Hindawi Publishing Corporation
Advances in Materials Science and Engineering
Volume 2014, Article ID 751973, 5 pages
http://dx.doi.org/10.1155/2014/751973

Hindawi

Research Article

Up- and Downconversion Luminescence Properties of Nd^{3+} Ions Doped in Bi_2O_3–BaO–B_2O_3 Glass System

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Received 13 November 2013; Accepted 16 December 2013; Published 28 January 2014

Academic Editor: Luigi Nicolais

Physical, optical, and luminescence properties of Nd^{3+} ions in bismuth barium borate glass system were studied. The glasses prepared by a melt quenching method were doped at various Nd_2O_3 concentrations in compositions $(40-x)B_2O_3 : 40Bi_2O_3 : 20BaO : xNd_2O_3$ (where x = 0.00, 0.50, 1.00, 1.50, 2.00, and 2.50 in mol%). Luminescence properties of the glasses were studied under two excitations of 585 and 750 nm for downconversion. From both excitations, the results show emission bands in NIR region corresponding to the transitions between $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (900 nm), $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1,060 nm), and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ (1,345 nm). The luminescence intensity obtained with 585 nm excitation was stronger than 750 nm, with the strongest NIR emission at 1,060 nm. The upconversion emission spectrum exhibits strong fluorescence bands in the UV region at 394 nm (λ_{ex} = 591 nm). The processes are associated with excited state absorption (ESA) from $^4F_{3/2}$ level to $^4D_{3/2}$ level and it is the radiative decay from the $^4D_{3/2}$ to ground levels ($^4D_{3/2} \rightarrow {}^4I_{13/2}$) which are responsible for the emission at 394 nm.

1. Introduction

The first demonstration of laser action in a neodymium doped glass was done by Snitzer in 1961 and since then considerable progress has been made in evaluating the effects of amorphous host materials on the lasing properties of various rare earth ions. A large variety of laser glasses doped with Nd^{3+} ions have been investigated with the purpose of generating efficient broadband laser emission around 1060 nm [1–3]. Recently, glass-ceramics containing neodymium oxides have been found in applications for several different purposes. First of such application has been Nd_2O_3 in special glasses for halogen lamps to absorb ultraviolet rays, harmful emissions to human. In application as refractory glasses, the glasses containing Nd_2O_3 can have high hardness and excellent chemical durability. Lastly, neodymium contained in glass can be used as a band rejection filter for image display devices, owing to absorption originating in the intertransition within the 4f shell of the Nd^{3+} ion [4, 5].

In addition to the rare-earth ion characteristics, the glass host matrices also play a fundamental role in determining the performance of photonic devices since the stimulated emission characteristics of a trivalent rare-earth ion depend on the surrounding host matrix in which the ions are incorporated. The surrounding ligand field can have a considerable influence on the optical absorption cross-section, stimulated emission cross-section and fluorescence decay, and the quantum efficiency of the system [5]. Bi_2O_3 containing glass possesses higher refractive index and exhibits high optical basicity, large polarizability, and large nonlinear optical susceptibility [6]. It was also reported that glasses containing

Bi_2O_3 have been developed for nuclear engineering applications because they accomplish the double task of allowing visibility while absorbing radiations like gamma rays and neutrons [7]. Bi_2O_3 cannot be considered as actual network former due to small field strength of Bi^{3+} ion. However, in the presence of conventional glass-forming cations such as P^{5+}, Si^{4+}, and B^{3+} it may have this property [8, 9]. Borate glasses are structurally more intricate as compared to silicate or phosphate glasses due to two types of coordination of boron atoms with oxygen (3 and 4) and the structure of vitreous B_2O_3 consisting of a random network of boroxyl rings and BO_3 triangles connected by B–O–B linkages. In addition, the additional modifier oxide causes a progressive change of some BO_3 triangles to BO_4 tetrahedra, resulting in the formation of various cyclic units including diborate, triborate, tetraborate, or pentaborate groups [9]. The presence of two network forming oxides, the classical B_2O_3 and the conditional Bi_2O_3 glass former, the possible participation in the glass structure of both boron and bismuth ions with more than one stable coordination (and, thus, the presence of several structural units namely, BO_3, BO_4, BiO_3, and BiO_6), the capability of the bismuth polyhedra and of the borate structural groups to form independent interconnected networks [4]. Over the last several years, bismuth barium borate glasses have been also useful for variety of optical applications such as radiation shielding window, gamma rays shielding materials, and scintillation counters [10, 11].

Many literatures have been studied on Bi_2O_3–BaO–B_2O_3 glass system and its related properties [12–16]. However, study on rare earth ion doped to this glass structure and its luminescence properties are very lacking. Only one literature doped with Eu^{3+} has been studied by Egorysheva et al., [17] and good luminescence property was obtained. So, the studies of other rare earth ions doped in this glass are needed. In this present work has been to study the effect of Nd^{3+} content on physical, optical, and luminescence properties from excitations and their responding emission spectra of the glass system. The variety of the emission from Nd^{3+} ions in the glasses system could be potential applications to be developed for various fields such as new light sources, display devices, UV-sensors, and interestingly tunable visible lasers. This work is the first report on luminescence properties of Nd^{3+} on Bi_2O_3–BaO–B_2O_3 glass system.

2. Experimental Detail

2.1. Glass Preparation. The glasses with their chemical compositions $(40\text{-}x)B_2O_3 : 40Bi_2O_3 : 20BaO : xNd_2O_3$ (where x is the mol% of Nd_2O_3 content in the glass systems which varied between 0.0, 0.5, 1.0, 1.5, 2.0, and 2.5) were prepared by the normal melt-quenching technique and the glass compositions in mole percent for different Nd_2O_3 dopings are given in Table 1. For each batch composition, 20 g of homogeneous mixture of starting chemicals was melted in high purity alumina crucibles by an electric furnace at a temperature of 1,100°C for 3 hours. The melts were quenched by pouring into preheated stainless steel molds. The glasses were then annealed at 500°C for about 3 hours to remove thermal strains. Finally, the as-prepared glass samples were cut and then finely polished to a dimension of 1.0 cm × 1.5 cm × 0.3 cm.

Table 1: Chemical compositions of the glass systems prepared in this work.

Nd_2O_3 (mol%)	Glass system
0.00	$40.00Bi_2O_3 : 20.00BaO : 40.00B_2O_3$
0.50	$40.00Bi_2O_3 : 20.00BaO : 39.50B_2O_3 : 0.50Nd_2O_3$
1.00	$40.00Bi_2O_3 : 20.00BaO : 39.00B_2O_3 : 1.00Nd_2O_3$
1.50	$40.00Bi_2O_3 : 20.00BaO : 38.50B_2O_3 : 1.50Nd_2O_3$
2.00	$40.00Bi_2O_3 : 20.00BaO : 38.00B_2O_3 : 2.00Nd_2O_3$
2.50	$40.00Bi_2O_3 : 20.00BaO : 37.50B_2O_3 : 2.50Nd_2O_3$

2.2. Measurements. The density (ρ) at room temperature of the glass samples was determined by a method based on Archimedes' method principle. The weights of the prepared glass samples were measured in air and xylene immersion by using a 4-digit sensitive microbalance (AND, HR-200). The molar volume (V_M) was calculated using the relation $V_M = M_T/\rho$, where M_T is the total molecular weight of the multicomponent glass system. The optical absorption spectra of the prepared glass samples in the UV-VIS-NIR region from 300 to 1,800 nm were recorded at room temperature using UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu). In the NIR luminescence measurement, the Nd^{3+} doped in glass sample was excited by two wavelengths at 585 and 750 nm. The emission spectra were recorded at room temperature using a Quanta Master 3 luminescence spectrometer from Photon Technology International (PTI). For the upconversion luminescence studies, the Nd^{3+} doped glass samples were excited with a 591 nm wavelength. The emission spectra were recorded at room temperature using a spectrofluorophotometer (Shimadzu RF-5301PC, Japan) with a 150 watts Xenon lamp as a light source.

3. Results and Discussions

3.1. Physical Properties. The density and molar volume of the glasses determined with the described methods are shown in Figure 1. As can be seen from the figure, by adding of Nd_2O_3 into the Bi_2O_3–BaO–B_2O_3 glass network, the density of the glass is increased with the increasing of Nd_2O_3 content. This indicates the increase of the molecular weight by the replacement of B_2O_3 with a heavier Nd_2O_3 oxide in the glass and this as expected increases the density of these glasses. However, the variation of density is nonlinearly increasing with composition of Nd_2O_3. This is may be due to different loss rates of Bi_2O_3 at high melting temperature process (melting point of Bi_2O_3 is 817°C [18].) The molar volume of the glass systems, however, shows a decrease trend with increasing of Nd_2O_3 content. The molar volumes of glasses were decreased with increasing of Nd^{3+} ions concentration, reflecting increase compactness of the glass structure with higher concentration of Nd^{3+}, that is, the decrease of average atomic separation.

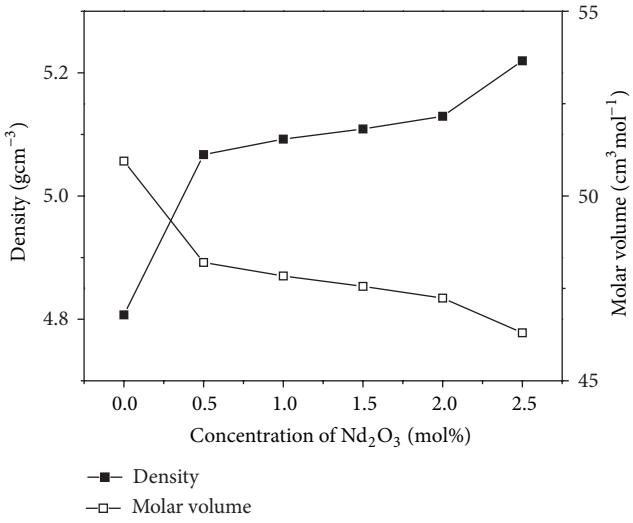

Figure 1: Density and molar volume of Nd^{3+} doped Bi_2O_3–BaO–B_2O_3 glasses.

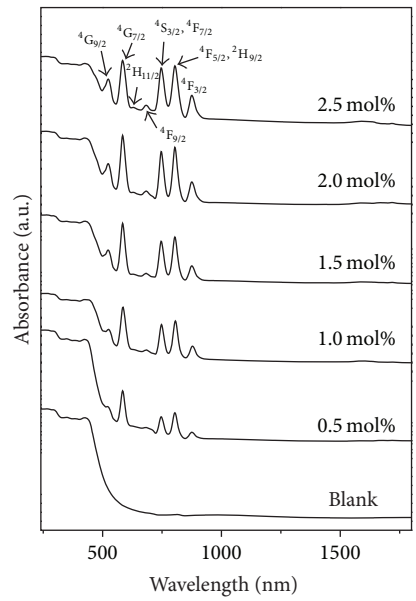

Figure 2: Ground state absorption spectra of Nd^{3+} ions in Bi_2O_3–BaO–B_2O_3 glasses at room temperature.

The variations of density and molar volume with concentration of Nd_2O_3 are presented in Figure 1.

3.2. Absorption Spectra. The absorption spectra of Nd^{3+} doped bismuth barium borate glasses in the range of 300–1,800 nm at room temperature are shown in Figure 2. It is clearly observed that the height of the absorption bands increase with the increase of Nd_2O_3 concentration. Seven absorption bands were observed and assigned to transitions from the $^4I_{9/2}$ ground state to $^4F_{3/2}$, $^4F_{5/2}$ + $^4H_{9/2}$, $^4F_{7/2}$ + $^4S_{3/2}$, $^4F_{9/2}$, $^2H_{11/2}$, $^4G_{7/2}$, and $^4G_{9/2}$ levels [19, 20]. The absorptions in the UV-visible and NIR regions were slightly increased with increasing composition of Nd^{3+} in the glass system.

3.3. Emission Spectra

3.3.1. Downconversion Spectra. The downconversion emission spectra of Nd^{3+} doped bismuth barium borate glass recorded when excited by 585 and 750 nm wavelengths at room temperature are shown in Figure 3. The emission bands in NIR region were assigned to the corresponding transitions: $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (900 nm), $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1,060 nm), and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ (1,345 nm) [19, 20]. The emission for the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition was not observable, probably due to its low intensity. Owing to its importance as a high-power and high-energy laser line, the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1,060 nm) emission is probably the most thoroughly characterized transition for both glass and crystalline hosts. All the luminescence peaks (900, 1,060, and 1,345 nm) obtained when excited with the 585 nm have been shown with stronger emissions than when excited by the 750 nm wavelength. The luminescence peak intensity was decrease with higher Nd_2O_3 concentration with the strongest NIR emission intensity is at 1,060 nm and then 1,345 and 900 nm respectively.

3.3.2. Upconversion Spectra. Figure 4 shows upconversion emission spectra of bismuth barium borate glass doped Nd^{3+} ions under 591 nm excitation. The emission spectra exhibit strong fluorescence bands in the UV region at 394 nm. The upconversion process may be associated with the excited state absorption (ESA) from $^4F_{3/2}$ to $^4D_{3/2}$ levels. Figure 5 shows the possible upconversion mechanisms. In the first step, Nd^{3+} in the ground level ($^4I_{9/2}$) was excited directly by absorbing the excitation wavelength 591 nm photons to the excited $^4G_{5/2}$ level and then these ions relax nonradiatively to the metastable $^4F_{3/2}$ level. The cross-relaxation process between the $^4G_{5/2}$ and $^4F_{3/2}$ levels causes the population of the $^4D_{3/2}$ level by absorbing a second photon. Finally, the excited Nd^{3+} at $^4D_{3/2}$ state can decay radiatively to ground levels and cause the upconversion emission at 394 nm ($^4D_{3/2} \rightarrow {}^4I_{13/2}$ or $^2P_{3/2} \rightarrow {}^4I_{11/2}$). Through a nonradiative process Nd^{3+} ions at the $^4D_{3/2}$ level can relax to the lower ($^2P_{3/2}$) levels due to a small energy gap between the two levels. This nonradiative decay has the possibility to cause upconversion emissions from the levels at 467 nm ($^2P_{3/2} \rightarrow {}^4I_{15/2}$), but this was not observed in these glass structures.

4. Conclusions

The physical and luminescence properties of Nd^{3+} doped B_2O_3–Bi_2O_3–BaO–Nd_2O_3 glasses prepared by a conventional melt-quenching method were studied for Nd_2O_3 compositions. Density of glasses was found to increase with increasing of Nd_2O_3 composition. The behavior of molar volume mainly depends on the density of glasses, but it follows an opposite trend with density. The molar volume of

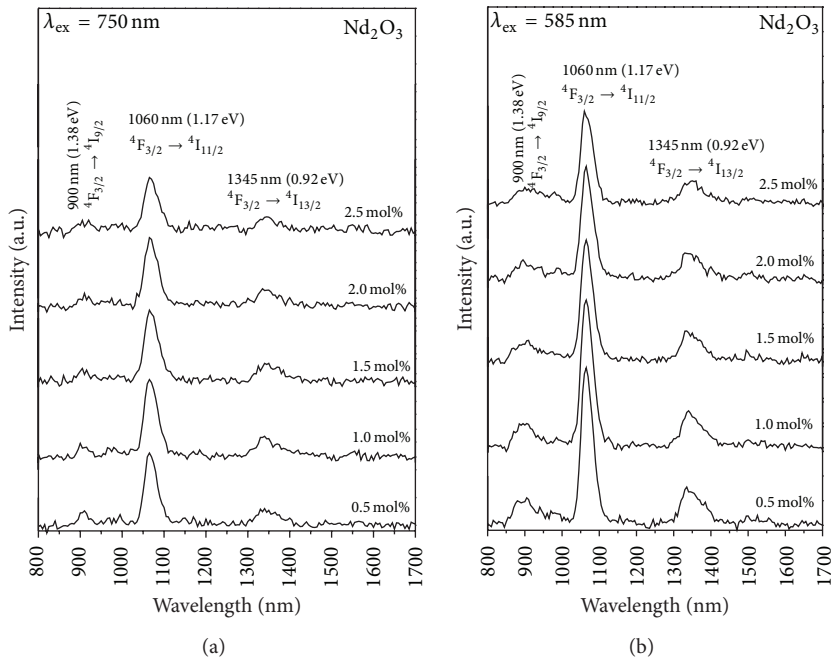

Figure 3: NIR luminescences spectra of Nd^{3+} doped Bi_2O_3–BaO–B_2O_3 glasses show downconversion at room temperature when excited by 585 and 750 nm excitation wavelengths.

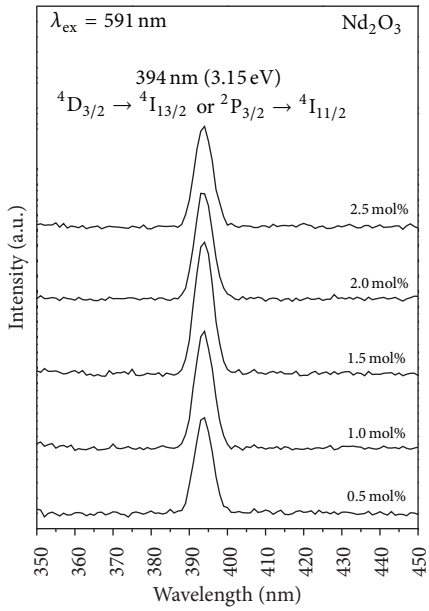

Figure 4: Upconversion luminescence spectra of Nd^{3+} ions in Bi_2O_3–BaO–B_2O_3 glasses when excited with 591 nm at room temperature.

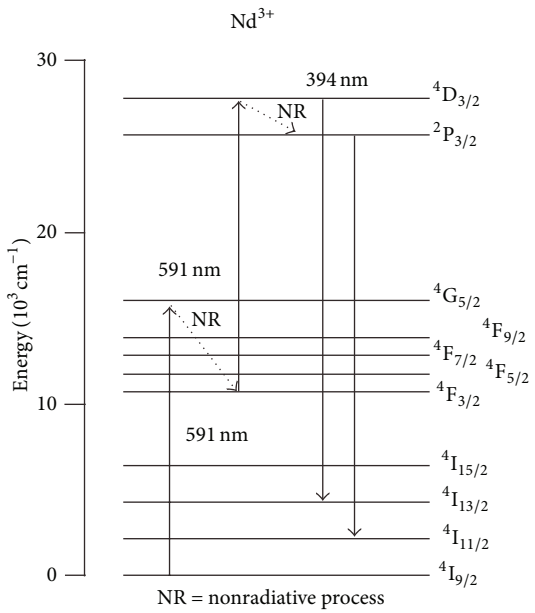

Figure 5: Energy levels and possible transition pathways of Nd^{3+} ions in Bi_2O_3–BaO–B_2O_3 glasses.

glasses was decreased with increasing of Nd_2O_3 concentration, reflecting more compact of the glass structure. The optical absorption spectra in UV-VIS-NIR region were observed with seven absorption peaks assigned to $^4I_{9/2}$ ground state transition to $^4F_{3/2}$, $^4F_{5/2}$ + $^4H_{9/2}$, $^4F_{7/2}$ + $^4S_{3/2}$, $^4F_{9/2}$, $^2H_{11/2}$, $^4G_{7/2}$, and $^4G_{9/2}$ levels. Downconversion of Nd^{3+} in the glasses was studied under two excitations at 585 and 750 nm. The result shows luminescence peaks at 900, 1,060, and 1,345 nm. Stronger luminescence peak intensity was observed when excited by 585 nm in comparison to 750 nm excitation wavelength. Upconversion observed with 591 nm excitation showed emission spectra at 394 nm. The mechanisms for the excited state absorption (ESA) were purposed as the possible emission pathways from $^4D_{3/2} \rightarrow {}^4I_{13/2}$ or $^2P_{3/2} \rightarrow {}^4I_{11/2}$ transitions. These results showed that the Nd^{3+} doped

B_2O_3–Bi_2O_3–BaO glass system can be used in laser or optical devices design.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

P. Limsuwan would like to thank King Mongkut's University of Technology Thonburi (KMUTT) for partially funding the project under the National Research University. J. Kaewkhao, N. Chanthima, and S. Ruengsri would like to thank National Research Council of Thailand (NRCT) for a partial financial support. R. Ruamnikhom would like to thank Institute for the Promotion of Teaching Science and Technology (IPST) for his Ph.D. grant.

References

[1] I. Pal, A. Agarwal, S. Sanghi, Sanjay, and M. P. Aggarwal, "spectroscopic and radiative properties of Nd^{3+} ions doped zinc bismuth borate glasses," *Indian Journal of Pure & Applied Physics*, vol. 51, pp. 18–25, 2013.

[2] G. Blasse and B. C. Grabmaier, *Luminescenct Matetials*, Springer, Berlin, Germany, 1994.

[3] J. E. Shelby, *Introduction to Glass Science and Technology*, TJ International Padstow, New York, NY, USA, 2nd edition, 2005.

[4] P. Becker, "Thermal and optical properties of glasses of the system Bi_2O_3—B_2O_3," *Crystal Research and Technology*, vol. 38, no. 1, pp. 74–82, 2003.

[5] K. Azman, M. R. Sahar, and M. S. Rohani, "The upconversion of co-doped nd^{3+}/er^{3+} tellurite glass," *World Academy of Science, Engineering and Technology*, vol. 64, pp. 414–417, 2010.

[6] B. Karthikeyan and S. Mohan, "Structural, optical and glass transition studies on Nd^{3+}-doped lead bismuth borate glasses," *Physica B*, vol. 334, no. 3-4, pp. 298–302, 2003.

[7] N. Mott and E. Davis, *Electronic Process in Non-Crystalline Materials*, Clarendon Press, Oxford, UK, 2nd edition, 1979.

[8] E. Culea, L. Pop, M. Bosca, V. Dan, P. Pascuta, and S. Rada, "Structural and physical characteristics of $xGd_2O_3(100-x)[Bi_2O_3\ B_2O_3]$ glasses," *Journal of Physics*, vol. 182, no. 1, Article ID 012062, 2009.

[9] S. L. S. Rao, G. Ramadevudu, Md. Shareefuddin, A. Hameed, M. N. Chary, and M. L. Rao, "Optical properties of alkaline earth borate glasses," *International Journal of Engineering, Science and Technology*, vol. 4, no. 4, pp. 25–35, 2012.

[10] J. Kaewkhao, A. Pokaipisit, and P. Limsuwan, "Study on borate glass system containing with Bi_2O_3 and BaO for gamma-rays shielding materials: comparison with PbO," *Journal of Nuclear Materials*, vol. 399, no. 1, pp. 38–40, 2010.

[11] K. Boonin, J. Kaewkhao, and P. Limsuwan, "Optical Investigation of Bi_2O_3-B_2O_3 Glass System," *Advanced Materials Research*, vol. 93-94, pp. 336–339, 2010.

[12] S. Sindhu, S. Sanghi, A. Agarwal, V. P. Seth, and N. Kishore, "Effect of Bi_2O_3 content on the optical band gap, density and electrical conductivity of $MO{\cdot}Bi_2O_3{\cdot}B_2O_3$ (M = Ba, Sr) glasses," *Materials Chemistry and Physics*, vol. 90, no. 1, pp. 83–89, 2005.

[13] A. V. Egorysheva, V. D. Volodin, and V. M. Skorikov, "Glass formation in the Bi_2O_3-B_2O_3-BaO system," *Inorganic Materials*, vol. 44, no. 11, pp. 1261–1265, 2008.

[14] C. Feifei, D. Shixun, N. Qiuhua, X. Tiefeng, S. Xiang, and W. Xunsi, "Glass formation and optical band gap studies on Bi_2O_3-B_2O_3-BaO ternary system," *Journal Wuhan University of Technology, Materials Science Edition*, vol. 24, no. 5, pp. 716–720, 2009.

[15] H. Doweidar and Y. B. Saddeek, "FTIR and ultrasonic investigations on modified bismuth borate glasses," *Journal of Non-Crystalline Solids*, vol. 355, no. 6, pp. 348–354, 2009.

[16] W. Qiao and P. Chena, "Study on the properties of Bi_2O_3-B_2O_3-BaO lead-free glass using in the electronic pastes," *Glass Physics and Chemistry*, vol. 36, no. 3, pp. 304–308, 2010.

[17] A. V. Egorysheva, V. D. Volodin, A. A. Chistyakov, Y. A. Kuzishchin, V. M. Skorikov, and T. D. Dudkina, "Luminescence of europium-doped BaO-Bi_2O_3-B_2O_3 glasses," *Inorganic Materials*, vol. 46, no. 12, pp. 1384–1390, 2010.

[18] Go. Dhanaraj, K. Byrappa, V. Prasad, and M. Dudley, *Springer Handbook of Crystal Growth*, Springer, New York, NY, USA, 2010.

[19] B. S. Reddy, S. Buddhudu, S. R. K. Rao, and P. N. Babu, "Spectral analysis of Nd^{3+} & Er^{3+}: $B_2O_3(TeO_2/CdO/ZnO)$-Li_2O-AlF_3 glasses," *Journal of Optoelectronics and Advanced Materials*, vol. 10, no. 10, pp. 2777–2781, 2008.

[20] R. Balda, J. Fernández, M. A. Arriandiaga, and J. M. Fernández-Navarro, "Spectroscopy and frequency upconversion in Nd^{3+}-doped TeO_2-TiO_2-Nb_2O_5 glass," *Journal of Physics Condensed Matter*, vol. 19, no. 8, Article ID 086223, 2007.