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# Properties of silver phosphate glass in the presence of nanosize cobalt and nickel oxides

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ABSTRACT

Silver phosphate glasses, undoped and doped with 0, 5, 10, 15 & 20 wt.% CoO/NiO were prepared by quench melt technique. The prepared glasses were characterized by using X-ray diffraction and FTIR spectroscopic techniques. Glass transition temperatures were determined by Differential Scanning Calorimetric technique whereas morphological changes in the freshly prepared and aged glasses were examined by SEM technique. Electrical conductivities and dielectric constants of all the glasses were measured at different temperatures and frequencies. Structural changes and changes in electrical conductivities and dielectric constants with temperature and frequencies have been discussed and a plausible mechanism is given.



## 1. Introduction

During the last decades, phosphate glasses have received substantial attention due to their wide range of possibilities for tailoring physicochemical properties for specific technological applications. These glasses have many desirable properties in comparison with silicate or borate glasses such as high thermal expansion coefficient, low softening temperature and low preparation temperature. Because of these properties, they may be potential host materials for certain high-level radioactive nuclear wastes, laser glasses, energy transfer materials, battery materials for ultra-fast charging and discharging, amplifiers, phosphors, solar cells, glasses for sealing in electronics, biomaterials, magneto-optical devices, etc. [1–5]. However, the poor chemical durability and corrosion of phosphate glasses limited the process of their industrialization [2]. The chemical durability of phosphate glasses can be increased by the addition of transition metal oxides. The introduction of transition metal oxides into phosphate glasses induces structural changes and it is found that the replacement of P–O–P bonds with M–O–P bonds in the glass networks significantly improves the chemical durability [6]. Due to their technological importance, phosphate glasses have been the subject of continuous investigations over the years in understanding structure–property correlations which facilitated the design of new materials with advanced properties [7–10]. For understanding the structure at molecular level, transport behaviour and potential applications of the phosphate glasses, it is essential to understand the properties in the presence of various dopants. Recently the authors studied the effect of SrO doping in silver phosphate glass on structural and electrical properties and found interesting results [11]. In this paper we present a systematic study on the preparation of silver phosphate glasses doped with CoO and NiO, electrical conductivity measurements over a wide range of frequencies and temperatures, and dielectric properties, e.g. dielectric constant and loss. DSC studies have been made to find out the $T_g$ values and FTIR spectral studies were made for structural investigations.

## 2. Material and methods

### 2.1. Materials

All the chemicals used in the preparation of silver phosphate glass were of analytical grade. $AgNO_3$, ammonium dihydrogen phosphate and nickel sulphate, cobalt sulphate, and NaOH pellets were used as such without any further purification.

### 2.2. Preparation of nickel oxide/cobalt oxide

In a typical procedure, a known weight of nickel sulphate/cobalt sulphate was dissolved separately in distilled water and stirred for half an hour. Dilute NaOH solution was added drop by drop for 4 h where nickel hydroxide/cobalt hydroxide was precipitated. Precipitates were kept overnight and then filtered, washed with hot water several times and dried in hot air oven at 80 °C for 12 h. Dried samples were heated at 500 °C where NiO/CoO was obtained [12].

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### 2.3. Preparation of glasses

Undoped silver phosphate glass and 5, 10, 15 & 20 wt.% CoO & NiO doped silver phosphate glasses were synthesized by melt-quench method [11]. Silver nitrate and ammonium dihydrogen phosphate were taken in 1:1 M ratio and mixed thoroughly in an agate paste mortar. The mixture was then taken in a platinum crucible and heated in an oven at 150–200 °C till the evolution of gases ceased. The mixture was heated strongly in an electric muffle furnace at 800–900 °C for 4 h, where melting took place. The melt was then suddenly quenched on an ice cooled stainless steel plate at 0 °C to form a glassy product. These glasses were then dried in an oven at 100 °C, stored in sample tubes, and kept in a desiccator under a cover of black cotton. In a similar way silver phosphate glasses doped with 5, 10, 15 and 20 wt.% CoO/NiO were prepared and stored till measurements were made.

### 2.4. Characterization of glasses

For the structural characterization, the X-ray diffraction patterns (X-ray powder diffractometer using Cu $K_\alpha$ radiation) and scanning electron microscopy (Quanta FEG 250 ESEM) were used. FT-IR spectra of the glasses were recorded with the help of a Shimadzu IR AFFINITY-1 spectrometer at room temperature in the range of 2000–400 $cm^{-1}$ using KBr pellets. The uncertainty in FTIR spectrometer was $\pm 5$ $cm^{-1}$. Glass transition temperatures of undoped $Ag_2O$–$P_2O_5$ and CoO/NiO doped $Ag_2O$–$P_2O_5$ glasses were obtained using DSC technique (METTLER TOLEDO, DSC 822e at a heating rate of 10 °C/min in nitrogen atmosphere). The uncertainty in measurements from DSC instrument was $\pm 1$ °C. The electrical conductivities, dielectric constants and dielectric losses of all glasses were measured by a HIOKI 3532-50 LCR Hi TESTER in the temperature range of 303 to 373 K at different frequencies ranging from 100 Hz to 10 KHz. The uncertainty in measurements from LCR metre was $\pm 0.1\%$. Hydraulic press machine and die were used to make pellets of all the glasses by applying a pressure of 5 tons. The pellets were coated with silver paste on both the sides and kept between two electrodes (two probe method). The sample holder was kept in a PID controlled furnace.

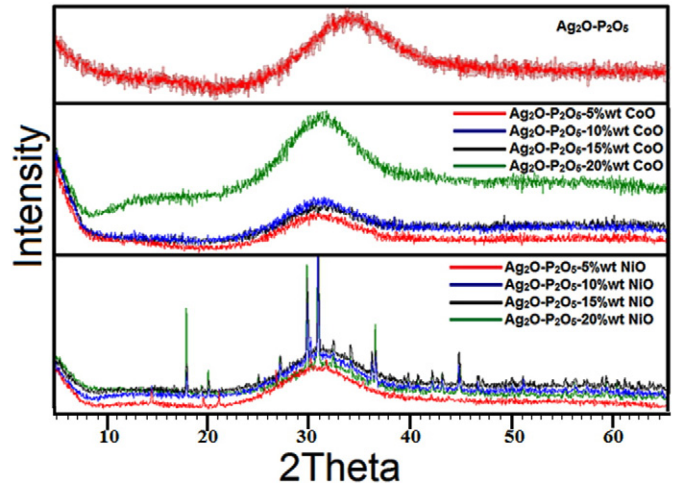



**Fig. 1.** X-ray diffraction patterns of undoped and doped silver phosphate glasses.

## 3. Results

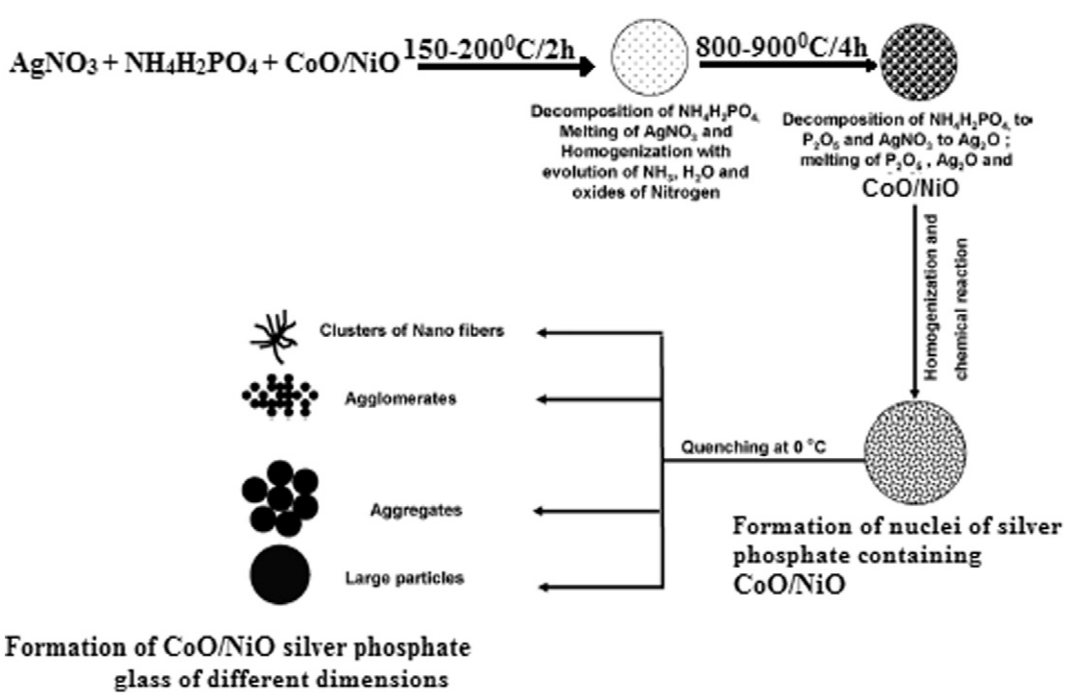
Formation of CoO and NiO can be represented by the following reaction.

$$MSO_4\ (M=Co/Ni) + 2NaOH \rightarrow M(OH)_2 + Na_2SO_4$$

$$M(OH)_2 \xrightarrow{500^{\circ}C} MO + H_2O$$

The formation of doped glasses can schematically be represented by Scheme 1 [13].

Fig. 1. shows the X-ray diffraction patterns of $Ag_2O$–$P_2O_5$ and (5, 10, 15, 20 wt.%) CoO & NiO doped $Ag_2O$–$P_2O_5$ glasses. Undoped silver phosphate glass was found to be very poorly crystalline or amorphous in nature. In the presence of CoO, the glass remained almost poorly crystalline or amorphous. However in the presence of 15 and 20 wt.% NiO, sharp diffraction peaks appeared at about two theta values of 36 and




**Scheme 1.** Formation of CoO/NiO doped silver phosphate glasses [13].