curve of the sample with 1 mm thickness. The glass transmittance is the highest, and the optical transmittance of the prepared glass-ceramic gradually decreased with the increase of the treatment time. Because of the different heat treatment system of glass ceramics in the crystal size, number and distribution are different, so that the prepared glass ceramic light transmittance will be different. D1 sample transmittance was not significantly different from that of the untreated glass because of crystallization degree is low. The transmittance of the D2 sample was slightly lower than that of the D1 sample, the transmittance of the sample reach 88% at 850 nm in the near infrared region. The transmittance of D3 samples in the near - infrared region can reach 79% at 850 nm, but the transmittance of the visible region decreases obviously. D4 transmittance is very low, because it not only a large number of

Fig. 6. Up-conversion spectra of Er³⁺/Yb³⁺ ions in glass and glass-ceramics.

Fig. 7. Up-conversion spectra of different Er³⁺/Yb³⁺ ions in glass-ceramics.

crystals, but also the emergence of overlapping and reunion in the long heat treatment process, and scattering will be great because of the light is blocked in the passage.

Figure 6 shows the emission spectra of Er³⁺/Yb³⁺-doped glass and glass ceramics at an excitation wavelength of 980 nm. The glass-ceramic sample is obtained after crystallization at 700°C for 2 h, and the rare-earth ion doping concentration of the matrix glass and the glass-ceramic is the same. It can be seen from the figure that the emission peak intensity of the glass-ceramic sample is obviously higher than that of the matrix glass. It shows that a small amount of Er³⁺ and Yb³⁺ earth incorporated into the sodium niobate crystal. Because of the crystal doesn't have preferable rare earth site, so solid solubility limit would be small. If the amount of rare earth exceed it, photoluminescence intensity would also decrease. The emission spectrum of the sample shows three emission peaks at 525, 543 and 660 nm, respectively. The emission peak at 525 nm is a ²H_{11/2}→⁴I_{15/2} transition, and the green emission at 543 nm is the strongest, which is a ⁴S_{3/2}→⁴I_{15/2} transition, and the emission peak at 660 nm is a ⁴F_{9/2}→⁴I_{15/2} transition.

Figure 7 shows the up conversion emission spectra of Er³⁺/Yb³⁺-doped series glass-ceramic samples excited at 980 nm. In this experiment, Er³⁺/Yb³⁺ co-doped glass ceramics with different concentration of Yb³⁺ were prepared. The glass-ceramic samples were obtained after crystallization at 700°C for 2 h. The ratios of doped Yb³⁺/Er³⁺ are 5:1, 7.5:1, 10:1, 12.5:1. It was

found from the emission spectra that the intensity of the emission peak first increased and then decreased with increasing the concentration of Yb³⁺ doping when the Er³⁺ doping concentration was fixed. The luminescent intensity is the strongest when the ratio of Yb³⁺/Er³⁺ doping is 7.5:1, and it is the most suitable rare earth doping concentration. The absorption band of ²F_{7/2}→²F_{5/2} of Yb³⁺ is overlapped with the absorption band of ⁴I_{15/2}→²I_{13/2} of Er³⁺, so Yb³⁺ ions can pass through the Yb³⁺ to Er³⁺ energy transfer to improve the luminous intensity of Er³⁺. Yb³⁺ ions act as sensitizers throughout the process.

In this study, the transparent niobium silicate glass ceramics with the molar ratio of 50SiO₂–15Nb₂O₅–25Na₂O–10K₂O–0.2Er₂O₃–1.5Yb₂O₃ (mol %) were prepared by crystallization of glass method. The results show that NaNbO₃ nanocrystal particles were formed of the glass ceramics, and heat treatment is 700°C for 2 h, and the transmittance is up to 79% in the near infrared region at 850 nm. By analyzing the fluorescence spectra of glass-ceramic samples, we found the intensity of emission peak increases at first and then decreases with the increase of Yb³⁺ concentration when the concentration of Er³⁺ doping is fixed, which indicates that Yb³⁺ to the energy transfer of Er³⁺ plays a major role effect. The optimal Yb³⁺/Er³⁺ doping concentration molar ratio is 7.5:1 because the luminous intensity is the highest, which shows excellent fluorescence properties on the matrix glass.

Acknowledgments This work was financially supported by The National 863 Project (2011AA030204), Key Research Project of Jilin Provincial Science and Technology Department (20160204027GX).

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