Spectroscopic study of Inner Transition metal Mn\(^{2+}\) ion in CeSO\(_4\)Cl Phosphor

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Abstract

CeSO\(_4\)Cl: 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\(_4\)Cl: 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 materials\(^1\). 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 \(^4T_1\) (G) 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\(_2\)O\(_4\): 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\(_6\)O\(_{10}\): Mn\(^{2+}\) in which the Mn\(^{2+}\) emission is at 512 nm\(^2\). 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 cube\(^3\).

Lammer and Blass\(^4\) 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\(^3,6\) 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 Kapsar\(^11\) 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\(_4\)Cl (pure); and CeSO\(_4\)Cl: 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\(_4\)Cl (equation 1). Water-soluble sulphate salt of manganese was then added to the solution to obtain CeSO\(_4\)Cl: Mn.

Confirming that no undissolved constituents were left behind and all the salts had completely dissolved in water and thus reacted.

\[ \text{CeCl}_3 + \text{Ce}_2(\text{SO}_4)_3 \rightarrow 3\text{CeSO}_4\text{Cl} \]
The compounds CeSO$_4$Cl (pure) and CeSO$_4$Cl: 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 CeSO$_4$Cl: 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 hosts$^{12}$ for luminescence with emission range from 490 to 750 nm. According to reports, the 3d 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 emission$^{13}$.

Mn$^{2+}$ emission at 535 nm was observed in the present host due to $^4T_1 \rightarrow ^6A_1$ 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$_4$Cl 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$_4$Cl host in which 535 nm emissions comes from $^4T_1$ to $^6A_1$ ground state excited at 254 nm.

**Conclusion**

The primary objective to present this paper is the development and implementation of inexpensive CeSO$_4$Cl: Mn green emitting material for photoluminescence study. Mn$^{2+}$ emission at 535 nm was observed at green region in the present host due to $^4T_1 \rightarrow ^6A_1$ transition excited at 254 nm. Here we report an investigation of CeSO$_4$Cl: Mn material which have very low toxicity and cost, and can be prepared in open air atmosphere using simple wet chemical method. The CeSO$_4$Cl: Mn phosphor may be used as a lamp phosphor.
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References