

Luminescence of Cesium Thiocyanate (CsSCN) doped with Eu^{2+} ($\text{CsSCN}:\text{Eu}^{2+}$)

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Abstract:-Many host lattices have been investigated, as it is known that the effect of the host lattice in luminescence is complex, therefore this work seek to investigate Cesium Thiocyanate (CsSCN) as a suitable host lattice in luminescence. Cesium Thiocyanate is doped with Eu^{2+} and the Luminescence of the doped compound measured. CsSCN was prepared from $\text{Cd}(\text{SCN})_2$ and $\text{Ca}(\text{CO})_3$. The prepared CsSCN was then doped with 0.05% Eu^{2+} at 220°C . The Luminescence spectra of the $\text{CsSCN}:\text{Eu}^{2+}$ was measured using a D5000-diffractometer. The emission spectra obtained is broad with the maximum at 1980cm^{-1} . The spectra obtained were in agreement with typical thiocyanate spectra that were doped with Eu^{2+} . CsSCN can therefore be used as a host lattice with some minor problems of decomposition by products.

Key Words: Cesium Thiocyanate, Luminescence, Host lattice.

I. Introduction

The energy of luminescence of Eu^{2+} ions depends very strongly on the host lattice. Also increased covalence shifts the centre of gravity and therefore, shifts the lowest excited state to lower energy; that is why phosphors which emit in this low energy range are of considerable interest for the lamp industries. Many host lattices have been investigated such as oxides, chlorides and some pseudohalogens. But thiocyanates are receiving attention as host lattice only of recent, among them Strontium Thiocyanate ($\text{Sr}(\text{SCN})_2$) and Barium Thiocyanate ($\text{Ba}(\text{SCN})_2$) have been doped with Eu^{2+} and measured[1]. Most Thiocyanates have the cations coordinated to S or N, example is $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ [2] as such have similar environment towards the activator.

One outstanding feature of the $\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$ crystal structure is the coordination of the Ca^{2+} by four water molecules and four thiocyanate ions through S and N, in form of a distorted square antiprism. This environment which is typical of thiocyanates doped with Eu^{2+} makes them to produced very intense green emission at low temperature [2]. There are many thiocyanates known, Michel Fleck [3] made a detailed search of the literature in 2004 and claimed the literature revealed more than 80 inorganic thiocyanates. Table 1 gives some of these known thiocyanates and their crystal data, with priority given to the binary thiocyanates which are of interest in this work. Given the vase number of thiocyanates already known and with their properties relevant for the production of luminescence in the low energy range, more efforts should be made to investigate their luminescence properties as host lattice.

Table 1: Some known thiocyanates and their crystal parameters

S/N	Compound	Space group	Unit cell	Crystal system
1	NaSCN	PNCN	$a=4.047(1)$ $b=5.604(1)$ $c=13.279(2)$ $z=4$	Orthorhombic
2	CsSCN	Pnma	$a=7.978$ $b=6.332$ $c=8.332$ $z=4$	Orthorhombic
3	$\text{Ba}(\text{SCN})_2$	C12/C1	$a=10.188(2)$ $b=6.872(1)$ $c=8.522(1)$ $z=4$	Monoclinic
4	$\text{Ca}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$	Pnma	$a=12.8013(16)$ $b=7.9028(13)$ $c=7.2694(10)$ $z=4$	Orthorhombic
5	$\text{Ca}(\text{SCN})_2$	C12/C1	$a=9.6172(2)$ $b=6.4240(17)$ $c=7.8717(18)$ $z=4$	Monoclinic

Chemically speaking, thiocyanate is a salt of thiocyanic acid formed when alkaline cyanides are fused with sulphur. It is a pseudo-halogen, due to its similarity with halogen ions, for example it is a monovalent anion. The presence of sulphur and/or nitrogen in their coordination sphere makes the thiocyanates to be covalent, but compared to sulphides and nitrides they are less covalent [6]. Luminescence which is basically the science where light is emitted after absorption is measured with the help of spectrofluorometer. This consists mainly of a lamp, monochromator, sample holder, photomultiplier and a detector [7]. Because of the nature of its covalence, thiocyanates are considered to be very interesting new types of host lattice in luminescence.

In this work, CsSCN as a host lattice is studied using Fluorolog-3 spectrofluorometer, which consist of an excitation source, a sample module chamber, an emission spectrometer and a detector. Host lattices consist of cations combined with one of several different anions, hence have closed electron shells, and therefore are optically inactive. It is important that the host is optically transparent, for the absorption- excitation process to take place at the activator site. CsSCN seems to fulfil these conditions, therefore it is doped in this work with EU²⁺ and the emission and excitation measured.

II. Experimental Work

2.1 Preparation of Caesium Thiocyanate

To avoid the problem due to oxides in commercial compounds, CsSCN was prepared in the laboratory from Cd(SCN)₂ and Cs₂(CO)₃, by dissolving their stoichiometric ratio in distilled water, CdCO₃ precipitate out and was filtered. The CsSCN obtained in solution was evaporated slowly at 70°C to dryness. The X-Ray powder diffraction of the prepared CsSCN was measured and compared with the theoretical X-Ray pattern to ascertain its purity.

2.2 Doping of CsSCN with Eu²⁺

The melting point of CsSCN is 207°C [4], therefore CsSCN was doped using the melt method at a temperature of 220°C with 0.05% Eu²⁺. CsSCN was mixed with 0.05% Eu²⁺, which was then put in an oven and the oven heated slowly to reach the doping temperature. The doping temperature was maintained for one day to allow the Eu²⁺ to get doped into the host lattice. Because of the decomposition problems faced, attempt was made to dope it at lower temperature (200°C) to check the decomposition problems of the host lattice, CsSCN.

2.3 X-Ray Powder Diffraction

The X-ray powder diffraction was measured using a D5000-diffractometer from company Siemens (Karlsruhe) as depicted in fig. I. Fat and film were used in the sample holder preparations. CuK α 1 ($\lambda = 154\text{pm}$). Ge was used as irradiation source. The used detector was a PSD- 50M from company Braun (München). The sample was always grinded to fine powder. A small amount of the film was cut, put on one of the sample holder part and a very little amount of fat was applied before the sample was introduced to the film, after which the whole assembly were put into the big sample holder. The prepared sample holder was put into the diffractometer and the measurement run using a computer.



figure 1: X-Ray powder diffractometer (D5000)

2.4 Measurement of luminescence spectra of CsSCN:EU²⁺

The luminescence measurement was done using a Fluorolog-3 (FL3-22) spectrofluorometer from Jobin Yvon which is shown in fig. II below. This spectrofluorometer is equipped with a 450w xenon lamp, two double grated monochromators for emission and excitation. It also contains a photomultiplier with a photon counting system. The measurement procedure is as follows:- The cryostate was evacuated for about 15minutes and then floated with N₂ gas, then cooled down to 80K using liquid nitrogen cryostat, (model, VNF-100, Janis Research).

After cooling the heater was started and the sample intensity adjusted to obtain maximum intensity possible. The spectra were then measured using DATAMAX computer program and the obtained spectra drawn using a computer program called Origin. During measurement emission spectra was corrected for the photomultiplier sensitivity and excitation spectra corrected for the intensity of the excitation source. Three measurements of the luminescence were taken and the best used for this analysis.



Figure II: Fluorolog-3 (FL3-22)

III. Results and Discussion

X-ray diffraction spectroscopy lies in the range of 0.1 \AA to 25 \AA , this is within the range of interatomic distances, and therefore x-rays provides a convenient and practical means for the identification of crystalline compounds. X-ray diffraction pattern is normally unique for each crystalline substance, so if an exact match can be found between the pattern of the unknown and an authentic sample, chemical identity can be assumed [8]. CsSCN as the host lattice was successfully prepared and with the help of the theory of X-ray above, the X-Ray pattern of CsSCN was checked for purity. The X-ray powder diffraction shown below in fig III shows the peaks from the prepared CsSCN (above) which fit the theoretical pattern (below). CsSCN crystallised in an orthorhombic crystal system with Pnma space group [3], since the prepared CsSCN was compared with the theoretical X-Ray pattern and its fit, it must be pure crystals of the compound.

The luminescence spectra of CsSCN:Eu²⁺ measured are shown in fig IV. Three measurements were carried out and the best taken for this report. The emission spectrum has a maximum at 1980 cm^{-1} (505nm), which can be assigned to the f-d transition of Eu²⁺. The emission band is broad, not completely Gaussian, but rather nearly symmetrical with a steep drop on the high energy side. This is characteristics of Eu²⁺ doped thiocyanates as seen in Ca (SCN)₂·2H₂O:Eu²⁺ [5].

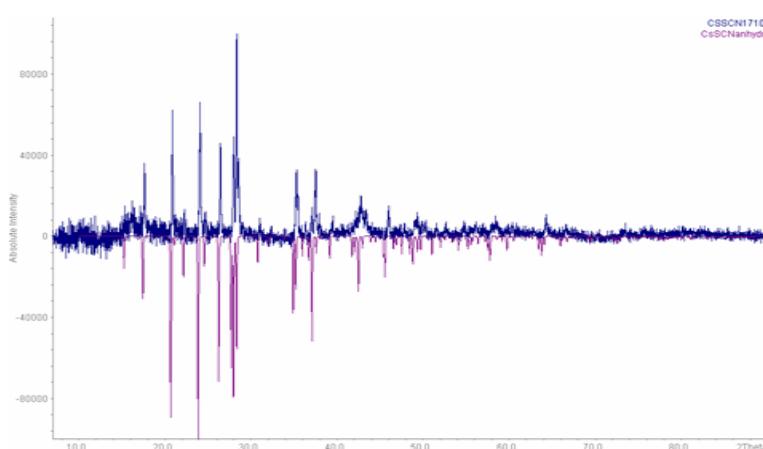


figure. III: X-Ray powder diffraction pattern of CsSCN.

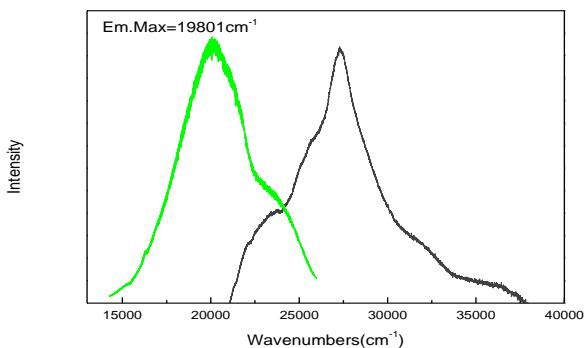


figure IV: Emission and Excitation Spectra of $\text{CsSCN}:\text{Eu}^{2+}$ Vex = 27397cm^{-1} , Vem = 20000cm^{-1}

At 23529cm^{-1} a thick peak can be seen on the emission spectra which may be due to some unresolved peaks. This can be due to some impurities in the doped compound. The doping temperature was 220°C but because thiocyanates are generally thermally unstable, therefore at this temperature, decomposition of the SCN could have taken place to some extent. Some of the impurities could be some decomposition products, such as Cs_2S . An attempt to dope it at 200°C gave similar results. The excitation spectrum is broad as expected for Eu^{2+} phosphors [9], but the shape could have been affected by the impurities observed in the emission.

$\text{CsSCN}:\text{Eu}^{2+}$ shows an intensive luminescence in the green spectral region at low temperature because of the energetically low lying $4f^65d^1$ state of Eu^{2+} . The emission spectra obtained in this work are all due to the f-d transitions of the Eu^{2+} ions. Apart from the band due to some impurities possibly from decomposition by-products as discussed above, only one band is observed for the $4f^65d^1 \rightarrow 4f^7$ transition of the Eu^{2+} . This shows that all Eu^{2+} ions occupy identical sites; this is expected since there is only one crystallographically distinct Cs ion.

The ligands (SCN) in this host lattice are covalent. It is known that for increasing covalence the interaction between the electrons is reduced since they spread out over wider orbital. Consequently, electronic transitions between energy levels with an energy difference which is determined by electron interaction shift to lower energy for increasing covalence (nephelauxetic effect). This effect shifts the centre of gravity to lower energy, hence shifting the lowest excited $5d(7F_0)$ state to lower energy. Since the excited d state depends very strongly on the host lattice, this emission is therefore influenced by the Cs^+ surrounding. Another factor that could lead to broadening of emission band is the nature of the substance used. This happens when powder is been handled, because external and internal surface are different. In this case the Eu^{2+} near the surface experience a covalence and a crystal field which differs from the bulk and can lead to spectra broadening. In this work the host lattice is crystal, hence the amount of covalence is the main factor of influence that lead to spectra broadening.

IV. Conclusion

Caesium Thiocyanate was successfully doped with Eu^{2+} using the melt method. The luminescence spectra of $\text{CsSCN}:\text{Eu}^{2+}$ was measured with the help of Fluorolog-3 (FL3-22) spectrofluorometer from Jobin Yvon. The measured spectra of $\text{CsSCN}:\text{Eu}^{2+}$ shows typical features of spectra from Thiocyanate doped with Eu^{2+} . Since Thiocyanate are generally known to be thermally unstable, the problem of decomposition by-products was observed in the spectra. Caesium Thiocyanate is therefore a good host lattice, but the small problem associated with decomposition by-products need to be addressed.

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