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Temperature Dependence Of $Ca(Scn)_2.2h_2o:Eu^{2+}$ Emission.

Bertha Abdu Danja[1]*
1(Fakultät 4 Inorganic Chemistry II University of Siegen, Germany) Department of Chemical Sciences, Faculty of Science, Federal University Kashere, Gombe – Nigeria.

Abstract: *Temperature dependence of luminescence of alkaline earth metal thiocyanantes doped with Eu^{2+} is measured in this work. In the early part of this research $Ca(SCN)_2 \cdot 2H_2O$ was doped with Eu^{2+} and the emission measured at 80K. The emission of $Ca(SCN)_2 \cdot 2H_2O$: Eu^{2+} are influenced by many factors, such as the crystal field, polarity, second coordination sphere, temperature, etc all these factors influence the energy of the f-d states, that is why this study seek to focus on the effect of temperature. To investigate the temperature effect, the emission spectra were measured at different temperatures from 80K to 240K using Fluorolg-3 (FL3-22) spectrofluorometer from Jobin Yvon. The measured spectra showed that there is an inverse linear relation between temperature and intensity of the emission.*

Keywords*: Luminescence, Thiocyanates, Emission, Temperature, alkaline earth metals*

I. Introduction

Luminescence is a term which describes a process in which energy is emitted from a material at a different wavelength from that at which it is absorbed. This implies that the luminescence centre can emit only when excitation energy is absorbed, to which many types of energy is known, e.g. photoluminescence by electromagnetic radiation, electroluminescence by an electric voltage, chemiluminescences by the energy of a chemical reaction, etc. In this work the energy absorbed and emitted is photoluminescence. For this energy to be absorbed and emitted an activator and a host lattice are needed. The 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. Temperature effect is important because luminescence process consist of the excitation energy being absorbed by the activator as already mentioned above and then the activator is raised to an excited state followed by return to the ground state with emission of radiation, but this competes with non-radiative return, this competition makes the effect of temperature in luminescence very important. The absorption and excitation can be explained in details using the configurational coordinate diagram showed in **fig** 1 which shows clearly the steps in absorption, excitation and relaxation. The activator used here is Eu^{2+} and the host lattice $Ca(SCN)_2 \cdot 2H_2O$, the emission spectra of this activator and host lattice have already been reported [1]. Thiocyanates as host lattice have also been studied in detail and reported [3] [4]. This work is focused on the temperature effects on the emission of $Ca(SCN)_2 \cdot 2H_2O$ as discussed above, the effect of temperature on the energy absorbed and emitted are studied here by measuring the emissions spectra at different temperatures.

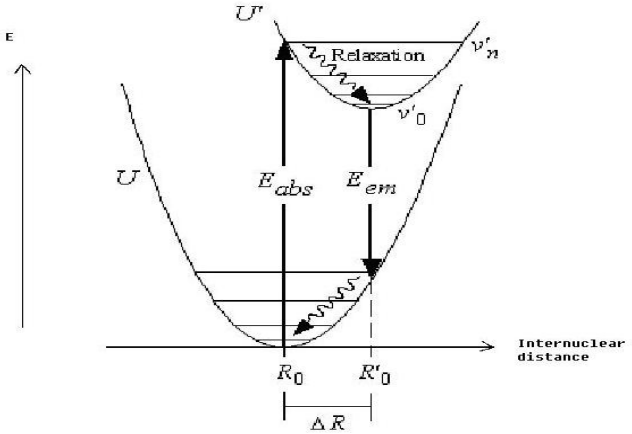

Fig 1; Configurational coordinate diagram for divalent lanthanides

II. Materials And Methods

The luminescence measurement was done using a Fluorolg-3 (FL3-22) spectrofluorometer from Jobin Yvon. 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 N_2 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 origin. During measurement emission spectra was corrected for the photomultiplier sensitivity and excitation spectra corrected for the intensity of the excitation source. The same procedures were followed with different temperatures, instead of cooling to 80K it was cooled to 100K, 120K, 140K, 160K, 180K and 200K and measurements taken.

III. Results And Discussion

The emission of $Ca(SCN)_2 \cdot 2H_2O:Eu^{2+}$ is strongly quenched with increasing temperatures. The emission spectra measured at different temperatures from 80K to 240K are given below in fig 2.

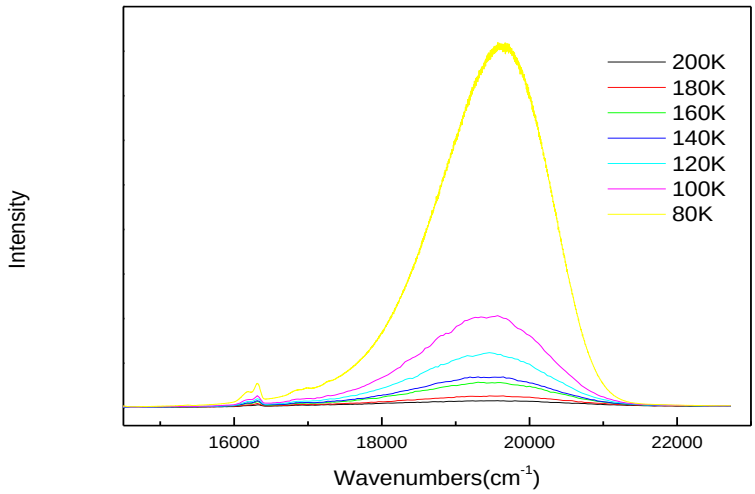

Fig. 2 Temperature dependence emission of $Ca(SCN)_2 \cdot 2H_2O:EU^{2+}$. V_{ex} = 25000cm^{-1}

The spectra above show that there is an inverse linear relation between the temperature and the intensity of the emission. That means the higher the temperature, the lower the intensity of the emission as can be seen clearly in fig 2. Figure 3 is a plot of relative intensity against temperature. At 100K the intensity was reduced to more than 50% of that at 80K. The drop between 80K and 100K is very sharp, indicating how strong the emission is quenched with temperature. An increase of 20K makes a great difference in the intensity.

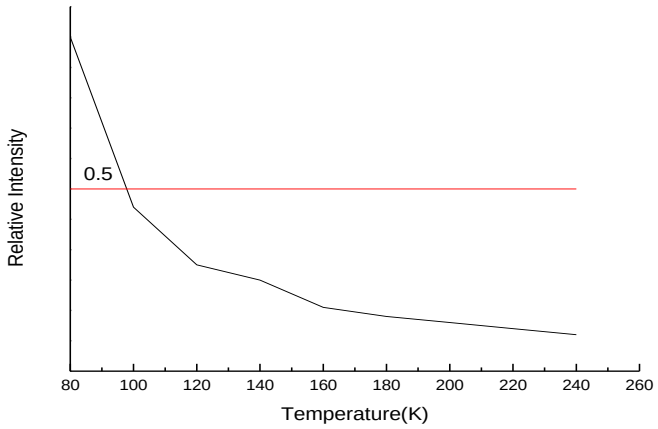

Fig. 3: Decay of emission of $Ca(SC)_2.2H_2O:Eu^{2+}$ with Temperature.

$Ca(SCN)_2 \cdot 2H_2O:Eu^{2+}$ shows an intensive luminescence in the green spectral region at low temperature because of the energetically low lying $4f^65d^1$ state as can be seen in fig 4 below, which has earlier

on been reported [1], but this green intensive luminescence is largely dependence on temperature. This reduction of emission intensity with temperature can be explained by the increase in non-radiative process in higher temperatures as explained in the introduction above. This is likely due to the proximate of the $4f^{6}5d^{1}$ states to the conduction band, therefore easily populated with temperature which leads to non-radiative return to ground state. Another observation that can be made is the increase in the full width with temperature. Which can be explained by the fact that the higher the temperature, the higher the occupation of the excited states, resulting into more transitions.

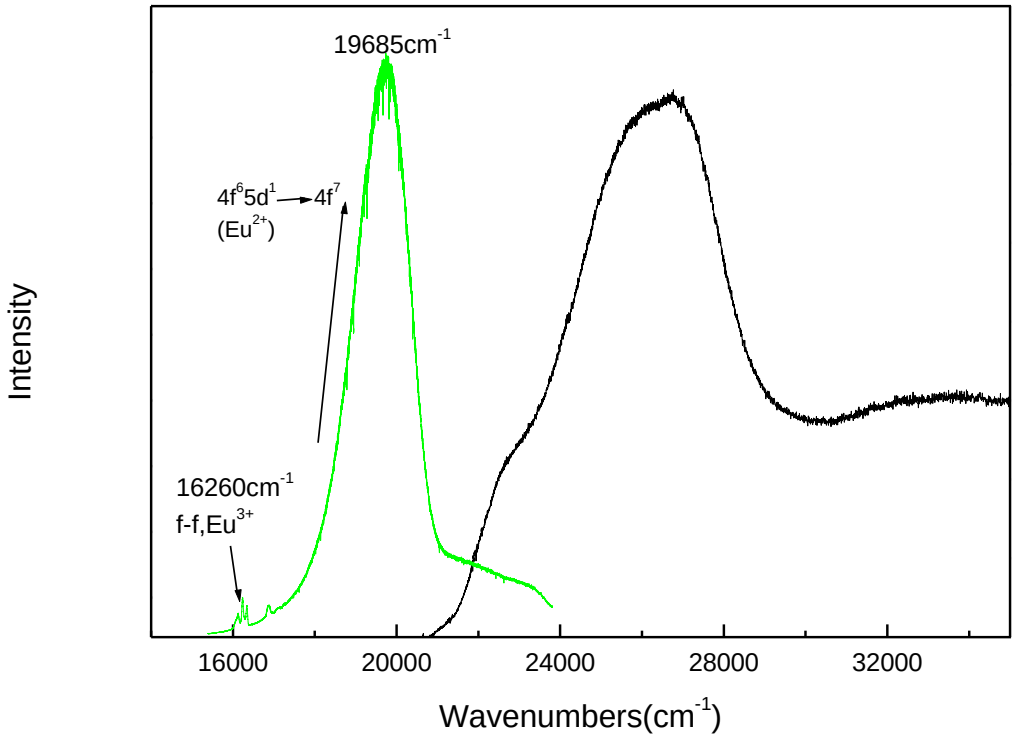

Fig 4: Emission and excitation Spectra of $Ca(SCN)_2 \cdot 2H_2O:Eu^{2+}$.
V_{ex} = 24390cm^{-1}, V_{em} = 19608cm^{-1}, T = 80K [1]

IV. Conclusions

From the results obtained as shown above, it can be concluded that the effect of temperature is very great, the inverse relation between temperature and the intensity of emission is outstanding. Therefore it is clear that the higher the temperature, the lower the intensity of emission. This is of importance to the lamb industries, as they make materials for lamps, the effect of temperature on the emission must be put to considerations.

References

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