

OPTICAL PROPERTIES OF Er³⁺/Nd³⁺ CO-DOPED MAGNESIUM PHOSPHATE GLASS

Md Rahim Sahar, Mazlini Mazlan, Ramli Ariffin, and Md. Supar Rohani

*Department of Physics, Faculty of Science, Universiti Teknologi Malaysia,
81310 Skudai, Johor, Malaysia*

ABSTRACT

Series of glass based on $(P_2O_5)_{0.5}-(MgO)_{0.5-x}-(Er_2O_3 / Nd_2O_3)_x$ have been successfully prepared by melt quenching technique. Their amorphousity is confirmed using the X-ray diffraction technique. The optical properties of the glass have been measured using Infrared and UV-Visible spectroscopy. It was found that the vibrational frequency is observed to be around 3420-3560, 1312-1319, 1060-1083, 933-938, 764-769, and 471-474 cm^{-1} which is predominately due to the OH⁻ band, P=O, P-O-P, P-O⁻ stretching vibrations respectively. The absorption cut-off wavelength is in the range of (318 nm – 322 nm) and is very much depend on the MgO contents.

Keywords: Phosphate glass; Optical Properties; Cut-off wavelength;

INTRODUCTION

There has been much research of phosphate glasses due to their unique high thermal expansion, low melting temperature, high transmission in the UV region and radiative properties [1, 2]. The main advantage of a phosphate glass over other oxide glasses (e.g. silicate and borate) is its ability to accommodate high concentration of transition metal ions and remain amorphous. In addition, phosphate glasses enjoy a range of compositional and structural possibilities (ultra, meta, pyro, and ortho) that facilitate tailoring chemical and physical properties of interest for specific technological applications [3]. However, metaphosphate glasses containing rare-earth ions have potentially important applications in optical communications and laser technologies. Glasses of the R (PO₃)₃ formulas (where R represents one of the lanthanide ions) have been reported to exhibit the largest magnetic contributions to the low temperature specific heats known in oxide glasses. Even though there have been studies of phosphate glasses doped with the lanthanide ions, there have been limited studies of phosphate glasses co-doped with the lanthanide ions [4]. The aim of this work is to investigate the optical properties of phosphate glass co-doped with the lanthanide ions through Infrared and UV-Visible spectroscopies.

EXPERIMENTAL DETAILS

The glass samples were prepared from starting material constituents of P_2O_5 , MgO, Er_2O_3 and Nd_2O_3 (all from Aldrich products, 99.99% pure) by melt-quenching technique with constant phosphate content at 50 mol% and by changing the MgO content as the Er_2O_3 and Nd_2O_3 change. Four samples co-doped with constant of the Er_2O_3 contents at 2.5 mol% and 0.25, 0.50, 0.75 and 1 mol% of Nd_2O_3 were prepared. Another three samples co-doped with constant of Nd_2O_3 contents at 0.50 mol% and 1.50, 2.00 and 3.00 mol% respectively.

An appropriate mixture of 20 gram batch is placed in Silica crucible. The mixture was then mixed to become homogenous by using milling machine at about 30 minutes. The mixture being heated in an electrical furnace at 1100 °C and being kept there for 1 hour for the glass to melt. The melts were quenched into a steel plate mould before transferred to another furnace at 450 °C for 3 hours and then the sample is allowed to cool down to room temperature.

The X-ray diffraction (XRD) analysis was used to verify the amorphousness of the samples. Infrared absorption spectra of the glass samples were measured using a Perkin-Elmer Spectrum One FT-IR spectrometer in the 4000-400 cm^{-1} frequency range using pellets of KBr. The UV-Vis spectroscopy is recorded to determine the absorption characteristic at 200 – 700 nm.

RESULTS AND DISCUSSION

The compositions and the XRD patterns of the glasses obtained are shown in Table 1 and Figure 1. All the glass samples are in amorphous state showing broad halo which is a characteristic of amorphous structure [5].

Table 1: The compositions (mol %) of the magnesium phosphate glasses

Sample No.	P_2O_5 (mol%)	MgO (mol%)	Er_2O_3 (mol%)	Nd_2O_3 (mol%)
S1	50.00	47.25	2.50	0.25
S2	50.00	47.00	2.50	0.50
S3	50.00	46.75	2.50	0.75
S4	50.00	46.50	2.50	1.00
S5	50.00	48.00	1.50	0.50
S6	50.00	47.50	2.00	0.50
S7	50.00	46.50	3.00	0.50

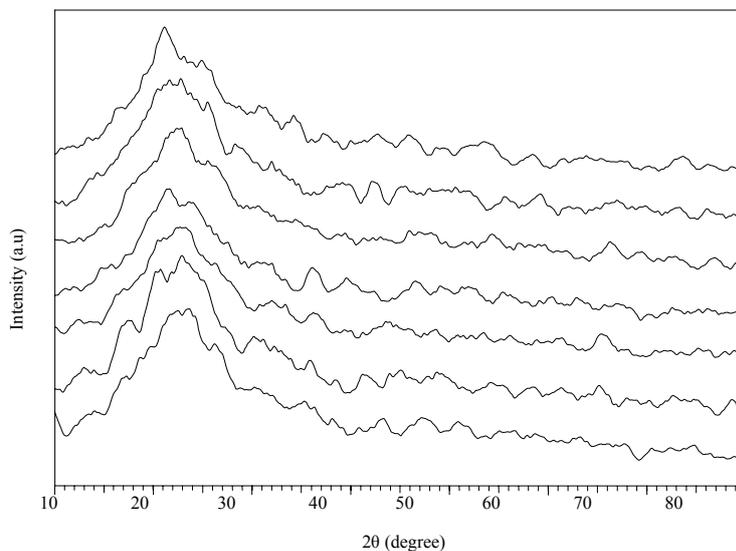


Figure 1: X-ray diffraction pattern of the glass samples

Figure 2 show the absorption bands around $3420-3560\text{ cm}^{-1}$, which can be assigned to the vibration peaks of OH^- band. It is quite strong which would reflect the higher degree of the hygroscopicity of the glass and can be avoiding by using a very high purity materials. This problem can also be met by preparing the glass sample in a vacuum condition or in nitrogen gas environment.

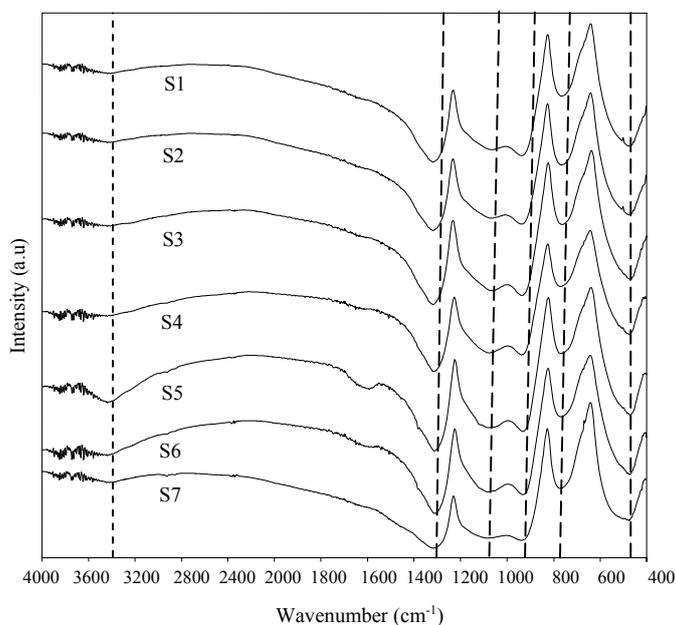


Figure 2: FTIR spectra for the glass samples

As can be seen in Figure 2, the strong absorption peaks around $1312\text{-}1319\text{ cm}^{-1}$ which can be assigned to the P=O stretching vibration [6, 7], in the branching group of Q^3 tetrahedral site are observed to exist in most phosphate glass system. However, this peaks shifted towards a lower wavenumber as the amount of $\text{Er}^{3+}/\text{Nd}^{3+}$ content increase. This would indicate that there are some structural changes occur in the glass network

The bands around $1060\text{-}1083\text{ cm}^{-1}$ is assigned to the asymmetrical stretching vibration of P-O-P bond, respectively. The bands for $(\text{P-O-P})_{\text{as-s}}$ shifts to lower wave number with increasing of Er_2O_3 and Nd_2O_3 content. Presumably due to the changes in the phosphate chain length and the chain P-O-P band angle.

Another absorption peaks are located around $933\text{-}938\text{ cm}^{-1}$ are due to the stretching vibration of P-O⁻ [8]. A shift towards lower bands is believed to be attributed by the existence of the bonds between $\text{Er}^{3+}/\text{Nd}^{3+}$ ions and the non-bridging oxygen.

A small absorption peaks occur around $764\text{-}769\text{ cm}^{-1}$ are due to the symmetric stretching modes of the P-O-P linkages, $(\text{P-O-P})_{\text{s}}$. The other absorption peaks around $471\text{-}474\text{ cm}^{-1}$ can be assigned to the P-O-P bending vibration are actually one of the characteristic of the phosphate glass IR transmission spectra [9].

Figure 3 shows the UV-Vis spectra for the sample 1 with the thickness is about 2.90 mm. From Figure 3, the cut off wavelength can be obtained and the results for all the samples can be summarized in Table 2.

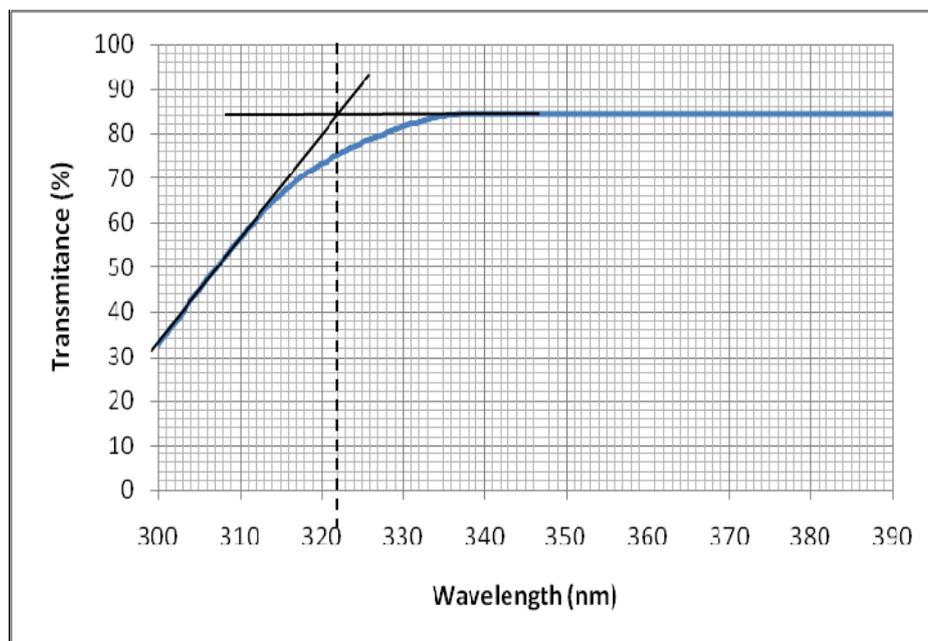


Figure 3: Optical transmittance spectra for Sample 1

Table 2: Cut-off wavelength as a function of MgO contents in phosphate glasses

Sample	MgO	λ cut-off
S1	47.25	322
S2	47.00	321
S3	46.75	319
S4	46.50	318
S5	48.00	321
S6	47.50	320
S7	46.50	318

From Table 2, a plot of cut-off wavelength against sample no. is can be made and the result are shown in Figure 4. It can be seen that as the cut-off wavelength gradually shifts to the lower wavelength with decreasing the MgO contents. It is due to the changing in glass network structures.

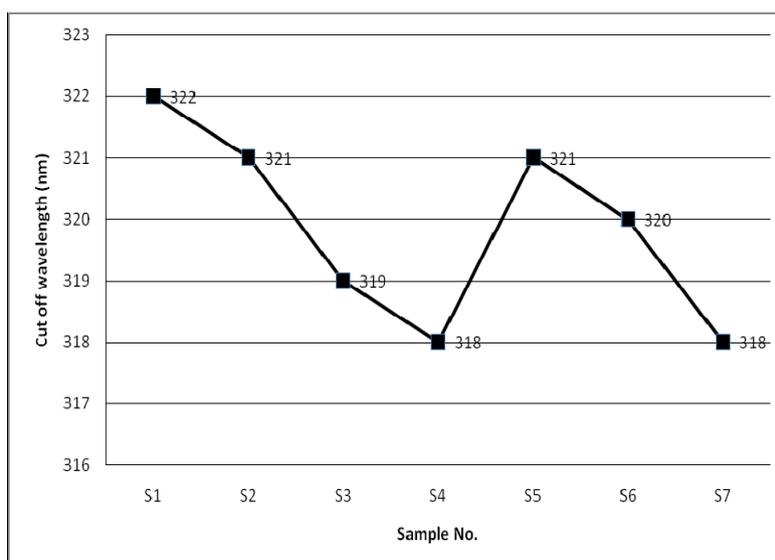


Figure 4: Cut off wavelength versus sample no

CONCLUSION

From the discussion above, some conclusions can be drawn. The phosphate glass sample has successfully been made and their amorphousity has been confirmed by X-ray diffraction technique. The IR spectra show that there are six broad absorption peaks corresponding to the OH⁻ band, P=O, P-O-P, P-O⁻ stretching vibrations. The absorption cut off wavelength in the range of 318 nm to 322 nm is very much dependent on the concentration of MgO contents.

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