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Spectroscopic Studies on Znf_2-Pbo-P_2o_5 Glasses Containin Pr^3+ Ions

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ABSTRACT

Spectroscopic Studies on ZnF_2 –PbO–P_2O_5 Glasses doped withPr^{3+} ions

Praseodymium doped glasses are being widely investigated, in view of the fact that these glasses exhibit very rich emission from UV to infrared region and used as the most promising candidates for communication window up-conversion. Due to these applications we have synthesized ZnF_2–PbO–P_2O_5 Glasses doped with Pr_2O_3 and the infrared spectra, optical absorption in the visible region and photoluminescence in the visible region are carried out. By the analysis of the results of above studies the glasses indicated an increase of intensity of all the optical and emission bands with the increase in the concentration of Pr_2O_3. From these results it may be attributed to the larger population of $^3H_6$ and $^3F_2$ energy levels due to increase in the concentration of Pr^{3+} ions.

Introduction

different colors. It is hard, brittle and stands up to the effects of wind, rain or Sun. In more precise terminology, glass is an amorphous solid completely lacking in long range, periodic atomic structure and exhibiting a region of glass transformation behavior. Any material, inorganic, organic or metallic, formed by any technique, which exhibits glass transformation behavior, is a glass.

Scope of the present work:

Interest in amorphous phosphates was stimulated by their use in a variety of industrial applications, including sequestering agents for hard water treatments and dispersants for clay processing and pigment manufacturing [1]. The melting point and boiling point of P_2O_5 glasses are 560 ^oC and 605 ^oC respectively. Some other properties of pure P_2O_5 glass are (refractive index = 1.4930 at λ = 546.1 nm; thermal expansion coefficient = 13.7 x 10^{-6} / ^oC [2]. Hypothetically P_2O_5 glass has a UV edge less than 150 nm (~ 8.27 eV). However, P_2O_5 glass generally contains water and shifts the edge towards longer wavelength. A comparative

diagram of the UV edges of various glass formers is shown in Fig1.

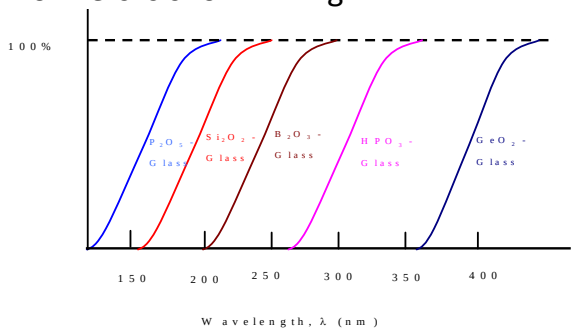

Fig.1 Comparative diagram of the UV edges of various glass formers.

P_2O_5 glasses have several advantages over conventional silicate and borate glasses due to their superior physical properties such as high thermal expansion coefficients, low melting and softening temperatures and high ultra-violet transmission [3]. The advent of solid state lasers in 1960's heralded a new era of phosphate glass research. Certain compositions of these glasses have large rare-earth stimulated emission cross-sections and low thermo optical coefficients (compared with silicate glasses) and are the materials of choice particularly for high power laser applications [3]. During the last two decades phosphate glasses have been investigated intensively, but there is still a great interest in developing new glasses related to the demands of both industry and technology. Many phosphate glasses are prone to crystallization or devitrification either during processing or in applications where they may be held at high temperatures for long periods. Therefore it would seem that a detailed study of the thermal behavior of such glasses is of some importance. In the particular field of thermo luminescence (TL) dosimetry, much recent work is concentrated on optimizing the glass compositions to give the best TL characteristics. However the poor chemical durability, high hygroscopic and volatile nature of phosphate glasses prevented them from replacing the conventional glasses in this field [4, 5].

Glass preparation

Composition of the Glass

The details of compositions of the glasses investigated are:

1. $10ZnF_2–30PbO–60P_2O_5$
2. $10ZnF_2–30PbO– (60–x)P_2O_5$:x Pr_2O_3 $(0.5 \leq x \leq 1.5)$

Methods of preparation of glasses

The glasses used for the present study are prepared by the melting and quenching .Techniques [6-7]. The starting materials used for the preparation of the present glasses were Analytical grade reagents (99.9 % pure) of ZnF_2, P_2O_5, PbO and Pr_2O_3. The

compounds of required compositions were thoroughly mixed in an agate mortar and melted in a platinum crucible. The furnace used was a PID temperature controlled furnace .The glasses were melted at about 900 ^{o}C for ½ an hour till a bubble free liquid was formed. The samples were subsequently annealed at 300 ^{o}C in another furnace. The resultant melt was poured on a rectangular brass mould (containing smooth Polished inner surface) held at room temperature. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for studying the electrical and optical properties are 1 cm x 1 cm x 0.2 cm.

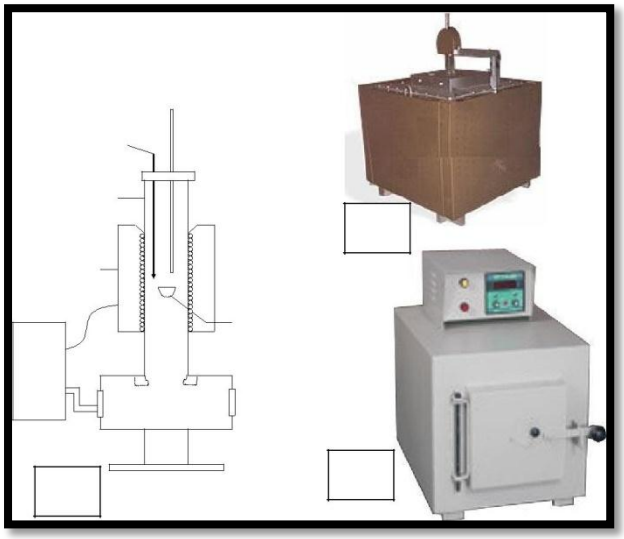

Fig.2(a) Schematic sketch high temperature furnace and the photographs of (b) Melting furnace (c) Annealing furnace

Characterization of the samples

X–Ray diffraction

The crystalline phases if any in the glasses samples were checked by X-ray diffraction spectra recorded on Rigaku D/Max ULTIMA III X-ray diffractometer with CuKα radiation. represents the schematic diagram of general X-ray diffractometer.

Fig.3 Rigaku D/Max ULTIMA III X-ray

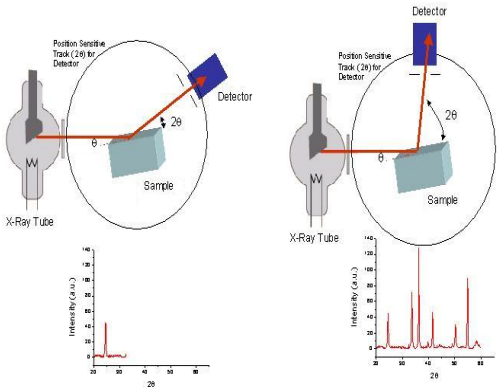

Fig.4 Schematic representation of X-ray

Characterization

X-ray diffraction

The X- ray diffraction spectra recorded for these ZnF2–PbO–P2O5:Pr3+.the curves have no sharp peaks ensuring amorphous nature of thesamples.

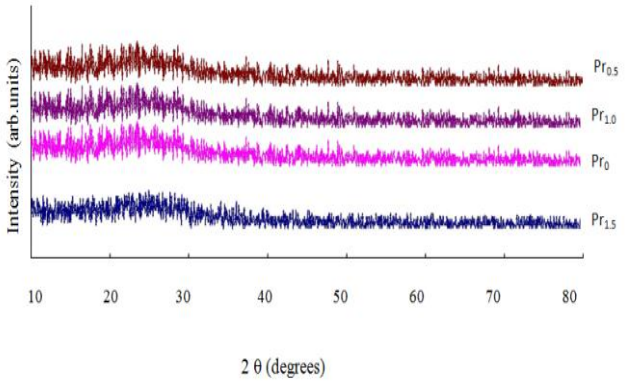

Fig. 5 X-Ray diffraction pattern of ZnF_2–PbO–P_2O_5 glasses doped with different conc. of Pr_2O_3.

Physical parameters

Table 1 Summary of data on various physical parameters of ZnF_2–PbO–P_2O_5: Pr_2O_3 glasses

Property	Density d (g/cm^3)	Avg. mol.wt $\overline{M}$	Ionic conc. N_i (10^{21} ions/cm^3)	Inter ionic distance of Pr^{3+} ions R_i (Å)	Polaron radius R_p (Å)	Field strength F_i (10^{16}, cm^{-2})
Pr_0	3.851	162.46	-	-	-	-
$Pr_{0.5}$	3.786	163.40	23.01	3.51	1.41	1.49
$Pr_{1.0}$	3.857	164.34	46.62	2.77	1.11	2.39
$Pr_{1.5}$	3.961	165.28	71.40	2.41	0.97	3.18

Results

1- Infrared spectral studies

The IR transmission spectra recorded for the pure glassesexhibited conventional bands due phosphate groups and they are attributed to the P=O stretching units (at 1270 cm-1), (PO4)3-(at 1060cm-1), P-O-P asymmetric(at 920cm-1), symmetric (at 740 cm-1) bendings. Another band due to the vibrations of PbO4/ZnO4 structural units is also located at about 485 cm-1 in these spectra. With the introduction of Pr2O3 into the glass network, no additional bands are observed; however, the intensity of the bands due to phosphate structural units is observed increase but no significant shift in the bands is observed.

Fig.6 IR spectra for ZnF_2–PbO–P_2O_5 glasses doped with Pr^{3+} ions.

2- Optical absorption studies

The optical absorption spectra of ZnF2–PbO–P2O5:Pr3+ glasses exhibited absorption bands corresponding to 3H4→3P2, 3P1, 3P0, 1D2 transitions of Pr3+ ions Out of these 3H4→1D2 in the orange region, whereas 3H4→3P2, 3P1, 3P0 are in the blue region . represents the comparison plot of optical absorption spectra doped different concentrations of Pr3+. The intensity of the bands is observed to be the highest is the spectra of the glasses doped with 1.5 mol% of Pr2O3. The details of the optical absorption data of theseglasses.

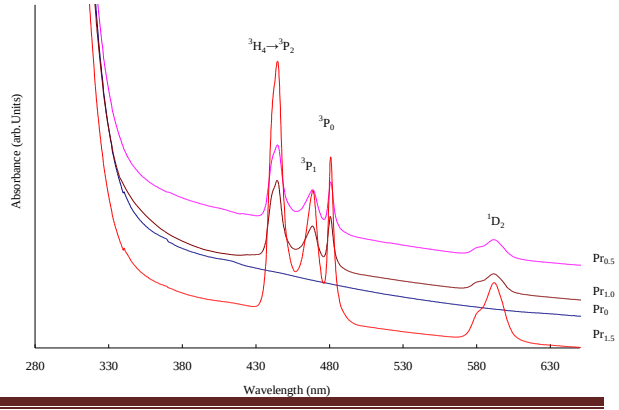

Fig.7 Optical absorption spectra for ZnF2–PbO–P2O5 glasses doped with different conc. of Pr3+ ions.

3- Photoluminescence (PL) studies

The PL spectra of ZnF2–PbO–P2O5: Pr3+glasses recorded in the visible region excited at 440 nm exhibited the five emission bands originated from 3P0 and 1D2 excited levels .The detailed emission transitions are as follows:

3P0 → 3F2, 3F4, 3H6, 3H5; 1D2 → 3H5.

An increase in the intensity of these emission bands is observed with increase in the concentration of Pr2O3 in the glass matrix. The energy level diagram involving all the absorption and emission transitions of Pr3+ ions in ZnF2–PbO–P2O5 is presented in the

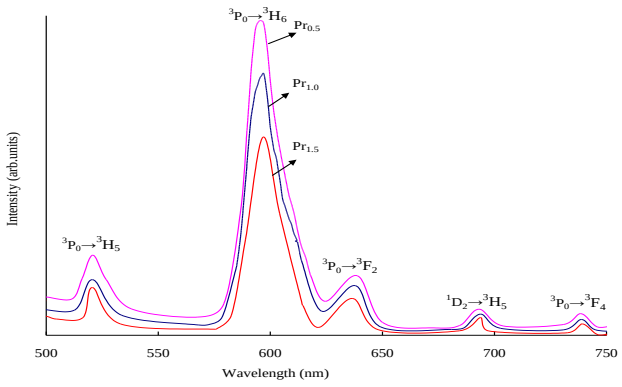

Fig.8 Photoluminescence spectra for ZnF_2–PbO–P_2O_5: Pr^{3+}glasses recorded at room temperature (λ_{exc}=440 nm)

Discussion

In general, the properties of a glass depend upon its composition and to a considerable extent upon its structure. Lead phosphate glasses containing tungsten oxide have a complex composition and are an admixture of network formers, intermediates and modifiers. P2O5 is a well-known network former with PO4 structural units with one of the four oxygen atoms in PO4 tetrahedron is doubly bonded to the phosphorous with a substantial π –bond character to account for the pentavalency of phosphorous [8]. The PO4 tetrahedrons are linked together with covalent bonding in chains or rings by bridging oxygen's. Neighboring phosphate chains are linked together by cross bonding between the metal cations and two non-bridging oxygen atoms of each PO4 tetrahedron. In general P–O–P bond between PO4 tetrahedron is much stronger than the cross bond between chains via the metal cations [9].PbO is in general a glass modifier and enters the glass network, by breaking up the P–O–P bonds (normally the oxygen'sof PbO break the local symmetry while Pb2+ ions occupy interstitial positions) and introduces co-ordinated defects known as dangling bonds along with non-bridging oxygen ions; in this case Pb2+ is octahedrally co-ordinated.

However, PbO may also participate in the glass network with PbO4 structural units when lead is linked to four oxygen ions in a covalency bond configuration. Further when PbO is present in larger quantities the π¯bond of P = O may be ruptured with the creation of new non bridging oxygen ions facilitating the formation of P–O–Pb linkages [10].

The patterns of the optical absorption spectra give some information regarding the coordination number of the Pr3+ ions with oxygen in amorphous materials. To be more specific the energy associated with the absorption transition of 3H4 →3P0 (~20700 cm-1) of Pr3+ ions in the titled glasses suggest predominantly 8 coordination for this rare earth ion
[11, 1]. These distorted PrO8 structural units form a one-dimensional chain through edge-sharing in the glass network and may alternate with phosphate structural units [2].
Among the three emission bands (green, orange and red) in the visible region, the intensities of orange (3P0 → 3H6) and the red (3P0 → 3F2) emission bands are found to be enhanced with increase in the concentration of Pr2O3 in the glass matrix. This may be attributed to the larger population of 3H6 and 3F2 energy levels due to increase in the concentration of Pr3+ ions.

Summary

A systematic study on, optical absorption, luminescence and infrared spectral properties of Pr3+ doped ZnF2–PbO–P2O5 glasses have been presented.
The details of compositions of the glasses investigated are:
10ZnF2–30PbO–60P2O5

$10ZnF_2–30\ PbO–\ (60–x)\ P2O5:\ x\ Pr_2O_3$

$(0.5 \leq x \leq 1.5)$ (all in mol %)

The glasses were prepared by the usual melting, quenching and subsequent annealing techniques.
The following studies were made:
(a) Infrared spectra in the region 400 to 4000 cm –1.
(b) Optical absorption in the visible region.
(c) Photoluminescence in the visible region.

Conclusions

The analysis of the results of various studies viz. optical absorption, luminescence and infrared spectra of ZnF2–PbO–P2O5: Pr2O3 glasses indicated an increase of intensity of all the optical and emission bands with the increase in the concentration of Pr2O3.
The main conclusions drawn from the results of above studies are summarized below:

1. Optical absorption spectra:

The optical absorption spectra of Pr2O3 doped ZnF2–PbO–P2O5 glasses exhibited four prominent absorption bands corresponding to the 3H4→3P2, 3P1, 3P0, 1D2
transitions. An increase in the intensity of these bands is observed with increase

in the concentration of Pr2O3 in the glass matrix.

2. The infrared spectra:

The IR transmission spectra recorded for the pure glasses exhibited conventional bands due phosphate groups and they are attributed to the P=O stretching units (at 1270 cm-1), (PO4)3-(at 1060 cm-1), P–O–P asymmetric (at 920 cm-1), symmetric (at 740 cm-1) bendings. Another band due to the vibrations of PbO4/ZnO4 structural units is also located at about 485 cm-1 in these spectra. With the introduction of Pr2O3 into the glass network, no additional bands areobserved [10,11]; however, the intensity of the bands due to phosphate structural units is observed increase but no significant shift in the bands is observed.

3. Luminescence spectra:

The PL spectra of all the investigated glasses in the visible region exhibited the six emission bands originated from 3P0 1D2 excited levels. The detailed emission transitions are as follows:

3P0 → 3F2, 3H6, 3H4, 3H5; 1D2 → 3H5

An increase in the intensity of these emission bands is observed with increase in the concentration of Pr2O3 in the glass matrix.

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