Resonant energy transfer from $Ce^{3+} \rightarrow Dy^{3+}$ and Mn^{2+} in $NaZnSO_4Cl$ chlorosulphate phosphor

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A B S T R A C T

Newly prepared $NaZnSO_4Cl$ chlorosulphate material investigated by a wet chemical method was confirmed by the X-ray powder diffraction (XRD) pattern. Photoluminescence (PL) of $NaZnSO_4Cl:Ce^{3+}$ shows strong emission at 330 nm, and it is also efficient for $Ce^{3+} \rightarrow Dy^{3+}$ and $Ce^{3+} \rightarrow Mn^{2+}$ energy transfer for different concentrations. The Dy^{3+} emission by $Ce^{3+} \rightarrow Dy^{3+}$ under UV wavelength peaking at 473 nm and 573 nm for an excitation of 254 nm due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^6H_{13/2}$ transitions, whereas $Ce^{3+} \rightarrow Mn^{2+}$ is peaking at 515 nm due to $^4T_1 \rightarrow {}^6A_1$ transitions. In this phosphor the energy transfer takes place via the resonant process which is dependent on the concentration of the ions. The purpose of the present study is to develop and understand the photoluminescence and effect of Dy^{3+} or Mn^{2+} co-doping in $NaZnSO_4Cl:Ce^{3+}$ luminescent material, which can be used as a lamp phosphor.

1. Introduction

There are two different processes of energy transfer that are distinguishable from an experimental point of view, resonant and non-resonant [1]. The transfer via the resonant process depends on the concentration of the ions while the non-resonant case strongly depends on the structure of the crystal [2]. In the non-resonant case, when the excitation of the activator promotes it to the state with energy smaller than the portion emitted by the sensitizer, a phonon is emitted, and the energy conservation principle is satisfied [3–5]. In some of them the energy transfer processes are regarded as a resonance between two allowed non-radiative (virtual) electric dipole transitions; this is the common case observed in organic and inorganic systems. Through these two transitions the energy state of the sensitizer is lowered to elevate the activator, which after the excitation, radiates. This is the first step that has to be performed in order to sensitize the luminescence. There are also investigations devoted to the transition processes that result from the resonance of an allowed electric dipole transition in the sensitizer and forbidden transitions in the activator; this mechanism is observed in inorganic materials.

Energy transfer process is observed when there are two different ions in a matrix. We may excite one ion, the donor, and observe fluorescence from another ion, the acceptor. We shall discuss in this paper the energy transfer between ions in sulfate matrix. Rare earths are especially suitable for energy transfer studies because of their well-defined and narrow electronic levels, to which absorption occurs and from which fluorescence is observed.

In case of the rare earth, the transfer is a non-radiative one, i.e. no phonon will appear in the system, during the transfer. Forster [6,7] predicted that for the organic system, the rate of energy transfer is proportional to the overlap of the donor emission, and the acceptor absorption spectra. The discussion of Forster was extended by Dexter [8] for ions in inorganic crystals.

A new concept of energy transfer (ET) sensitization is developed, based on nearly resonant energy migration through a RE ion subsystem in the glass matrix, followed by a single-step transfer towards the emission centers created by Ce^{3+} or Tb^{3+} doping. Energy transfer between pairs of rare earth ions at dilution levels below the self-quenching limits has been known to take place generally through multipolar interaction like dipole–dipole interactions or dipole–quadrupole interactions [9–11]. The Ce^{3+} ion can be used as sensitizer as well as an activator, depending on the splitting of 5d excited levels by the crystal field symmetry. Much works have been done on the energy transfer from Ce^{3+} to different activator ions in different host lattices [12–15]. In recent years we have reported several phosphors on rare earth (RE) ions doped mixed sulfate [16–24] and showed how those ions can exist in different valence states, as result to irradiation, which can induce valence changes. It has been verified that under irradiation the doped ions in the crystal can cause defects easily and form

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color centers, the doped ions in the crystal act as trapping sites by capturing electrons or holes that are produced by irradiation, which change the chemical valence of doped ions.

In this paper, we report the synthesis of $NaZnSO_4Cl$ material by wet chemical technique and explain resonant energy transfer mechanism in $Ce^{3+} \rightarrow Dy^{3+}$ and $Ce^{3+} \rightarrow Mn^{2+}$ ions in $NaZnSO_4Cl$ sulfate phosphor. We have not aimed at the highest luminescence efficiency materials but the work shows that very efficient phosphor can be obtained by sensitizer Ce^{3+} ions on the basis of the Dy^{3+} or Mn^{2+} ions.

2. Experimental

$NaZnSO_4Cl$ (pure); $NaZnSO_4Cl$:Ce; $NaZnSO_4Cl$:Ce, Dy; and $NaZnSO_4Cl$:Ce, Mn phosphors were prepared by a wet chemical method. The constituents NaCl (99.99%) and $ZnSO_4$ (99.99%) were taken in a stoichimetric ratio and dissolved separately in double distilled deionized water, resulting in a solution of $NaZnSO_4Cl$. Water soluble sulfate salts of cerium (99.99%), and dysprosium (99.99%) or manganese (99.99%) were then added to the solution to obtain the $NaZnSO_4Cl$:Ce; $NaZnSO_4Cl$:Ce, Dy and $NaZnSO_4Cl$:Ce, Mn (here $MnSO_4 \cdot 2H_2O$ was taken as a sulfate salt of manganese).

The compounds in their powder form were obtained by evaporating on 80 °C for 8 h. The dried samples were then slowly cooled down to room temperature. The resultant polycrystalline mass was crushed to fine particle in a crucible. The pure compound was confirmed by taking the X-ray diffraction (XRD). The photoluminescence (PL) emission spectra of the samples were recorded using Fluorescence spectrometer (Shimadzu, RF 5301 PC). 2 g Sample was used in each case. The emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

3. Results and discussion

3.1. Ce^{3+} emission in $NaZnSO_4Cl$

Fig. 1 shows the X-ray diffraction (XRD) pattern of $NaZnSO_4Cl$ material. No JCPDS or ICDD file is available of this material. The XRD pattern did not indicate the presence of constituents $ZnSO_4$ or NaCl and other likely phases, which is an indirect evidence for the formation of the desired compound. These results indicate that the final product was formed in homogeneous form. Fig. 2 shows the photoluminescence (PL) excitation spectra of $NaZnSO_4Cl$:Ce^{3+} phosphor. A broad band is observed at around
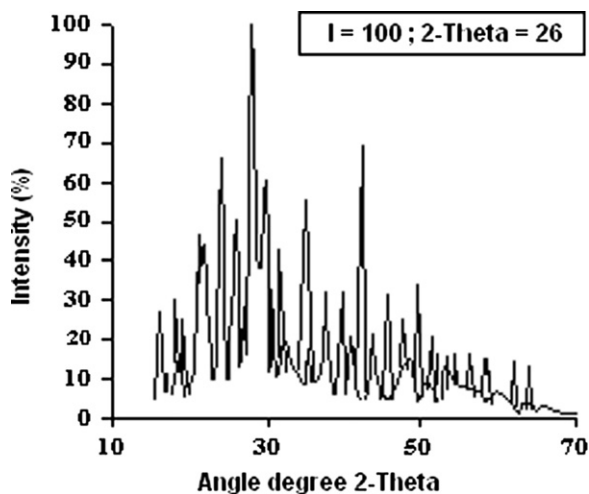
254 nm (λ_{em}=330 nm). Fig. 3 shows the PL emission spectra of Ce^{3+} ions in $NaZnSO_4Cl$ phosphors with different concentrations under the excitation 254 nm wavelengths of light. The peak is observed at 330 nm, which are assigned to the $5d \rightarrow 4f$ transition of Ce^{3+} ions. At higher concentrations of Ce^{3+} ion, an intensity of peaks also increases. This indicates a change of the surrounding of the Ce^{3+} ions at higher concentration in the $NaZnSO_4Cl$ lattice. For lower concentrations (0.1 mol%, 0.2 mol%, and 0.3 mol%) of Ce^{3+} the positions of peaks are slightly shifted toward shorter wavelength side i.e. 325 nm. With increasing concentration of Ce^{3+} ions intensity of peaks increases and relative intensity of 330 nm peaks also increases.

3.2. $Ce^{3+} \rightarrow Dy^{3+}$ energy transfer

Rare earths are especially suitable for energy transfer phenomenon because of their well-defined and narrow electronic levels to which absorption occurs and from which fluorescence is observed. Symbolically, energy transfer can be written as

$$2(S) \rightarrow 1(S) \rightarrow 1(A) \rightarrow 2(A) \text{ or } S* + A \rightarrow S + A*$$
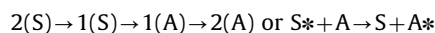
The donor system returns from an excited state 2(S) to the ground state 1(S) and the energy released is used to bring an
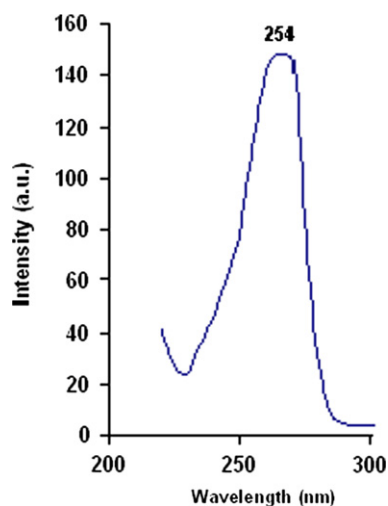
Fig. 2. Excitation spectra of $NaZnSO_4Cl$:$Ce_{1\ mol\%}$.
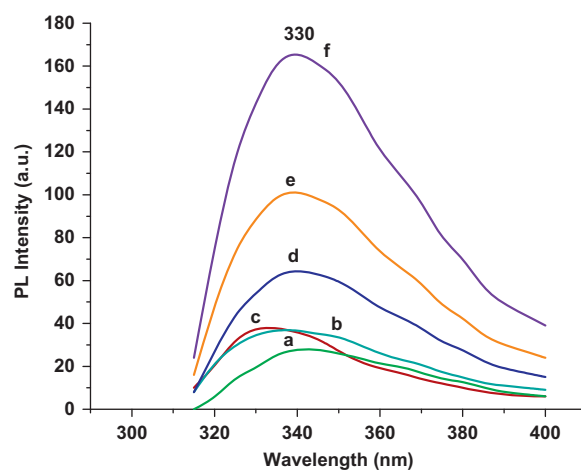
Fig. 1. XRD pattern of $NaZnSO_4Cl$.

Fig. 3. PL Emission spectra of $NaZnSO_4Cl$:Ce (a) 0.1 mol%. (b) 0.2 mol% (c) 0.3 mol% (d) 0.5 mol% (e) 1 mol% and (f) 5 mol% (for λ_{exci}=254 nm).