Correlation between spectral properties and optical basicity for oxide gels doped with chromium(II) ions

ANDRZEJ M. KŁONKOWSKI, TERESA WIDERNIK, MARIUSZ BICZKOWSKI

Faculty of Chemistry, University of Gdańsk, ul. Jana Sobieskiego 18, 80-952 Gdańsk, Poland.

For oxide xerogels of the types: $Na_2O-B_2O_3-SiO_2$ and SiO_2-TiO_2 prepared by the sol-gel procedure a correlation between one of the absorption bands of Cr^3 ion (attributed to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition) and theoretical optical basicity has been found. The experimental results show that Cr^{3+} ion can play the role of basicity probe in Lewis sense for oxide xerogels. Additionally, its band position can be a relative measure of water content in the same material.

1. Introduction

In oxide materials the oxygen in a M–O bond behaves as a base in the Lewis sense and correspondingly the M metal (or semimetal) behaves as a Lewis acid. The polarisation of O^{2-} results in the negative charge being drawn from the oxygen ion to the M^{n+} metal (*i.e.*, covalent bond formation). The oxygen is therefore less able to donate charge to another solute metal ion (*e.g.*, a transition metal ion), *i.e.*, it is less able to function as a Lewis base.

Certain metal ions undergo observable changes (*e.g.*, a shift in the absorption band) depending upon the degree of electron donation that they receive from the oxygen ions, and they may therefore be used as "probes" for basicity in oxide materials. Spectral measurements of Tl^+, Pb^{2+} and Bi^{3+} in these materials have shown that the frequency of the absorption band is dramatically lowered by increasing basicity of the material [1]. The reason for this appears to be due to orbital expansion effect within the probe ion brought about by electron donation by the oxygens. This effect is known as the nepheloauxetic effect, and is fundamentally linked to that for transition metal ions [2], [3]. Therefore, transition metal ions may also be used as probe ions. However, they are less satisfactory type of probe than the *p* block metal ions (Tl^+, Pb^{2+}, Bi^{3+}) [1].

Thus, the optical basicity concept is based on direct spectroscopic measurements of the shift of frequency in the UV region of a selected absorption band of a doping agent from the *p* block. Values have been assigned to most common oxides and a summation procedure has been derived to provide optical basicity values for oxide mixtures. This is particularly relevant to systems containing transition metal oxides, where UV absorption edge prevents direct measurement of optical basicity. An alternative method has been developed by DUFFY and INGRAM [1] for calculating theoretical optical basicity. To calculate the optical basicity of an oxide system it

is necessary to have available the Λ value of the individual oxides composing the system ($AO_{a/2}$, $BO_{b/2}$, ...) for substituting in the following equation [4]:

$$\Lambda = X(AO_{a/2})\Lambda(AO_{a/2}) + X(BO_{b/2})\Lambda(BO_{b/2}) + ... \tag{1}$$

where the equivalent fractions $X(AO_{a/2})$, $X(BO_{b/2})$ ... are defined as the proportion of oxide$(-II)$ they contribute to the total oxide$(-II)$ of the system. Another way to calculate Λ is as in the following equation [1], [5]:

$$\Lambda = 1 - \{(z_A r_A/2)(1 - 1/\gamma_A) + (z_B r_B/2)(1 - 1/\gamma_B) + ... \tag{2}$$

where: z_A, z_B ... are oxidation numbers of the cations A, B, ... , r_A, r_B ... are their ionic ratios with respect to the total number of oxides and γ_A, γ_B ... are basicity moderating parameters of these cations ($\gamma = 1.36(x - 0.26)$, where x is Pauling electronegativity).

Experimental optical basicity values can be measured only for some acidic oxides (SiO_2, P_2O_5, B_2O_3 and SO_3) and the oxides of alkali and alkaline earth metal ions and Al^{3+} [1], [4]. Experimentally, optical basicity is obtained typically by measurements of Tl^+ or Pb^{2+} probe ion s-p spectra and, since these are in the UV region, this metod cannot be used for oxide materials doped with transition metal ions because of their UV opaqueness.

Recently, the optical bistability concept has been most often used for oxide glasses. We tried to use them to oxide gel systems doped with transition metal ions prepared by the sol-gel procedure. Obviously, the gels are opaque in the UV region [5] and therefore in this study we characterise these materials by the theoretical optical basicity proposed by DUFFY and INGRAM [1], [6]. Further, we systematically studied the absorption band shifts brought by changes in optical basicity in the gels doped with such transition metal ions as Cr^{3+}.

2. Experimental

2.1. Chemicals

$Si(C_2H_5O)_4$, $B(CH_3O)_3$ and $Ti(C_4H_9O)_4$ (from Aldrich Co.) as well as $Cr(NO_3)_3 \cdot$ $\cdot 9H_2O$ and sodium metal (from Polish Chemical Reagents) of analytical grade were used without further purification. Methanol, ethanol and buthanol were of analytical grade purity. The water used was doubly distilled.

2.2. Sample preparation

Oxide gels in the system NaO_2–B_2O_3–SiO_2 doped with Cr^{3+} (3 mol%) were prepared as follows. Firstly, to the mixture of alkoxides such as $Si(CH_3O)_4$ and $B(CH_3O)_3$ in methanol $NaOC_4H_9$ and $Cr(NO_3)_3$ were added in appropriate amounts [7]. $NaOC_4H_9$ was obtained by reaction of sodium with buthanol at elevated temperature (70 °C). During gelation the reaction polyethylene beaker with the reaction mixture was irradiated in ultrasonic apparatus. The wet gel after

gelation was dried at 100 °C and then analyzed, because the B_2O_3 changed during the gelation process. Analytical data of the compositions of the dried gels (xerogels) are collected in Tab. 1.

T a b l e 1. Composition of xerogels of the type NaO_2–B_2O_3–SiO_2 doped with 3 mol% Cr^{3+}.

Xerogel	Composition [mol%]		
	Na_2O	B_2O_3	SiO_2
a	5.8	11.6	82.6
b	11.6	5.8	82.6
c	12.5	12.5	75.0
d	13.3	20.0	66.7

Another gel system of the type SiO_2–TiO_2 doped with Cr^{3+} (3 mol.%) was also prepared by the sol-gel method [7]. Firstly, the reaction mixture $Si(CH_3O)_4 + H_2O$ in methanol was prepared. After one day $Ti(C_4H_9O)_4$ and $Cr(NO_3)_3$ were added to this mixture in appropriate amounts. The obtained gel was dried as mentioned above. Compositions of the xerogels are as in Tab. 2.

T a b l e 2. Composition of xerogels of the type SiO_2–TiO_2 doped with 3 mol% Cr^{3+}.

Xerogel	Composition [mol%]	
	SiO_2	TiO_2
a	100	—
b	75	25
c	50	50
d	25	75
e	—	100

2.3. Apparatus

UV-Vis absorption spectra were recorded on a Perkin-Elmer Lambda 18 spectro-photometer equipped with a Harrick internal reflection accessory. The MgO was used as a standard. Spectra were recorded between 300 and 900 nm.

3. Results and discussion

In Figure 1, absorption spectra of the Na_2O–B_2O_3–SiO_2 xerogels doped with Cr^{3+} ions are shown. The spectra consist of two distinct bands peaked at ca. 420 and 590 nm. They are related to the transitions: ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, respectively [8].

The long wavelength band is shifted further if the optical basicity change than the band at 420 nm. Therefore we use the 590 nm band as an indicator of basicity [1]. Changes of the calculated optical basicity for the xerogels of the type Na_2O–B_2O_3 –SiO_2 are in a very narrow range (between 0.51 and 0.57). This is due to a small
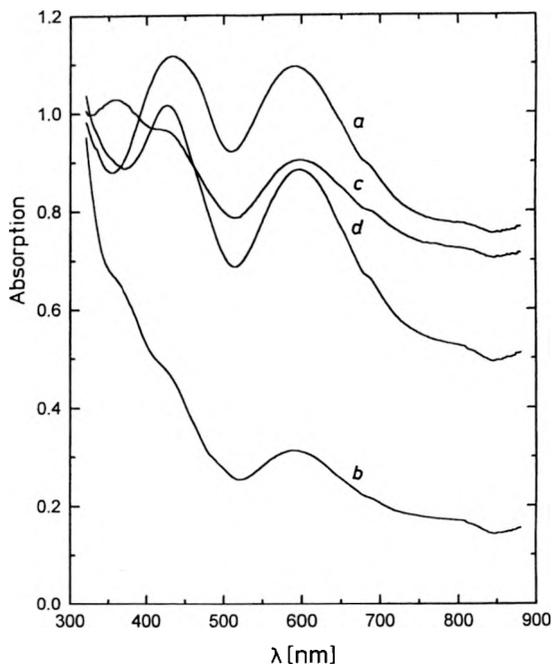
Fig. 1. UV-Vis absorption spectra of xerogels of the type NaO_2–B_2O_3–SiO_2: $5.8Na_2O$–$11.6B_2O_3$ –$82.6SiO_2$ (curve a), $11.6Na_2O$–$5.8B_2O_3$–$82.6SiO_2$ (curve b), $12.5Na_2O$–$12.5B_2O_3$–$75.0SiO_2$ (curve c), $13.3Na_2O$ –$20.0B_2O_3$–$66.7SiO_2$ (in mol%), doped with 3 mol% Cr^{3+}.
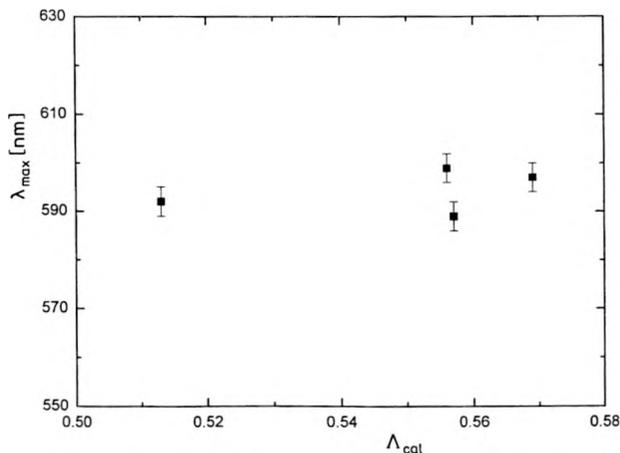

Fig. 2. Variation in the band position λ_{max} (attributed to the $^4A_{2g} \rightarrow {^4}T_{2g}$ transition) with calculated optical basicity Λ_{cal} for xerogels of the type Na_2O–B_2O_3–SiO_2.

difference between the optical basicity values of SiO_2 and B_2O_3 (*cf.* [1] or [4]). This fact should cause rather small changes in the $^4A_{2g}(F) \rightarrow {^4}T_{2g}(F)$ band position. Actually, the band shifts as predicted above (Fig. 2).
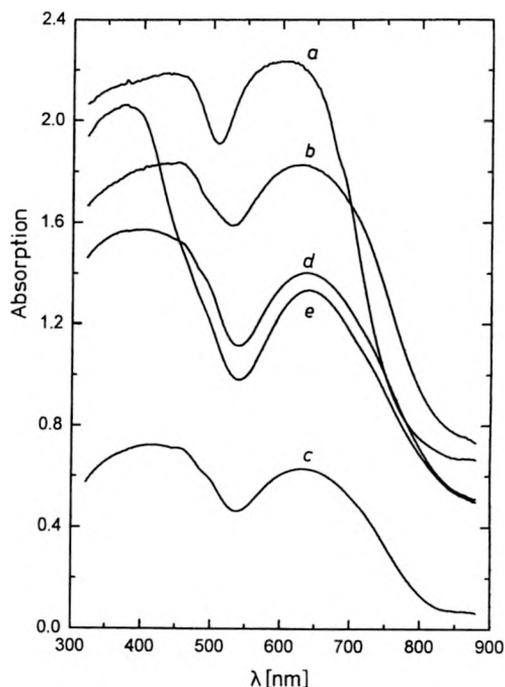
Fig. 3. UV-Vis absorption spectra of xerogels of the type SiO_2–TiO_2: $100SiO_2$ (*a*), $75SiO_2$–$25TiO_2$ (*b*), $50SiO_2$–$50TiO_2$ (*c*), $25SiO_2$–$75TiO_2$ (*d*), $100TiO_2$ (*e*), in mol%, doped with 3 mol% Cr^{3+}.
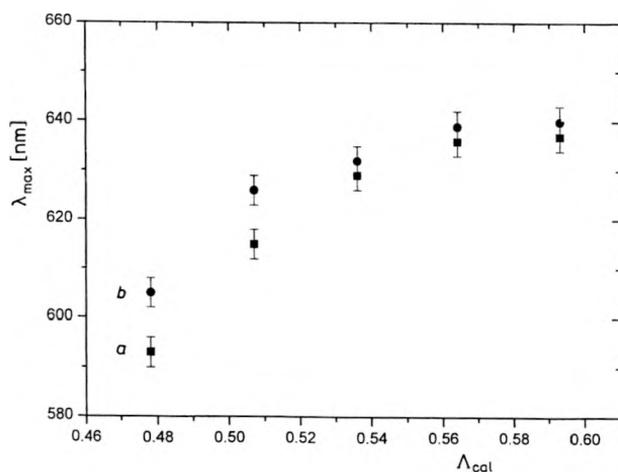

Fig. 4. Variation of the band position λ_{max} (attributed to the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition) with calculated optical basicity Λ_{cal} for xerogels of the type SiO_2–TiO_2. The xerogels were dried at 30 °C (*a*) and 100 °C (*b*).

Optical absorption spectra for the xerogel SiO_2–TiO_2 system doped with Cr^{3+} are quite similar to the ones previously shown (*cf.* Figs. 1 and 3). However, the optical basicity Λ_{cal} for the xerogels from this system changes in a rather broad

range of values. This causes that the long wavelength band changes distinctly, as shown in Fig. 4. It can be observed from this figure that for the xerogels dried at a higher temperature the band is shifted to red. It means that in this case Cr^{3+} ions are more probable to interact with oxygen atoms bonded to Si or Ti than with oxygen in water molecules in pores of the xerogels.

4. Conclusions

The theoretical optical basicity Λ_{cal} appears in this study to be a straightforward parameter characterizing electron-donor properties of oxide xerogels prepared by the sol-gel method, if any practical measure is known. The results for the mixed oxide xerogels doped with Cr^{3+} ions are as follows:

1. Position of the absorption band attributed to the $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition for Cr^{3+} ion may serve as a practical measure of the basicity of such oxide materials as xerogels prepared by the sol-gel method.

2. Shift of this Cr^{3+} band could indicate changes of water content in pores of the same oxide xerogel.

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