

The FTIR Analysis of Nd₂O₃ Substitution on (35-x)CuO-xNd₂O₃-65P₂O₅ glasses

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Abstract. Melt quenching technique (MQT) has been used to prepare the series of (35-x)CuO-xNd₂O₃-65P₂O₅ (0 ≤ x ≤ 10 mol%) glasses, The thermal properties and structure of those glasses were investigated. The glass transition temperature increases as the Nd₂O₃ is substituted for CuO. This behaviour indicates that the replacement of CuO by Nd₂O₃ improves the strength of the cross-links between the phosphate chains of the glasses. The analysis of the infrared spectra of the studied glasses reveals that the increase of Nd₂O₃ content decreases the formation of the end groups in phosphate chain structure.

1. Introduction

Phosphate glasses offer several advantages over silicate and borate glasses [1,2]. Compared with conventional oxide glasses, phosphate glasses are technologically important materials because they possess some superior physical properties such as high thermal expansion coefficients, low melting temperature, low softening temperature, low transition temperature and high electric conductivity. These glasses have considerable potential for application in optical data transmission, solid state batteries, sensing and laser technology. The study of glasses by means of the analysis of the optical absorption edge provides a simple method for explaining some features concerning the band structure of the materials [3]. The optical absorption in this region depends strongly on the electronic structure and involves interactions between the incoming radiations and the electronic state of the glasses under consideration. The electronic states depend on the glass composition. The absorption depends on how tightly the electrons are bound in the microstructure. The electrons in the excited states usually occupy their lowest energy level with the emission of photons. The principle involved is that the photons with energies greater than the band gap energy are absorbed and the less energetic photons are transmitted [4]. The aim of this work was to study the structure and properties of CuO-Nd₂O₃-P₂O₅ glasses in terms of the substitution of CuO by rare earth oxide neodymium.

2. Experimental

2.1. Preparation of Sample.

The glasses were prepared by melting dry mixtures of neodymium oxide (Nd₂O₃), cuprum oxide (CuO) and phosphate (P₂O₅) in silica crucible with composition [Nd₂O₃]_(x)-[CuO]_(35-x)-[P₂O₅]₍₆₅₎, where 0 ≤ x ≤ 10 mol %. To react the constituents, the mixed powders were heated in an electrical furnace at 350 °C for 1h, and then melted in another furnace at 1200 °C. To ensure proper mixing and homogeneity, the molten liquid was shaken frequently and vigorously. After being checked, the melt

was cast by pouring as fast as possible into a hot steel split mould to quench it to form a glass. The glass was immediately transferred to an annealing furnace at 350 °C where it was kept for 3 h to relieve any residual stress which could cause embrittlement. At the end of this annealing process, the furnace was switched off and the glass left to cool down to the room temperature gradually by controlled thermal treatment at cooling rate of 0.5°C/min. The sample were selectively cut, ground, and polished. After preparation, samples were stored in plastic containers in a dessicator until the FTIR and DTA measurement was performed. The amorphous nature of the samples was checked by X-ray diffraction.

2.2. Measurement of DTA

The equipment used to carry out the thermal measurement was a Perkin-Elmer DTA 7 Series system, which was operated under standard atmospheric conditions. The maximum temperature that could be reached by the instrument was approximately 1400°C. The same weight of fine standard and sample (± 5 -20 mg) were loaded in an alumina crucibles and were heated at a rate of 10 °C/min for all samples. With the combination of built-in computer and UNIX operating system. It was possible to obtained DTA curves and the required data for analysis.

2.3. Measurement of IR spectra

A Perkin Elmer 1600 Fourier Transform infra red (FTIR) have been used to investigate to all sample prepared using the KBr pellet technique. Typically around 2 mg of the finely ground sample is mixed with 200 mg of KBr powder and the mixture then pressed for 4 minutes, in evacuabale die under 10 tons of pressure to give a transparent disk with a surface area of 1 cm³. The FTIR spectra were recorded in the spectral range of 4000 – 400 cm⁻¹ resolution and 64 scans to ensure a good signal to noise ratio.

3. Results and discussion

Composition, density, molar volume and glass transition temperature for all the samples are listed in Table 1.

Table 1. Data for CuO-Nd₂O₃-P₂O₅ glasses, batch composition (mol%), density (g/cm³), D, molar volume (cm³/mol), V_m and glass transition temperature T_g (°C) of the studied samples.

| Batched | | | D | V _m | T _g |
|---------|--------------------------------|-------------------------------|-------|----------------|----------------|
| CuO | Nd ₂ O ₃ | P ₂ O ₅ | | | |
| 35 | - | 65 | 2.725 | 44.07 | 314 |
| 33 | 2 | 65 | 2.759 | 45.39 | 315 |
| 31 | 4 | 65 | 2.777 | 46.94 | 316 |
| 29 | 6 | 65 | 2.808 | 48.26 | 317 |
| 27 | 8 | 65 | 2.831 | 49.68 | 318 |
| 25 | 10 | 65 | 2.861 | 50.95 | 319 |

3.1. Glass transition temperature

As shown in the Fig. 2, the replacement of CuO by Nd₂O₃ increases T_g from 31°C for Nd₂O₃ = 0 mol% to 319 °C for 10 mol% Nd₂O₃. This is attributed to the lower field strength of the Cu²⁺ than of the rare earth ion Nd³⁺. A similar trend in variation of properties in the rare earth copper phosphate glasses has been observed by Arzeian et.al [5].

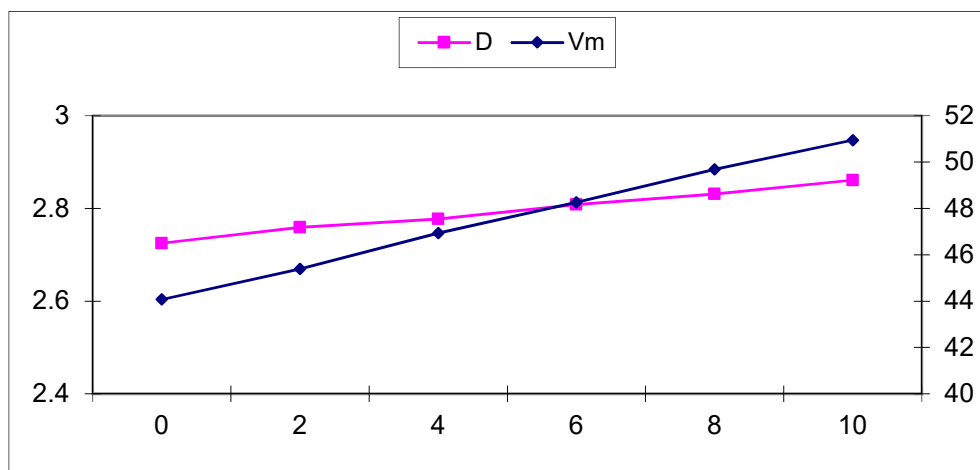


Fig. 1. Density and molar volume of (35-x)CuO-xNd₂O₃-65P₂O₅ glasses

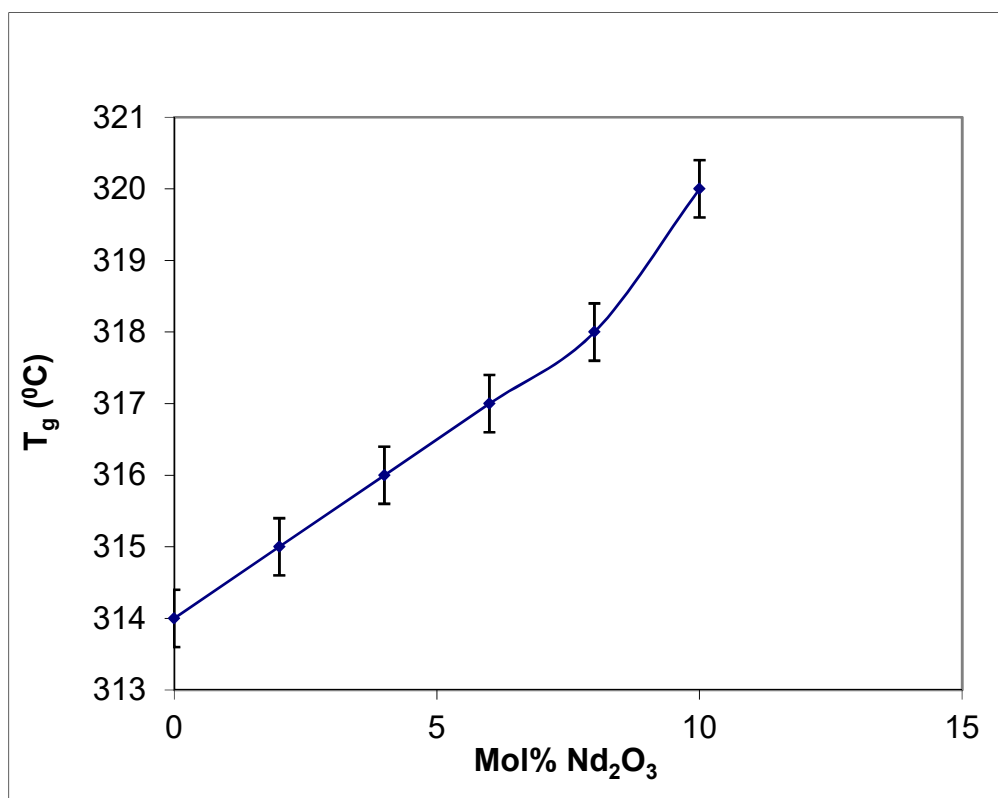


Fig. 2. Glass transition temperature of (35-x)CuO-xNd₂O₃-65P₂O₅ glasses.

3.2. FTIR

The Fourier Transform Infra Red (FTIR) absorption spectra of neodymium copper phosphate glasses are shown in Figure 3.

The infra-red spectrum of neodymium copper phosphate glasses lies in the region of 4000 cm⁻¹ to 200 cm⁻¹. The majority of the resonant vibrational frequencies are present in this region and can

be seen in Table 2. There are six important absorption bands within the frequency range from 3428 cm^{-1} to 470 cm^{-1} . For $\text{Nd}_2\text{O}_3\text{-CuO-P}_2\text{O}_5$ glasses, the measurements of the infra-red absorption spectra in many respects are similar to the one obtained by Hogarth and Moridi [6]. However, absorption peak for CuO, which 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 by P-O-Cu-O-Nd bands.

The addition of very small amount of Nd_2O_3 also affects the absorption band positions compared with ternary copper phosphate glass. A very slight shift in the position of some band is observed. The absorption band at 470 cm^{-1} has shifted to 476 cm^{-1} as the rare-earth content is changes from sample to sample.

Table 2: 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 | - | - |

The absorption band observed in this study at 770 cm^{-1} would seem to be attribute to the P-O-P ring frequency, which is in close agreement with other results [7,8]. 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 water trapped in the glass.

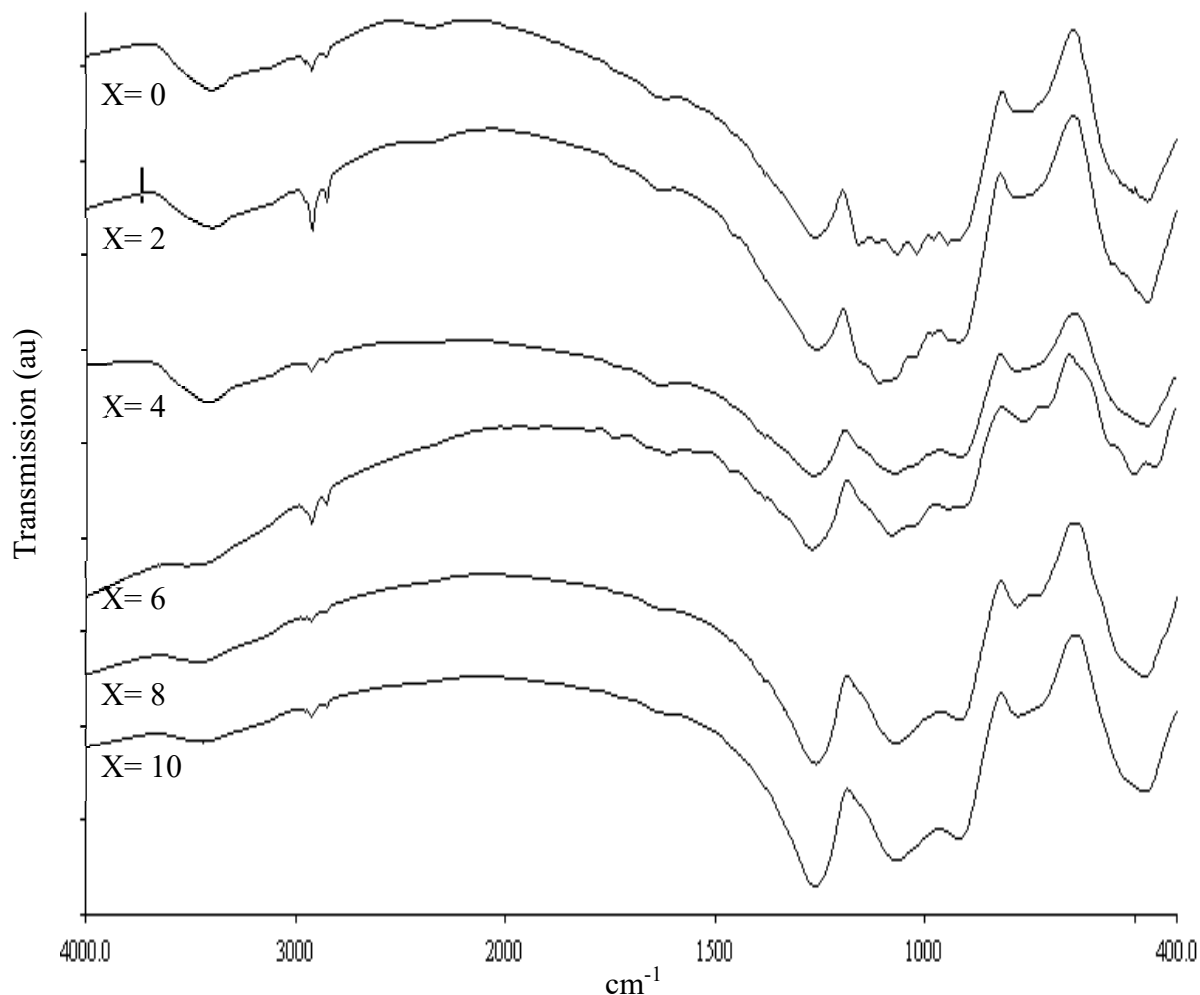


Fig. 3: IR spectra of $(\text{Nd}_2\text{O}_3)_x-(\text{CuO})_{35-x}-(\text{P}_2\text{O}_5)_{65-x}$, with, $0 \leq x \leq 10$

4. Conclusions

The infra red spectroscopy of these glasses showed that the dominance of the phosphate tetrahedral in lattice vibrations. The strong broad band at 938 cm^{-1} to 1270 cm^{-1} are assigned to P-O⁻ stretching in CuO-P₂O₅. Two absorption bands were observed in Nd₂O₃-CuO-P₂O₅ network at about 2925 cm^{-1} to 3406 cm^{-1} .

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