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The Importance of Using Some Glass Systems as Standard in Transmission Spectrophotometry in the Visible and Ultraviolet Regions

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Abstract: This study deals with the possibility of using a system of glass borates as a former, Na₂O and PbO as modifiers doped with Cu⁺⁺ 0.1 wt.%, 3 wt.% Er₂O₃, 3 wt.% H₂O₃ and 0.2 wt.% H₂O₃ chromophors in the system, as a standard filter in the visible, UV and IR regions. In an instrument as complex as a spectrophotometer there are many sources of error. Because of this it is useful to have available standard materials whose spectral transmittance are known accurately. Periodic measurements of such standards provide a useful indication of whether a spectrophotometer is producing accurate results. If the spectral transmittance functions of these standards are chosen suitably, the measurements can provide diagnostic information to indicate what type of error is occurring. The results of the spectral transmittance and optical band gap show that the suggested glass is stable for environmental conditions, so we can consider that system as good as commercial standard.

Key words: UV and IR regions, Optical band gap, spectral transmittance

INTRODUCTION

Interest in the optical properties of glasses has been stimulated by their possible application as optical transmission media as well as by their use as standard filters in spectrophotometry.

Two of the most commonly used materials are didymium^[1] and holmium oxide glasses^[2]. One difficulty with these glasses is that the positions of the transmittance minima vary with both the width and the shape of the waveband transmitted by the spectrophotometer.

It must be noted that colored glasses can only be used to check a photometric and wavelength scales if the transmittances of the glasses have been established in advance with an instrument whose linearity has been checked by a fundamental method such as the double aperture method. Minima are not symmetrical or consist of two slightly separated individual minima. Holmium oxide is better than didymium in this respect but there is still some uncertainty if the waveband is not very narrow.

The effect of temperature on these filters is to increase or decrease the transmittances at the minima without changing the wavelengths significantly^[3].

$$T_1(\lambda) = 10^{-d_1 \alpha(\lambda)} \text{ and } T_2(\lambda) = 10^{-d_2 \alpha(\lambda)} \quad (1)$$

Where T_1 and T_2 are the spectral transmittances of the samples, $\alpha(\lambda)$ is the absorption coefficient of the sample. Thus the ratio of the absorbances $A_1(\lambda)$ and $A_2(\lambda)$ is:

$$A_1(\lambda)/A_2(\lambda) = \log T_1(\lambda)/\log T_2(\lambda) = d_1/d_2 \quad (2)$$

It is then assume that if the ratio of the measured spectral absorbances is d_1/d_2 the photometric system is linear. This is not necessarily true. It is possible that the photometric system is such the measured spectral internal transmittance (d_1 and d_2 are the thicknesses of two known samples).

$$T'(\lambda) = [T(\lambda)]^x \quad (3)$$

Where, $x \neq 1$. In this case the measured spectral absorbance will be given by:

$$\begin{aligned} A'(\lambda) &= -\log T'(\lambda) \\ &= -x \log T(\lambda) \\ &= x A(\lambda) \end{aligned}$$

$$\text{and the relation: } A_1(\lambda)/A_2(\lambda) = d_1/d_2 \quad (4)$$

will hold, despite the nonlinearity.

Most of the examples of diagnostics standards given in the preceding section were for the visible spectrum.

Exactly the same principles apply in the ultraviolet region of the spectrum, but there are greater difficulties in finding suitable materials. In particular most glass filter cannot be used below 350 nm because of their strong absorption below this wavelength. For this reason liquid standards such as solutions of potassium chromate, copper sulphate and cobalt ammonium sulphate have often been used^[4].

In this study the spectral transmittance has been examined i.e the minima of the spectra for the prepared glass systems of 0.8 B₂O₃ - 0.199Na₂O - 0.001 CuO, 0.2 B₂O₃ - 0.8 pbO - 0.2 wt. % H₂O₃, 0.2 B₂O₃ - 0.8 pbO - 3 wt.% H₂O₃ and 0.2 B₂O₃ - 0.8 pbO - 3 wt.% E₂O₃ considering the fact as the ligand energy increases the absorption band towards the ultraviolet arises in the spectra, hence they can used as standard material for the wavelength scale, the measurements have been achieved through two years for studying the stability of these sample.

MATERIALS AND METHODS

The mixture was melted in ceramics crucibles in an electric furnace at 1100°C. The mixture was stirred for 3 h and we used the cooling rate cycle.

The melts were poured into brass molds with different shapes to correspond with the different optical measurements. The final glasses were submitted to machining and optical grinding. The glass samples were prepared using appropriate amounts of grade reagents boron oxide, lead oxide, holmium oxide and erbium oxide, the weighted quantities of the starting materials glass batch corresponding to the glass composition were mixed homogeneously. The mixture was placed in a ceramic crucible and heated slowly in an electric furnace.

The temperature was raised gradually depending upon the glass composition.

The crucible containing the melt was constantly agitated to ensure homogeneous mixing. Sufficient time was allowed for the melt to become visibly homogeneous and bubble free. The melt was rapidly quenched to room temperature between two stainless-steel plates. There was no noticeable reaction of the melt with crucible walls. The typical weight loss on melting under the experimental conditions can be neglected with respect to the values quoted for the components. The composition of the glass system was prepared in a series of 3 samples (composition).

The transmittances of the glass samples were measured using master shimadzu spectrophotometer 3031 with total uncertainty $\sim \pm 1\%$ through different times, the results show that these glass system is more stable and the change in transmittance around 0.1%

Table 1: The data of the optical band gap E_{opt} of the two glass systems

Glass system	Cut off wavelength λ , nm	Optical band gap E_{opt} , eV
B ₂ O ₃ -Na ₂ O- CuO (Cu ⁺⁺)	300	4
B ₂ O ₃ - pbO - Ho ₂ O ₃	300	4.14
B ₂ O ₃ - pbO - Er ₂ O ₃	350	3.55

The optical band-gaps of the glasses were obtained from the absorption spectra. the absorption coefficient $\alpha(\omega)$ is given by^[5]:

$$\alpha(\omega) = 1/d \log (I_0/I) \quad (5)$$

$$= 1/d \log 1/T$$

Where, d is the thickness of the glass sample in cm, T is the spectral transmittance measured by the spectrophotometer as shown in fig. 1 and 2 for sample of each glass system, $\alpha(\omega)$ is related to E_p the optical band-gap is given by^[4,5]:

$$\alpha(\omega) = \text{Const.} \left[\frac{h\omega - E_p}{\eta\omega} \right] \quad (6)$$

RESULTS AND DISCUSSION

If one introduces 3D elements into the base glasses e.g., Fe, Mn, Ni, Cu, Co, Cr, etc one obtains the simplest type of colored glasses.

The electrons in the subgroups of periodic system are particularly mobile. As their tendency to change valency. These elements when doped cause resonance absorption in their electron clouds under white- light irradiation.

It is well known from crystal chemistry that even a small change in the ligand field may cause enormous changes in absorption behavior, thus in coloration^[6,7].

The cuprous ions Cu⁺ do not add any colouration to glasses but in case of Cu⁺⁺ ions contribute blue colouration in commercial sodium-borate glasses as shown in Fig. 1, Cuprous ions in combination with cupric ions give rise to the disturbance of the optical electrons resulting in an increase in the light absorption. For the Cu²⁺⁺ ion (d⁹) the d-d transition can be interpreted as if it is an ion of (d¹) configuration. It is well known that ion with ground state are subjected to a large Jahn-Teller distortion.

Also there is a dependence of the absorption behavior on the modifiers in the glass systems. In our suggested glass system the Na₂O represent the modifier, according to Weyl's^[8] concept of screening, the positive field of alkali ions are not completely screened by the surrounding O²⁻ ions.

As a result, the effective negative charge of O²⁻ ions on the coloring ion decrease. The larger the radius of

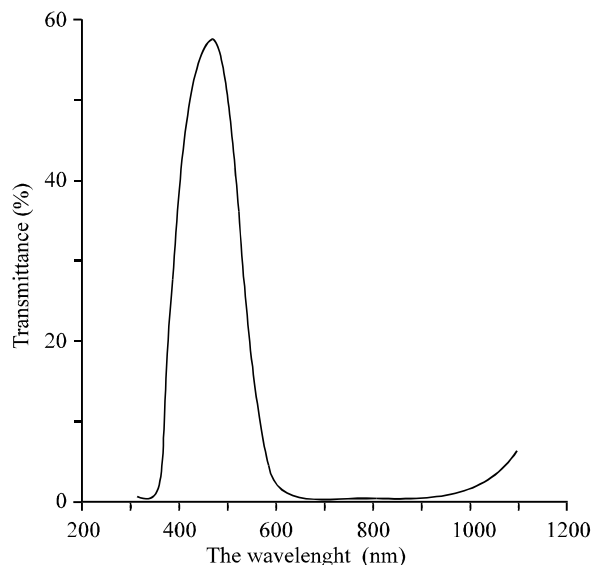


Fig. 1: The Spectral transmittance of 0.8 B₂O₃-0.1999 Na₂O-0.1 wt.% CuO glass system

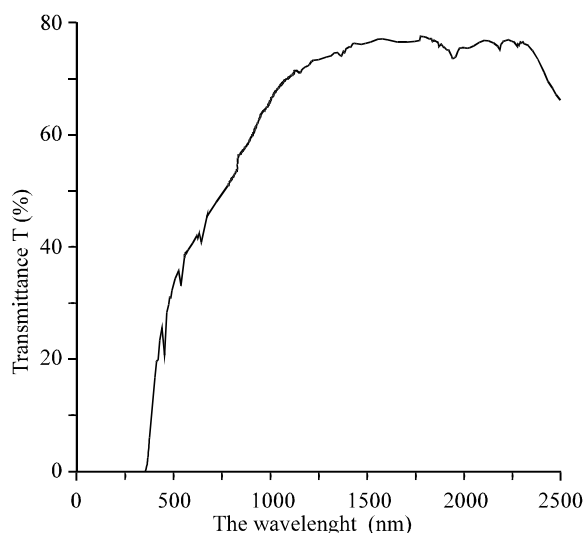


Fig. 2: The spectral transmittance for the lead borate doped with 0.2 wt.% H₂O₃ glass system

the alkali ions the less perfect is the screening and hence, the smaller the effective charge. These principles may give a possible explanation for the shift of the ligand field towards higher energy in the presence of alkali ion as modifier.

So we can say that, an absorption band can be created by adding one of the above cations to the glass system.

The minima in fig. 2- 4 explain the absorption spectra, which characterize the transition elements of rare earth (Lanthnides, Ho and Er). It is well known that the oxides

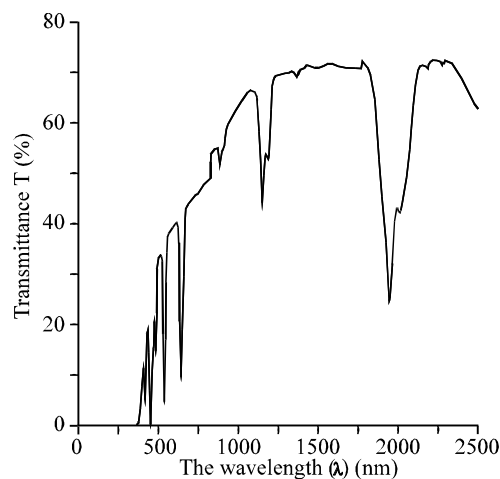


Fig. 3: The spectral transmittance for the [0.2 B₂O₃-0.8 PbO] doped with 3 wt.% H₂O₃ glass system

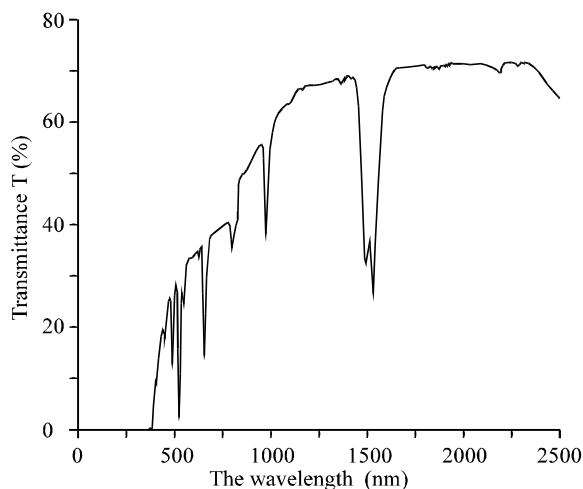


Fig. 4: The Spectra of transmittance for the lead borate doped with 3 wt.% Er₂O₃ glass system

of these elements have high valence and their electronic structure is 1s², 2s², 2p², 3s², 3p⁶, 3d¹⁰, 4fⁿ. Without any details, we can say that H₂O₃ or Er₂O₃ contribute some absorption peaks or transmittance minima as a result of electronic transitions in orbital p,d and f of the outer shells of their atoms especially in UV and visible regions. The minima at 1500 nm in case of Er₂O₃ and 2000 nm in case of H₂O₃ may be due to the vibrational mechanism i.e the ionic vibration of the glass oxide system in the two cases.

The pb²⁺ ion possesses two single 6s electrons in its outermost shell. These two single 6s electrons are responsible for the high polarizability of pb²⁺, which can be polarized even by oxygen anion. This polarization distorts the electron shell to such an extent that one can

attribute dipole character to the lead ions more like pb^0 , the other like pb^{2+} . This concept also helps to explain the behavior of surfaces of high lead content glasses. On the surface, pb^{2+} is exposed to oxygen only, on the inside which gives the surface the metal-like character affecting its behavior.

CONCLUSIONS

Our glass systems $0.8 \text{ B}_2\text{O}_3 - 0.199 \text{ Na}_2\text{O} - 0.001 \text{ CuO}$, $80 \text{ wt.}\% \text{ PbO} - 20 \text{ wt.}\% \text{ B}_2\text{O}_3 - 0.2\% \text{ H}_2\text{O}_3$, $80 \text{ wt.}\% \text{ PbO} - 20 \text{ wt.}\% \text{ B}_2\text{O}_3 - 3\% \text{ H}_2\text{O}_3$ and $80 \text{ wt.}\% \text{ PbO} - 20 \text{ wt.}\% \text{ B}_2\text{O}_3 - 2 \text{ wt.}\% \text{ Er}_2\text{O}_3$ can be used as a commercial standard materials, it provide a very useful and convenient way to check the performance of the spectrophotometer and to diagnose malfunctions, although they can never completely replace more fundamental methods of checking for errors. Materials are available with some of the desired properties, especially for the visible region. Often the spectral transmittance functions are less than ideal and many cases they are instable to environmental conditions such as temperature and are not sufficiently permanent over long periods of time. For these reasons it is very desirable that new and better standard materials such as glass systems should be developed in the future.

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