

COLOURED SULPHATE GLASSES

Vasilica DIMA,*¹ Petru BALTĂ and Roxana ȘERBAN

University “Politehnica” Bucharest, Faculty of Applied Chemistry and Materials Science,
Dept. Science and Engineering of Oxide Materials and Nanomaterials,
Catedra SIMONA, P.O. Box 12 134 Bucharest-Roumania, E-mail v.dima@oxy.pub.ro

Received August 16, 2005

Using a previously selected low melting glass from the system $\text{ZnSO}_4\text{--K}_2\text{SO}_4\text{--P}_2\text{O}_5$ the behaviour in this medium of some 3d colouring ions was studied. The recorded electronic spectra show the presence of redox equilibriums between different ions of each 3d element established in spite of the very low temperature. Even at 500 °C, the same redox mechanisms as above 1,000 °C act in this fluid melt. Some of the used 3d ions determine the increase of the crystallization tendency of the glass. The experimentally determined basicity is close to that of many industrial glasses.

INTRODUCTION

Although the sulphate glasses have been known for a longtime, their structure is far from being understood and the properties have not been entirely studied.¹⁻⁴ Among their most interesting features are their very low melting temperatures, for some compositions even under 500 °C. At such low temperatures, the melt is fluid enough for refining and homogenizing the processes and for pouring. As is known, the low melting temperature is related to less complex structures with low energy chemical bonds and consequently with a lower chemical stability. The predictable advantages of low melting glasses concerning the energy saving and processing facilities deserve the continuation of researches including the structure, properties and possible diminution of hygroscopy.

In the previously developed research works the field of glass forming melts in the system $\text{K}_2\text{SO}_4\text{--ZnSO}_4$ has been delimited. Only the compositions in the central part of the system – approximately between 30 and 60 mol.% K_2SO_4 – may be under-cooled in usual laboratory conditions. Finally, a ternary composition containing a small amount of P_2O_5 was selected.⁵

The accessible specialized literature seems to show that the colouring of these kinds of glasses with 3d ions was not studied. It is of interest to observe the behaviour of some, usual in glass field, 3d colouring ions in sulphate melts and glasses at quite low temperatures compared to those normal in industrial glasses technology. Such a study was undertaken and the obtained results are presented in this work.

EXPERIMENTAL

The sulphate glass used for experiments had the composition: 50% K_2SO_4 + 40% ZnSO_4 + 10% P_2O_5 (molar percents). The raw materials were: K_2SO_4 ; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$.

The used colouring agents were: CuO , Cu_2O , Cr_2O_3 , CoO and Fe_2O_3 , introduced as such, the proportion being up to one wt. %.

Ceramic crucibles were used and an electric furnace. Melt quantities of 10 or 30 g were maintained for 3 hours at 500 °C. By pouring into metallic forms, discs with a diameter of 20 mm and a thickness of about 2 mm were obtained, for optical spectra recording and rods of about 50 mm length, for expansivity and other properties measurement. The annealing was conducted at 200 °C for 10 minutes followed by cooling in the furnace.

With the obtained samples the same usual properties were first determined. For expansivity, values of the order of $308 \cdot 10^{-7} \cdot \text{K}^{-1}$ were obtained, corresponding to the known simple structure of these glasses with low energy chemical bonds. The very low values of the glass transition temperature T_g , of the order of 205 °C, are in agreement with the low melting temperatures. The absorption spectra in

* Corresponding author : E-mail v.dima@oxy.pub.ro

the range of 200–1100 nm were recorded by means of a double beam spectrophotometer Shimadzu UV-160 A, having in the reference beam the glass without a 3d ion.

THE ELECTRONIC SPECTRA OF SULPHATE GLASSES COLOURED WITH COPPER

Fig. 1 the spectrum of a glass containing copper ions is presented. The used copper sources were, for different glasses, CuO and Cu₂O. Only one record is shown because, irrespective of the copper source, the established redox equilibrium resulted in practically the same spectrum in spite of the low elaboration temperature. The three maxima specific for copper ions are clearly visible, namely: for Cu²⁺ the d-d electronic transitions at about 850 nm, conferring to glass the specific green colour, and the charge transfer transition at about 290 nm and for Cu⁺ at about 240 nm.

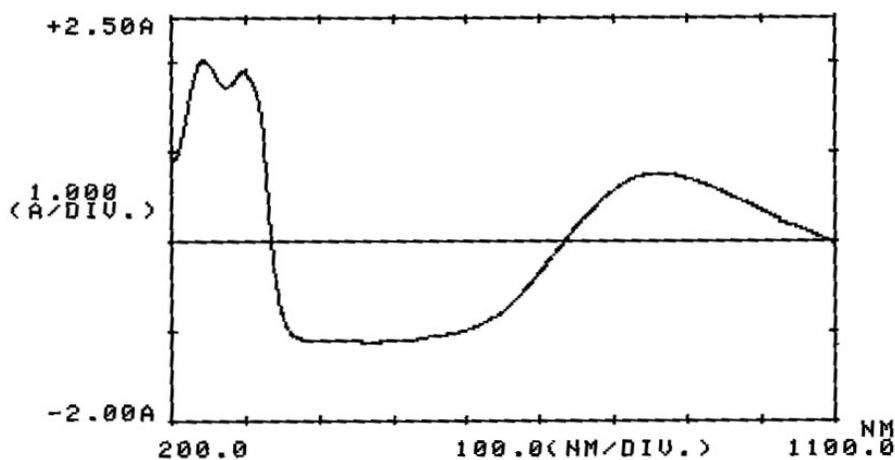


Fig. 1 – Absorption spectrum of glass coloured with copper introduced as CuO.

Taking into account that in the frame of the glass basicity scale elaborated in our laboratory^{6,7} the experimental method uses copper as a probe ion, a special glass sample was prepared observing the experimental conditions previously established.⁸ The obtained spectrum in the range 200–400 nm is presented in the Fig. 2. The two maxima of the copper ions are clearly visible and, using a cursor of the spectrophotometer software, the frequency of the maximum of Cu²⁺ was exactly determined, namely: 290.5 nm, respectively $\nu = 34,423 \text{ cm}^{-1}$. The frequency of the charge transfer absorption maximum of Cu²⁺, expressed in cm^{-1} , is used in formula (1) for experimental basicity value determination.

$$pB_e = 151 - 0.00259 \cdot \nu \quad (1)$$

The resulted basicity is $pB = 61.8\%$. It is of interest to observe that the maximum position in the studied glass is very close to that in an usual oxide glass with basicity 60% (respectively 284 nm).⁹ On the basis of the accumulated data⁷ it was established that the glass forming compositions have a basicity lower than 60% and those with basicity between 60 and 70% have intermediate glass forming properties. The basicity value of the studied sulphate glass is close to that of some important industrial glasses like window glass, E-fiber glass, TV screen glasses, etc.¹⁰

ELECTRONIC SPECTRA OF SULPHATE GLASS COLOURED WITH OTHER 3d IONS

CoO is a classic colouring agent used from antiquity to obtain blue colour in glasses and in glazes for ceramics and being less or even not influenced by the technological parameters. The absorption spectrum of sulphate glass coloured with CoO is presented in Fig. 3. The two maxima in the visible range correspond very well with those observed in other glasses.¹¹ The maxima in the UV region show that two cobalt ions are present: Co²⁺ absorbing farther in the UV and Co³⁺ having the corresponding maximum at about 280 nm, its

amplitude indicating a lower concentration.¹² Unlike copper, the cobalt oxide diminishes the glass forming aptitude of sulphate glass, the sample being less transparent but having the specific blue colour.

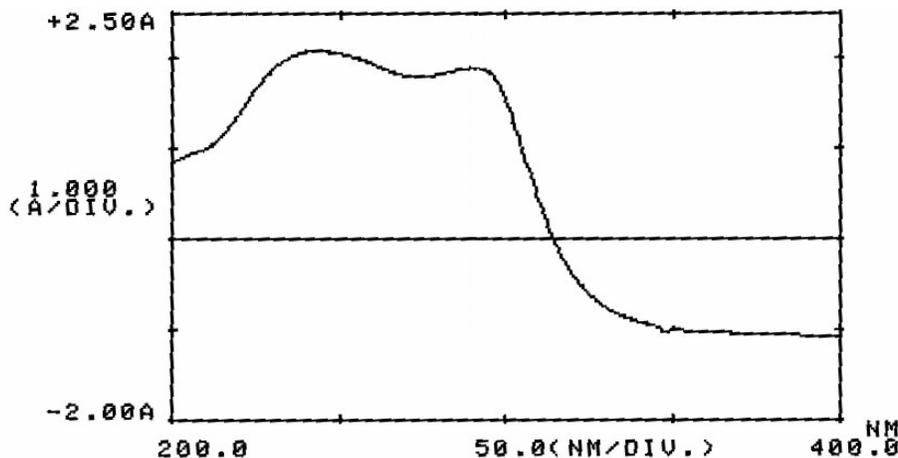


Fig. 2 – The absorption spectrum of the glass with Cu^{2+} as probe ion for basicity determination.

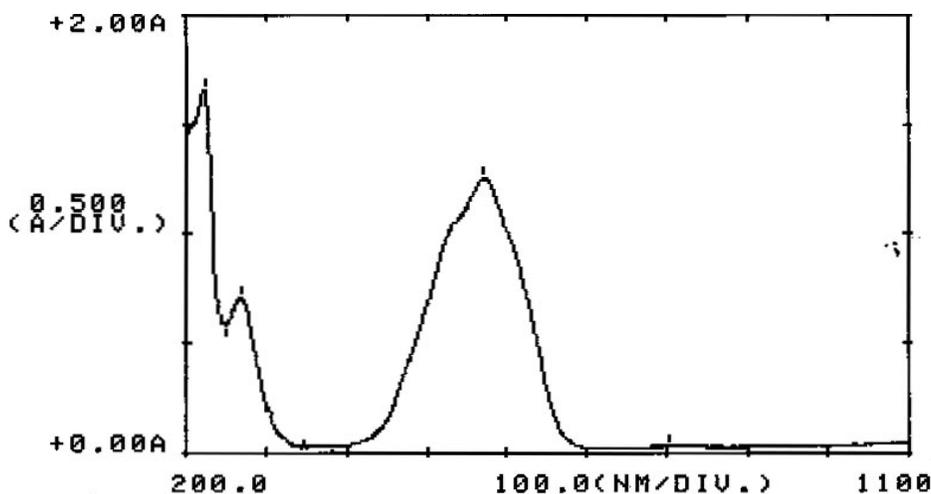


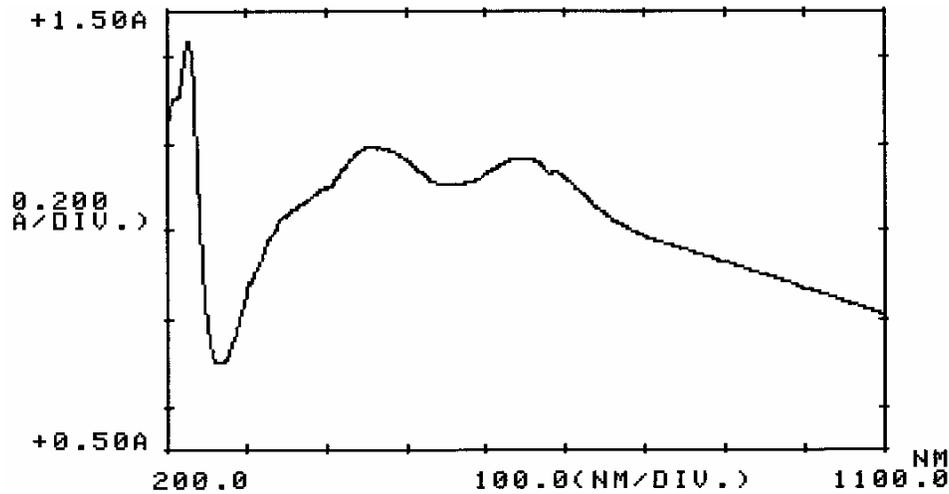
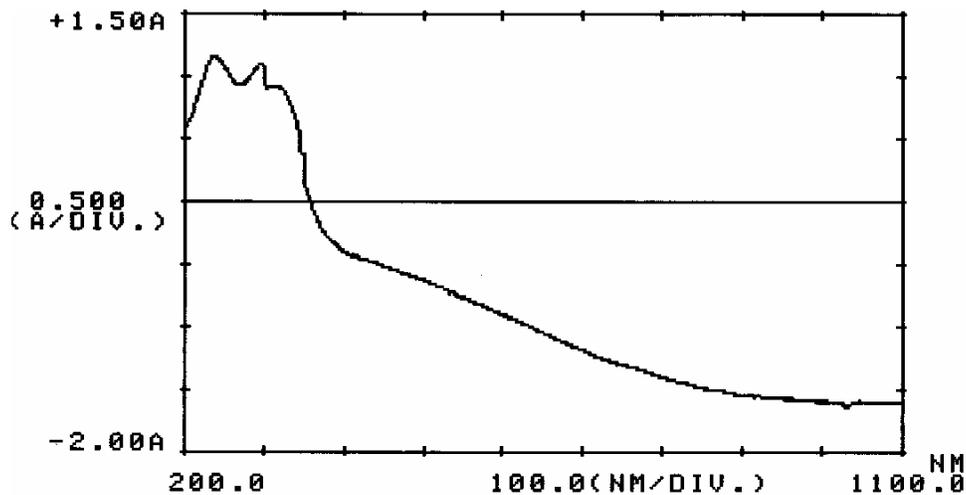
Fig. 3 – Absorption spectrum of glass coloured with CoO .

Cr_2O_3 , being a refractory oxide, it is of interest to observe its integration in a so low melting glass. The recorded spectrum is presented in Fig. 4. Using the ideas from⁶ and¹³ and the interpretations from⁹ it is possible to discuss the maxima attribution. The absorptions at 637 and at 432 nm seem to be d-d transitions specific for Cr^{3+} a d^3 ion. The shoulder at about 350 nm might be determined by Cr^{6+} , a d^0 ion. Finally, at 228 nm, is the charge transfer absorption of Cr^{3+} .

Like in the case of other 3d ions, complex redox equilibrium is present. It seems that chromium oxide does not integrate completely into the sulphate glass structure, determining the increase of the crystallization tendency. So the sample is partly crystallized and less transparent even when the Cr_2O_3 content was reduced to 0.1%.

The absorption spectrum of the glass containing Fe_2O_3 shown in Fig. 5 presents the usual characteristics with some peaks in the UV region and a long tail towards the visible.^{9,13} The maximum shoulder at 312 nm belongs probably to Fe^{3+} , a d^5 ion. The peak at 297 nm is due to Fe^{2+} and probably also that at 238 nm.

The complex redox equilibrium is again evidenced and also the pronounced tendency to devitrification.

Fig. 4 – Absorption spectrum of glass coloured with Cr_2O_3 .Fig. 5 – Absorption spectrum of glass coloured with Fe_2O_3 .

DISCUSSION

One of the general observed phenomena is the realization of a redox equilibrium involving the ions of each 3d element. According to the redox mechanism enounced in⁶ the determinant role in such equilibrium belongs to the oxygen diffusion from glass to the external atmosphere and vice-versa. At high temperatures, the thermal dissociation of the superior oxide takes place and the liberated oxygen leaves the melt or, sometime, is partly retained as peroxy groups. When the temperature decreases, the penetration into the glass atmospheric oxygen reoxidizes the ions in a lower oxidation state. In the absence of special redox agents (reducer or oxidizer) at equilibrium ions in different oxidation state are present showing that both mentioned processes are active with different rates. These rates depend on diffusion, that means on composition and temperature.

In the case of the studied glasses, the presence of both copper ions, irrespective of the oxidation state in the source, shows that due to the melt composition and structure, even at 500 °C both processes have high enough rates to realize in 3 hours the same equilibrium. So, in an indirect way, information is acquired that this sulphate glass has at 500 °C approximately the same viscous and redox properties as the industrial oxide glasses at 1,400-1,500 °C. As the recorded spectra show such low temperature redox equilibrium takes place for all tested 3d ions.

Another interesting phenomenon is the nucleating action of some of the used 3d ions in this sulphate glass. By the basicity value the used sulphate glass is placed at the higher limit of the glass forming compositions, the crystallization tendency being pronounced. The nucleating action of 3d ions might be related to the fact that at 500 °C the chemical reactivity of oxides of the 3d elements is low and they form separate nanocrystalline clusters. Usually these ions may have two coordination numbers, namely with four and with six oxygen atoms.^{6,9} The four coordinated ions have a higher tendency to form own structures which may play the role of crystallization nuclei. So, copper which prefers CN 6 integrates better as a glass modifier, forming homogeneous transparent coloured glasses. Possibly, for other 3d ions used in this work the proportion or the influence of the four-coordinated part is more important.

CONCLUSIONS

As 3d glass coloring agents CuO, Cu₂O, CoO, Cr₂O₃ and Fe₂O₃ were used. Only with copper ions homogeneous, transparent glasses were obtained. The rest of 3d oxides determined the increase of the devitrification tendency and the obtained samples were more or less crystallized.

The recorded electronic spectra showed the establishment of redox equilibria between different ions of each 3d element even at so low elaboration temperature as 500 °C, the high fluidity of melts facilitating the oxygen diffusion from melt to the external atmosphere and vice-versa.

The increase of the crystallization tendency in the presence of 3d oxides may be explained by their low chemical reactivity at a so low temperature and by the presence of four coordinated 3d ions which form own clusters acting as nuclei.

The experimentally determined basicity is comparable with that of many usual industrial glasses, one of the consequences being the similarity of the recorded spectra to those of other glasses colored with the same 3d ions.

REFERENCES

1. C. A. Angel, *J. Amer. Ceram. Soc.* **1965**, *48*, 540.
2. S. L. Narasimham and K. I. Rao, *J. Non-Cryst. Solids*, **1978**, *27*, 225-246.
3. H. G. Sundar, B. Govinda Rao and K. I. Rao, *Phys. Chem. Glasses*, **1982**, *23*, 90.
4. D. R. Uhlmann and N. J. Kreidl, "Glass Science and Technology, vol. I – Glass forming systems", Academic Press, New York, 1983, p. 212-231.
5. P. Baltă and the Staff of the Laboratory of Glass Chemistry and Technology, "Very low melting glasses", Research work supported by MCT, **1995-2000** (Unpublished).
6. P. Baltă, "Glass technology", Ed. Didactică și Pedagogică, Bucharest, 1984, p. 179-188 (in Roumanian).
7. P. Baltă, "The basicity of glasses", Invited paper presented to the 5th Conference of the European Society of Glass Science and Technology (ESG) "Glass science and technology for the 21st century", Prague June **1999**, Proceedings on CD, B4, Glass structure, p. 3-14.
8. P. Baltă, "The charge transfer absorption of 3d ions as means for oxide glasses basicity measurement", XVth International Congress on Glass – Leningrad, 1989, vol. 1b, p. 213-214.
9. P. Baltă, *Mat. Constr.*, **1988**, *XVIII*, 293-298 (in Roumanian).
10. P. Baltă, "Determinant factors in glass obtaining by melts under cooling", The conference on glass and ceramics, Varna-Bulgaria, **1999**, Proceedings, vol. 1, p. 9-16.
11. W. A. Weyl, "Colored glasses", London **1959**, p. 132-144, 169-191.
12. P. Baltă, M. Biale, *Rev. Roum. de Chim.*, **1989**, *34*, 1301-1306.
13. P. Baltă and E. Baltă, "Introduction to the Physical Chemistry of the Vitreous State", Ed. Academiei, Bucharest and Abacus Press UK, 1976, p. 232-256.