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Journal of Alloys and Compounds 300–301 (2000) 230–233

Journal of ALLOYS AND COMPOUNDS

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Spectroscopic studies of samarium doped CdF_2 crystal

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Abstract

Absorption and emission spectra of CdF_2:0.5% SmF_3 crystal were investigated. The emission spectra were studied in the temperature range 6–300 K. It has been demonstrated that apart from the narrow f–f transitions of the Sm^{3+} ion there appears a broad band emission whose nature is briefly discussed.

Keywords: Samarium-doped CdF_2; Spectroscopy

1. Introduction

An interest in studying the optical properties of samarium ions in CdF_2 crystal has been associated with the discovery of laser emission in 1961 by Kaiser, Garret and Wood [1] and in principle with the more important effect of conductivity due to free electrons by Kingsley and Prener [2]. This crystal doped with lanthanide ions demonstrates also an efficient electro-luminescence discovered by Langer et al. [3]. As known the Ln^{3+} ions in CdF_2 crystal may substitute different crystallographic sites. It may lead to different spectroscopic behaviour.

In this paper we present the absorption and emission spectra of samarium doped CdF_2. We have found that the crystal demonstrates the broad band emission after exciting in UV region with 275 and 308 nm lines. The nature of broad band emission is discussed.

2. Experimental

Absorption spectra were measured at room temperature on a Cary Varian 5 spectrophotometer. Emission spectra were measured by means of a GDM 1000 spectrometer (C. Zeiss Jena) with an argon laser as excitation and with TRW 1000 spectrophotometer (JobinYvon) with an excimer laser as excitation. The crystal was kindly supplied by Dr. G. Denisenko from the Institute of Crystallography of the Russian Academy of Sciences, Moscow.

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3. Results and discussion

Absorption spectrum of samarium doped CdF_2 crystal is shown in Fig. 1. The assignment of Sm^{3+} transitions is given in the figure. It is interesting to note that apart from the f–f transitions associated with the Sm^{3+} ion there are evident features at 550, 590 and 620 nm. Their origin may be most probably assigned to the Sm^{2+} ions.

The sample was then annealed for 20 h at 200°C. Its absorption spectrum is shown in this same figure. It is important to note that the absorption bands combined with OH groups at 2900 nm were significantly reduced. In result all the band 2850–3200 nm is reduced.

The emission spectra of samarium doped CdF_2 crystal measured after exciting 488 nm of argon laser in a temperature range 6–300 K are shown in Fig. 2. The observed narrow bands are assigned to the $^4G_{5/2}-^6F_J$, where $J=5/2$, $7/2$, $9/2$ and $11/2$ located around 570, 600, 650, and 710 nm, respectively.

The temperature dependence of the integrated emission intensities is shown in Fig. 3. The results show that the emission intensities increase with increasing temperature. This increase is most probably associated with the increase of thermal population of the $^4G_{5/2}$ term. It points also to a negligible small channel of nonradiative relaxation of the $^4G_{5/2}$ state.

In the course of our emission measurements we have used different excitation lines. We have found that we could not observe the Sm^{3+} emission after excitation with 275 nm. This line does not excite directly Sm^{3+} ion as may be revealed from absorption spectrum (see Fig. 1). In

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PII: S0925-8388(99)00775-6

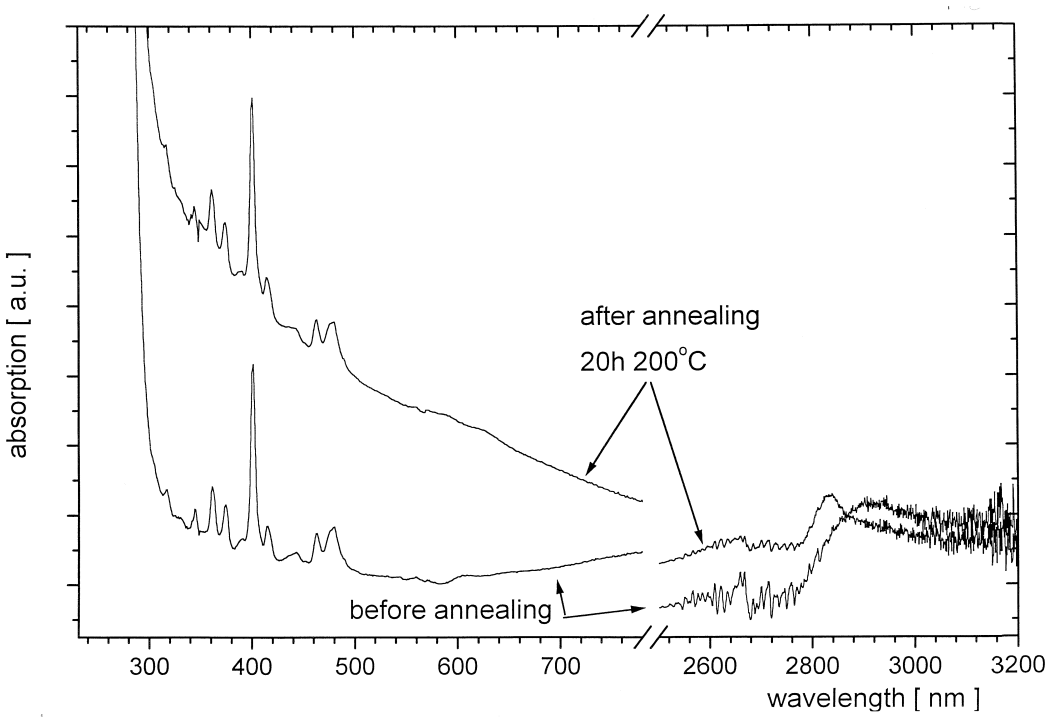

Fig. 1. Absorption spectra of CdF_2:0.5% SmF_3 crystal measured at 300 K.

spite of this a broad band centred at 580 nm appeared at room temperature (see Fig. 4). It was unhomogenously broadened and consisted of two different bands. We have found that when the sample was excited with a more focused beam the band maximum was observed at 560 nm. For less intensity the maximum was shifted to 500 nm. This observation needs further studies to explain the nature of such behaviour. We have measured also the emission spectra by pumping with a 308 nm line of excimer laser (see Fig. 5). This line also does not excite directly the

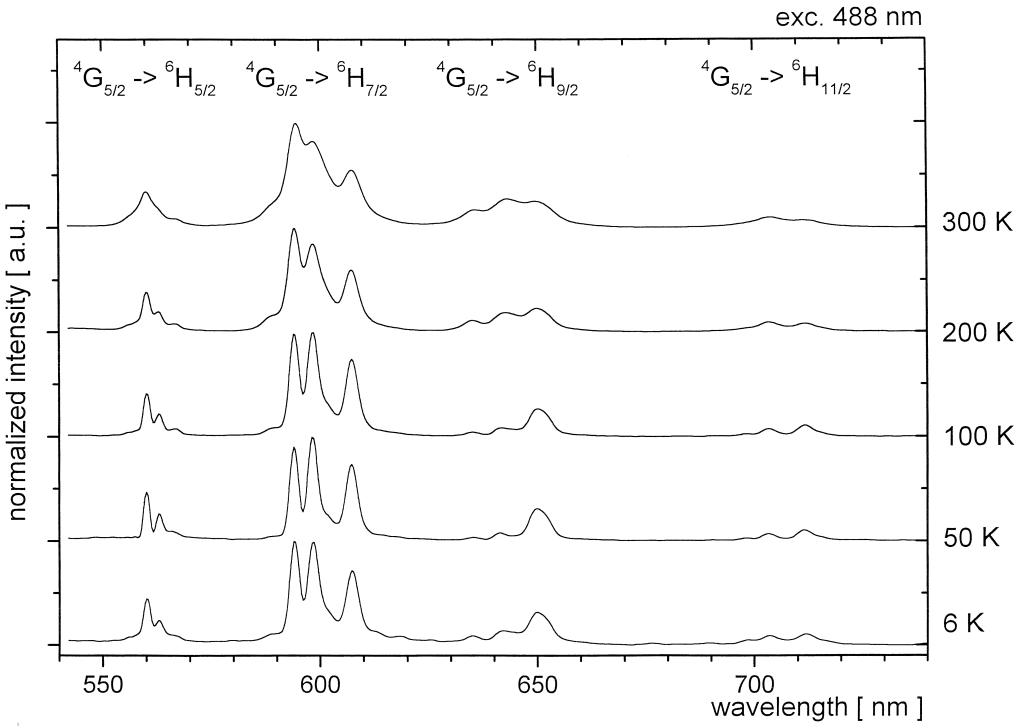

Fig. 2. Emission spectra of CdF_2:SmF_3 crystal measured at the temperature range 6–300 K.

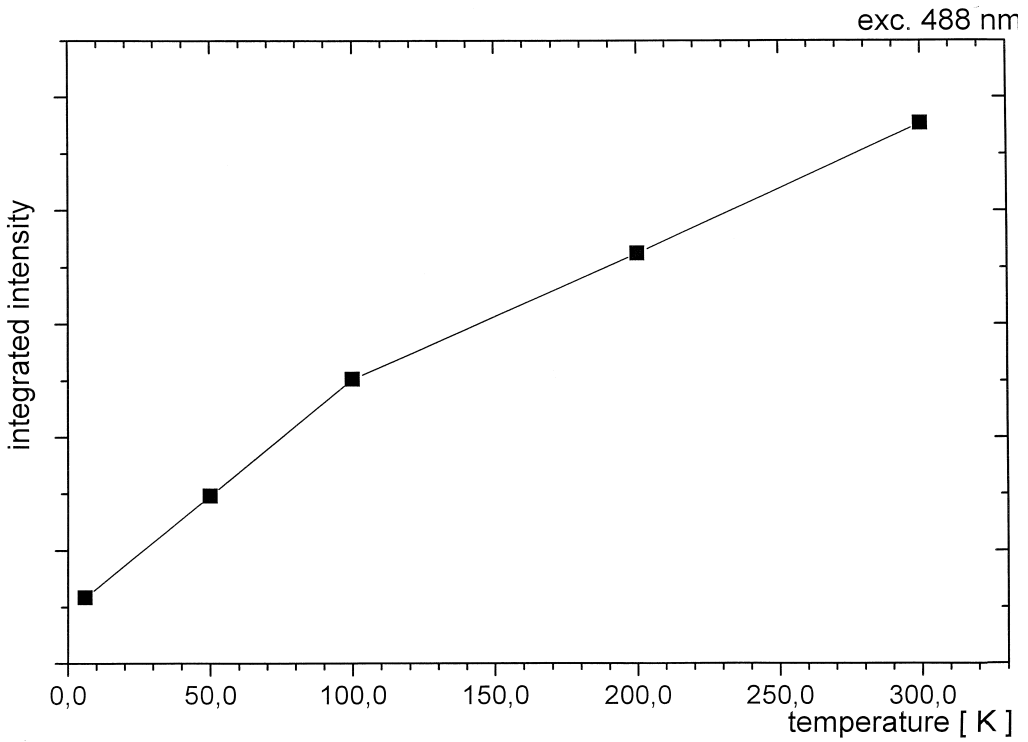

Fig. 3. Temperature dependence of integrated emission intensity of the $^4G_{5/2}$–^6F_J (J=5/2, 7/2, 9/2, 11/2) transition in CdF_2:SmF_3 crystal.

Sm^{3+} bands. We have observed also the broad band emission with the maximum around 610 nm, however the overall spectrum was drastically different. It was much broader ranging from 350 up to 800 nm. It is interesting to note that at 400 nm there appeared a hole. Its position corresponds energetically to the $^4L_{13/2}$ absorption bands of Sm^{3+}. So we can conclude that the hole is due to the self absorption in the crystal.

The broad band we observed is similar to the emission spectrum of Eu^{2+} ions [4]. So the question is – are Sm^{2+}

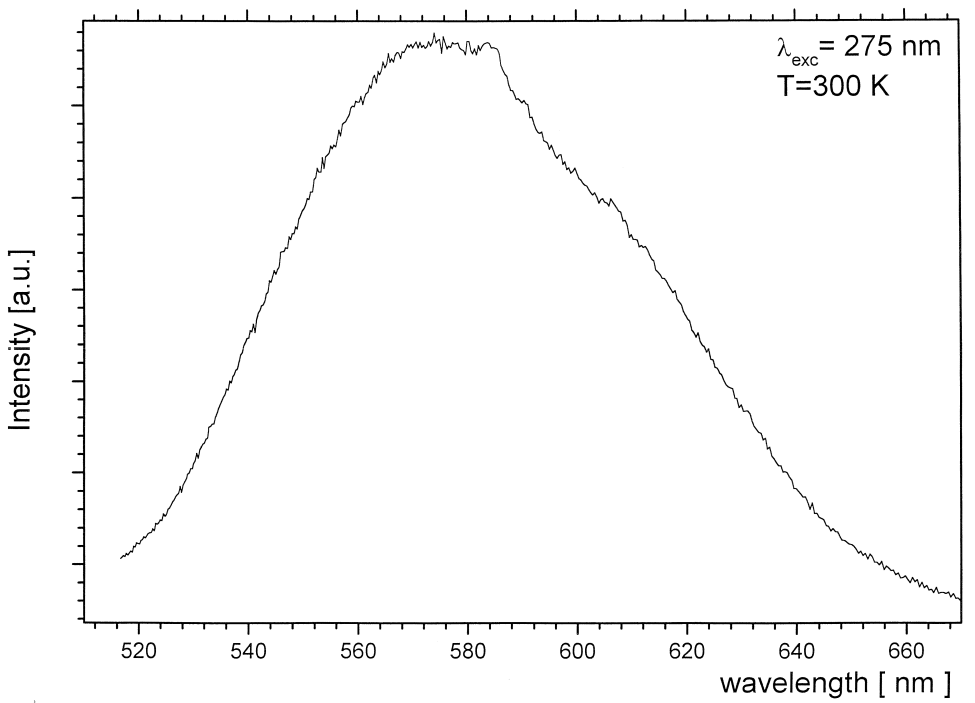

Fig. 4. Emission spectrum of CdF_2:SmF_3 crystal measured at 300 K under 275 nm excitation line of argon laser.

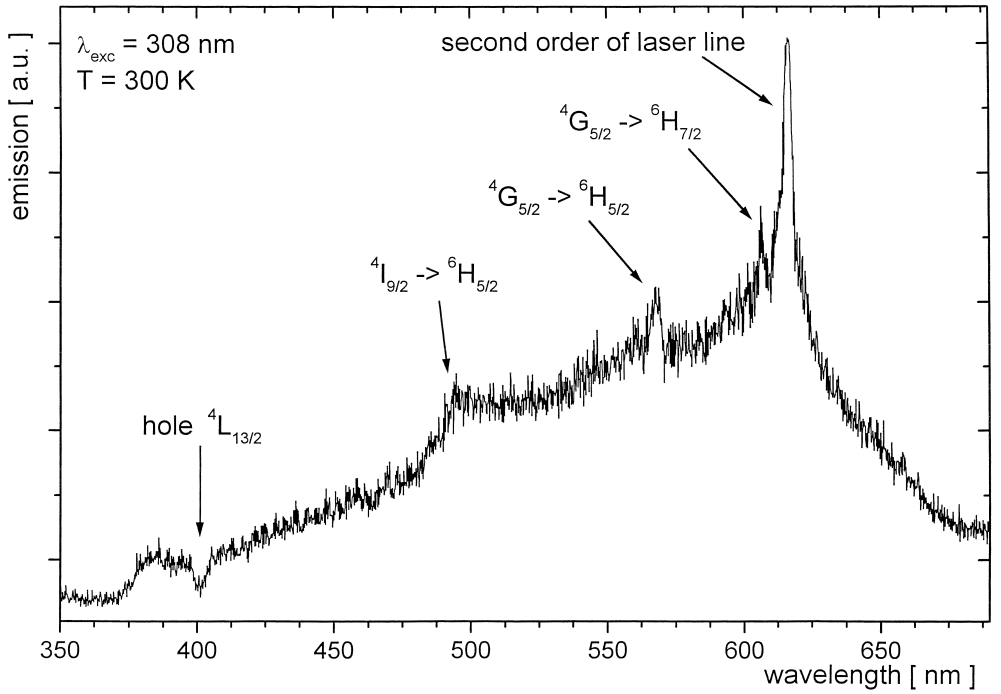

Fig. 5. Emission spectrum of CdF_2:SmF_3 crystal measured at 300 K under a 308 nm excitation line of excimer laser.

ions responsible for broad band emission because among rare earth ions samarium is also very often incorporated in different hosts as divalent ion? However as known [5,6] Sm^{2+} ions should demonstrate sharp emission lines assigned to the f–f transitions in the near IR region. Moreover they are also expected to be more intense [7] than those resulting from the Sm^{3+} ions. We did not observe such emission lines. So we can conclude that there are no Sm^{2+} ions in the CdF_2 crystal under investigation and we suppose that the origin of the broad band emission is rather due to some impurities present therein, probably with the OH^- groups.

In conclusion, we have reported the absorption and emission spectra of samarium doped CdF_2 crystal. We have found that apart from the emission lines assigned to the Sm^{3+} ion there appeared a broad band emission centred around 560 nm whose origin is not associated with Sm^{2+} but rather with some impurities present in the crystal.

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