Spectra of doped transition metal ions in K_2SO_4–$ZnSO_4$ glasses

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Abstract. Sulphate glasses prepared from K_2SO_4–$ZnSO_4$ system were doped with Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions in the form of their sulphates. The spectra in the visible region indicated octahedral coordination of these ions. The spectral features remain unaffected in the entire composition range. Hence the zinc ion in these binary sulphate glasses is likely to retain octahedral coordination in the entire glass forming compositions.

Keywords. Sulphate glasses; zinc ion coordination; transition metal ion spectra.

1. Introduction

Glasses can be obtained over a wide range of compositions in the binary zinc sulphate-alkali sulphate system. They are typical ionic glasses and investigation of many other properties of these glasses has been published elsewhere (Narasimham and Rao 1978). The d-d transitions of doped transition metal ions in a 60 mole % $ZnSO_4$-40 mole % K_2SO_4 glass was earlier reported by Duffy and coworkers (Duffy *et al* 1968, 1970; Duffy and McDonald 1970; Ingram and Duffy 1970). This indicated a possibility that zinc ions could be octahedrally coordinated in these glasses. The glass forming regions have now been extended considerably in this system. Many properties such as molar volumes and polarisabilities indicate that the sulphate glasses conform to an ideal mixing of the components and that the high degree of ionicity of these glasses remains unchanged. Therefore it appears as if the environment of zinc ions vary continuously in these glasses. In order to investigate the local environment of ions, doped transition metal ion spectra has come to be recognised as a powerful tool (Wong and Angell 1976). Therefore these glasses were doped with small percentages of transition metal ions in the entire composition range and their visible spectra were investigated. It is assumed in these spectroscopic investigations, as elsewhere (Wong and Angell 1976) that the doped divalent transition metal ions occupy zinc ion positions of the host glass.

2. Experimental

The glasses were prepared by melting together BDH samples of K_2SO_4 and $ZnSO_4 \cdot 7H_2O$ of better than 99% purity in appropriate proportions along with approximately

2 mol % of the transition metal ion sulphate (Riedel-De Haen AG Seelze-Hannover sample of anhydrous $Fe_2(SO_4)_3$, S.D. A.R. sample of $FeSO_4 \cdot 7H_2O$, Albright & Wilson Ltd. sample of $CoSO_4 \cdot 7H_2O$ and Sarabhai Chemicals Ltd. samples of $NiSO_4 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$). The melt was dehydrated by using dry nitrogen for about 3 hr and thin discs of these glasses suitable for spectroscopic investigation were prepared by a procedure described elsewhere (Narasimham and Rao 1978). The spectra of these samples were recorded using Unicam SP 700A in the region 400–1500 mμ. Care was taken to see that the thin glass discs were not exposed to moisture before recording their spectra. The spectra were all recorded at the laboratory temperature.

3. Results and discussion

Out of the five transition metal ions (d^5-d^9) employed in these investigations ferric ion doped glasses did not yield good spectra in spite of repeated efforts. Fe^{2+} (d^6) ion gave a broad absorption band centered round 9300 cm^{-1}. However Co^{2+}, Ni^{2+} and Cu^{2+} ions gave rise to sufficiently intense absorption bands. They are shown in figures 1 and 2. The spectrum for Fe^{2+} is given as inset of figure 2. The kink at 7200 cm^{-1} is an instrumental feature and is disregarded.

Although the spectra of only extreme compositions have been shown in the figures, the spectra of the intermediate compositions remained identical. The compositions and the positions of the absorption maxima in a few typical compositions are given
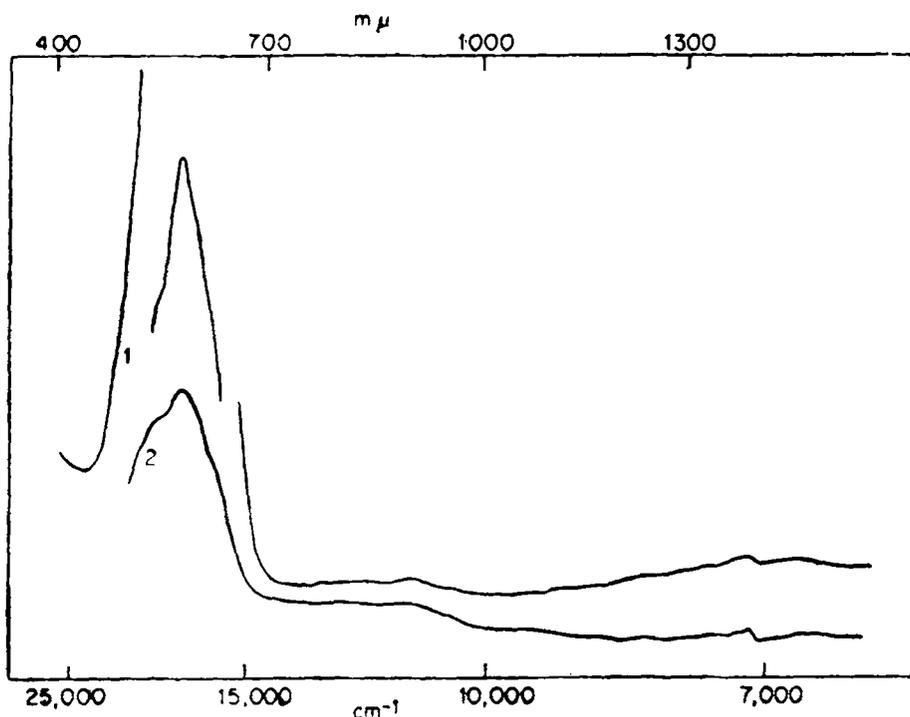

Figure 1. Spectra of Co^{2+} in (1) 70 : 30 and (2) 20 : 80 K_2SO_4 : $ZnSO_4$ glasses.

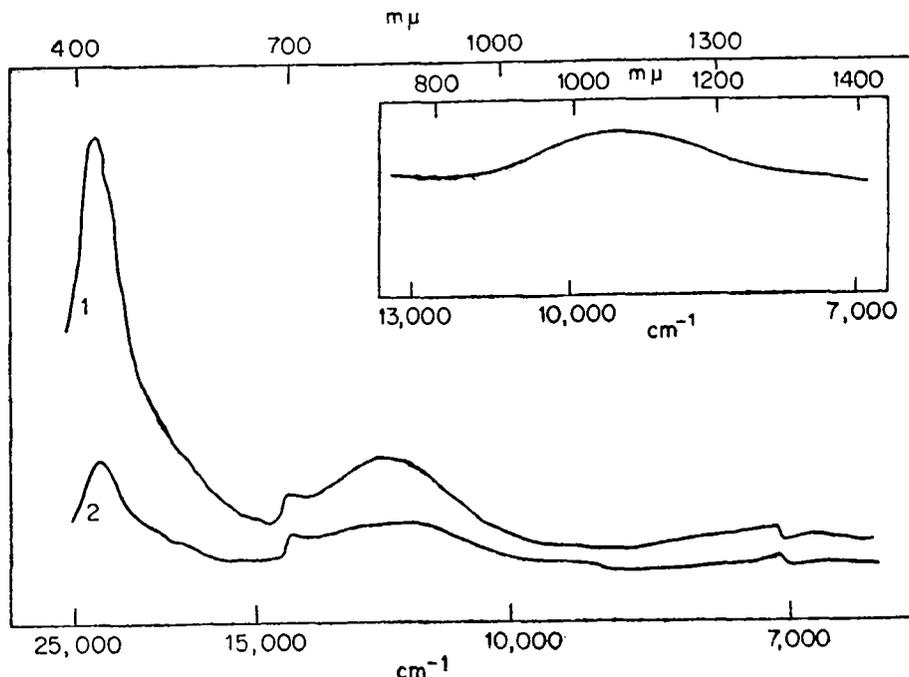**Figure 2.** Spectra of Ni^{2+} in (1) 70 : 30 and (2) 20 : 80 K_2SO_4 : $ZnSO_4$ glasses. Inset : spectrum of Fe^{2+} in 35 : 65 K_2SO_4 : $ZnSO_4$ glass.

in table 1. The molar absorptivities in the extreme compositions were calculated from the knowledge of the densities, the thicknesses, and the observed absorbances of thin glass discs and are given in parantheses in table 1. The observed peaks were assigned to the appropriate *d-d* transitions, the knowledge of which is available in the literature (Bates 1962). From a reference to the Orgel diagrams values of both the ligand field splitting energy, 10 Dq (Δ) and the Racah parameter B were obtained. In the cases of Co^{2+} and Ni^{2+} ions, there are sufficient number of absorption peaks. Therefore the effect of sulphate ligancy on the value B and hence the nephelauxetic parameter could be evaluated. However, Cu^{2+} (d^9) and Fe^{2+} (d^6) gave single broad absorptions and only 10 Dq values could be roughly estimated. In table 2 the crystal field splitting energies and the values of B parameter along with the observed and calculated (by the use of Orgel diagram) energies for the transitions are given.

It is known that the only allowed transition in the case of Fe^{2+} ion in octahedral symmetry is $^5\Gamma_5$ (D) $\rightarrow$ $^5\Gamma_3(D)$ and the observed single broad peak around 9300 cm^{-1} is consistent with its value of approximately 9100 cm^{-1} in sodalime silica glasses (Varguine and Weignberg 1955) and is in good agreement with 9200 cm^{-1} value reported by Duffy and McDonald (1970) in the case of 40:60 glass. Cobalt ion gives rise to spin allowed transitions from its ground $^4\Gamma_4$ (F) state to the excited $^4\Gamma_5$ (F), $^4\Gamma_2$ (F) and $^4\Gamma_4$ (P) states. The $^4\Gamma_4$ (P) however shows a shoulder due to Jahn-Teller distortion of the excited state (Bates 1962). Choice of the value of B which gives the best agreement with the experimental transition energies is difficult to make uniquely. However our choice of 720 cm^{-1} gives better agreement on an average for all the three peaks. Nickel ion shows typically allowed transitions from the ground $^3\Gamma_2$ (F) state to higher $^3\Gamma_5$ (F), $^3\Gamma_4$ (F) and $^3\Gamma_4$ (P) states. However

Table 1. Absorption maxima in cm⁻¹ from the spectra

Glass composition $K_2SO_4 : ZnSO_4$ / Dopant ion*	70 : 30		60 : 40	50 : 50	35 : 65	20 : 80	
Fe³⁺	—		—	—	9300 wb	—	
Co²⁺	6890 wb	(15·1)	—	—	—	6870 vw	(39·5)
	11100 wb	(13·4)	11900 wb	—		11040 vw	(44·6)
	17360 vs	(73·7)	17240 s	17240 s		17360 s	(82·3)
	18450 sh		18380 sh	18690 sh		18690 sh	
Ni²⁺	6910 vw	(12·1)	7350 vwb	7140 vw		6800 vw	(20·2)
	12050 s	(19·4)	11980 wb	12120 b	—	11700 wb	(26·6)
	14160 w	(16·2)	14140 w	14290 s		14290 w	(24·3)
	22520 vs	(48·3)	22220 s	22220 vs		22730 s	(37·6)
Cu²⁺	11270 b	(71·2)	11630 b	11630 b	—	11150 b	(48·9)

*the concentrations of the dopant ion in the (70 : 30) and (20 : 80) compositions were 0·32 and 0·39 moles/litre respectively and the dopant ion concentrations in all other glasses are approximately 0·2 moles/litre

s : strong, w : weak, b : broad, sh : shoulder, vs : very strong, vw : very weak, wb : weak and broad.

Molar absorptivities in the extreme compositions are given in parantheses.

Table 2. Assignment of transitions and the transition energy parameters

Dopant ion	Observed transition cm⁻¹	Assignment	Calculated transition cm⁻¹	Ligand field splitting energy cm⁻¹	Racah parameter cm⁻¹
Fe³⁺	9300	$^5\Gamma_3(D) \rightarrow {}^5\Gamma_5(D)$	9300	9300	—
Co²⁺	6870	$^4\Gamma_4(F) \rightarrow {}^4\Gamma_5(F)$	6870	7490	720
	11040	$\rightarrow {}^4\Gamma_2(F)$	13880		
	17360	$\rightarrow {}^4\Gamma_4(P)$	16360		
Ni²⁺	6800	$^3\Gamma_2(F) \rightarrow {}^3\Gamma_5(F)$	6880	6860	880
	11700	$\rightarrow {}^3\Gamma_4(F)$	11450		
	14290	$\rightarrow {}^1\Gamma_3(D)$	14910		
	22730	$\rightarrow {}^3\Gamma_4(P)$	22360		
Cu²⁺	11150	$^2\Gamma_3(D) \rightarrow {}^2\Gamma_5(D)$	11200	11200	

Ni²⁺ ion is known to give rise to spin forbidden transition (Ballhousen 1962) and the transition around 14300 cm⁻¹ is assigned to transition from $^3\Gamma_2$ (F) to $^1\Gamma_3$ (D). These transitions which are marked in figure 2 and given in table 2 are well accounted for with B = 880 cm⁻¹. The corresponding 10 Dq value is given in table 2. Copper ions, however, lead to a single absorption peak around 11200 cm⁻¹ in good agreement with those reported by Duffy and McDonald (1970) (see table 2).

Therefore the spectra very clearly indicate that the transition metal ions have an octahedral site symmetry in these glasses, in the entire composition range of 30 to 80 mol % of zinc sulphate. The values of B for transition metal ions being close to

that of the free ion also indicates that the degree of ionicity is very high and hence the bonding is similar to that of Zn ions in the host glass. Therefore if the divalent transition metal ions namely Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} are occupying positions of zinc ions, the octahedral site symmetry of zinc ions should remain unaltered in the entire composition range. It may be noted that the ionic radii of these isovalent ions (Fe^{2+}, 0·74Å; Co^{2+}, 0·72Å; Ni^{2+}, 0·6Å and Cu^{2+}, 0·72Å) are very close to the radius of zinc ions itself 0·74Å. Hence it is reasonable to assume that the transition metal ions occupy the zinc ion sites in these glasses. It may be noted that the same octahedral coordination of zinc ions occur in other crystalline sulphates containing zinc like in $ZnSO_4$ (Muller and Roy 1974) and $K_2Zn_2(SO_4)_3$ (Langbeinite structure; Wyckoff 1964). This pronounced preference of zinc ions for octahedral coordination introduces unique structural features in these sulphate glasses and it has been discussed elsewhere in detail (Narasimham and Rao 1978).

4. Conclusions

The spectra of doped transition metal ions is consistent with octahedral site symmetry. The spectral features are unaffected by the composition of the host glasses. Hence the zinc ions maintain octahedral coordination in these glasses.

Acknowledgements

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