Study of Nd$_2$O$_3$-CuO-P$_2$O$_5$ glass system by elastic properties

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Abstract: Longitudinal and shear ultrasonic velocities were measured in different compositions of the glass system Nd$_2$O$_3$($x$r$CuO$($35-x$r$P_2$O$_5$) at temperature range between 270 K and 323 K. From the transit time data and density, we found that all the elastic properties for these glasses decrease as the Nd$_2$O$_3$ content increase, which indicates a weakening of the binding energy in the network.

Introduction: P$_2$O$_5$ 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 ultraviolet transmission [1-3]. However the poor chemical durability, high hygroscopic and volatile nature of phosphate glasses prevented them from replacing the conventional glasses in a wide range of technological applications. In recent years there has been enormous amount of research on improving the physical properties and the chemical durability of phosphate glasses by introducing a number of glass formers and modifiers, such as Al$_2$O$_3$, MoO$_3$, As$_2$O$_3$, Sb$_2$O$_3$, Ta$_2$O$_5$, etc., into glass network [4-5].

The transition metal oxides glasses are those in which the transition metal oxide is a major constituent and they are typical of the charge transfer or mixed valence type of semiconductors. Glasses containing rare-earths ions may also exhibit different valency states and may contribute to electronic conduction. Most research has been carried out on transition metal oxide glasses with added lanthanides from either end of the rare-earth series, e.g. cerium with two 4f electrons, or prasodymium with three 4f electrons, at one end of the series, and erbium with eleven 4f electrons, or lutetium with fourteen 4f electrons, at the
other end of the series, in order to investigate how the addition of any of these might control the properties of the glass [6]. Neodymium lies in the lanthanide series with four 4f electrons. The doping of Nd to the copper phosphate glass systems is therefore an interesting investigation to be carried out. It was predicted that perhaps praseodymium with three 4f electrons being more stable and considerably shielded by outer electron shells might result in behavior more like that crystal with sharp optical absorption edge, but have little additional effect on such properties as the electrical conductivity, etc. Although conductivity and optical absorption data [7-8] on some binary and ternary copper phosphate glasses are available, no ultrasonic measurement on copper phosphate glass containing the rare-earth neodymium has so far been reported. So it is instructive to undertake the elastic properties of these glasses by ultrasonic technique.

**Sample preparation**: Glasses of composition \( \text{Nd}_x \text{O}_{35-x} \text{CuO}_{35} \text{P}_2 \text{O}_5 \) were prepared, where the compositions are given in mol % and \( 0 \leq x \leq 10 \) mol %. The oxide components were carefully weighed out and mixed in silica crucible of 80 cm³ capacity. To react the constituents, the mixture of neodymium oxide, copper oxide and phosphorus pentoxide in the crucible was 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 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 that 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 samples were selectively cut, ground, and polished. After preparation, samples were stored in plastic containers in a dessicator. A simple Archimedes process using toluene as the immersion liquid measured the density of the glass samples. The measurement of velocity of longitudinal and shear ultrasonic wave were performed at frequencies 5 and 10 MHz and within the temperature range 270 K - 323 K. The contribution to the loss due to the bonding agent between the transducer and the sample was neglected, because its typical thickness was less than 10 μm.
Result and Discussion: The density of $\text{Nd}_2\text{O}_3 - (35-x)\text{CuO} - 65\text{P}_2\text{O}_5$ glasses is shown in the Table 1 and the density variation with $\text{Nd}_2\text{O}_3$ content is shown in Figure 1. The results show that the density increases with the increase of $\text{Nd}_2\text{O}_3$ content: $2.725 \text{ g/cm}^3$ for $x = 0\%$ and $2.861 \text{ g/cm}^3$ for $x = 10\%$. This may be due to the network modifying ions tend to occupy interstitial sites within the highly open glass network.

The temperature dependence of longitudinal and shear ultrasonic velocities for different samples is shown in Figure 2(a) and Figure 2(b). It is observed that for both polarizations of the sound waves, the ultrasonic velocity decreases monotonically with increasing temperature for all the samples. From the longitudinal, shear velocities of the sound, and the density data, the value of elastic moduli ($\lambda$, $\mu$, Bulk modulus, $B$, Young's modulus, $E$) at different temperatures are obtained using the relevant relation given in our earlier works [9].

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$_6$</td>
<td>2.725</td>
</tr>
<tr>
<td>S$_7$</td>
<td>2.759</td>
</tr>
<tr>
<td>S$_8$</td>
<td>2.777</td>
</tr>
<tr>
<td>S$_9$</td>
<td>2.808</td>
</tr>
<tr>
<td>S$_{10}$</td>
<td>2.831</td>
</tr>
<tr>
<td>S$_{11}$</td>
<td>2.861</td>
</tr>
</tbody>
</table>

The decrease of sound velocity with increasing temperature in the present case is attributed to a thermally activated relaxation process proposed by Anderson and Bommel [10]. The presence of such relaxation process has its origin in the disorder inherent in amorphous materials. The relaxation process can be ascribed to a particle moving in a double-well potential corresponding to two structure in amorphous network. The relaxation time, $\tau(V)$ depends on temperature, $T$ and activation energy, $V$, according to Arrhenius relation.
\[ \tau(V) = \tau_0 e^{\frac{V}{kT}} \text{ where } \tau_0 \text{ is constant; the activation energy, } V, \text{ will have a distribution because of the amorphous phase of substance. The variation of } \Delta \nu, \text{ of sound velocity due to such a relaxation process is given by formula \[11].} \]

**Figure 1**: Density of the glass for various Nd$_2$O$_3$ contents (mole %)
Figure 2. The temperature dependence of (a) the longitudinal velocity, (b) shear velocity of various mol % Nd$_2$O$_3$ in xNd$_2$O$_3$ – (35-x)CuO – 65P$_2$O$_5$ glasses

We also showed that in glass induce more significant changes in longitudinal velocity if compared with shear velocity. From Figure 3, it is observed that the value of elastic constant C$_{44}$ is smaller than the value of elastic constant C$_{11}$. Apparently the characters of the glass so
produced are easy to bend but difficult to compress. From the graph, the elastic constant $C_{11}$ and $C_{44}$ decrease with increases in temperature.

A similar trend as the elastic constant is observed in the case of bulk modulus. Figure 4(b) shows the variation of bulk modulus with mol % of Nd$_2$O$_3$ in xNd$_2$O$_3$ - (35-x)CuO - 65P$_2$O$_5$ glasses. This shows that the elasticity of the glass increases with the increase in mole % of Nd$_2$O$_3$. It is apparently that the stiffness of the ternary glasses decreases with the increase of content of Nd$_2$O$_3$.

Sample with higher Nd$_2$O$_3$ has a lower value of bulk modulus. The bulk modulus B and the elastic constant ($C_{11}$ and $C_{44}$) of the PbO phosphate glass are 27, 47 and 15 Gpa respectively [12]. Comparison of these data with those of our ternary neodymium phosphate glasses shows that the values of elastic modulus is much higher, but those of binary neodymium phosphate glasses shows that the values of elastic modulus is lower. This might be due to the ability of the atoms to maintain their original neighbors, thus the interatomic spacing has not been altered.

From Figure 5, the Young's modulus shows the ability of the glass with higher Nd$_2$O$_3$ to afford the exerted force per unit area or experience stress is stronger. According to Cahn et al. [13], the glass with high Young’s modulus should contain components with high dissociation energies and high package densities but small molecular weights.
Figure 3: The temperature dependences of the second order elastic stiffnesses $C_{11}$ and $C_{44}$ of 8 mol % Nd$_2$O$_3$
Figure 4: The temperature dependences of (a) Young’s modulus, (b) the bulk modulus, of various mol% Nd₂O₃
Conclusions: The variations of ultrasonic wave velocity and hence elastic constant, bulk modulus, Young’s modulus and Poisson’s ratio for \( x\text{Nd}_2\text{O}_3(35-x)\text{CuO-65P}_2\text{O}_5 \) glasses with temperature has been interpreted in term of thermally activated relaxation process.

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References