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# Conductivity and dielectric properties of $Na_2O$-$K_2O$-$Nb_2O_5$-$P_2O_5$ glasses with varying amounts of $Nb_2O_5$

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ABSTRACT

Niobium phosphate glasses with a composition of $15K_2O$-$15Na_2O$-$xNb_2O_5$-$(70-x)$ $P_2O_5$ ($x = 20, 25, 30, 35, 40$) have been prepared using the conventional melt-quenching technique. The influence of $Nb_2O_5$ on the structure of the prepared glasses was investigated by infrared spectroscopy. The density, chemical stability and glass transition point of the glasses were measured and compared. The dielectric properties were evaluated using impedance spectroscopy. The results show that the increase of $Nb_2O_5$ results in more compact and integrated glass network, which contributes to the observed increases in the density, chemical stability and glass transition point of the glasses. Both the conductivity and dielectric parameters show a significant decrease when $Nb_2O_5$ increases from 20–25 mol%. Further increasing $Nb_2O_5$ up to 35 mol%, the reductions become small. With the addition of 40 mol% of $Nb_2O_5$, the conductivity and dielectric parameters become to increase again. The variations of electric and dielectric parameters are the combined results of the changes of glass network and the polarizability of niobium ions.



## 1. Introduction

Among oxide glasses, phosphate glasses are very important because of their superior physical properties [1–3], versatility to accept several cation and anion exchangers [4–6] and wide glass formation regions [7–9]. However their poor chemical durability, associated with the structure of phosphate chains, limits their practical application and prevents them from replacing conventional silicate glasses. The low chemical stability arises from the presence of $[PO_4]$ units with non-bridging oxygen atoms, which can react with moisture forming detrimental phosphorus acid. In recent years, there has been an enormous research to improve the chemical stability by introducing suitable dopants [10–13]. It is suggested that the addition of niobium oxide could increase the cross-linking of the glass network which is expected to improve the chemical stability [14]. Phosphate glasses in the alkali niobium system have attracted particular interest in recent decades [15–27], because they have a wide range of applications such as radioactive waste immobilization [15], fast ion conducting materials [16], rare-earth hosts for laser glasses and photonic materials [17,18], biomedical materials [19] and agriculture applications [20]. The structure and properties of the niobium phosphate glasses have been studied mainly in the ternary sodium [21,22], potassium [23,24], lithium [25], strontium niobium systems [26] and in quaternary barium potassium niobium systems [27], etc. Niobium silicate glasses with mixed potassium and sodium have been widely studied [28–31] because of the pronounced Kerr optical effect [31] in these materials, the possible precipitation of alkali niobate crystals with electrooptical [32] and dielectric properties [33], etc. In our knowledge, studies on the property and structure of niobium phosphate glasses containing both sodium and potassium are quite limited.

Impedance spectroscopy over a wide frequency range is a well-known technique to determine the electrical properties of different materials. This technique has been applied to understand the frequency dependence of complex conductivity of various glassy materials. The dispersion in conductivity has been widely evaluated. The study of frequency dependent conductivity spectra is a well-established method for characterizing the hopping dynamics of ions. At low frequencies, a random diffusion of the ionic charge carriers via activated hopping results in a frequency-independent conductivity. The frequency independent conductivity corresponds to the conductivity value to zero frequency ($\sigma_0$), which is known to be equal to the dc conductivity ($\sigma_{dc}$). At higher frequencies the conductivity exhibits dispersion following a power law behavior [34–35]. The dispersion depends on the material composition and temperature which determines the strength of polarizability and the degree of interaction between mobile ions in the network [36].

The main purpose of this work is to investigate the influence of niobium oxide content on the structure and properties, mainly the electric and dielectric properties, of the glasses with a general composition of $xNb_2O_5$-$(70-x)P_2O_5$-$15Na_2O$-$15K_2O$.

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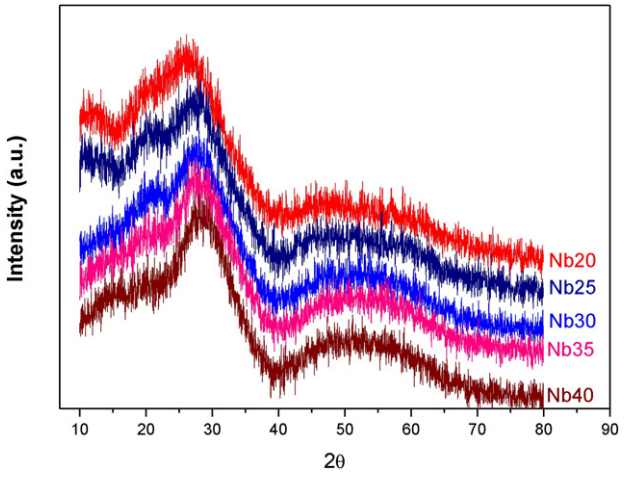


**Fig. 1.** XRD patterns of the prepared glass samples.

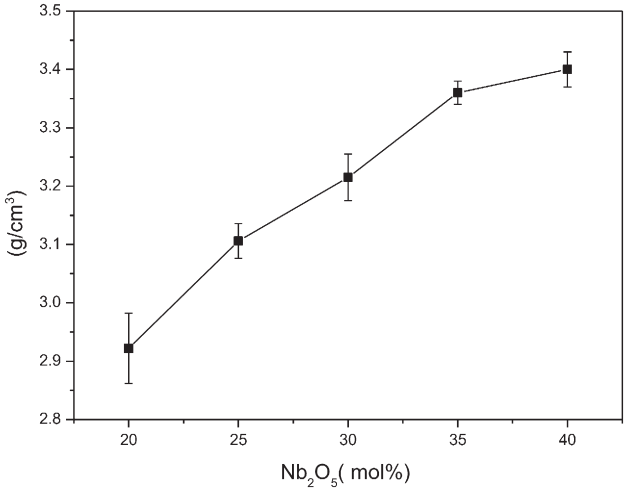


**Fig. 3.** The density of the glasses containing different amounts of $Nb_2O_5$.

## 2. Materials and method

Glasses with a composition of 15 $K_2O$-15$Na_2O$-(70-$x$) $P_2O_5$-x$Nb_2O_5$ (where $x$ = 20, 25, 30, 35, 40 mol%) were prepared by conventional melt quenching method. Analytical grade chemicals of $Na_2CO_3$, $K_2CO_3$, $NH_4H_2PO_4$, and $Nb_2O_5$ were used as precursors. The batches were melted at 1300 °C for 1 h and poured into a stainless steel mold, followed by annealing at 500 °C for 2 h. The prepared glasses were denoted respectively as Nb20, Nb25, Nb30, Nb35 and Nb40 corresponding to 20, 25, 30, 35, 40 mol% of $Nb_2O_5$.

The amorphous nature of the prepared glasses was confirmed using X-ray diffraction analysis with a Cukα radiation on a D8 ADVANCED diffractometer (Bruke, Germany). Infrared spectra of the samples were recorded on an IS10 FTIR spectrometer (Thermofisher, USA). The measurements were made on glass powder dispersed in KBr pellets. Differential thermal analysis was carried out with a heating rate of 10 °C/min on an HCT-1 analyzer (Henven, China) using glass powders sized 120–140 μm. The density, ρ, of the glasses was evaluated at room temperature by the standard Archimedes method with distilled water as immersion liquid. The chemical stability of the glasses was evaluated by measuring the weight loss after glass particles sized 300–600 μm were leached in distilled water at 98 °C for 1 h. For a comparative purpose, we also examined the weight loss of a commercial borosilicate glass under the same conditions. Both the density and stability measurements were conducted on five parallel samples and the mean values of the data are presented along with the standard deviation bars. The electrical and dielectric measurements were carried out on silver paint coated samples using an impedance analyzer (Agilent 4294A, USA).

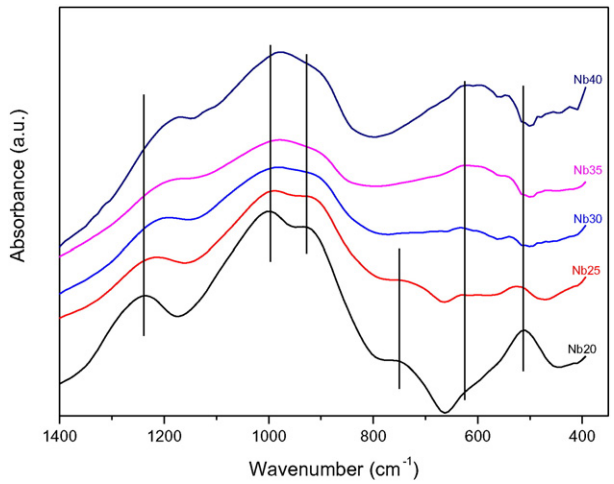


**Fig. 2.** FTIR spectra of the glass samples.

## 3. Results

The XRD patterns (Fig. 1) consist of broad halo peaks at low diffraction angles, which confirm the amorphous nature of the obtained samples. The obtained FTIR spectra in the wave number range of 1400–400 $cm^{-1}$ are presented in Fig. 2. The absorbance band at around 1250–1170 $cm^{-1}$ corresponds to the asymmetric stretching vibration of P═O bonds as well as the asymmetric stretching vibrations of $PO^{2-}$ mode in the $Q_2$ units [36]. This band becomes weak and shifts to lower wave numbers with increasing the niobium oxide content. The band at around 1000 $cm^{-1}$ is ascribed to the P—$O^-$ group vibrations [20]. The band at around 900 $cm^{-1}$ is the result of the asymmetric stretching vibration of P-O-P bonding [20]. The band at 730–750 $cm^{-1}$ ascribed to the symmetric stretching vibration of P-O-P [20] is weakened when $Nb_2O_5$ increases from 20 to 25 mol% and disappears when $Nb_2O_5$ is 30 mol% and above. In contrast to this band change is the gradual appearance of a new band at around 620 $cm^{-1}$, which can be assigned to the bending vibration of P-O-Nb bonds. The band at 530 $cm^{-1}$ corresponds to the bending vibration of O-P-O groups [19], and it shifts toward higher wave numbers with increasing $Nb_2O_5$.

The composition dependent glass density is showed in Fig. 3. It can be seen that the density increases with $Nb_2O_5$. The chemical durability data are listed in Table 1. The data show that with increasing the content of $Nb_2O_5$, the weight loss of the glass decreases from 0.275% to 0.009%. The weight loss of sample Nb40 (0.009%) is much lower than that of the commercial borosilicate glass (0.075%) measured under the same conditions.

Fig. 4 shows the DTA curves of the glass samples. We noticed that the glass transition temperature increases with the increase of the amount

**Table 1**
Weight losses and electrical properties data of the samples.

| Sample | Weight loss (%) | $E_{ac}$ (ev) | $E_{dc}$ (ev) | $\ln\sigma_{dc0}$ |
|---|---|---|---|---|
| Borosilicate glass | 0.075 ± 0.005 | | | |
| 20 Nb | 0.275 ± 0.009 | 0.85 | 0.84 | 14.32 ± 0.6 |
| 25 Nb | 0.175 ± 0.008 | 0.88 | 0.95 | 15.31 ± 0.9 |
| 30 Nb | 0.110 ± 0.006 | 0.92 | 0.96 | 16.14 ± 0.8 |
| 35 Nb | 0.095 ± 0.005 | 0.91 | 0.88 | 13.82 ± 0.9 |
| 40 Nb | 0.009 ± 0.0006 | 0.9 | 0.95 | 15.53 ± 0.7 |