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THERMAL, OPTICAL CHARACTERIZATION AND JUDD-OFELT ANALYSIS OF Nd^{3+}-DOPED $BaO-TeO_2-B_2O_3$ GLASSES

TERMIČNO-OPTIČNA KARAKTERIZACIJA IN JUDD-OFELTOVA ANALIZA $BaO-TeO_2-B_2O_3$ STEKEL, DOPIRANIH Z Nd^{3+}

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Barium-tellurite-borate glasses doped with Nd^{3+} ions were prepared by the melt-quench technique. The amorphous nature of the glasses was confirmed by XRD. The thermal stability of the borate glass was calculated from DTA profiles and TG. The absorption and the luminescence spectra of the glass were measured at room temperature. The spectrum properties of the glass were carried out by using Judd-Ofelt (J-O) theory, the intensity parameters Ω_k (k= 2, 4, 6) and radiative lifetimes were also calculated. The absorption band at 804 nm has a full-width at half-maximum of 18 nm. The fluorescence spectra revel three major bands. The strongest fluorescence spectrum-emission peak is located at 1062 nm, which can be attributed to the $^4F_{3/2}$–$^4I_{11/2}$ of the emission band of Nd^{3+}, and the full-width at half-maximum is 29 nm. These properties show that the $BaO-TeO_2-B_2O_3$ glass doped with Nd^{3+} ions is expected to be a better laser glass.

Keywords: barium-tellurite-borate glasses, Judd-Ofelt theory, thermal properties

Avtorji so barij-teluritno-boratna stekla, dopirana s kationi Nd^{3+}, pripravljali s talilno-kalilno tehniko. Amorfno naravo stekel so potrdili z rentgensko strukturno analizo (XRD). Termično stabilnost boratnega stekla so izračunali iz profila, dobljenega z diferencialno termično analizo (DTA) in termo gravimetrijo (TG). Absorpcijske in luminiscenčne spektre stekla so določili pri sobni temperaturi. Spektralne lastnosti stekla so določili z uporabo Judd-Ofeltove (J-O) teorije. Izračunali so tudi intenzitetne parametre Ω_k (k= 2, 4, 6) in življenjsko dobo radiacije. Absorpcijski pas pri 804 nm ima polno širino pri polovičnem maksimumu 18 nm. Fluorescenčni spektri imajo tri glavne pasove. Najmočnejši vrh fluorescenčne emisije je lociran pri 1062 nm, ki so ga pripisali $^4F_{3/2}$–$^4I_{11/2}$ emisijskemu pasu Nd^{3+}, in polna širina polovičnega maksimuma je pri 29 nm. Te lastnosti pričakovano kažejo, da so $BaO-TeO_2-B_2O_3$ stekla, dopirana s kationi Nd^{3+}, boljša laserska stekla.

Ključne besede: barij-teluritno-boratna stekla, Judd-Ofeltova teorija, termične lastnosti

1 INTRODUCTION

Over the past several years, a great deal of work has been carried out by performing detailed analyses on rare-earth-ions-doped glassy materials, because of their wide range of applications in optoelectronic devices, lasers and sensors, and colour display devices.[1,2] Borate glass is an attractive host matrix for rare-earth ions because of its high transparency, high thermal stability, different coordination numbers and the good solubility of the rare-earth ions.[3]

TeO_2-doped oxide glass is a good-quality material owing to a high linear and non-linear refractive index, low photon energies, and the good solubility of rare earth ions.[4] Tellurium dioxide and borate are appropriate oxide glass hosts due to the advantages mentioned above, but the chemical stability of the glass host is relatively poor.[5] Also, a small amount of alkali metal oxide in the host can improve the thermal stability of the glass matrix and strengthen the physical properties.

As tellurium dioxide and borate are suitable oxide glass hosts, they have been widely studied and have a large variety of applications. Extensive work has been carried out on rare-earth-ions-doped tellurite and borate glasses, such as Ho^{3+} ions in the $B_2O_3-TeO_2-ZnO-Na_2O$ glass system,[6] Dy^{3+} ions in the $B_2O_3-PbO_2-MgF_2-NaCl$ glass system and $LiO_2-B_2O_3$ glasses doped with Nd^{3+}.[3,7]

In the present work, the new glass system was prepared using the melt-quench technique. The absorption spectrum and fluorescence spectrum of the glass were measured at room temperature. J-O theory was applied to analyse the spectrum properties of the Nd^{3+} in the $BaO-TeO_2-B_2O_3$ glass.

2 EXPERIMENTAL PART

Glasses with varying compositions of $(BaO-TeO_2-B_2O_3)_{100-x}$ $(Nd_2O_3)_x$ where x= 0, 0.2 were prepared using H_3BO_3, $BaCO_3$, TeO_2 and Nd_2O_3 as the starting materials. Those powders were then collected in a platinum crucible and heated in a furnace at 850 °C. Then the melt was cast into a stainless-steel mould and annealed at 300 °C for 12 h to release the thermal strains.

The phase identification was determined by a single-crystal X-ray diffraction on a Bruker SMART APEX-II diffractometer and the SAINT program. Thermogravi-

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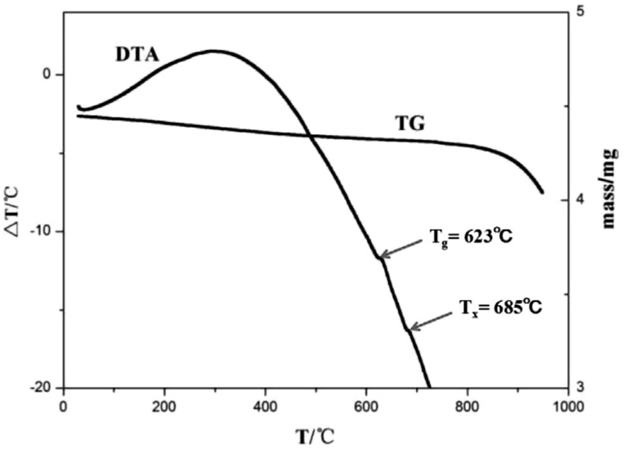

Figure 1: DTA/TG analysis curves of Nd^{3+}-doped glass

metric (TG) and differential thermal analysis (DTA) curves were acquired with a heating rate of 10 °C min^{-1} in a N_2 atmosphere. The absorption spectra were recorded with a Hitachi-340-UV-VIS spectrophotometer (Hitachi.Co.Ltd, Japan) at 300–1000 nm. The fluorescence spectra were recorded using a FLS920 spectrophotometer (Edinburgh Instruments Co. Ltd, UK).

3 RESULTS and DISCUSSION

3.1 Thermal stability

The thermal stability of a glass is a very important factor for potential applications. The DTA was carried out in order to establish the thermal stability of the glass and the results are shown in **Figure 1**. Thermal characterization can provide valuable, indirect information about the structural changes that take place in a glass system.[8] From the DTA we obtained the glass-transition temperature (T_g = 623 °C) and the crystallization temperature (T_x = 685 °C). The quantity ΔT = T_x – T_g was employed to estimate the thermal stability of the glass. The value of ΔT is 62 °C, which suggests good thermal stability of the glass. The TG curve shows that the total mass of the glass powder is almost constant in the measured temperature range.

3.2 XRD

The X-ray diffraction (XRD) patterns of the glass samples shown in **Figure 2a** exhibit a broad hump and there is the absence of discrete sharp peaks. This reveals the absence of long-range periodicity of the prepared samples. **Figure 2b** shows the XRD patterns of the samples a few months later, and there is also an absence of sharp crystallization peaks. The doped glass sample has good thermodynamic stability, from comparing the blue lines in **Figures 2a** and **2b**.

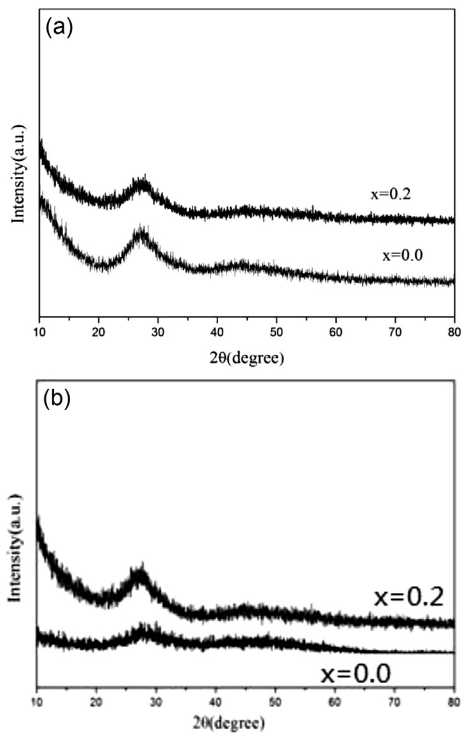

Figure 2: XRD patterns of $(BaO\text{-}TeO_2\text{-}B_2O_3)_{100-x}$ $(Nd_2O_3)_x$ where x= 0, 0.2: **(a)** the samples with very short storage times and **(b)** the samples after a few months

3.3 FT-IR spectral studies

Figure 3 shows the FT-IR spectra of the prepared glass system. IR spectroscopy can provide information about the structural units present in the amorphous materials. The band at ≈620 cm^{-1} is attributed to the B–O bending vibration of the BO_3 triangles and stretching vibrations of the Te–O bonds in TeO_4 units.[9,10] The band at ≈948 cm^{-1} is due to the stretching vibration of the BO_4 units in X various structural groups. The band at ≈1300 cm^{-1} is characteristic of the B–O stretching vibrations of the trigonal BO_3 units in various types of borate groups. The band at ≈2900 cm^{-1} is attributed to the OH bond group. The O–H absorption improves the optical attenuation and decreases the quantum efficiency

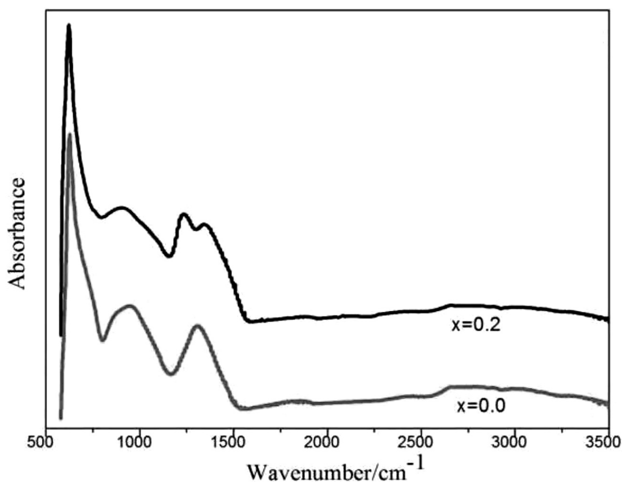

Figure3: Room-temperature IR spectrum of the Nd^{3+} doped glass

Table 1: Spectroscopic parameters of Nd^{3+}-doped BaO-TeO_2-B_2O_3 and those of other Nd^{3+}-doped crystals

Materials	Peak absorption wavelength /λ_a (nm)	FWHM(at ≈808) /nm	σ_{abs}(at ≈808) /×10^{-20}cm^2	σ_{em}(at ≈1062 nm) /×10^{-19} cm^2	Ref
1%Nd:$Lu_3Al_5O_{12}$	808	5	1.86	0.967	[14]
1%Nd:YVO4	808.7	2	2.7	14.1	[15,16]
0.94%Nd:LaVO4	808	17	1.67	0.65	[17]
0.2%Nd:BaO-B_2O_3-TeO_2	804	18	4.93	8.72	This work

of the rare-earth-excited levels.[11] The absorption coefficient of the OH in the doped sample is 3.60 mm^{-1}, while its absorption coefficient in the undoped sample is 4.76 mm^{-1}. The lower intensity of the OH band indicates that the present glass system is suitable for high-quality optical material with a lower OH content.

3.4 Spectroscopic characteristics and Judd-Ofelt analysis

Optical absorption spectra for the glass were measured in UV and near infra-red regions at room temperature in the wavelength range 300–1000 nm. As shown in **Figure 4**, there are a number of absorption bands that corresponds to the f–f electronic transition of Nd^{3+} ions. The various spectroscopic transitions observed for Nd_2O_3-containing glasses are as follows: $^2P_{1/2}$(430 nm), $^2G_{9/2}$(476 nm), $^4G_{9/2}$(514 nm), $^4G_{7/2}$(526 nm), $^4G_{5/2}$(584 nm), $^4S_{3/2}$+$^4F_{7/2}$(748 nm), $^4F_{5/2}$(804 nm), $^4F_{3/2}$(878 nm).[12] From the absorption spectra, it is clear that the optical transition $^4I_{9/2}\rightarrow{}^4G_{5/2}$ is more intense than the other transitions. The absorption bands at 748 nm, 804 nm and 878 nm can be efficiently pumped using commercially available laser diodes.[13] The absorption band at 804 nm, the full-width at half-maximum (FWHM), is about 18 nm, which is close to the Nd:$LaVO_4$ crystal. The broad bandwidth is suitable for laser diode pumping because it is not temperature dependent.

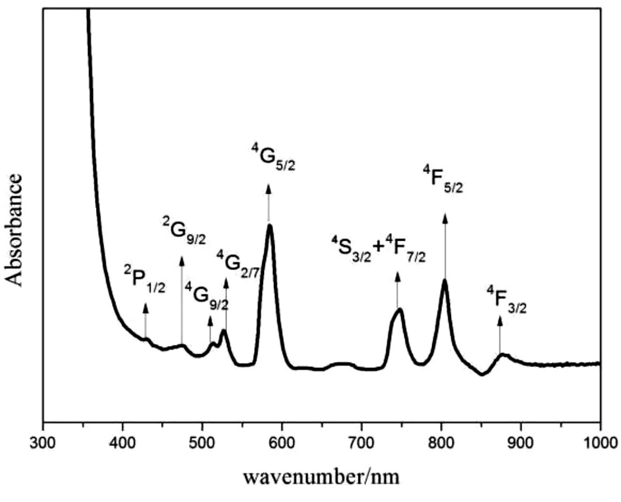

Figure 4: Room-temperature optical absorption spectra of the Nd^{3+}-doped glass

The absorption spectrum of the Nd^{3+} ions in the BaO-TeO_2-B_2O_3 glass was analysed using the J-O theory. The spectral parameters of the rare-earth glass and the doped crystal are different. The Nd active ion, due to the screening effect of $5s^2p^6$ lamella, can only produce a very faint perturbation to the 4f electrons. The absorption cross-section abs is given by

$$\sigma_{abs} = 2.303\ A/dN_c$$

Where A is the absorption, d is the sample thickness, and Nc is the concentration of Nd^{3+} in the doped glass. The absorption cross-section at 804 nm is 4.93 × 10^{-20} cm^2, which is higher than a Nd:YVO_4 crystal. A comparison of spectrum parameters is listed in **Table 1**.

The experimental oscillator strength can be obtained using the relation:[18–20]

$$f_{exp} = \frac{2.303mc^2}{\pi e^2 N_c d\lambda^2}\int OD(\lambda)d\lambda$$

where *m* and *e* are the mass and charge of the electron, *c* is the speed of the light, *Nc* is the Nd^{3+} concentration, $\int OD(\lambda)d\lambda$ is the integrated absorption coefficient.

$$f_{cal} = \frac{8\pi^2 mcv}{3h(2J+1)}\left[\frac{(n^2+2)^2}{9n}S_{ed} + nS_{md}\right]$$

where *v* is the mean energy of the transition, n is the refractive index (roughly 1.88),[21] *h* is Planck's constant, S_{ed} is the electric dipole line strength, S_{md} is the magnetic dipole strength, which can be neglected in comparison with S_{ed}. S_{ed} can be calculated as follows:

$$S_{ed} = e_2 \sum_{\lambda=2,4,6}\Omega_\lambda (\Psi J \| U^{(\lambda)} \| \Psi' J')^2$$

where the term $(\Psi J \| U^{(\lambda)} \| \Psi' J')^2$ is the reduced matrix element of the tensor operator, and Ω_λ (λ= 2, 4, 6) are the J-O intensity parameters.

Table 2 shows the calculation result. Among the three intensity parameters Ω_2, Ω_4 and Ω_6, Ω_2 is indicative of the crystal field symmetry of the rare-earth site and easily affected by the local structure changes of the host. The high value of Ω_2 implies that the prepared glass has a highly covalent nature. The spectroscopic quality factor χ ($\chi = \Omega_4/\Omega_6$) indicates the emission intensity of the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition of Nd^{3+}.[22] The small value of χ implies that the glass has a strong emission intensity of the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition.

Table 2: Optical parameters of the absorption spectrum of glass (Ω_2, Ω_4 and Ω_6 are in units of 10^{-20} cm^2)

Transition ^4I 9/2	$\bar{\lambda}$/nm	$f_{exp}(\times10^{-6})$	$f_{cal}(\times10^{-6})$
$^2P1/2$	430	0.28	0.20
$^2G9/2$	476	2.09	0.64
$^4G9/2$	514	0.74	1.87
$^4G7/2$	526	2.27	4.62
$^4G5/2$	584	33.03	27.80
$^4F7/2$, $^4S3/2$	748	8.49	8.02
$^4F5/2$	804	10.57	9.60
$^4F3/2$	878	2.31	1.74
Ω_2=9.79	Ω_4=1.20	Ω_6=9.19	

Figure 5 shows the fluorescence spectrum of the glass under excitation of 358 nm at room temperature in the wavelength range 800–1600 nm. In the spectrum three fluorescence peaks can be seen: 903 nm, 1062 nm, 1335 nm.

The main peak located at 1062 nm can be attributed to $^4F_{3/2}\rightarrow{}^4I_{11/2}$ and results from the emission of Nd^{3+} ions. The FWHM of this emission band is 29 nm. The emission spectrum of Nd^{3+} in the $BaO\text{-}TeO_2\text{-}B_2O_3$ glass is also investigated based on J-O theory.

$$A_{J,J'}=\frac{8\pi^2e^2n^2}{mc\lambda^2}f_{cal}$$

where $A_{J,J'}$ is the probability of the electric-dipole spontaneous transition from the excited level J' to the terminal level J.

$$\tau_{rad}=\frac{1}{\sum A(j-J')}$$

where τ_{rad} is the radiation lifetime of a given upper level. We obtained the radiation lifetime as 134 μs at the 1062 nm.

The emission cross-section σ_e can be derived using the formula:

$$\sigma_{em}=\frac{\lambda^5 I(\lambda)}{8c\pi n^2\tau_r\int\lambda I(\lambda)d\lambda}$$

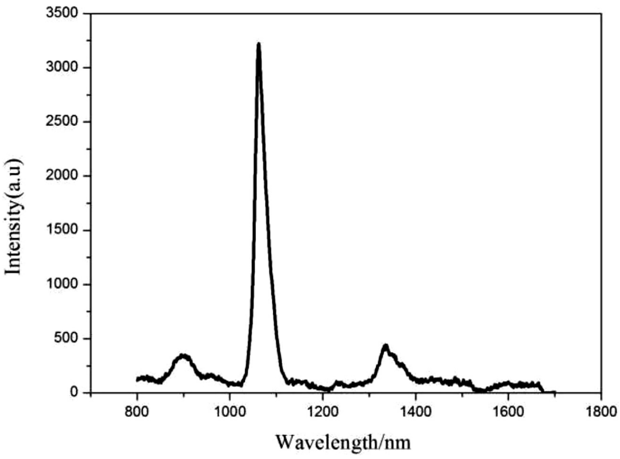

Figure 5: Luminescence spectrum of Nd^{3+}-doped glass

where $I(\lambda)$ is the intensity of the emission spectra and τ_r is the radiative lifetime. The emission cross-section is calculated with the formula is 8.72×10^{-19} cm^2 at the wavelength of 1062 nm.

4 CONCLUSIONS

In this work, Nd^{3+}-ions-doped barium-tellurite-borate glasses were prepared using the melt-quench technique. XRD confirmed the amorphous nature of the glass samples. DTA and TG were used to study the thermal properties of the samples and the results show that they have good thermal stability. The glass samples were characterized by using spectroscopic techniques such as optical absorption and fluorescence spectra. There are several main optical absorption peaks from 400 to 900 nm, whereas in the fluorescence spectrum three emission transition bands located at 903 nm, 1062 nm and 1335 nm were observed. The spectral properties were studied by applying the J-O theory. The intensity parameters Ω_2, Ω_4, and Ω_6 and the radiative properties of the emission levels of the Nd^{3+}: $BaO\text{-}TeO_2\text{-}B_2O_3$ glasses were calculated. The stimulated emission cross-section values are calculated for the present glasses, which are large when compared with other crystals. These properties show that the $BaO\text{-}TeO_2\text{-}B_2O_3$ glass doped with Nd^{3+} ions is expected to be a better laser glass.

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