Optical absorption study of manganese-doped Na$_2$O-K$_2$O-P$_2$O$_5$ glasses

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Abstract

The mixed alkali phosphate glasses with the general formula 49.95[xNa$_2$O-(1-x)K$_2$O]-0.1MnO$_2$-49.95P$_2$O$_5$ with x=0-1mol% were prepared and characterized using the optical absorption technique. The optical absorption spectrum of each glass exhibits a single band in the region around 200-400 nm. From the ultraviolet absorption edges, the optical parameters including optical band gap and the Urbach energy were evaluated. It is interesting to note that these optical parameters are composition-dependent. The optical band gap energy ($E_g$) and the Urbach energy ($\Delta E$) show the presence of a maximum and a minimum respectively around the intermediate composition x=0.5. The non-linearity behavior of the composition dependence of $E_g$ and $\Delta E$ is a fingerprint of the mixed-alkali effect in the glasses under study.

Keywords: Manganese, Phosphate, glasses, Optical properties, MAE.

1. Introduction

Glass is the most frequently used material in several applications fields. Topical progression in the glass field facilitates the researcher to design numerous kinds of oxide glasses such as borate, phosphate, tellurite, silicate, germinate, etc. Due to the specific properties of phosphates glasses, such as low thermal characteristics, higher thermal expansion coefficients, UV transparent and they can incorporate large amounts of oxides [1,2], they are considered as the more important glasses compared to other glass families. So, the study of their properties is a crucial interest in order to use them in various fields of applications.

Most of the properties of the glassy materials are depending on the chemical composition of the glass system and the non-linear behaviour of certain properties with the substitution of one alkali by a dissimilar one while keeping the total alkali content constant is known as the mixed alkali effect [3]. The most evident manifestation of this effect has been observed in the variation of some dynamic properties. The experimental and theoretical investigations on the mixed alkali effect (MAE) of several glasses are reported in the literature [4,5]. The novelty of this work is double: firstly, to
formulate new low melting phosphate glasses; secondly, to understand the effect of the substitution of potassium by sodium on the optical properties of the glasses containing manganese oxide. Recently [6], we have reported on the thermal and structural properties of the 49.95[xNa2O-(1-x)K2O]-0.1MnO2-49.95P2O5 glasses by Differential Scanning Calorimetry (DSC), Fourier-Transform Infrared (FTIR), Raman, and Electron Paramagnetic Resonance (EPR). The above technique highlights the presence of the mixed alkali effect in these glasses. The foremost purpose of this work is to study the effect of mixed Na2O and K2O oxides on the optical properties of the above manganese phosphate glasses.

2. Experimental procedure

The glasses compositions in the system 49.95[xNa2O-(1-x)K2O]-0.1MnO2-49.95P2O5 with x=0-1 mol% (labelled NaxK1-xPMn) are prepared using the conventional melt quenching technique. The chemical reagent precursors are di-hydrogen ammonium phosphate (NH4H2PO4) (Aldrich, 99%), potassium carbonate (K2CO3) (LobaChemie, 99%), sodium carbonate (Na2CO3) (LobaChemie, 99%), and manganese oxide (MnO2) (Aldrich, 99.9%). The appropriate amount of the different reagents is crushed and grinded to fine powders. Details of the procedure adopted in the elaboration of these glassy-samples have been described elsewhere [6]. The obtained glasses are homogeneous transparent and colorless.

For the study of the optical properties of the glasses, a UV–Visible spectroscopy was performed on a Jasco-570 spectrophotometer over the spectral range of 200-800 nm. A barium sulfate (BaSO4) plate was used as the standard on which the finely ground sample from the glass was coated.

3. Results and discussions

3.1. Absorption spectra of the glasses

The absorption spectra of the studied glasses NaxK1-xPMn were recorded at room temperature in the region 200-800 nm and are displayed in Figure 1. These spectra have the same shape. They are characterized by a single absorption band over the region of 200–400 nm. As the amount of sodium oxide increases in the glassy matrix, one can note a shift of this absorption band to lower wavelengths. This shift may result from the variation of the content of the non-bridging oxygen atoms in the glassy system as sodium oxide increases. The present absorption band can be assigned to the presence of trace unavoidable of iron impurities in the raw materials and specifically to the predominance of trivalent Fe3+ ions [7]. Also, it may be due to the transfer charge (TC) between the oxygen 2p and the 3d orbital of manganese ion [8]. Furthermore, it is worth noting that no visible band could be detected in the region 400-800 nm in the optical spectra of the investigated glasses (Figure 1). This shows that the studied glasses are transparent in this region. This transparency is concomitant with the colorless appearance of these materials. However, the absence of color by visualization, although the glasses contain manganese, is due to the low content of the Mn2+ ion (0.1 mol %).
3.2. Optical parameters of the glasses

From the absorption ultraviolet edges, the optical parameters including optical band gap energy and the Urbach energy were determined for the studied glasses. The optical band gap energy values for the present samples were determined by employing the Tauc’s plots method. The absorption coefficient \( \alpha(\nu) \) near the edge is calculated according to the relation [9]:

\[
\alpha(\nu) = (2.303/d) A(\nu)
\]

where “A” is the absorbance and “d” is the thickness of the sample (in centimeters).

Generally, for the amorphous and vitreous materials, Davis and Mott [9] described the optical absorption \( \alpha(\nu) \) above the exponential tail by the following power-law expression:

\[
\alpha(\nu) = \alpha(\nu - E_g)^n
\]

where “n” is an index that can have different values: 2, 3, 1/2, and 1/3 corresponding to indirect allowed, indirect forbidden, direct allowed, and direct forbidden transitions. “B” is a constant called a band-tailing parameter, “\( E_g \)” is the optical band gap energy and \( h\nu \) is the incident photon energy.

The Tauc’s plots of the studied glasses Na\(_x\)K\(_{1-x}\)PMn are represented in figure 2. The optical band gap energy values are determined by extrapolation of the linear part of the curves to the x-axis at zero absorption.

In order to estimate the degree of the disorder induced by the substitution of K\(_2\)O by Na\(_2\)O in the Na\(_x\)K\(_{1-x}\)PMn glasses, we have explored the region of the lower photon energy of the edge for the glasses (Figure 3). In this region, the absorption coefficient changes into an exponential dependence, as given by the Urbach law [10]. The absorption coefficient \( \alpha(\nu) \) depends exponentially on the photon energy (\( h\nu \)). The exponential dependence known as the Urbach rule [10] may be written in the form:

\[
\alpha(\nu) = B \exp(h\nu/\Delta E)
\]

Where \( \Delta E \) is the Urbach energy and \( B \) is a constant.
Figure 2. Tauc’s plots for the Na$_x$K$_{1-x}$PMn glasses.

Figure 4 depicts the variation of the optical band gap energy and the Urbach energy as a function of Na/Na+K ratio. It is observed that the optical band gap energy $E_g$ varies from 2.99 eV to 2.94 eV when K$_2$O is replaced by Na$_2$O. $E_g$ presents a non-linear variation with the composition. It goes through a maximum at the intermediate composition $x=0.5$ (Na$_{0.5}$K$_{0.5}$PMn) (Figure 4). Namely, $E_g$ goes through a maximum when the content of Na$_2$O is equal to K$_2$O in the studied glasses. The observed maximum of the $E_g$ in the title phosphate glasses could be due to a distribution of defects resulting from the two alkali ions. A non-linear variation in the composition dependence of the optical band gap energy ($E_g$) has been observed with a maximum value at $x=0.5$ (Na$_{0.5}$K$_{0.5}$PMn). This non-linear variation indicates the existence of mixed alkali effect in the present glass system. This MAE could be explained by the formation of some defects in the band gap and the composition dependence of these defects varies non-linearly according to the K$_2$O/Na$_2$O ratio.

The variation of the absorption coefficient ln($\alpha$), as a function of energy $h\nu$, allows one to determine the Urbach energy for each glass. It is the inverse of the slope relative to the linear of the curve. The $\Delta E$ values are found to vary from 0.34 to 0.31 eV. The variation of the $\Delta E$ versus the composition for the Na$_x$K$_{1-x}$PMn glasses reveals the presence of a minimum for the Na$_{0.5}$K$_{0.5}$PMn glass. This discontinuity trend is an indicative to the presence of mixed alkali effect. It is interesting to note that the Na$_{0.5}$K$_{0.5}$PMn glass exhibits the lower value of the Urbach energy, so one can conclude that the disorder is important for this glass.

It is evidenced that the composition dependence of the optical band gap energy and the Urbach energy are particularly sensitive to the substitution of potassium by sodium oxide and indicating the presence of mixed alkali effect in the studied glasses Na$_x$K$_{1-x}$PMn. Similar behaviour is also observed for other mixed alkali glasses [11,12].
Figure 4. Variation of the band gap energy and Urbach energy with Na/Na+K ratio.

4. Conclusion

The optical properties of glasses belonging to the general formula 49.95[xNa2O-(1-x)K2O]-0.1MnO2-49.95P2O5 with x= 0-1 mol% have been studied. The experimental results concerning absorption spectra of manganese-doped alkali phosphate glasses, show the presence of a single band in the region 200-400nm which is attributed to the iron impurities (Fe3+) present in the vitreous composition and/or to the transfer charge (TC) between the oxygen 2p and the 3d orbital of manganese ion. The optical properties of the glass compositions showed that the optical band gap energy and the Urbach energy present maxima and minima, respectively when mixing equal amounts of K2O and Na2O in the Na,xK1-xPMn. One can conclude that the optical properties are sensitive to the mixed alkali effect in the glasses under study.

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