



Short Communication

Spectroscopic study of Inner Transition metal Mn^{2+} ion in $CeSO_4Cl$ Phosphor

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Abstract

CeSO₄Cl: Mn phosphor is prepared by wet chemical method. The spectroscopic study and electronic states of Mn^{2+} are derived from excitation spectra for green-emitting $CeSO_4Cl: Mn$ phosphor and is found to give a spectrum consistent with linear symmetry in increasing intensity of Mn^{2+} ion. Mn^{2+} emission at 535 nm was observed in the present host due to ${}^4T_1 \rightarrow {}^6A_1$ transition. The emission spectra shows single peak having sharp shape and strong intensity at 535 nm. It can be used as a green phosphor.

Keywords: Inorganic material, wet chemical, photoluminescence, lamp phosphor, Transition metal.

Introduction

The luminescence properties of divalent manganese have been studied intensively and are used in many luminescent materials¹. Transition metal ions have an incompletely filled d-shell i.e. their electron configuration is d^n ($0 < n < 10$). The energy levels originating from such a configuration have been calculated by Tanabe and Sugano, taking the mutual interaction between the d-electron as well as the crystal field into account. The example is the d^5 configuration, of which Mn^{2+} , used in many luminescent materials, is a well-known representative. In fact the Mn^{2+} ion is practically colorless. However, Mn^{2+} compounds, like MnF_2 and $MnCl_2$, have a high rose colour. The presence of a transition metal (TM) impurity in an insulating material leads to the appearance of physicochemical properties which are absent in the pure host lattice and may be useful for applied devices such as solid-state lasers, storage phosphors, etc. Despite a doped material being certainly more complex than a pure one.

Mn^{2+} has the $3d^5$ configuration and from the Tanabe-Sugano diagram it follows that the ground level is 6A_1 . Emission arises from the 4T_1 (4G) level, which shifts to lower energies for higher crystal field strengths. All optical absorption transitions are parity and spin forbidden.

Generally, Mn^{2+} -activated phosphors are divided into two classes: those with green emission and those with orange-to-red emission. In octahedral surroundings with large crystal field the emission is usually red; in tetrahedral surroundings with a much smaller crystal field the emission is usually green. A well-known example belonging to the latter class is $ZnGa_2O_4: Mn^{2+}$. Another possibility to obtain a green Mn^{2+} emission is to choose a lattice in which Mn^{2+} is on a site, which is considerably larger than the Mn^{2+} radius. This requirement is met in compounds like $SrB_6O_{10}: Mn^{2+}$ in which the Mn^{2+} emission is at 512 nm². Also

$GdF_3: Mn^{2+}$ offers a large site for Mn^{2+} . If the Mn^{2+} ion is positioned on a regular Gd^{3+} site, it is surrounded by eight F- ions. The F- coordination resembles that of a twisted cube³. Lammer and Blasse⁴ reported for $GdF_3: Mn^{2+}$ emission with a maximum at 520 nm.

Rare earth impurity ions was extensively studied because of its high sensitivity and its ability to store the incident energy^{5,6} giving it suitability for radiation dosimetry. The material has been marketed as a commercial TL dosimeter, $CaF_2: Eu$, under the commercial name TLD-200. On the other hand, luminescence studies of SrF_2 and BaF_2 ⁷⁻¹⁰ doped with rare earths has received much less attention, despite their intense luminescence. For BaF_2 Lucas and Kapsar¹¹ studied the luminescence properties of $BaF_2: Eu$ and the possibility of using this material in radiation measurements. $CaF_2: Mn$ does not give any fluorescence under the UV excitation while $CaF_2: Ce$ gives a characteristic Ce^{3+} fluorescence emission with UV light excitation. The combination of Ce, Mn in the CaF_2 lattice however gives brilliant Mn^{2+} fluorescence emission in addition to that of Ce^{3+} on UV excitation due to energy transfer from Ce^{3+} to Mn^{2+} ions.

Material and Methods

$CeSO_4Cl$ (pure); and $CeSO_4Cl: Mn$ phosphors were prepared by a wet chemical method. $CeCl_3$ and $Ce_2(SO_4)_3$ of analar grade were taken in a stoichiometric ratio and dissolved separately in double distilled de-ionized water, resulting in a solution of $CeSO_4Cl$ (equation 1). Water-soluble sulphate salt of manganese was then added to the solution to obtain $CeSO_4Cl: Mn$. Confirming that no undissolved constituents were left behind and all the salts had completely dissolved in water and thus reacted.



The compounds CeSO_4Cl (pure) and $\text{CeSO}_4\text{Cl}:\text{Mn}$ in its powder form was obtained by evaporating on 80°C for 8 hours. The dried samples were then slowly cooled at room temperature. The resultant polycrystalline mass was crushed to fine particle in a crucible. The powder was used in further study. Formation of the compound was confirmed by taking the x-ray diffraction (XRD) pattern that matched with the standard data available. Formation of the compound was confirmed by taking the x-ray diffraction (XRD) pattern. The photoluminescence (PL) emission spectra of the samples were recorded using Fluorescence spectrometer (Hitachi F-4000). The same amount of sample was used in each case. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

Results and Discussion

Photoluminescence (PL) in $\text{CeSO}_4\text{Cl}:\text{Mn}$: Transition metal ions have been widely used in luminescent materials, e.g., Mn^{2+} , a transition metal center, has been doped into more than 500 inorganic hosts¹² for luminescence with emission range from 490 to 750 nm. According to reports, the $3d^5$ multiplet energies of Mn^{2+} in crystals depend largely on the covalency interaction with the host crystal or the crystal field, because the 3d electrons of the transition metal ions are the outermost electrons. The tetrahedral coordinated Mn^{2+} ion gives a green emission, while the octahedral coordinated Mn^{2+} ion exhibits an orange-to-red emission¹³.

Mn^{2+} emission at 535 nm was observed in the present host due to ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition. This corresponds to blue-green part of the visible spectrum. An excitation spectrum is peaking at 254 nm wavelength whereas Ce^{3+} contained in a host peaking an emission at 310 nm due to $5d \rightarrow 4f$ transition as shown in figure-2. Figure-3 shows emission spectrum with various contents of Mn^{2+} ions. In the figure the excitation spectrum (monitoring at 535 nm emission) has intense broad bands with maxima at 235 nm. Selecting 235 nm excitation wavelength, it was recorded the emission spectra for Mn doped ions in CeSO_4Cl host. The curves a, b, c, d, and e show the emission spectra for the same host with Mn a) 1, b) 0.5, c) 0.3, d) 0.2, and e) 0.1 mol.%, concentrations respectively. The emission spectra shows single peak having sharp shape and strong intensity at 535 nm (green emission). Figure-4 shows schematic Mn^{2+} energy level diagram in CeSO_4Cl host in which 535 nm emissions comes from ${}^4\text{T}_1$ to ${}^6\text{A}_1$ ground state excited at 254 nm.

Conclusion

The primary objective to present this paper is the development and implementation of inexpensive $\text{CeSO}_4\text{Cl}:\text{Mn}$ green emitting material for photoluminescence study. Mn^{2+} emission at 535 nm was observed at green region in the present host due to ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition excited at 254 nm. Here we report an investigation of $\text{CeSO}_4\text{Cl}:\text{Mn}$ material which have very low toxicity and cost, and can be prepared in open air atmosphere using simple wet chemical method. The $\text{CeSO}_4\text{Cl}:\text{Mn}$ phosphor may be used as a lamp phosphor.

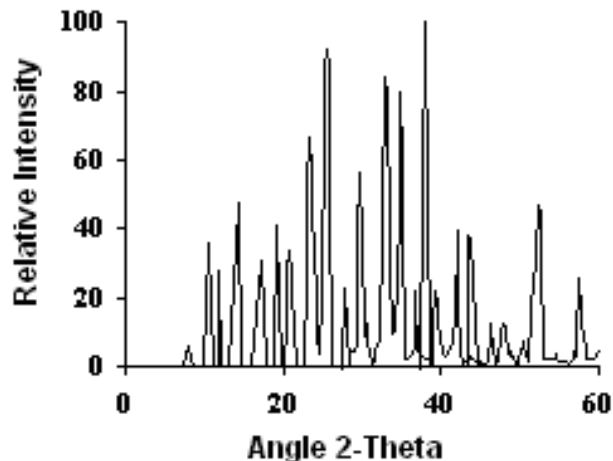


Figure-1
 XRD Pattern of CeSO_4Cl

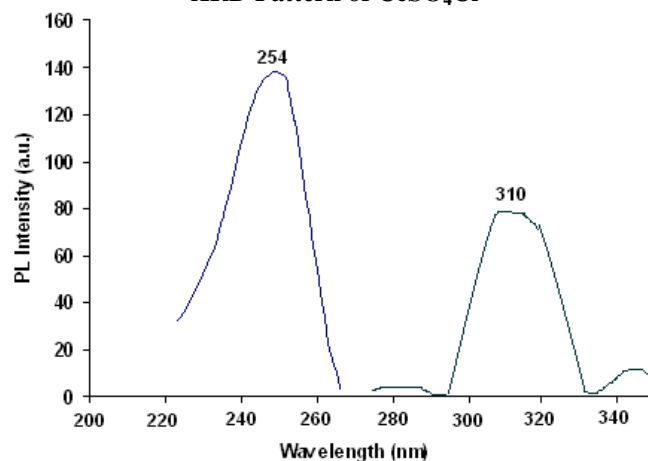


Figure-2
 PL excitation spectrum ($\lambda_{\text{exc}} = 254 \text{ nm}$) of $\text{CeSO}_4\text{Cl}:\text{Mn}_{0.1}$ mole%

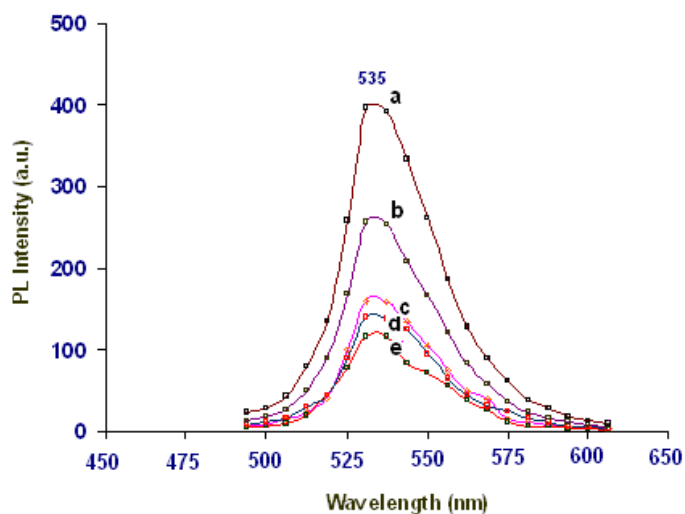


Figure-3
 PL emission spectra ($\lambda_{\text{emi}} = 535 \text{ nm}$) of $\text{CeSO}_4\text{Cl}:\text{Mn}$ a) 1, b) 0.5, c) 0.3, d) 0.2, e) 0.1 mol.%

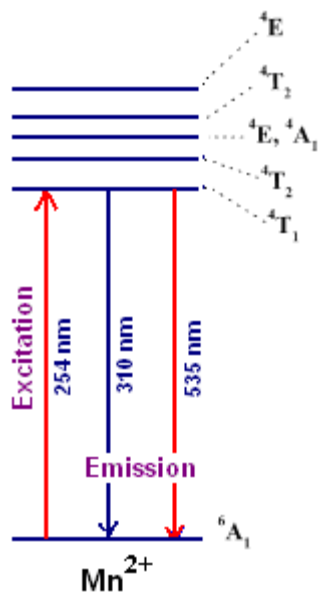


Figure-4
Schematic Mn²⁺ energy level system in CeSO₄Cl

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