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Ultraviolet absorption of cerium(III) and cerium(IV) in some simple glasses

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The optical absorption spectra of cerium (III) and cerium (IV) in $Na_2O-B_2O_3$, Na_2O-SiO_2, $Na_2O-P_2O_5$ glasses, and in $H_2O-H_2SO_4$ and $H_2O-H_3PO_4$ solutions have been studied. Individual molar extinction coefficients of cerium (III) and cerium (IV) at different wavelengths (350 to 200 nm) have been estimated. In all the glasses and solutions, cerium (IV) produces a very strong and broad charge transfer band around 250 nm; the intensity, half-width, and position of this band change appreciably with glass composition. Cerium (III) in glass and in aqueous solution produces a number of absorption bands in the ultraviolet region corresponding to the f → d transitions. The cerium (III) bands are sharp and well resolved in $Na_2O-P_2O_5$ and in low-alkali borate glasses; the sharpness of resolution deteriorates in Na_2O-SiO_2, and in high-alkali borate glasses. The intensity of cerium (III) absorption also changes with glass composition. In all the glasses the molar extinction coefficient of cerium (IV) is 5 to 10 times stronger than that of cerium (III).

1. Introduction

Cerium dioxide is used in making various types of commercial glasses. In some opthalmic glasses, as for example, Crookes lenses, as much as 10 wt% CeO_2 is added for ultraviolet protection [1, 2]. The presence of cerium ions, particularly cerium (IV), makes the glass completely opaque to near ultraviolet radiations. Since cerium absorption in these glasses has a steep cut-off edge, the visible contribution of cerium is very low and thus almost colourless glasses can be obtained with complete absorption to the ultraviolet. This is an unique property which hardly can be achieved with any other known colourants in oxide glasses. CeO_2 is used in container glasses as a decolourizer [3–5], where cerium (IV) oxidizes part of iron (II) and minimizes the objectionable bluish-green tinge of the glass. In photosensitive glasses containing noble metal ions, a small amount of CeO_2 is often added as a sensitizer [6, 7]. The presence of a small amount of cerium ions is known to alter the mechanism of damage caused by high energy radiations to glasses [8]; silica fibre wave guides doped with CeO_2 has been reported to undergo less damage when irradiated with pulsed laser sources [9]. Most of the above-mentioned beneficial properties, imparted by cerium ions in glass, depend critically on their ultraviolet absorption characteristics. It is known that under normal conditions of melting, cerium in glass distributes between cerium (III) and cerium (IV); the ratio of these two oxidation states being dependent mainly on the composition of the glass [10, 11], furnace atmosphere [12], and the temperature of melting. Although nominal absorption spectra of cerium containing glasses have been reported in some cases [13], the individual absorption spectrum of cerium (III) and cerium (IV) in glass, and their variation with glass composition is not available in the literature. It is generally believed that cerium being a rare earth metal (with well shielded incomplete inner electronic shell) absorption spectrum of its ions will be least affected by changing glass composition.

In the present investigation we have studied the ultraviolet absorption of cerium (III) and cerium (IV) in binary sodium–borate, sodium–phosphate, and sodium–silicate glasses; and here we report the quantitative individual absorption spectrum of these ions in different glasses. Contrary to conventional belief the absorption spectrum of both cerium (III) and cerium (IV) changes critically with the glass composition.

2. Experimental

Three series of glasses (Na_2O–B_2O_3, Na_2O–SiO_2, and Na_2O–P_2O_5) were melted. The batch materials, Na_2CO_3, H_3BO_3, $NaH_2PO_4.2H_2O$ were all of Analar quality. Acid washed Indian quartz (iron content less than 0.001 wt% as Fe_2O_3) was used as silica. Total cerium concentration in these glasses was varied from 0.02 to 0.50 wt% (as CeO_2); and the concentrations of cerium (III) and cerium (IV) were made to vary over a wide range by adjusting the oxygen pressure of the furnace from 1 to 10^{-10} atm.

All the glasses were chemically analysed; the major components were estimated with conventional methods. Total cerium was estimated colorimetrically with 8-hydroxy quinoline [14, 15]. Cerium (IV) was estimated by dissolving a suitable amount of glass powder in 50 ml 3N H_2SO_4 in the cold and measuring optical density at 310 nm. Optical absorption of a similar solution containing the same amount of blank glass was subtracted. In the case of sodium–silicate glass, a wieghed amount of finely powdered glass was dissolved in a mixture of 43 ml 3N H_2SO_4 + 7 ml 40% HF in cold in a polythene beaker; after complete dissolution of the glass the excess HF was neutralized with 2 g H_3BO_3 powder, and optical density measured at 310 nm. The appropriate blank absorption was subtracted. Concentration of cerium (III) in all the glasses was calculated from the difference of total and tetravalent cerium in that glass.

Thin polished samples (of appropriate thicknesses) of the glasses were used to measure ultraviolet absorption on a Cary 14 spectrophotometer.

3. Results

Fig. 1 shows the absorption spectra of cerium (III) in sodium–borate and sodium–phosphate glasses. The sodium–phosphate glass on melting at 1000° C with air as the furnace atmosphere contained only cerium (III); even melting with oxygen as the furnace atmosphere did not produce any measurable amount of cerium (IV). Thus absorption spectrum of cerium (IV) in this glass could not be estimated. Two series of sodium–borate glasses of molar compositions 15 Na_2O, 85 B_2O_3 and 25 Na_2O, 75 B_2O_3 were studied; fifteen glasses were made in each series with random variation of cerium (III) and cerium (IV) content. All the glasses contained a mixture of cerium (III) and

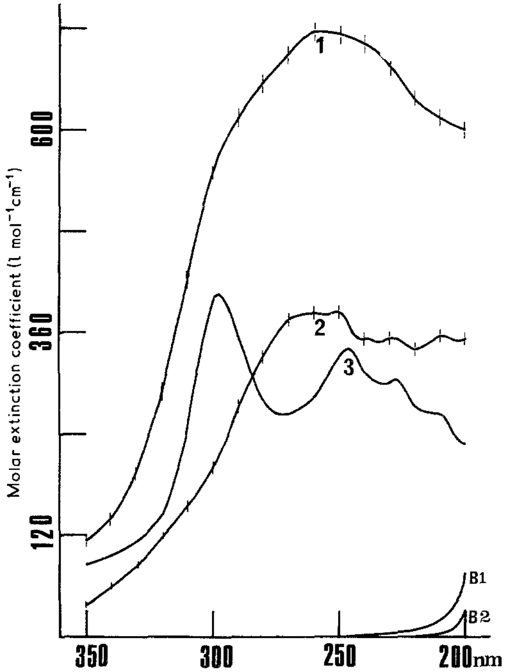

Figure 1 Ultraviolet absorption of cerium (III) in different glasses. Curve 1 : $25Na_2O \cdot 75B_2O_3$ glass; curve 2 : $15Na_2O \cdot 85B_2O_3$ glass; curve 3 : $50Na_2O \cdot 50P_2O_5$ glass.

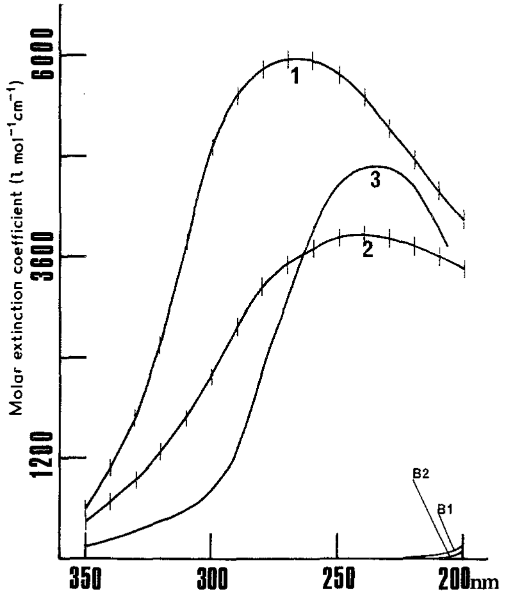

Figure 2 Ultraviolet absorption of cerium (IV) in different glasses. Curve 1 : $15Na_2O \cdot 85B_2O_3$ glass; curve 2 : $25Na_2O \cdot 75B_2O_3$ glass; curve 3 : $30Na_2O \cdot 70SiO_2$ glass.

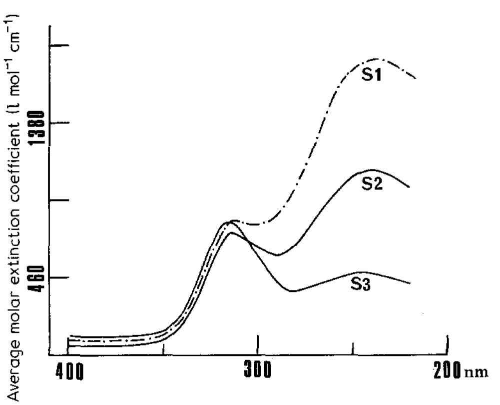

Figure 3 Ultraviolet absorption of $30Na_2O\cdot70SiO_2$ glasses containing cerium (III) and cerium (IV). Curve S1 : melted in air at 1400° C; curve S2 : melted with $p_{O_2} = 10^{-6}$ atm at 1400° C; curve S3 : melted with $p_{O_2} = 10^{-14}$ atm at 1400° C.

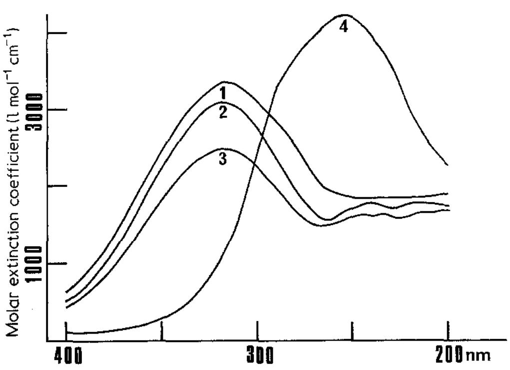

Figure 4 Ultraviolet absorption of cerium (IV) in different aqueous acidic solutions. Curve 1: 36 N H_2SO_4 ; curve 2: 1 N H_2SO_4 ; curve 3: 80% $HClO_4$; curve 4: 41 N H_3PO_4.

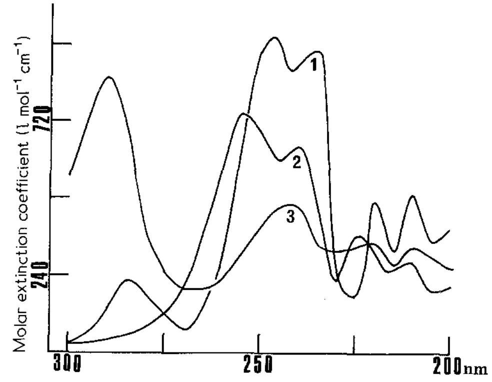

Figure 5 Ultraviolet absorption of cerium (III) in different aqueous acidic solutions. Curve 1 : 36 N H_2SO_4; curve 2 : 1 N H_2SO_4; curve 3 : 41 N H_3PO_4.

cerium (IV) which were estimated chemically as described before. Absorption spectra of all the glasses were measured, and for an individual series of glass, the optical densities per cm at a particular wavelength were calculated. Since these glasses were prepared with Analar raw materials, the ultraviolet absorption of these glasses arise from the individual absorptions due to cerium (IV), cerium (III) and that of the blank glass itself [18]. If it is assumed that for a particular series of glass at any wavelength the extinction coefficients of cerium (IV) and cerium (III) remain unchanged over the concentration range studied, then

$$D_\lambda = B + \epsilon_{III}\cdot C_{III} + \epsilon_{IV}\cdot C_{IV} \qquad (1)$$

where D_λ is the optical density/cm of a glass at the wavelength λ, C_{III} and C_{IV} are the concentrations of cerium (III) and cerium (IV) respectively expressed as mol per litre of glass; and ϵ_{III} and ϵ_{IV} are the extinction coefficients of cerium (III) and cerium (IV) respectively at the wavelength λ; B is the absorption due to the blank glass at λ. Multiple regression equations of the form of Equation 1 were set up for wavelengths at 10 nm intervals in the range 350 to 200 nm, and solved with a standard computer program. B, ϵ_{III} and ϵ_{IV} at various wavelengths with their standard deviations (as vertical bars) are shown in Figs. 1 and 2. Fig. 3 shows the absorption spectra of cerium containing sodium–silicate glasses. No measurable amount of cerium (IV) could be detected in glass S3; assuming this glass produces only cerium (III) spectrum, the molar extinction coefficient of cerium (IV) in the silicate glass as represented in Fig. 2 (curve 3) was calculated from the difference of absorption due to glasses S3 and S1, and normalized with respect to cerium (IV) concentration of glass S1. Figs. 4 and 5 show the absorption spectra of cerium (IV) and cerium (III) in different acidic aqueous solutions

4. Discussion

In oxide glasses, under normal conditions of melting, cerium distributes into tri- and tetravalent states. Cerium (IV) is a $4f^0$ system, and cannot have any f → f transition; the colour of cerium (IV) salts arises from tails of strong charge transfer band in the near ultraviolet region. Cerium (III) has a $4f^1$ ground electronic configuration with two free ion states separated by about 2000 cm^{-1}; the first excited configuration is 5d, and lies about 40000 cm^{-1} above the ground state. The energy

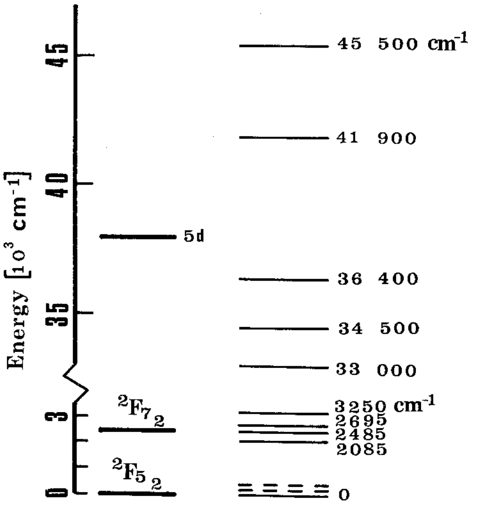

Figure 6 Energy level diagram of cerium (III) in $YAlO_3$ at 300 K.

level diagram of cerium (III) is $YAlO_3$ is shown in Fig. 6 [16]. The optical spectra of cerium (III), therefore, consists of f → f transitions in the near infra-red, and f → d transitions in the ultraviolet. Cerium (III) in oxide glasses has very little, if any, absorption in the visible region. In the ultraviolet region a maximum number of five absorption bands may be expected for cerium (III), which indeed is fulfilled in low-alkali borate and alkali phosphate glasses (Fig. 1). In the high-alkali borate glasses, the cerium (III) absorption spectrum appears as an envelope containing at least two absorption bands; the number and position of other component bands, if any, could not be discerned from these spectra. In alkali borate glasses the absorption intensity (oscillator strength) of cerium (III) increases almost by a factor of two by increasing the soda content from 15 to 25 mol%. Absorption spectrum of cerium (III) in alkali silicate glasses is similar to that in alkali phosphate glasses except in the lack of fine structure at shorter wavelengths, and small differences in energies of absorption maxima.

Absorption spectra of cerium (IV) change significantly with the composition of glass. One very broad absorption band is obtained in all the glasses and aqueous acidic solutions; the position of its maximum and particularly the intensity of absorption, change remarkably with changing glass composition. This is hardly surprising for cerium (IV) is well known for complexation even with reasonably inert ligands so much so that the electrode potential of the cerium (III)/cerium (IV) couple in an aqueous acidic medium is critically dependent on the nature of anions of the acid as shown in Table I. In spectroscopic conformity, Fig. 4 shows clearly that the ligation sphere of cerium (IV) indeed changes with H_2O/H_2SO_4 ratio in the solution (compare curve 1 with curve 2 of Fig. 4). It should be pointed out, however, that the ligation sphere of cerium (III) also changes with the H_2O/H_2SO_4 ratio in aqueous solutions as evidenced in Fig. 5. Comparison of the electrode potentials of Table I indicate that cerium (IV) in perchloric acid will easily oxidize water, for

$$O_2 + 4H^+ + 4e = 2H_2O \qquad E^\circ = +1.229\,V.$$

Indeed, in Fig. 4 it can be seen that a part of cerium (IV) has been reduced in 80% perchloric acid medium even after only 5 min of standing at room temperature (curve 3). In fact from Table I it appears that cerium (IV) even in aqueous sulphuric acid solution is only metastable.

TABLE I Electrode poential of Ce(IV)–Ce(III) complex in some aqueous acidic media

	E°	Medium
Ce(IV) + e = Ce(III)	+ 1.28	2 M HCl
	+ 1.44	1 M H_2SO_4
	+ 1.61	1 M HNO_3
	+ 1.70	1 M $HClO_4$

There is a common belief that cerium being a member of rare earth group (shielded incomplete 4f shell), its absorption will be insensitive to changing composition of glass. However, it should be remembered that electronic transitions responsible for the ultraviolet absorption with cerium (IV) in glass are of charge transfer in nature, and charge transfer transitions are well known to depend critically on the nature of the complex; a very small change in the symmetry of the complex or a change in the electronegativity of the ligated ligands influencing the overlap of atomic orbitals, alter the nature of charge tansfer bands appreciably [17].

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