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A Review on the Preparation, Characterization and Applications of Yttrium Based Glass Materials

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Abstract*: Rare-earth elements are of interest in several high-tech and environmental application areas, the two major ones concerning magnetic and optical devices. Yttrium-based inorganic optical materials generally are of practical interest for their applications such as solid state lighting/displays, lasers, and scintillators. Solid-state lighting is particularly desirable commercially for its efficiency and lifetime compared to traditional incandescent alternatives. For lighting and display applications, low-cost, low-temperature synthesis methods for materials that meet or exceed the quality of the materials currently on the market are highly desirable. The aim of the present paper is to highlight the preparation, characterization and applications of yttrium based glasses*

Keywords: *Yttrium, glass, optical, laser and displays*.

1. INTRODUCTION

Recently, many new alloy systems requiring a relatively low critical cooling rate for glass formation have been developed, enabling the fabrication of large size bulk metallic glass components [1, 2]. The large rare earth elements, such as yttrium, scandium, gadolinium, erbium even in small addition have been shown to be advantageous in bulk glass formation [3]. The rare earth elements have similar atomic size, physical and chemical properties. Therefore, proper addition of different rare earth elements should have the influence on the glass forming ability of the bulk metallic glasses-forming alloys. The rare earth elements are the important minor addition materials which have an important impact on the glass production. Since the beginning of the bulk metallic glasse development, rare earth elements have been used as the bulk metallic glasse-forming base and the minor alloying additions [4]. They have a serious effect on the manufacturability of some bulk metallic glasses, which depends on preparation and processing conditions such as vacuum and impurity of environment. Oxygen or other impurities would significantly reduce the glass forming ability.

Rare earth phosphates find their place in wide variety of applications such as optical materials including lasers [5], phosphors [6], and more recently as anti-UV materials [7]. Rare earth orthophosphates exhibit certain properties that make them of interest as scintillators for gamma-ray detection [8–10], as thermophosphors for remote measurement of temperature on moving components [11], and as rare earth analytical standards [12]. Rare earth codoping in inorganic materials has a long held transition of facilitating highly desirable optoelectronic properties for their potential applications to the laser industry. Rare earth compounds were extensively applied in luminescent and display, such as lighting, field emission display (FED), cathode ray tubes (CRT), and plasma display panel (PDP) [13–15]. Several other authors reported the synthesis of rare earth phosphate compounds by different methods such as high temperature solid state reaction technique, wet chemical precipitation technique, and sol-gel and hydrothermal synthesis [16–20]. The physicochemical properties of the material, which depends on the synthesis route, that is, chemical composition, grain size, morphology, and the crystalline structure, influence the thermal behavior the end product, and therefore their final physicochemical properties. So these factors are of prime importance in the manufacturing processes. The present study is focused on the investigation of preparation and applications of Yttrium based materials.

2. RARE EARTH ELEMENT OF YTTRIUM

Yttrium is a transition metal of group 3 (IIIB). It is moderately abundant element in the Earth's crust. Its abundance is estimated to be about 28 to 70 parts per million. Traditionally, yttrium has had many of the same uses as the rare earth elements. For example, it has been used in phosphors. Yttrium phosphors have long been used in color television sets and in computer monitors [21]. They have also been used in specialized fluorescent lights. Other uses include the production of electrodes, electronic filters, lasers, superconductors, computer monitors, trichromatic fluorescent lights, temperature sensors, X-ray intensifying screens [22] and various medical applications and also as traces in various materials to enhance their properties. Yttrium is an important element used in atomic reactors for control rods. It is also used in manufacturing of glass and ceramics. It is also used for the production of labeled monoclonal antibodies for tumor therapy studies Yttrium also used in making of alloys and Laser. In spite of being such huge applications in different areas it’s accurately measurement of concentration always problematic. Yttrium is lighter than the light rare earths, but included in the heavy rare earth group because of its chemical and physical associations with heavy rare earths in natural deposits. Yttrium phosphors are used in energy efficient fluorescent lamps and bulbs. Yttria stabilized zirconium oxide is used in high temperature applications, such as thermal barrier coating to protect aerospace high temperature surfaces. Yttrium is used extensively in the electronics industry to manufacture LCDs and colour TVs. Used as phosphors they enable colour changes as electrical currents are transmitted through them. Terbium and Europium are used in energy efficient lighting applications. Light emitting diodes (LEDs) are 80% more efficient than incandescent lighting and 40% more efficient than compact fluorescent bulbs.

3. MATERIALS AND METHODS

3.1. Chemical Processing

Rare earth mineral concentrates are chemically processed to extract intermediate groups of mixed rare earth compounds. Chemical treatment of mineral concentrates derived from hard rock deposits may start with roasting in air (calcining) to drive off carbon dioxide and oxidize cerium to the tetravalent state. This is in many situations followed by treatment with hydrochloric acid to dissolve non-cerium rare earths, yielding a marketable cerium concentrate which can be used directly as a low value product (for instance, for glass polishing) or further separated into high purity individual rare earths. Alternatively, high temperature direct chlorination is a universal ore treatment process that easily integrates with subsequent process steps. The process produces an anhydrous rare earth trichloride product that is well suited for the production of mischmetal. Chemical processing of mineral concentrates derived from placer deposits is usually accomplished using sodium hydroxide.

3.2. Extraction and Purification of Individual Rare Earths

Individual rare earth compounds are produced from mixed rare earth chloride using methods such as selective oxidation, selective reduction, fractional precipitation, fractional crystallization, solvent extraction and ion exchange. The compounds produced include chlorides, fluorides, oxides, carbonates and nitrates. The production of rare earth metals with purities generally in the range of 98–99% is achieved using various reduction routes. Higher levels of purity, while sometimes achievable with reduction methods, are normally obtained through a sequence of refining processes.

3.3. Manufacture of Rare Earth Products

Rare earth products are manufactured using a variety of processes, depending on the nature of the product and degree of purity required. Some rare earth products may be manufactured directly from mineral concentrates such as bastnäsite and monazite. Others are produced as end products of chemical processing or as intermediates in the preparation of rare earth metals. Many rare earth products, particularly those of a more sophisticated nature, can only be obtained by further processing of intermediates or metals.

3.4. Formation of Glass

Many different techniques can be used to prepare glass, but the most widely used and certainly the most important historically, is melt quenching. When changes is specific volume and thermal capacity are investigated for a glass melt that has been slowly cooled, the results obtained are shown in Fig.1. As the temperature drops, the specific volume decreases. When the melting point T_m is reached an ordinary liquid releases its fusion heat and changes into a crystal. Afterward, the volume decreases in accordance with the expansion coefficient of the crystal. However a substance that solidifiers into a vitreous state does not crystallize at the melting point, but continues to be cooled in a liquid state. In other words, it's supercooled. Accordingly, this state is metastable, although thermodynamically, it is not a stable state. A supercooled liquid however has a fixed volume at a constant temperature regardless of time. As the temperature drops even further, through, the change in volume becomes more gradual, as shown in Fig.1. In the end the volume decreases with almost the same expansion coefficient as in crystal.

The temperature T_g at which a shift is seen from the expansion coefficient of a liquid to that of a solid is called the transition point. Expressed as a coefficient of viscosity, this corresponds to 10^{13} Poise. A supercooled liquid below this temperature is called a vitreous state. Above this temperature, the liquid is simply in supercooled state. When a glass is maintained at a constant temperature below the transition point, the volume decrease with time until it reaches a certain equilibrium value. This phenomenon is called stabilization. If the maintenance temperature is in the vicinity of the transition point, a longer time is required for equilibrium to be reached as temperature is lowered. At ordinary room temperatures, the time required is close to infinity. The equilibrium values at various temperatures are on an extension of the volume-temperature curve of the supercolled liquid. When a glass is cooled at constant rate, the relaxation time of the glass structures is increased. As a result, the structure cannot follow changes in temperature and frozen at a certain fixed temperature. At ordinary temperatures, therefore, glass structure shows no change over time. In other words, glass can be defined as substance in which a supercooled state is maintained at temperatures below the melting point so that no devitrification (crystallization) occurs, and the structure is frozen in the vicinity of the transition point. As shown in Fig.1, a glass has a greater specific volume than in corresponding crystal at ordinary temperature. Similarly, a glass also shows higher values of enthalpy than a crystal. We can say that glass is in a thermodynamic state in which the free energy, entropy, or enthalpy is somewhat higher than in corresponding crystal. The physical properties of glass depend to a certain extent on the rate at which it is cooled, specifically through a glass transformation range

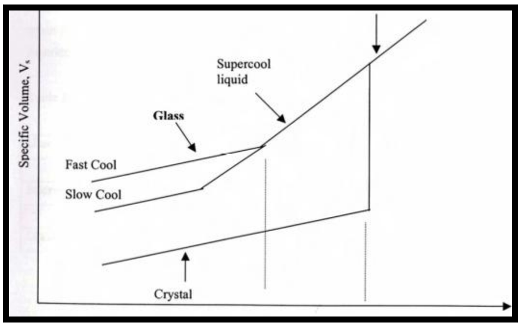

Fig1. *The changes of specific volume against temperature*

4. Yttrium-Based Materials for Optical Applications

As mentioned, yttrium-based materials are commonly used in such applications as lighting and displays. A well-known example, though less frequently used since the advent of flat-screen televisions and monitors, is the cathode ray tube. [23, 24] In a cathode ray tube (CRT), a cathode emits three electron beams, which are focused by a series of lenses and accelerated until they hit a phosphor screen, as depicted in Fig.2 [23].

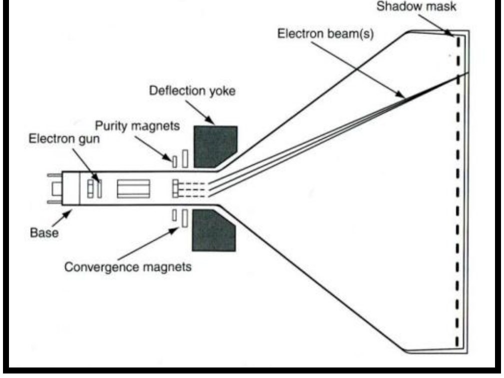

Fig2. *Image depicting the basic process behind the function of cathode ray tubes [23]*

As early as 1964, yttrium-based single-crystalline lasers were reported, particularly room-temperature operating Nd: YAG. [25] Nd: YAG has since become one of the most common laser media compositions. In the 1990s, Ikesue, et al., reported the first high efficiency polycrystalline Nd:YAG laser, making ceramic laser materials commercially attractive [26, 27].Yttrium-based materials are particularly desirable for laser applications because of their mechanical strength, chemical stability, and their high thermal conductivity [27]. Scintillators were developed for particle detection in the 1940s [28-31]. Most simply defined, scintillation is the energy loss of radiation traveling through the scintillator medium [32-36]. More technically, scintillation can be defined as luminescence induced by ionizing radiation in transparent dielectric media. It is important to differentiate scintillation from luminescence, which is the radiation of a material as a result of direct excitation by light. Scintillation is a three-step process: hole-pair creation, thermalization, and recombination [32, 33]. First, incident radiation releases energy by forming electron/hole pairs. Next, hole-pair interaction leads to excitation transfer to luminescent centers. Finally, recombination leads to relaxation and emission (or quenching). Scintillation materials are employed to detect X-ray and gamma-ray photons, neutrons or accelerated particles. Usually the wide band-gap insulator materials of a high degree of structural perfection are used in the form of artificially made single crystals. They accomplish fast and efficient transformation of incoming high energy photon/particle into a number of electron-hole pairs collected in the conduction and valence bands, respectively, and their radiative recombination at suitable luminescence centres in the material. Generated UV or visible light can be then detected with high sensitivity by conventional solid state semiconductor- or photomultiplier-based photodetectors, which are an indispensable part of scintillation detectors.

4.1. Yttria (Y_2O_3) for Optical Applications

Yttria (Y_2O_3) is commonly used for a variety of optical applications including as a solid-state laser host material, scintillator, lighting and display applications [37-41]. There are several qualities that make yttria a desirable material for these applications. It is resistant to thermal expansion, having a thermal expansion coefficient of around 6-7x10^{-6} K^{-1}; this gives rise to its resilience in high-power laser applications [42,43]. Its high thermal conductivity, around 12 W/mK, is also desirable for several of these applications [44, 45]. In addition, it has a high resistance to corrosion and good atmospheric stability, which is desirable in both laser and lighting applications. Crystalline yttria is cubic, with space group $Ia\bar{3}$ [46-48]. Each yttrium is trivalent and is bonded to six oxygen atoms. Yttria boasts a broad transparency across the visible range and into the infrared region, from 0.23 to 8 μm. This quality makes yttria a good host material for a broad range of light-emitting trivalent lanthanide ions. For example, yttria doped with europium (Eu^{3+}) is a well-studied material for a variety of applications. Eu:Y2O3 is most commonly used as a red phosphor in solid state lighting and in displays of all types, including cathode ray tubes, liquid crystal displays, and plasma display panels, due to its high emission efficiency. Another lighting application unique to Eu:Y_2O_3 is as the red phosphor in three band-fluorescent lamps. Small particles with low size distribution, and uniform morphology are advantageous for most of these applications because of the potential for high packing density at lower volume, good chemical stability, and luminescent efficiency. During manufacture of traditional red phosphors for commercial use, the materials themselves are often damaged by the manufacturing process itself; the thermal properties of yttria are yet another reason why it is a good candidate for commercial red phosphors. Crystallographically, in Y_2O_3, Eu^{3+} substitutes into the site generally occupied by the yttrium ions [46]. It emits in the 600-640 nm range, which is the emission we will examine during this work, particularly because of its high efficiency and because of the desirability of Eu:Y_2O_3 for lighting and display applications.

4.2. Applications of Yttrium Based Materials

Significant progress has been made over the past few years in the development of laboratory-based and commercial high-power Yb^{3+}-doped silica fiber sources [49–52]. Fused silica is a very useful host for some applications where very long amplifiers can be used. However, it is generally found to be less suitable for small laser devices, because the rare earth concentration is limited by ion clustering, low solubility, concentration-quenching [53], photodarkening [54] and other undesirable effects [55]. In silica, the Yb_2O_3 concentration can only be increased maximally to the level of 1–2 wt%. More complex silicate glasses can overcome some of these problems. However, the Yb^{3+} emission cross-section and the laser efficiency are generally low for these glasses. Phosphate glasses allow one to overcome most of these problems [55]. These hosts are attractive laser oscillator/amplifier materials, because unlike silicate, fluoride and other laser glass materials, they combine such useful properties, as good chemical and mechanical durability, ion-exchangeability, high cross-sections for stimulated emission, high gain, low concentration quenching and no clustering effects, low upconversion losses, a wide bandwidth capability, and they can be readily drawn into fibers of complex design.

Phosphate glasses also exhibit a very high solubility for rare earth ions and high photodarkening resistance. These features permit the introduction of large concentrations of active ions into relatively small volumes, resulting in smaller laser devices with high energy storage capabilities. The high concentration of rare earth ions in phosphate glasses has several advantages. These high doping concentrations result in highly efficient pumping in short lengths of fibers, high energy storage per unit volume, high gain per unit length and very rapid and efficient energy transfer between rare earth ions.

5. Sol-Gel Process and Applications

Sol-gel can be defined as a sum of its two parts: sols and gels. A sol is defined as a stable suspension of colloidal solid particles within a liquid [56]. A gel is defined as a porous three-dimensionally interconnected solid network that expands in a stable fashion throughout a liquid medium and is only limited by the size of the container [56]. From these definitions, sol-gel can be defined as the preparation of a suspension of solid particles in liquid, which then forms an interconnected solid-network. Sol-gel processing refers, then, to the synthesis process rather than to the end product, however the term has been used in both ways. Sol-gel can be used as a coating, cast as a monolith or thin film, spun as a fiber, or crushed into a powder, as well as other applications [57-59]. In the case of this work, the material will be cast to form bulk glass materials.

Sol-gel is often selected due to its many desirable qualities, including the versatility of the final product. Because the materials are prepared in a solution at low temperatures, the process allows more control over the composition and the homogeneity of the final product without expensive equipment or the need for high-temperature processing equipment. This quality is of particular interest in this case, as it allows the preparation of a glass composite containing nanoparticles using only conventional laboratory equipment. Sol-gel containing fibrous material has been produced, though generally for mechanical purposes. In these cases, the fibrous material has been added as a means of strengthening the glassy matrix and increasing its modulus. Organic dyes have also been added to a sol-gel system for optical applications [60].

6. Rare-Earth–Doped Glasses

Optical glasses are the corner stone in a huge number of technological applications. This is definitely true for laser systems. Over almost 40 years there has been extensive research covering a large number of active ions in every known glass system. Neodymium, however, remains the primary RE element of interest for most commercial applications of glass lasers, and, more generally, of solid-state lasers. Only recently, a growing interest has been focused on erbium and ytterbium: the former ion is fundamental for applications in the optical telecommunications (but also has interest for eye-safe laser applications, such as in rangefinders), while the latter is useful as co-dopant of erbium (because of the energy-transfer effect that increases pumping efficiency at 980 nm) but is assuming larger and larger importance for the development of medium-to-high power fibre lasers. Ytterbium-doped silica fibres exhibit a broad-gain bandwidth, high optical conversion efficiency, and large saturation fluence. A cladding-pumped Yb-doped fibre laser with continuous-wave optical power of 1.36kW at 1.1 μm, with 83% slope efficiency and near diffraction-limited beam quality, has been demonstrated [61]. By combining an assembly of highly reliable diode-pumped single Yb-fibre lasers, industrial systems with output up to 50kW are also available. Other rare-earth ions under investigation include samarium and holmium for visible emission, praseodymium for the 1.3 μm window, thulium and again holmium for longer near-infrared wavelengths. There are three major applications for optical amplifiers in modern optical networks; they can be used as power amplifier/boosters (placed directly after the laser diode transmitter), in-line amplifiers (repeaters), or preamplifiers (placed in front of the detector to enhance its sensitivity). The corresponding requirements may be different, especially in terms of input signal power handling, maximum optical gain, and signal-to-noise ratio. The application of optical amplifiers, especially in local access networks, has to do with the loss compensation of passive components (such as interleavers and $1 \times N$ splitters). The goal of developing fibre systems operating over an ultra-wide band, covering the wavelengths between 1.3 and 2 μm, would require the use of different rare-earth elements and different glass matrices.

7. CHARACTERIZATION OF GLASS

The characterization of a material can be defined as a complete description of its physical and chemical properties. A thorough and extensive characterization of a single crystal is very difficult, because it requires a variety of tests using a number of sophisticated instruments, an accurate analysis of the results of these tests and their confirmations. The use of instrumentation is an exciting and fascinating part of any analysis that interacts with all the areas of chemistry and with many other fields of pure and applied sciences. In most cases of chemical analysis, a signal is produced which reflects the chemical or physical property of a chemical system. The prepared glasses will be subjected to the following characterization studies

7.1. Powder X-Ray Diffraction

Powder diffraction is a scientific technique using X-ray or neutron diffraction on powder or microcrystalline samples for structural characterization of materials. Ideally, every possible crystalline orientation is represented equally in the sample, leading to smooth diffraction rings around the beam axis rather than the discrete Laue spots observed for single crystal diffraction. In accordance with Bragg's law, each ring corresponds to a particular vector in the sample crystal with intensity proportional to the number of such planes. The machine which is used to perform such measurements is called a powder diffractometer.

7.2. Fourier Transform Infrared Spectroscopy (Ft-Ir)

Fourier Transform Spectroscopy is a simple mathematical technique to resolve a complex wave into its frequency components. The conventional IR spectrometers are not of much use for the far IR region, as the sources are weak and the detectors are insensitive. FT-IR made this energy-limited region more accessible. It also made the mid–infrared (4000 - 400 cm^{-1}) more useful. The infrared spectrum is formed as a consequence of the absorption of electromagnetic radiation at frequencies that correlate with the vibration of specific sets of chemical bonds from a molecule. Thus, the vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule.

7.3. Uv-Vis-Nir Spectroscopy

UV-Vis-NIR spectroscopy is defined as the measurement of the absorption or emission of radiation associated with changes in the spatial distribution of electrons in atoms and molecules. In practice, the electrons involved are usually the outer valence or bonding electrons, which can be excited by the absorption of UV or visible or near IR radiation.

7.4. Thermal Studies

Recent trends indicate that thermal analysis has become well established method in the study of the thermal behaviour of materials and finds widespread applications in diverse industrial and research fields. Thermal analysis is a general term, which covers a group of related techniques in which the temperature dependence of the parameters of any physical property of a substance is measured. Thermal studies not only provide valuable information on the thermal stability of the compounds and the decompositions products but also provide an insight into their modes of decomposition.

7.5. Microhardness Studies

Hardness is an important factor in the choice of ceramics for abrasives, bearings, tool bits, wear resistance coatings etc. Hardness is a measure of resistance against lattice destruction or the resistance offered to permanent deformation or damage. Measurement of hardness is a destructive testing method to determine the mechanical behaviour of the materials.

7.6. Dielectric Studies

The useful method of characterization of electrical response is the dielectric studies. A study on the dielectric properties of materials gives an electric field distribution within material. The frequency dependence of these properties gives great insight into the material applications. The range of measurement depends on the properties and the materials of interest. From the study of dielectric constant as a function of frequency, temperature etc., the different polarization mechanisms in material such as atomic polarization of the dipoles, space-charge polarization etc., can be understood.

7.7. Scanning Electron Microscopy (Sem)

Electron microscopy is a powerful tool to investigate the microstructure of materials. External morphology, chemical composition, crystalline structure and orientation of materials making up the sample are revealed by SEM. Data are collected over a selected area of the surface of the sample, and a two-dimensional image is generated.

7.8. Energy Dispersive X-Ray Analysis (EDAX)

To study the elemental composition of materials, qualitative and quantitative analysis were performed by energy dispersive X-ray analysis.

8. CONCLUSION

Glasses have been known for a long time as a convenient host for rare earths and have been widely used for the fabrication of solid-state lasers. Recently, guided-wave format has added several advantages, namely the small size, the high pump power density, and the larger flexibility in design and fabrication. Thus, in the last few years, due to the great development of optical communications, an increasing research and development activity has been focused on the design and manufacture of fibre optic and integrated optic lasers and amplifiers, especially of those based on yttrium based glasses. As has been presented, there are three primary applications for yttrium-based materials: lasers, scintillators, and lighting and displays. In the case of scintillators, the high light-output necessary for detection is not likely to be improved by the use of a composite rather than a more densely doped ceramic material. We have concluded, however, that lighting and display technologies can benefit from the development of a low-cost, high-emission material. Rare-earth–doped glasses are a key factor for the development of some optical components, like integrated optical amplifiers, whose characteristics are critical for achieving the flat and broad-band optical gain that seems needed in future communication systems. Rare-earth–doped glasses are also fundamental for the development of several kinds of lasers, both in massive and integrated optics format. Since then, many remarkable results in the development of more efficient glass matrices and in the actual fabrication of rare-earth–doped glass integrated optical amplifiers have been achieved.

We can conclude that, besides their other significant properties, rare-earth elements are of great importance in the field of optics and that there is a continuous attempt of exploiting their photoluminescence properties for the development of novel glasses, in particular aiming at the production of higher-performance broad-band integrated optical amplifiers.

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