Effect of crucible material on optical bandgap and activation energy of Na_2O-CdO-P_2O_5 glasses

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In the sodium cadmium phosphate glasses, the effect of diffused alumina from alumina crucible has been assessed by measuring various properties such as mass density, refractive index, optical bandgap and dc conductivity. The results of measurements corresponding to glasses prepared in alumina crucible have been compared with those of glasses prepared in platinum crucible with and without adding Al_2O_3. The Optical bandgap and direct current (dc) electrical conductivity of the Na_2O-CdO-P_2O_5 glasses prepared in alumina and platinum crucibles have been determined at room temperature. These glasses have also been electrically characterised in the temperature range 293–423 K. Activation energy E_a of the samples prepared in alumina crucible lies in the range 0.60–0.96 eV whereas it stands in the range of 0.57–0.94 eV for the samples prepared in platinum crucible.

1. Introduction

Many investigations have been reported on the optical and electrical properties of non-crystalline materials such as inorganic glasses prepared with glass formers like silicon or boron oxides [1–5]. Ever since the discovery of the semiconducting nature of vanadium phosphate glasses by Denton *et al.* [6], a number of publications regarding the optical and electrical properties of phosphate glasses have been reported in scientific literature [7–10].

Density, refractive index, optical and electrical properties of glasses like cadmium-phosphate, cadmium-zinc-phosphate, sodium-cadmium-phosphate, lithium-cadmium-phosphate have been studied with the change of concentration of the modifier or glass former at room temperature. Temperature dependent electrical conductivity has also been studied by various researchers over a considerable temperature range [11–20].

Most of the researchers reported that the glasses were prepared in alumina crucible and few of them had also prepared the glasses in quartz, gold or platinum crucibles. However, no one described how the diffusion of crucible material effects various properties of the glass. The present work was taken in hand to study the role of diffused alumina in determining optical band gap and electrical conduction of sodium-cadmium-phosphate glasses.

2. Experimental

High purity (99.99%) chemicals Na_2CO_3, CdO, P_2O_5 were used for the glass preparation. The samples were prepared by using 15 gm ingredients in an alumina crucible and same series was prepared in platinum crucible under the same conditions. The samples were prepared by the melt quench technique and their starting batch compositions are listed in Table I. The rest of the details of sample preparation are given elsewhere [11, 13].

A weight loss of the alumina crucible was estimated after preparing each batch of glass samples. It was observed that loss in the crucible weight increases with the increase of sodium concentration in the glass samples. In order to verify that the weight loss in the alumina crucible was caused during glass preparation, an empty crucible was heated at the same temperature for the same period of time as for actual samples. The crucible was washed in dilute nitric acid (HNO_3) of the same concentration as used to wash the crucible after sample preparation. This experiment did not show any loss in the crucible weight and this confirmed that the crucible looses its weight during glass preparation.

Four samples of sodium-cadmium-phosphate glasses with 10, 20, 30 and 40 mole% sodium concentration were prepared in platinum crucible by adding an amount of Al_2O_3 equal to that of the weight loss of alumina crucible during sample preparation. Density, refractive index, activation energy and optical bandgap of the glasses prepared in platinum crucible with the addition of Al_2O_3 were then measured for comparison. The results are listed in Table I.

The mixture formulae

$$x\%\,Na_2CO_3 - (50 - x)\%\,CdO - 50\%P_2O_5 \quad (1)$$

$$x\%\,Na_2CO_3 - (50 - x)\%\,CdO - 50\%P_2O_5 - mAl_2O_3 \quad (2)$$

TABLE I

Composition mole%	Density ρ (g/cm^3)			Refractive index n			Conductivity (mho cm^{-1})			Activarion Energy Ea (eV)			Optical Bandgap Eopt (eV)		
Na_2O-CdO-P_2O_5	Platinum crucible	Alumina crucible	Platinum crucible + Al_2O_3	Platinum crucible	Alumina crucible	Platinum crucible + Al_2O_3	Platinum crucible	Alumina crucible	Platinum crucible + Al_2O_3	Platinum crucible	Alumina crucible	Platinum crucible + Al_2O_3	Platinum crucible	Alumina crucible	Platinum crucible + Al_2O_3
0 - 50 – 50	3.95	3.91	3.91	1.55	1.52	1.51	4.39×10^{-15}	3.89×10^{-15}	3.89×10^{-15}	0.94	0.96	0.99	3.50	3.50	3.51
10 - 40 - 50	3.58	3.44	3.45	1.51	1.47	1.46	9.20×10^{-15}	5.13×10^{-15}	5.13×10^{-15}	0.84	0.87	0.87	3.30	3.33	3.34
20 - 30 - 50	3.34	3.30	3.30	1.46	1.45	1.45	2.25×10^{-13}	8.13×10^{-14}	8.13×10^{-14}	0.74	0.82	0.82	3.05	3.11	3.13
30 - 20 - 50	3.12	3.22	3.22	1.42	1.43	1.43	1.61×10^{-13}	1.55×10^{-12}	1.55×10^{-12}	0.68	0.69	0.69	2.83	2.91	2.94
40 - 10 - 50	2.85	3.12	3.12	1.40	1.41	1.40	1.63×10^{-11}	4.47×10^{-11}	4.47×10^{-11}	0.58	0.61	–	2.90	2.87	2.89

are used to prepare the glasses, where m represents the loss in mass of the alumina crucible. The maximum possible error in E_a was calculated to be $+0.003$ eV.

3. Result and discussion

It was noted that the alumina crucible shows a decrease in its weight after the preparation of each batch as shown in Fig. 1. It was suspected that the amount of alumina lost in each reaction has become a part of the glass samples, and the loss in mass of the crucible increases with the increase of Na_2O in the composition. The composition of all glasses, presented in this study, can be described by the Equations 1–2. Starting batch composition of each sample is listed for reference in Table I.

The results of density ρ, refractive index n, activation energy E_a, and optical band gap E_{opt}, measurements corresponding to sodium-cadmium-phosphate glass samples prepared in alumina or platinum crucibles are listed in Table I for comparison. A close examination of these results would reveal that for a given composition, the magnitude of the measured quantities like density, refractive index, activation energy, and optical band gap decreases with the increasing concentration of alumina as shown in Figs 2–5 respectively.

Al_2O_3 is a glass former [21, 22], which have low glass forming ability, but when it is mixed with other glass formers, it becomes the part of the structure which

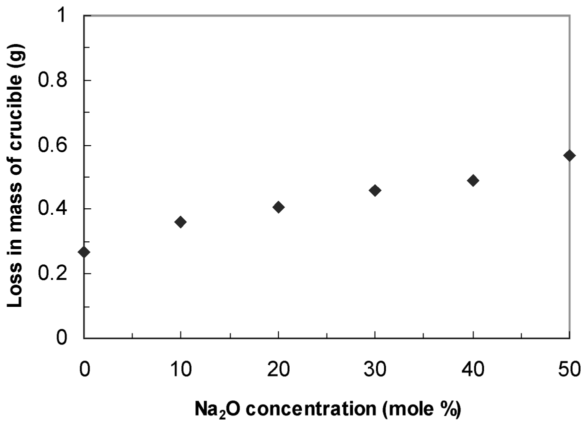

Figure 1 Decrease in weight of the alumina crucible with the increasing concentration of Na_2O.

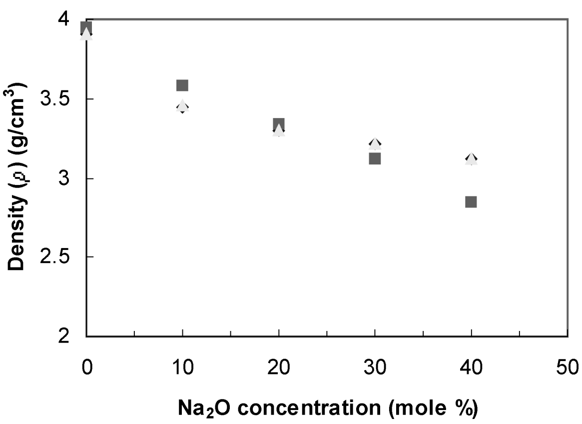

Figure 2 Variation of density with the increasing concentration of Na_2O in Na_2O-CdO-P_2O_5 glasses.

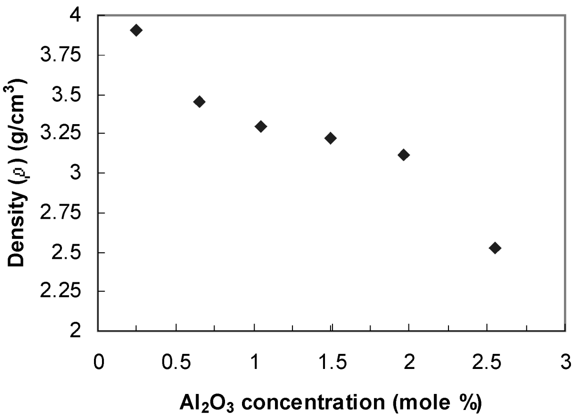

Figure 2a Figure 2a Decrease in density with the increase of diffusion of Al_2O_3 in the glass compositions.

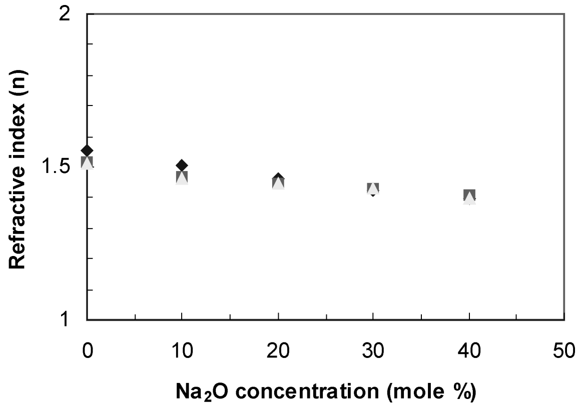

Figure 3 Variation of refractive index with the increasing concentration of Na_2O in Na_2O-CdO-P_2O_5 glasses.

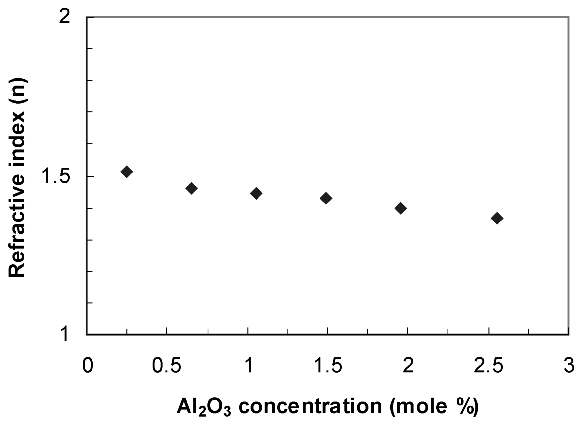

Figure 3a Figure 3a Decrease in refractive index with increase of diffusion of Al_2O_3 in the glass compositions.

may cause to flare up the structure. The expansion of structure causes the increase in the molar volume and decrease in the density of the glass with the increase of the alumina addition.

The refractive index depends on the density of the medium. As medium becomes denser velocity of the radiation decreases and as a result refractive index increases according to the relation.

$$n = c/v$$

where c is the velocity of the radiation in vacuum and v is its velocity in the medium.

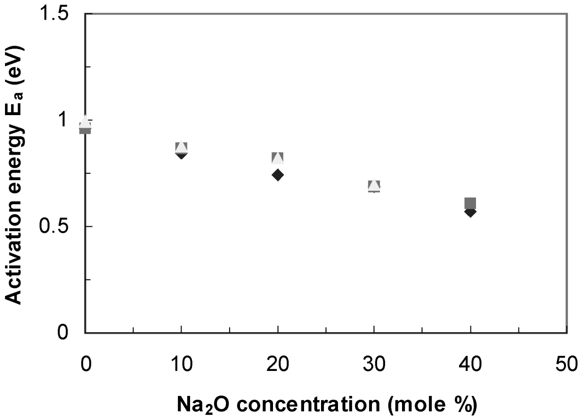

Figure 4 Variation of activation energy with the increasing concentration of Na_2O in Na_2O-CdO-P_2O_5 glasses.

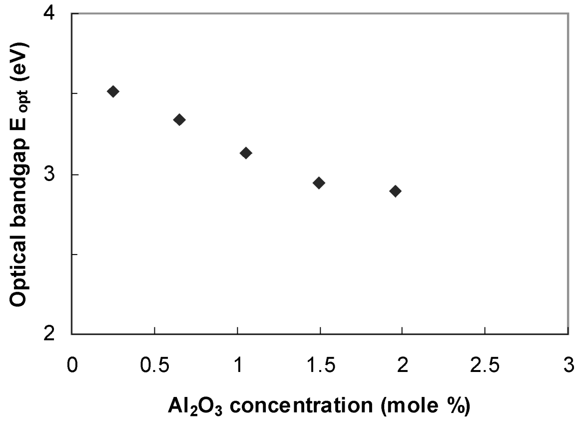

Figure 5a Figure 5a Decrease in optical bandgap with increase of diffusion of Al_2O_3 in the glass compositions.

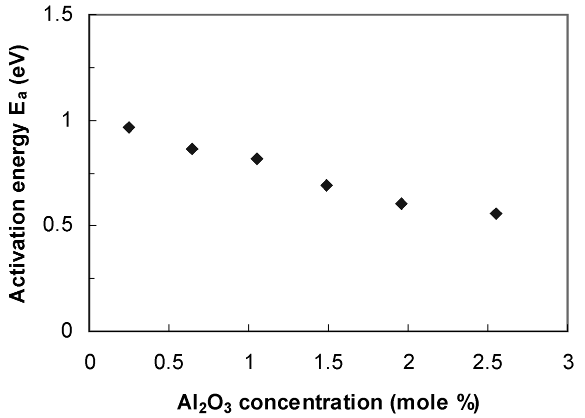

Figure 4a Figure 4a Decrease in activation energy with increase of diffusion of Al_2O_3 in the glass compositions.

The addition of Al_2O_3 to a given composition has caused a decrease in the density which implies that the system has lost its compactness to some extent and consequently the velocity of radiation would increase. This in turn would reduce the value of refractive index. The amount of Al_2O_3 has increased with the addition of more and more Na_2O to the glasses as indicated in Fig. 1. This is probably due to the reaction of alumina with the alkali to form alkali aluminate which would involve more alumina corresponding to high concentration of alkali material.

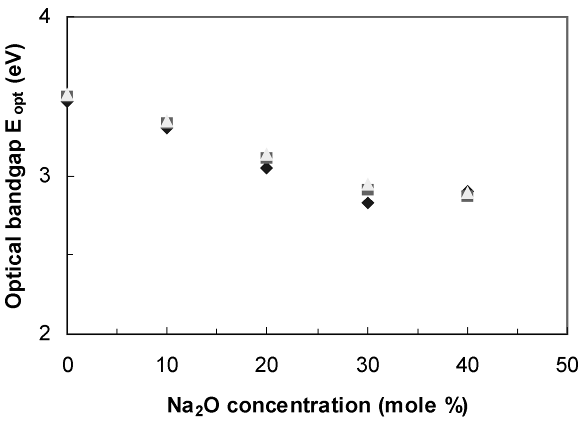

Figure 5 Variation of optical bandgap with the increasing concentration of Na_2O in Na_2O-CdO-P_2O_5 glasses.

The alumina is known to have both the acidic and the alkaline behaviour whereas Na_2O is a known alkali [23]. It can been noticed from Fig. 1 that a considerable amount of Al_2O_3 has passed into the glass samples at high concentration of Na_2O. The addition of two alkaline substances has decreased the activation energy which caused an increase in the conductivity of the glasses.

A glance of the results listed in Table I shows that optical bandgap energy, *E*opt decreases with the increasing amount of Al_2O_3, which is proportional to the concentration of the Na_2O. It seems as if the addition of alkali oxide has reduced the band gap energy by introducing some additional states in the gap.

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