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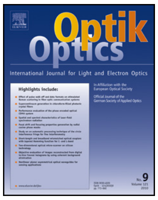

Mechano and photoluminescence spectra of cadmium sulphide and cadmium selenide doped phosphors

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ABSTRACT

The present paper deals with the mechanoluminescence and photoluminescence spectra of CdS and CdSe doped phosphors. It is found that PL spectra are similar to ML spectra of the phosphors within the limit of experimental errors. The activator concentration for which the PL intensity attains an optimum value is 1×10^{-3} and the ML intensity attains an optimum value for 4×10^{-3} concentrations. The PL spectra of CdSe:Mn, CdS:Au, CdS:Mn, CdS:Ag, and CdS:Cu phosphor have peak centered at 765 nm, 770 nm, 765 nm, 740 nm and 760 nm respectively at an activator concentration 4×10^{-3}. It is found that for a given phosphor the critical activator concentration for which the PL intensity attains an optimum value is always greater than that for the ML intensity. The mechanism of PL excitation and concentration quenching are discussed for the Cu, Mn, Ag and Au doped phosphors of CdS and CdSe. It is conclude that the centers which are responsible for PL emission should also be responsible for the ML emission.

1. Introduction

In the field of luminescence, spectroscopy has played an important role. It was believed in the beginning that the spectroscopy may be useful in ascertaining whether the ML emission is incandescent or gas discharge or it is a solid state luminescence from the excited state of the molecules comprising the crystals. However, ML intensity was very weak and of short duration. These reasons ruled out the use of congenital spectrograph for recording the ML spectra. The use of colored filters and the visual observation of color of the ML emission were the method initially adopted by some workers to understand the nature of ML [32,22,35,37].

The photograph of the ML spectra of few substances was taken by Longchambon [23] by giving exposures of many hours duration and by using a large amount of the materials.

The photograph of the ML spectra of a number of substances such as sphaletrite, colophane and artificial zinc sulphide has been taken by Nelson (1939) [25]. Since the present day devices were not available, the ML spectra of only a limited number of substances could be investigated earlier. The best devices for recording the ML spectra are monochrometor based spectrometer and images intensifier spectrometer.

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There are many unknown in the investigation of ML and it seems to be an extremely complex process. Nevertheless, much work has been done to interpret and understand the luminescence processes and to evaluate the nature of luminescent centers. It is useful to compare the ML emission properties with those of known emission processes such as photoluminescence (PL), in order to determine the emitting state in ML. PL is the phenomenon in which a material emits photon of wavelength when excited by electromagnetic radiation of certain other wavelength. PL spectrum provides useful information about the nature of luminescent and recombination centers. It is generally expected that the room temperature PL spectrum will correspond closely to that obtained from ML measurements. This indicates that identical excited electronic states are being populated in both the ML and PL, but by different mechanism. The four characteristics fundamentals to emission are energy, lifetime, quantum efficiency and polarization. Out of these, only the energy can be adequately compared in both ML and PL.

It is seen, generally that the spectral distribution of the emitted light as a function of energy (presented here as a function of the wavelength of the emitted light) is similar in samples which demonstrate both ML and PL. Although ML and PL occur at the same energies, there exist some differences in the relative intensities of the vibronic bands in the spectra. Koda et al. [18] have shown that large changes in the Franck- Condon factors can be induced by high pressure on the emitting molecule in ZnS phosphors. These changes could account for the differences observed in the ML and PL spectra of the molecules in mechanoluminescence while under stress.

Rothschild (1964) and Vav Gool [33] have investigated the emission bands of Cu, Ag, and Au in ZnS and CdS base phosphors. Avinor and Meiger [1] have observed the emission bands of CdSe activated by Ag, Cu and Au and co-activated with Aluminum at liquid nitrogen temperature. They reported that the band due to Ag activator was found to be completely quenched at the room temperature. The infrared emission spectra of new and already known phosphors in the region 1–3.5 μ are described. New phosphors include CdSe – Cu (1.2 μ), CdSe – HgS – Cu (1–1.75 μ), HgS (2.1 μ) and ZnS – Co (3.2 μ). The 2.6 μ band of PbS at 290 °K moves to 3.3 μ at 90 °K and 2.1 μ band for HgS at 290 °K. Garlick and Dumbleton [9], Grillot and Guintini [10] observed that the luminescence emission of CdS:Cu consists of a broad band from 0.7–1.4 μ. Analogies exist between the energy states due to copper and silver in CdS and those already known for ZnS.

The intensity and spectral distribution of CdS:Mn and CdS:Co crystals luminescence are studied at 4.2 K by Protsyuk and Rozhko [28]. The results are explained in an assumption that the pattern of the impurity arrangement in the crystal depend on the doping degree. The quenching effect of the impurity is due to change in the number of luminescence centers, energy transfer from excitons to the impurity and free carrier trapping in the impurity.

In the year 1990, Neukirch et al. [26] studied the luminescence of heavily doped, highly excited CdS:In crystals which exhibit a broad luminescence band in the region of the band gap energy. This band shifts to higher energies with increasing Indium concentration. The authors attribute this emission to non – k – conserving band to band transitions and compare the experimental data to theoretical calculations.

The nature of recombination centers in AgCl doped CdS phosphor was studied by Krustok et al. (1990). The intensity of photoluminescence emission bands in CdS:Ag:Cl depend on the added Ag(10 16–10 20 cm^{-1}) and Cl(10 16–10 19 cm^{-1}) concentration and the partial pressure of cadmium or sulphur is measured. It is shown that the intensity of photoluminescence band is a power function of the silver and chloride concentration and the partial pressure of components. The comparison between the experimental and theoretical curves permit one to determine the nature of the radiative and non-radiative recombination centers of Ag and Cl in CdS:Ag:Cl. This paper gives the PL and ML spectra of CdS and CdSe activated phosphor.

2. Determination of mechanoluminescence spectra

The ML is of a very short duration i.e. about a few miles- second and of low intensity. In 1969, Belyaev and Martyshev [2], used system based on two photomultipliers—one recording the luminescence directly and the other recording the luminescence via a monochromator. However, these suffer from the disadvantage that it is difficult to ensure that both photomultipliers record exactly the same proportion of ML in each and every stage and that the bulk of the light entering the monochromator at any one wavelength setting is absorbed within the instrument. Chapman and Walton [5] removed both disadvantages by using the image intensifier spectrograph. In this they used a four stage image intensifier (EMI type 9912) s20 photocathode. The output of the intensifier is photographed with a conventional 35 mm format camera and the developed film is microdensitometer. When a 600 mm^{-1} grating is used the spectrograph has an effective resolution of around 0.75 nm and disperses a spectrum from 400 nm to 800 nm approximately, across the input photocathode at a single grating setting.

Here we have used impulsive exciting device which had an arrangement for band- pass filters [3,11].

3. Experimental procedure

The phosphors used in the present investigation were crystallites of an average grain size 10 μm. The phosphor (20 mg) was placed on the Lucite plate of the device reported in previous publications [47–53]. The phosphor was covered with an adhesive tape. This technique eliminates the error in the ML intensity measurement due to the scattering of the fragments during the impact of the load on the phosphor. The ML in phosphor was excited impulsively using a load of weight 800 kg which was dropped with a velocity of 314 cm/sec. The ML emission received by the photomultiplier tube was fed to the digital storage oscilloscope. At least four independent observations were taken for a particular observation. The error in the ML intensity measurement was +8%. All the measurement was done inside a dark room. When the specimen of small-sectional