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Synthesis of Sm^{3+} doped Bismuth Borate Glasses by Melt Quenching Technique

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Abstract: *Trivalent rare earth ions exhibit specific electronic transitions that results in unique optical properties, such as sharp and well defined UV-Visible absorption and luminescence. Due to these properties rare earth doped materials have great technological applications in optical fibers, amplifiers, energy saving lighting devices, and lasers. This paper presents a systematic investigations on synthesis of* Sm^{3+} *doped bismuth borate glasses by melt quenching technique. Concentration of samarium ion is varied from 0 to 3 mol%. The presence of heavy metal ions reduces the phonon energy of the borate network, which increases the The phonon energy of borate network reduces in presence of heavy metal oxides such as lead oxide or bismuth oxide and so luminescence quantum efficiency of doped rare-earth ions increases. The prepared glass samples are ready for further physical and optical characterization.*

Keywords: Borate, rare-earths, phonons

I. INTRODUCTION

Rare-earth-doped oxide glasses constitute an important class of functional materials for modern photonic and optoelectronic technologies [1-2]. The incorporation of trivalent lanthanide ions into suitable glass hosts enables sharp electronic transitions arising from 4f–4f configurations, which are weakly influenced by the surrounding matrix [3]. Among these ions, Samarium (Sm^{3+}) has attracted significant attention due to its characteristic orange–red emissions originating from the $^4G_5/_2$ excited state to the ^6H ground multiplets. These emission bands are particularly useful in solid-state lighting, display devices, optical sensors, and visible lasers[4-5]. The effectiveness of such luminescent systems depends not only on the intrinsic properties of the dopant ion but also critically on the structural and physical characteristics of the host glass matrix.

Glasses based on borate networks are well known for their excellent glass-forming ability, low melting temperature, high optical transparency, and compositional flexibility. Boron oxide (B_2O_3) serves as a classic glass former capable of creating a highly interconnected network of trigonal (BO_3) and tetrahedral (BO_4) structural units. The ratio between these units strongly influences the physical properties of the resulting glass, including density, refractive index, thermal stability, and phonon energy[6]. The relatively high phonon energy of pure borate glasses, however, can promote non-radiative relaxation processes in rare-earth-doped systems, thereby reducing luminescence efficiency. To overcome this limitation, borate glasses are often modified with heavy metal oxides to tailor their structural and optical properties[7].Among heavy metal oxides, Bismuth oxide (Bi_2O_3) has emerged as an attractive component for advanced glass systems. Bismuth oxide-based glasses exhibit high refractive indices, wide infrared transmission windows, large nonlinear optical coefficients, and relatively low phonon energies compared to conventional borate glasses. The presence of Bi^{3+} ions, which possess a large ionic radius and high polarizability, significantly modifies the borate network by introducing non-bridging oxygens (NBOs) and enhancing structural compactness. These features contribute to improved rare-earth solubility and enhanced radiative transition probabilities. Consequently, bismuth borate glasses provide a favorable environment for hosting Sm^{3+} ions, combining the glass-forming ability of B_2O_3 with the optical advantages of Bi_2O_3[8-9].The interaction between Sm^{3+} ions and the bismuth borate glass matrix plays a crucial role in determining the optical performance of the material. The 4f electrons of Sm^{3+} are shielded by outer 5s and 5p orbitals,

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resulting in narrow emission bands and relatively weak sensitivity to crystal field variations. Nevertheless, the asymmetry and covalency of the surrounding glass network influence the intensity parameters of electric dipole transitions. Structural modifications induced by Bi_2O_3, such as increased NBO concentration and changes in local symmetry, can enhance the probability of hypersensitive transitions in Sm^{3+}. This leads to improved emission intensity and tunable chromaticity, which are essential for photonic applications[10-11]. Furthermore, the high density and refractive index of bismuth-containing glasses contribute to larger emission cross-sections, making them promising candidates for optical amplifiers and visible laser sources.

From a materials synthesis perspective, the selection of an appropriate preparation technique is vital for achieving homogeneous dopant distribution and optimal optical performance. Among various methods such as sol–gel processing, chemical vapor deposition, and microwave-assisted synthesis, the melt quenching technique remains the most widely employed route for preparing bulk rare-earth-doped glasses. This paper highlights the synthesis of heavy metal based samarium ion doped borate glasses. Borate act as a network former for synthesis of glasses and bismuth oxide taken as heavy metal oxide act as network former. Bismuth borate glasses were prepared with different concentration of samarium oxide.

Synthesis methods of rare-earth doped glasses

There are three main techniques for preparing a glass matrix. The sol-gel process, the chemical vapour deposition and finally the melt quenching technique which is used in this work. The melt quenching technique was the only method by which bulk glasses of acceptable sizes could be obtained and nowadays more than 99% of the glass is produced by this method.

Sol-gel process

The **sol–gel process** is a versatile wet-chemical method used for the preparation of glass and ceramic materials at relatively low temperatures. It is especially useful for producing high-purity and homogeneous glasses, thin films, fibers, coatings, and porous materials [12]. The process is based on the transition of a system from a liquid "sol" into a solid "gel" phase. In glass preparation, the sol–gel method typically uses metal alkoxides as starting materials. The process begins with **hydrolysis**, in which the alkoxide reacts with water in the presence of an acid or base catalyst. During hydrolysis, alkoxy groups (–OR) are replaced by hydroxyl groups (–OH). This is followed by **condensation reactions**, where hydroxyl groups react with each other. These reactions gradually build a three-dimensional network structure. As condensation continues, the solution becomes more viscous and eventually forms a semi-rigid network called a **gel and** this stage is known as **gelation**. After gelation, the material undergoes **aging**, during which further condensation strengthens the network and improves mechanical stability. The next critical step is **drying**, where the liquid inside the pores is removed. Careful drying is essential because rapid evaporation can cause cracking due to capillary stresses. Slow evaporation at ambient conditions produces a porous material known as a xerogel. If the liquid is removed under supercritical conditions, an aerogel with extremely high porosity and very low density can be obtained. After drying, the material is subjected to **heat treatment or sintering**. During this stage, residual organic groups and solvents are burned off, and the structure becomes denser. At higher temperatures, the porous network collapses and transforms into dense glass. Compared to traditional glass melting, which requires very high temperatures (often above 1500°C), the sol–gel method achieves similar results at much lower temperatures. The sol–gel process offers several advantages. It provides excellent control over chemical composition and ensures uniform mixing at the molecular level. High purity can be achieved because the process starts from high-quality chemical precursors. It also allows the formation of thin films, coatings, fibers, and complex shapes. However, the method also has some limitations. The process can be time-consuming, especially during gelation and drying. Shrinkage and cracking may occur due to solvent removal.

Chemical vapour deposition process

Chemical Vapor Deposition refers to a broad range of thin film deposition techniques that are widely used for producing high quality, high-performance solid coatings or polymers [13]. For thermal Chemical Vapor Deposition the substrate is heated and a precursor reactant gas is introduced into the deposition chamber which may either be directly absorbed onto the surface of the substrate to be coated, or may form an intermediate reactant in the gas phase which is then deposited onto the substrate. The processes are run at elevated temperatures and at atmospheric pressures. Chemical Vapor Deposition is a widely used manufacturing process that is used in electronics industry, solar panel and optical industries such as sunglasses, optical storage and architectural glass. The advantage of the Chemical Vapor Deposition is that it offers a wide variety of coating materials based on metals, alloys and ceramics. The major draw back of this method is that the byproducts are hazardous including being highly toxic, explosive or corrosive. Full consideration must be given to safely handling them in a way that is not harmful to humans or the environment.

Melt Quenching Technique

Melt quenching technique is frequently used technique for preparing glasses, especially rare-earth-doped glasses such as dysprosium, samarium, terbium, europium, neodymium, and erbium doped systems. It is a cost effective and versatile process that enables the formation of homogeneous, amorphous materials with controlled and desired composition. Glass is basically a super cooled melt of inorganic compounds having no tendency to crystallize during the cooling process. The melt quenching technique is based on two fundamental steps first is melting and second one is rapid cooling(quenching). For preparing glass samples raw materials are heated above their melting temperature until a homogeneous liquid is formed. The molten liquid is is then cooled below its freezing point so quickly that the atoms do not get sufficient time to arrange themselves into a crystal structure. The classical explanation for the formation of a glass is that when a liquid is cooled, its fluidity (reciprocal viscosity) decreases and at a certain temperature, below its freezing point, becomes almost zero and the liquid becomes rigid. The basic structural units, which make up the glass network known as glass formers such as for silicate, borate, phosphate, tellurite etc. The other compounds such as lithium oxide, lithium carbonate, sodium oxide, lead oxide etc added to the glass somewhat modify this network called modifiers. The network modifier disrupt the network and then rare-earth ions can be incorporated in glass. In the present work the molar composition of samarium doped borate based glasses with Bi_2O_3 are as follows: (the numbers in front of the chemical symbols are the mole percentage of the compound in the glass)

$(70-x)\ H_3BO_3 + 20Li_2CO_3 + 10Bi_2O_3 + xSm_2O_3$

$x=0,1,3$

All compounds are thoroughly crushed in an agate mortar in order to mix chemicals homogeneously. The mixture is then put in a alumina crucible and melted in an muffle furnace(fig-1) at 1100^0 C for one hour. The melt is then air quenched by pouring it on a rectangular iron cast kept at 500^0 C. It was then slowly cooled to room temperature to get a properly annealed glass. The glasses were polished to achieve good transparency.

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Fig-1

II. CONCLUSION

Bismuth borate glasses with good optical quality were prepared by doping them with different concentration of Sm^{3+}melt quenching technique. The structural analysis of theses glasses will be done through FTIR and spectroscopic properties will be investigated through UV-Visible absorption and emission spectra. The emission spectra of Sm^{3+}-doped glass exhibits three bands in the orange and red regions.This suggests the utility of Sm^{3+}-doped Bismuth borate glasses as a laser material and may be used as a luminescence material for the development of laser and photonic devices operating in the orange-red region.

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