Luminescence of Cu$^+$ in Na$_2$SO$_4$

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Cu$^+$ doped Na$_2$SO$_4$ was synthesized and Cu$^+$ emission has been studied. The changes in luminescence of Cu$^+$ with the phase of Na$_2$SO$_4$ are shown. The luminescence from phase III is observed at 357 nm while the phase V shows emission around 396 nm. Thus shift of almost 40 nm is observed. The excitations are also different and observed at 254 nm for phase III and 270 nm for phase V. Phase I, which is hexagonal shows emission at 456 nm with the excitation at 245 nm.

Keywords: Chemical synthesis, Crystal structure, Differential scanning calorimetry, Inorganic compounds, Luminescence

1 Introduction

The alkali sulphates have been studied for the possible applications in solid state batteries due to their high ionic conductivity. Of the several alkali sulphates, Na$_2$SO$_4$ has extensively been studied for the possible applications as a solid electrolyte in solid state batteries and as a SO$_x$ sensor. Interest in this material is also generated due to several phase transitions and a lot of work has been done on this material correlating the electrical properties with the various phases. Several phases of Na$_2$SO$_4$ exist which are labeled as V to I and exhibit phase transitions between them. The room temperature phase is labeled as Na$_2$SO$_4$-V phase, which crystallizes in the orthorhombic structure (space group Fddd). Na$_2$SO$_4$-III also exhibits orthorhombic crystal structure (space group Cmcm), while the high temperature phase stable above 250°C (phase I) shows hexagonal structure (space group P6/3mmc).

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The room temperature phase is labeled as Na$_2$SO$_4$-V phase, which crystallizes in the orthorhombic structure (space group Fddd). Na$_2$SO$_4$-III also exhibits orthorhombic crystal structure (space group Cmcm), while the high temperature phase stable above 250°C (phase I) shows hexagonal structure (space group P6/3mmc).

Phase I is stable up to just below the melting point 884°C and then transforms to metastable phase III on cooling to room temperature with an intermediate phase, phase II. On reheating phase III converts to phase I without going through the phase II. The phase V is stable at room temperature and converts to phase I at 240°C. The phase III also changes to phase V when exposed to ambient conditions for nearly a year. The phase I is of particular interest due to very high ionic conductivity. The electrical conductivity of Na$_2$SO$_4$ approaches $10^{-5}$ S/cm around 250°C, if such high conductivity could be established at room temperature then material will be very useful for various electrochemical applications and a lot of research is devoted to the stabilization of this phase at room temperature. Phase I can be stabilized by forming solid solutions with anions such as (CO$_3$)$^{2-}$ or some uni-, bi-, and trivalent cations such as K$^+$, Ni$^{2+}$, Mg$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Y$^{3+}$ etc., including rare earth$^{6,7}$ ions (La$^{3+}$, Gd$^{3+}$, Eu$^{3+}$). The phase transitions in Na$_2$SO$_4$ have been well studied by differential thermal analysis, Raman spectroscopy, X-ray diffraction, electrical conductivity$^{10}$, etc. The luminescence is used as a technique to study the phase transitions. Correcheer et al$^{11}$ observed changes in thermally stimulated luminescence (TSL) spectra correlated with V$\rightarrow$I phase transition. Rowland et al$^{12}$ studied the spectral resolved thermoluminescence (TL) and radioluminescence from Dy$^{3+}$ doped Na$_2$SO$_4$ and found dramatic changes in TL spectra with phases. Another way to study these phase transitions could be to observe changes in photoluminescence spectra of the luminescent ions with phase. The luminescence from 3d monovalent activators such as Cu, Ag are susceptible to environment due to unshielded 3d orbital. Also the ionic radii of Cu$^+$ (0.77 Å) is less than that of Na$^+$ ion (1.02 Å). Na$^+$ ions could be easily replaced by Cu$^+$ without any other changes in lattice. Therefore, these ions are the suitable choice to study these phase transitions. However, doping these ions in monovalent form in sulphate hosts is rather difficult task. Recently, we have succeeded in doping Cu$^+$ in several sulphate lattices$^{13}$. In the present paper, results on Cu$^+$ luminescence in various phases (I, III and V) of Na$_2$SO$_4$ are presented and discussed.
2 Experimental Details

Anhydrous Na$_2$SO$_4$ (Fluka) was sprinkled with CuCl$_2$ solution in the desired amount and the powder was dried under the drying lamp for several hours to drive away water. This powder was then heated in reactive atmosphere discussed elsewhere$^{14}$. The powder was then melted at 890°C in china crucible and cooled to room temperature by switching off the furnace. This sample will be called as Sample 1. Another sample was prepared in a similar way but quenching the melt by transferring it in another crucible maintained at ice temperature. This sample will be called as Sample 2. Yet another sample was prepared by moderately quenching the melt in air. This sample is labeled as Sample 3. These solidified materials were then crushed in agate mortar and the fine powders were used for measurements. Pure samples with similar methods of preparation were also prepared for reference. Na$_{1.9}$M$_{0.05}$SO$_4$ doped with Cu where M is Ca or Zn were also prepared in a way similar to that used for Sample I. These samples are labeled as Sample 4 and Sample 5, respectively. In all these samples the amount of Cu$^{+}$ doped is 200 ppm.

X-ray diffraction patterns were recorded on Philips PAN Analytical X’pert Pro diffractometer with Cu target. Photoluminescence was studied on Hitachi F-4000 Spectrofluorometer. Thermal analysis was done on Shimadzu DTG-60.

3 Results and Discussion

Figure 1(a) shows the X-ray diffraction pattern of Sample 3. This pattern could be identified with the orthorhombic phase with the space group Cmcm and similar to that of ICDD 89-4751 in the ICDD database. This phase is labeled as phase III in the literature$^{15}$. This phase can also be differentiated from phase V from the DTA pattern. Na$_2$SO$_4$ in phase V shows multiple peaks in DTA pattern corresponding to phase transition sequence V→IV→III→II→I and is well reported in literature$^{15}$. In contrast, the DTA pattern for phase III sample consists of only one peak around 240°C corresponding to III to I transition$^{10}$. When the DTA run for Sample 3 is carried out, the pattern shows a single peak around 230°C [Fig. 2(a)]. The peak for pure sample prepared in similar way also shows a peak around 230°C [Fig. 2(b)]. These peaks appeared to be shifted towards lower temperature compared to the available literature data. Such changes in phase transition temperature are observed earlier also. Various factors such as impurities, particle size, etc. are the reasons cited for such change$^{16,17}$. The Cu$^{+}$ luminescence in this phase is observed at 357 nm [Fig. 3(a)] with excitation at 254 nm [Fig. 3(b)]. The observed band is narrow and the full width at half maximum was found to be 42 nm. The DTA pattern of Sample 1 is quite different from that for sample 3. It consists of 3 peaks which could be identified with the sequence of phase transitions reported in literature$^{15}$. Figure 4(a) shows the DTA pattern for Sample 1. The first peak appears around 215°C which can be attributed to V→IV transition. The second peak corresponding to IV→III transition is observed at 230°C. The peak at 255°C corresponds to III→I transition. Similar peaks appear for pure sample prepared in similar way [Fig. 4(b)].
The X-ray pattern of this sample [Fig. 1(b)] matches with the orthorhombic phase with space group Fddd (ICDD 86-0803). Thus, it can be concluded that the Sample 1 is in phase V. The Cu$^+$ luminescence observed in this case is quite different compared to that for Sample 3. The emission is observed at 396 nm [Fig. 3(c)], 40 nm longer than that observed for Sample 3. The excitation is also shifted and is observed at 270 nm [Fig. 3(d)]. For rapidly quenched sample (Sample 2) the Cu$^+$ emission is observed around 419 nm [Fig. 3(e)] with the excitation at 245 nm [Fig. 3(f)]. This emission is very different from that observed for Sample 1 and Sample 2. When the XRD of this sample is examined, it can be clearly seen that it is qualitatively similar to what is described earlier [Fig. 1(a)] with the difference that intensity of lines for $(d = 3.5$ and $d = 2.8$ are in reverse order [Fig. 1(c)]. Such phase of Na$_2$SO$_4$ is reported in the ICDD database (ICDD 25-1111) but is not indexed. It is well reported in literature that the phase I can be stabilized by introducing divalent impurities inside lattice\cite{18}. One such reported phase is Na$_{1.90}$Zn$_{0.05}$SO$_4$, which is hexagonal in nature and reported in ICDD database (ICDD 29-1291). The XRD of Sample 4 could be identified with this phase with the space group P6$_3$mc and cited in literature, ICDD 29-1291 [Fig. 5(a)]. The Cu$^+$ luminescence in this phase is different from that observed for phase III. The emission is observed at 456 nm [Fig. 6(a)] with the excitation at 245 nm [Fig. 6(b)]. The emission band is broad compared to that observed for phase III with full width at half maxima equal to 82 nm. When Zn was replaced with Ca, the XRD pattern changes to monoclinically distorted hexagonal structure with the space group Cc [Fig. 5(b)]. This pattern is similar to that reported in the file ICDD 29-1196. The Cu$^+$ emission in this sample is double humped with maxima observed at
444 nm [Fig. 6(c)] and 357 nm. The excitation to this band is observed at 254 nm [Fig. 6(d)]. The emission is relatively weak compared to emissions discussed earlier. The significant changes in luminescence are observed for the different phases. The longest emission is observed in hexagonal phase and emission shifts to shorter side for orthogonal phase. Similar thing is observed in Ce doped $^{19}$CaSO$_4$. The shift of almost 100 nm is observed as sample goes from phase III to phase I. When phase I is distorted to monoclinic structure, shift of 12 nm is observed as compared to that of phase I. Thus, the small change in lattice amounts to significant change in luminescence.

Different PL spectra in various phases may be understood on the basis of the structural differences. Fig. 7 shows the lattice structure of Na$_2$SO$_4$ in phase V configuration. The structure is drawn using CIF file No. 100084. In this structure, two Na atoms along with sulphur ions form a dumbbell. Two oxygen atoms are attached to each Na atom. The Na-O bond length is 2.43 Å. From Fig. 7, it is very difficult to find exact coordination of Na atom but can be considered as distorted octrahedral configuration. Similar structure was constructed for phase III using atomic co-ordinates from Rasmussen paper. Figure 8 shows the two Na sites of which site Na$_1$ is octrahedrally co-ordinated with six oxygen atoms surrounding the Na atom. The Na-O bond length is 2.45 Å. The other Na ion (Na$_2$) along with sulphur and three oxygen ions form a tetrahedron. The Na$_1$ is surrounded by four such tetrahedra. Thus, the crystal field around Na$_1$ ion gets distorted due to these tetrahedra. Fig. 9 shows the structure for phase I. The atomic co-ordinates are taken from Naruse paper. The Na$_1$ is surrounded by six close equidistant O

![Fig. 7](image7.png)

![Fig. 8](image8.png)

![Fig. 9](image9.png)
atoms and thus in octahedral configuration. The immediate next surrounding are six equidistant tetrahedra. Thus, the crystal has strong distortion due to the presence of these tetrahedra. The Na₂ atom has four close, two intermediate and four rather distant O neighbours. Since the Sample 4 is stabilized phase using divalent Zn ions, some of the Na ions will be displaced by Zn ions with some vacancies. It has been found that in slowly cooled samples 94% of ions at site I are Na ions while only six per cent are occupied by substitute ions. The site II occupancy by Na ions is 85% whereas 15% by substitute ions.

Two Na sites exist in Na₂SO₄ and Cu⁺ ion is subjected to octahedral field with tetrahedral distortion. In octahedral field, the first excited state ¹D splits into levels ¹Eₕ and ¹T₂ₕ while the ¹D state splits ²g into ¹Eₕ and ¹T₂ₕ. The tetrahedral distortion further splits the ¹Eₕ state into two labeled as ¹Eₗ and ¹Eₗ⁺. Similar splitting occurs for ¹Eₗ state labeled as ¹Eₗ⁺, ¹Eₗ⁻ and ¹Eₗ⁻. The amount of splitting depends on the degree of distortion. It is, therefore, expected that in phase I, there is large splitting with the lowering of ¹Eₗ state and raising of ¹T₂ₕ state. This should shift the emission to the higher wavelength side and excitation to lower wavelength side. It is in fact observed that in hexagonal phase (phase I) the emission is at 456 nm, the longest, and excitation at 245 nm, the shortest among Na₂SO₄ phases studied in this work (Fig. 6). The excitation spectrum shows a shoulder at 256 nm. This corresponds to ¹A₁⁺⁻¹Eₗ transition.

The structure diagram for phase III shows that the Na ion is coordinated tetrahedrally with 4 oxygen ions. Thus, the crystal field is less distorted compared to phase I. This lowers the degree of splitting and therefore, compared to phase I, the emission is observed at shorter wavelengths while excitation at longer. Therefore, the emission is observed around 357 nm with the excitation at 258 nm. The excitation spectra for phase III consists of humps at 247 nm and 280 nm with the peak appearing at 258 nm. This corresponds to ¹A₁⁻¹T₂ₕ, ¹A₁⁻¹Eₗ and ¹A₁⁻¹Eₗ⁺ transitions, respectively.

The exact co-ordination for Na in phase V (Space group Fddd) is very difficult to determine as atomic arrangements are zigzag in nature. The field around Cu⁺ ion can be considered as mixed type and hence the splitting is expected intermediate to phase I and phase III. Therefore, the emission is observed at 396 nm with the excitation at 254 nm.

4 Conclusions

Various phases of Na₂SO₄ activated with Cu⁺ are synthesized. Excitation and emission spectra depend profoundly on the local symmetry of Cu⁺ (Table 1). Emission is at the shortest wavelength for phase III (orthorhombic Cmcm), and the longest for phase I (hexagonal P6₃ mc). From these results, it can be concluded that Cu⁺ luminescence changes according to phases of Na₂SO₄. Slight change in structure changes the luminescence significantly. Dependence of splitting of energy levels on the crystal field vis-à-vis co-ordination sphere can be studied using such measurements. Na₂SO₄ will prove to be a valuable host for such studies. Similar studies can be undertaken in Li₂SO₄ in which Cu emission is recently reported

References