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Studies on transmission behaviour of certain manganese containing, cerium and arsenic doped alkali–lime–silica glasses*

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Abstract. The transmission behaviour of manganese containing alkali–lime–silica glasses have been investigated with and without CeO_2 and As_2O_3 as dopants. The changes taking place owing to irradiation with solar and ultra-violet conditions are reported and the roles of arsenic and ceria in causing the observed changes are discussed.

Keywords. Glasses; transmission; arsenic; ceria; manganese; alkaline oxides.

1. Introduction

Manganese is usually present in glass as the bivalent manganous Mn^{2+} and trivalent manganic Mn^{3+} states which impart colours in the glass. The nature of the transmission curves in the visible range depends mainly upon the constituents of the glass (Bancraft and Nugent 1929). Ceria is believed to trible the decolorising power of manganese; while arsenic reduces manganic ion and is also reported to act as an oxidation reduction buffer, thus stabilizing the colour due to manganese in glass. Under suitable conditions Ce^{4+} oxidizes Mn^{2+} (Weyl 1951).

The change in transmission due to the exposure to radiation has been discussed by Weyl (1951) who has offered an explanation for the action of sunlight on glasses containing manganese, and the formation of the yellow and the purple hues. Soda-lime glasses containing As_2O_3, CeO_2, MnO_2 and Sb_2O_3 and with low and high iron contents were also reported by White and Silverman (1950). The effect on transmission after irradiation is pronounced in the case of glasses having low iron contents and it is marginal in the high iron containing glasses.

The shifting of maximum absorption towards higher wavelengths with increasing ionic radii of the alkali ions in the order $Li^+ < Na^+ < K^+$, in alkali–silicate glass has been explained (Kumar and Singh 1989).

The purpose of the present investigation is primarily to determine the transmission behaviour of manganese containing alkali–lime–silica glasses with and without CeO_2 and As_2O_3 as dopants. Emphasis has been laid on determination of the behaviour of transmission changes due to ultra-violet and solar radiations.

2. Experimental

Ternary glasses of molar compositions $2R_2O{\cdot}3CaO{\cdot}6SiO_2$ (where $R = Li^+, K^+$ ions) were selected as the base glasses. Raw materials used for the preparation of glasses were analar grade alkali carbonates, calcium carbonate and pure sand. Manganese,

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cerium and arsenic were added to batches as MnO_2, CeO_2 and As_2O_3 respectively. Batch compositions are shown in table 1.

The batches were weighed and mixed thoroughly in a porcelain pestle and motar. The glasses were prepared by melting the batches in the siliminate crucibles, in an electric muffle furnace. Samples of these glasses were obtained in the form of a disc by pouring the molten glass onto a steel plate. These discs were then annealed and ground to the shape of rectangular plates $3{\cdot}5 \times 0{\cdot}9 \times (0{\cdot}25\text{–}0{\cdot}35)$ cm^3, and then polished.

Spectrophotometric measurements were carried out using UV–Vis Shimadzu 240 Spectrophotometer, for all the glass samples in the visible range (300–700) nm of the spectrum, before and after exposure to ultraviolet and solar radiations. Ultraviolet and solar treatments were given for 4 h and 15 days respectively. Since the thickness of the samples varies over a range of 0·25 to 0·35 cm, thickness correction has been made for all the samples using the Bouguer's Law. Accordingly to this law, $T = t^x$ where T = light transmission of a material of thickness x having a unit transmission t. The transmission for all samples, calculated for a standard thickness of 0·3 cm, at 10 nm intervals in wavelength (for exposed and unexposed glasses), are indicated in the graphs.

3. Discussion and conclusion

The percentage transmission obtained for the various glass compositions under varying experimental conditions are indicated in table 2 and figures 1–7.

From figure 1 it is clear that in all the cases the addition of ceria as well as arsenic shifts the wavelength of maximum transmission towards the higher side as compared to the base composition. However, in the case of glasses containing arsenic, the shifting of transmission was from higher to lower wavelengths for lithia and potash containing glasses, respectively, while this effect was reversed in the case of ceria additions (table 2). Although it has been reported by earlier workers (Kumar and Singh 1989) that the shift is due to increase in the ionic radii, it seems that the addition of arsenic in the base glass under investigation reverses this effect

Table 1. Batch compositions of glasses, along with melting temperature, time and annealing temperatures.

	Glass number					
Materials	I	II	III	IV	V	VI
Lithium carbonate	25·07	—	25·07	—	25·07	—
Potassium carbonate	—	38·58	—	38·58	—	38·58
Calcium carbonate	51·05	41·90	51·05	41·90	51·05	41·90
Sand	61·19	50·32	61·19	50·32	61·19	50·32
Manganese dioxide	0·5	0·5	0·5	0·5	0·5	0·5
Cerium dioxide	—	—	1·0	1·0	—	—
Arsenic trioxide	—	—	—	—	1·0	1·0
Melting point (°C)	1360	1400	1360	1400	1360	1400
Melting time (h)	1·5	1·5	1·5	1·5	1·5	1·5
Annealing temperature (°C)	450–500	450–500	450–500	450–500	450–500	450–500

Table 2. Relation between ionic radii of alkali ion with maximum transmission % and dopant oxides.

Glass composition	Thickness of sample (cm)	Ionic radii of alkali ion (Å)	Dopant 0·5 wt% MnO_2		Dopants 0·5 wt% MnO_2 1·0 wt% CeO_2		Dopants 0·5 wt% MnO_2 1·0 wt% As_2O_3	
			Wavelength (nm)	Max. tr.%*	Wavelength (nm)	Max. tr.%	Wavelength (nm)	Max. tr.%
$2Li_2O{\cdot}3CaO{\cdot}6SiO_2$	0·3	0·60(Li^+)	400	29·5	410	21	450	75
$2K_2O{\cdot}3CaO{\cdot}6SiO_2$	0·3	1·33(K^+)	403	35·5	450	52·5	410	84

tr. = transmission.

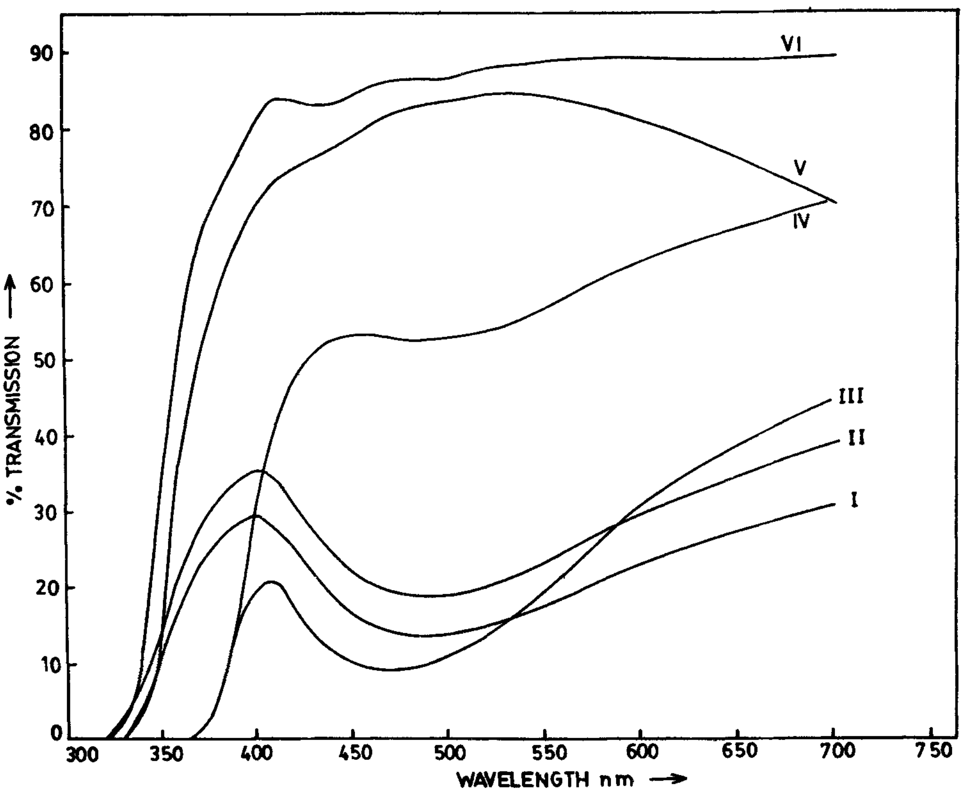

Figure 1. Transmission curves of alkali–lime–silica glasses: (I) lithium, (II) potassium with 0·5 wt% MnO_2; (III) lithium, (IV) potassium with 0·5 wt% MnO_2 + 1 wt% CeO_2; (V) lithium, (VI) potassium with 0·5 wt% MnO_2 + 1 wt% As_2O_3 (sample thickness 3 mm).

which could be due to the varying oxidation state of arsenic and would require detailed investigation.

Other observations based on our experimental results were as follows:

(i) In all cases the percentage transmission in potash containing glasses was higher.
(ii) The transmission in the case of arsenic containing glasses was higher when compared to ceria-containing glasses.

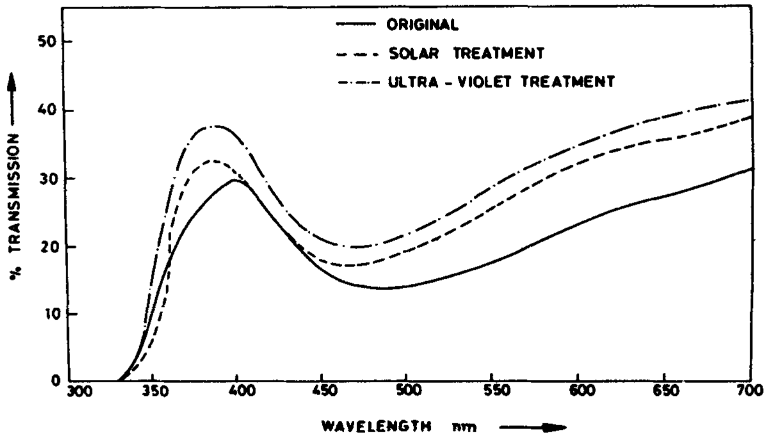

Figure 2. Effect of solar and ultraviolet radiations on lithium–lime–silica glass with 0·5 wt% MnO_2 (sample thickness 3 mm).

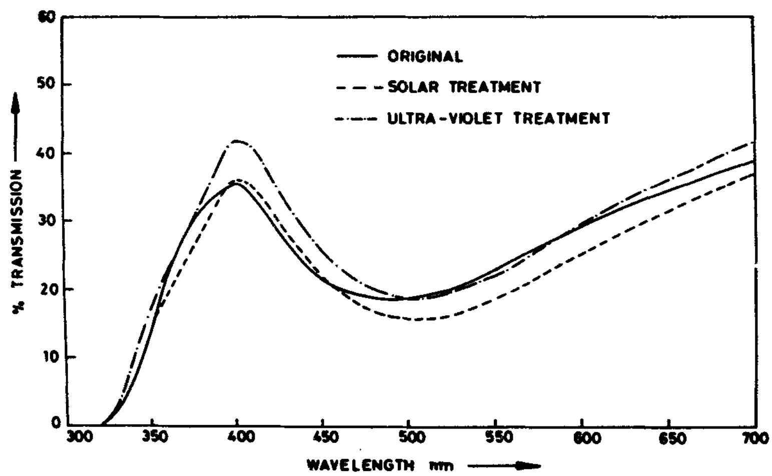

Figure 3. Effect of solar and ultraviolet radiations on potassium–lime–silica glass with 0·5 wt% MnO_2 (sample thickness 3 mm).

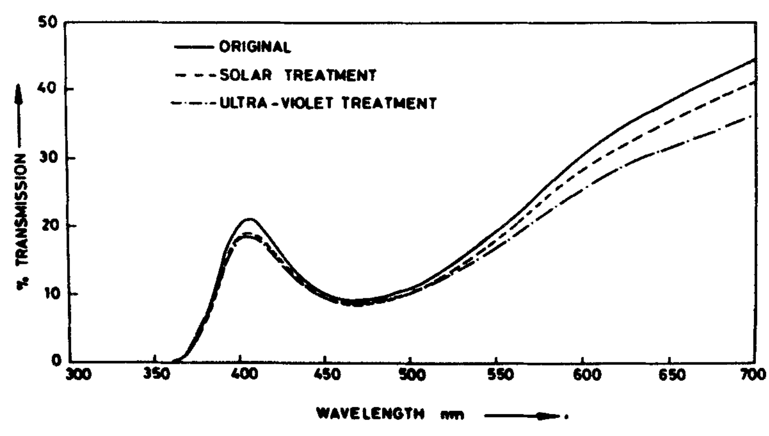

Figure 4. Effect of solar and ultraviolet radiations on lithium–lime–silica glass with 0·5 wt% MnO_2 and 1 wt% CeO_2 (sample thickness 3 mm).

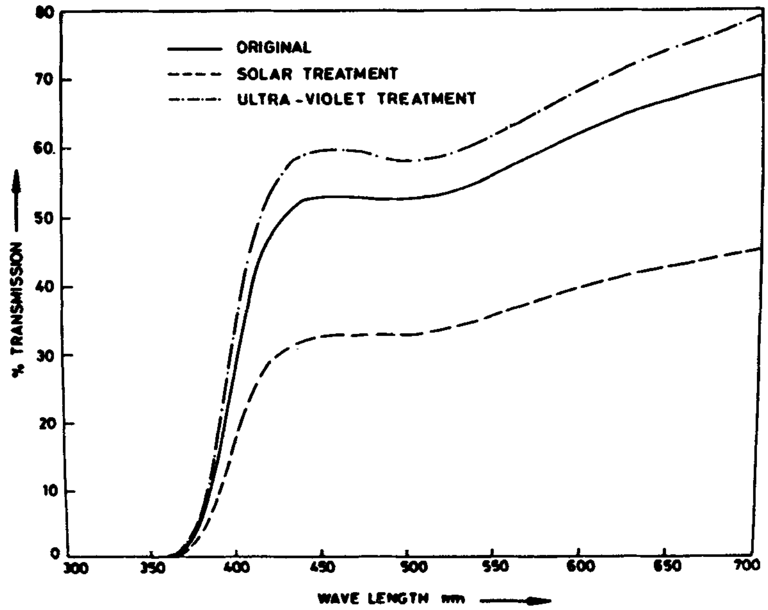

Figure 5. Effect of solar and ultraviolet radiations on potassium–lime–silica glass with 0·5 wt% MnO_2 and 1 wt% CeO_2 (sample thickness 3 mm).

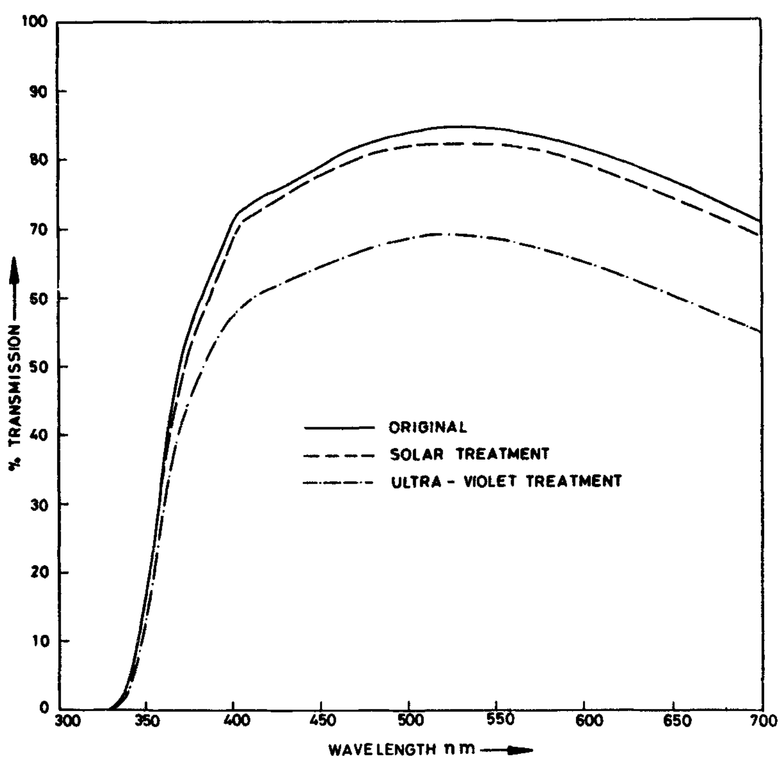

Figure 6. Effect of solar and ultraviolet radiation on lithium–lime–silica glass with 0·5 wt% MnO_2 and 1 wt% As_2O_3.

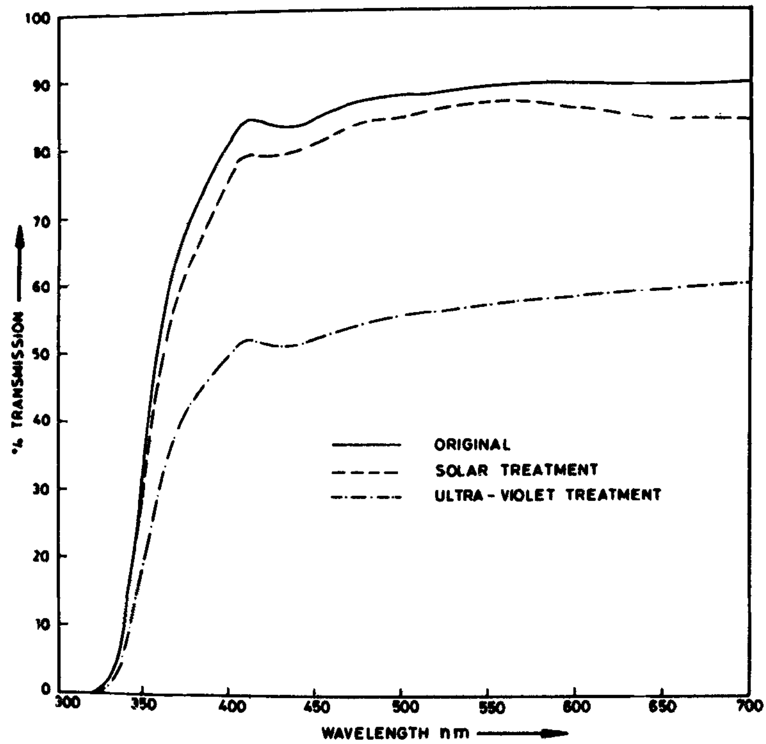

Figure 7. Effect of solar and ultraviolet tradition on potassium–lime–silica glass with 0·5 wt% MnO_2 and 1 wt% As_2O_3.

(iii) The base glass has a marginal effect on the nature of transmission after solar and ultraviolet irradiations (figures 2–3). The same trend is found in the case of base glasses containing ceria (figures 4–5).

(iv) The addition of arsenic alone in the base glass has a pronounced effect on the nature of the transmission curves after ultraviolet irradiation (figures 6–7) and has a marginal effect in the case of solar irradiation, this could be due to the ease with which electron can be liberated from arsenic.

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