

OPTICAL BAND GAP AND IR SPECTRA OF GLASSES IN THE SYSTEM [Nd₂O₃]_(x)-[CuO]_(35-x)-[P₂O₅]₍₆₅₎

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ABSTRACT

The infra red and ultraviolet-visible spectroscopy of neodymium copper phosphate glasses on the [Nd₂O₃]_(x)-[CuO]_(35-x)-[P₂O₅]₍₆₅₎ system with $0 \leq x \leq 10$ mol.% has been studied. The study shows existence of phosphate tetrahedral dominates in lattice vibrations. It is also found out that The Urbach energy lie between 0.451 and 0.634 eV, and the optical energy gaps between 0.79 eV to 2.34 ± 0.01 eV.

INTRODUCTION

Rare-earth doped glasses have a particular interest in many areas such as in communications for fibers and optical amplifiers, as remote chemical sensors, and as solid state lasers for medical applications [1]. Their ions are characterised by partially filled d and f shells that can frequently exist in a number of oxidation states. The electronic conduction can occur as a result of electron transfers from ions in a lower to those in a higher oxidation state. Several papers have also reported some properties of these glasses [2,3]. In such systems rare-earth ions may give rise to a sharp absorption edge and absorption peaks.

The spectroscopic behaviour of rare-earth ions are strongly affected by the local structure at the rare-earth sites [4,5] and the distribution of the doped ions in the glass matrix [6]. The relationship between the structure of the host glass and the properties of the doped ions is useful for designing the glasses for different applications. Rare-earth ions are used as dopants in glasses mainly for two reason: firstly, their well defined and sharp energy levels may serve as structural probes for the environment of the dopant and secondly, the modifications of the energy level structure of the rare earth ions caused by the glassy environment may lead to interesting applications. Even though the electronic spectra and the optical band gap of these glasses has been elsewhere reported [7], but the optical characteristic of Nd³⁺ as a dopant might be interested. Thus, it is the aim of this paper.

EXPERIMENTAL

Preparation of Sample

Glasses of composition [Nd₂O₃]_(x)-[CuO]_(35-x)-[P₂O₅]₍₆₅₎ were prepared, where $0 \leq x \leq 10$ mol %. The oxide components were carefully weighed and well mixed in silica crucible. The mixture was then heated in an electrical furnace at 350 °C for 1h, and then at 1200 °C for 2h . To ensure the proper mixing and homogeneity take place, the molten liquid was shaken frequently and vigorously. The melt was then cast into a hot steel split mould before immediately transferred to an annealing furnace at 350 °C where for

3 h to relieve any residual stress which could cause embrittlement. Then the furnace was switched off and allowed to cool down to the room temperature at cooling rate of $0.5^{\circ}\text{C}/\text{min}$. The amorphous nature of the samples were characterised by an X-ray diffraction. Meanwhile, the density of the glass was measured by a simple Archimedes process using toluene as an immersion liquid.

Measurements of IR spectra

Typically about 0.02 mg of the relatively fine sample powder is mixed with 2 mg of KBr powder before being pressed into a pellet with a surface area of 1 cm^2 . The FTIR spectra were recorded in the spectral range of $4000 - 400\text{ cm}^{-1}$ using Perkin Elmer 1600 Fourier Transform infra red (FTIR)

Optical Absorption in UV and Visible Region

Samples with the thickness range from 100 to 200 nm are prepared using the evaporation technique on grounded glass. The absorption spectra of the glasses were taken using a UV-VIS-NIR scanning spectrophotometer at room temperature.

RESULTS AND DISCUSSION

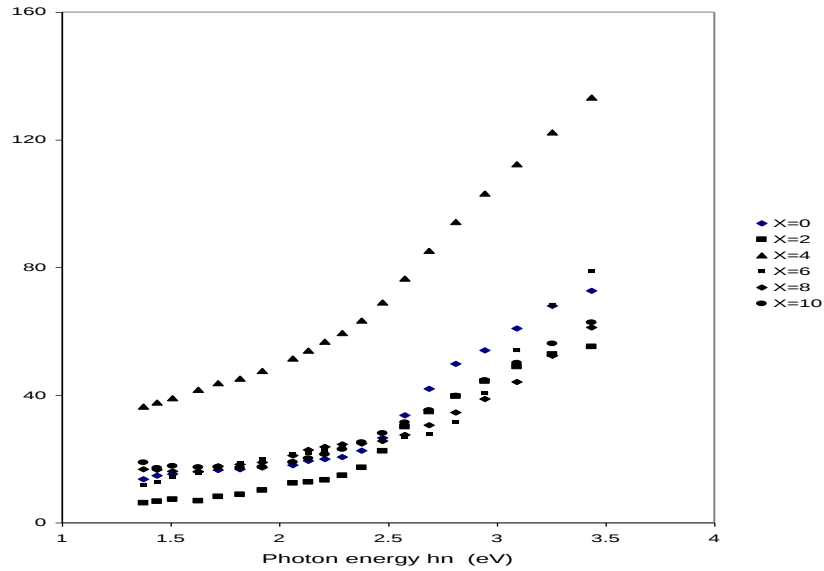


Figure 1: $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ for various $\text{Nd}_2\text{O}_3\text{-CuO-P}_2\text{O}_5$ glasses

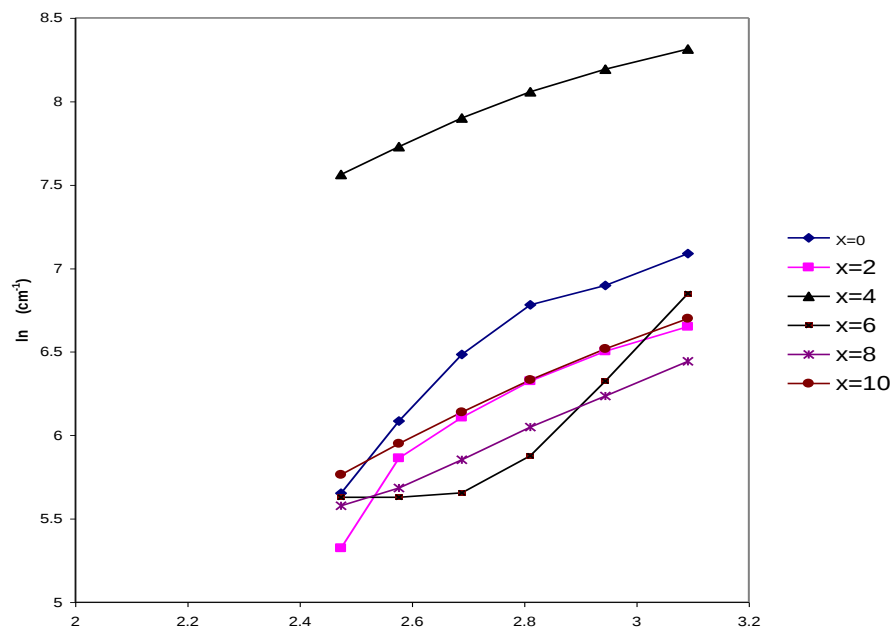


Figure 2: The $\ln \alpha$ versus $\hbar\omega$ for various Nd_2O_3 (mol%) content for $x\text{Nd}_2\text{O}_3-(35-x)\text{CuO}-65\text{P}_2\text{O}_5$ system

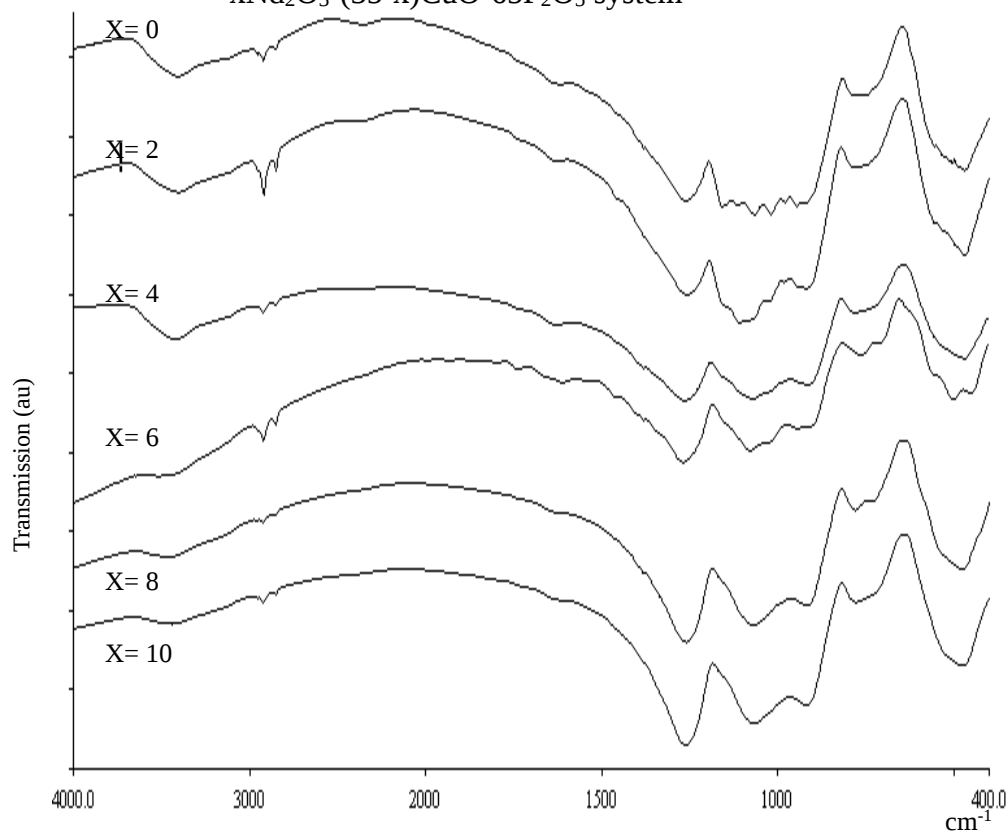


Figure 3: IR spectra of $(\text{Nd}_2\text{O}_3)_x-(\text{CuO})_{35-x}-(\text{P}_2\text{O}_5)_{65-x}$, with, $0 \leq x \leq 10$

IR spectra

The Fourier Transform Infra Red (FTIR) absorption spectra of neodymium copper phosphate glasses are shown in Figure 3. From Figure 3, it can be seen that the infra-red spectrum lies in the region of 4000 cm^{-1} to 200 cm^{-1} as can be seen in Table 1. There are six important absorption bands within the frequency range from 3428 cm^{-1} to 470 cm^{-1} , similar to those obtained by Hogarth and Moridi [8]. However the absorption peak for CuO, which should appear at 620 cm^{-1} has not appeared in these glasses. This band seems to be completely broken down as a consequence of the P-O-Cu stretching vibrations being modified into the P-O-Cu-O-Nd bands.

It is also found that the addition of small amount of Nd_2O_3 has affects the absorption band positions from 470 cm^{-1} to 476 cm^{-1} . This is due to the microstructural changes occurred in addition to the reduction of the Cu^{2+} content on annealing.

The absorption band observed in $755 - 779\text{ cm}^{-1}$ would seem to be attribute to the P-O-P ring frequency, which is in close agreement with other results [9]. The strong broad band at 938 cm^{-1} to 1270 cm^{-1} are assigned to P-O⁻ stretching in $\text{CuO-P}_2\text{O}_5$. Two absorption bands were observed in $\text{Nd}_2\text{O}_3\text{-CuO-P}_2\text{O}_5$ network at about 2925 cm^{-1} to 3406 cm^{-1} . These weak bands are probably associated with the water trapped in the glass.

Table 1: Infrared spectra of $x\text{Nd}_2\text{O}_3\text{-(35-x)CuO-65P}_2\text{O}_5$ glasses

Sample	Peak positions (cm^{-1})							
S ₁	470.55	506.91	755.65	945.62	1066.50	1262.5	-	3406.6
S ₂	473.55	-	783.66	941.93	1110.46	1260.5	2912.6	3405.6
S ₃	472.61	-	750.23	938.14	1075.56	1264.5	-	3428.6
S ₄	475.29	504.66	761.29	941.93	1080.60	1270.5	2925.6	-
S ₅	476.65	-	782.72	-	1072.58	1261.5	-	-
S ₆	476.63	-	779.71	-	1070.55	1263.5	-	-

Optical Absorption in UV and Visible Region

The optical absorption spectra for $x\text{Nd}_2\text{O}_3\text{-(35-x)CuO-65P}_2\text{O}_5$ glasses are shown in Figure 1. From Figure 1, there is no evidence of sharp absorption edges and this is a characteristic of most glassy oxide materials including transition metal ion phosphate glasses. It can also be seen, that the absorption edge moves towards the longer wave lengths as the thickness of the glass sample is being increased. This could be due to the transition from non bridging oxygens (which bind an exited electron less tightly) to a bridging oxygen (which tightly). The optical absorption coefficient $\alpha(\omega)$ was determined by using equation $\alpha(\omega) = (\hbar\omega - E_g^{\text{opt}})^r / \hbar\omega$ at different photon energies near the absorption edge. The quantity $(\alpha\hbar\omega)^{1/2}$ against photon energy $(\hbar\omega)$ was then plotted for each composition. The dependence of $(\alpha\hbar\omega)^{1/2}$ on photon energy for these systems and the derived curves are linear for higher absorption coefficients but tend to

deviate from linearity at low photon energy. The E_{opt} values were determined by extrapolating the linear parts of the curves to $(\alpha h\nu)^{1/2} = 0$ and the value lie within close limits between 0.79 eV to 2.34 eV. These energy seem to shift towards a higher value as the Nd_2O_3 content increases even at a small quantity. This may be due to the decrease in the band tailing arising from the disorder. It means that the addition of amount of Nd_2O_3 will disturb the disorder and consequently increase the optical gap.

It is known that phosphorus has a tetrahedral oxygen coordination with one of them is connected to the phosphorus through a double bond. In the glass the addition of CuO into the network is expected to form $[\text{CuO}_{4/2}]^{2-}$ units in which copper is coordinated to four oxygens in a covalently bonded configuration. The introduction of rare earth oxide into the P_2O_5 – CuO network would decreases the non-bridging oxygen concentration and thus creates different oxidation states due to the mixed ions in the form of oxygen-bridged. This could be the reason why the absorption edge has shifted towards the higher energy which lead to the increase in the optical gap.

Figures 2 show the variation of $\ln \alpha$ versus photon energy. The values of width of the band tails of the localized states E_e can be calculated from the slopes of the straight lines and found to be in the range of 0.451 to 0.634 eV depending on composition. These values are much higher than might be expected for neodymium phosphate glasses, thus This confirms the argument that there is some sort of different electronic behaviour which occurs in rare-earth copper phosphate glasses compared to other phosphate glasses.

CONCLUSIONS

The IR study shows that the dominance of the phosphate tetrahedral in lattice vibrations. The Urbach energy was found lie in range of 0.451 to 0.634 eV, and the optical energy gaps between 0.79 eV to $2.34 \pm 0.01\text{eV}$.

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