Journal of Luminescence 55 (1993) 187–191
North-Holland

JOURNAL OF
LUMINESCENCE

Spectra of magnetic circular dichroism of absorption and luminescence of Eu-doped CaS single crystals

Satoru Kijima[a], Katsuaki Sato[a], and Takao Koda[b]

[a] *Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan*
[b] *Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan*

Received 27 November 1992
Revised 25 January 1993
Accepted 17 February 1993

Fine structures on the absorption and emission bands due to the f–d transition between the ground state $4f^7(^8S_{7/2})$ and the excited state $4f^6(^7F_J)5d$ in the Eu^{2+} ion have been observed through measurements of magnetic circular dichroism of absorption and photoluminescence for Eu-doped single crystals of CaS at 20 K. The fine structures consist of zero-phonon lines and phonon side lines. The energies of phonons involved were determined as 20.9 and 33.3 meV in absorption, and 21.5 and 34.5 meV in emission, which are explained in terms of TO- and LO-phonons pseudolocalized at Eu–S.

1. Introduction

Recently, Eu-doped CaS (CaS:Eu) has been widely studied as a material for high quality red-emitting electroluminescence devices [1]. However, most of previous optical research has been done on thin films [2], which suffer from various problems due to the polycrystalline nature of the materials. Only a few fundamental studies have been reported on well-defined single crystals [3]. The reason is because the alkaline–earth chalcogenides such as CaS are chemically unstable and quite refractory with a melting temperature exceeding 2000° C, which makes the crystal growth quite difficult. Growth of single crystals with a good quality has been required for basic investigation of the optical properties inherent to CaS.

For this purpose Kaneko et al. [4] succeeded in obtaining single crystals of alkaline–earth chalcogenides (CaS, SrS, etc.) by the floating-zone (FZ) method using a Xe-arc image furnace. Single crystals thus obtained were sufficiently pure and large for reliable studies on their optical properties. They reported various optical studies including photoluminescence for undoped crystals of CaS, etc.

The bulk phonon energies in undoped CaS have been determined by Kaneko et al. [4] and Drofenik et al. [5]. Some detailed analyses on the photoluminescence and absorption properties of Eu-doped CaS have been also carried out by other investigators [6–8]. Nakao [6] reported pseudo-localized phonon energy (33.5 meV) in the vicinity of Eu^{2+} ion in CaS.

Magnetic circular dichroism (MCD) spectroscopy has provided much information on the electronic structures in transition metal atoms doped in semiconductors and insulators [9–11]. For example MCD of absorption (MCDA) and MCD of photoluminescence (MCDPL) for single crystal of ruby ($Al_2O_3:Cr$) gave new information on localized electronic states of Cr^{3+} [10].

Detailed MCDA spectra of Eu^{2+} ions have been reported by Weakliem [12] for $CaF_2:Eu^{2+}$, in which the Eu^{2+} ion is surrounded by a hexahedron of F ions. On the other hand, the Eu^{2+} ion in CaS:Eu is surrounded by the octahedron of S ions

Correspondence to: Dr. K. Sato, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan. Telefax: + 81-423 85 5395.

0022-2313/93/$06.00 © 1993 – Elsevier Science Publishers B.V. All rights reserved

making the detailed splittings of energy levels slightly different from those of $CaF_2 \cdot Eu^{2+}$.

We measured spectra of optical absorption (ABS) and photoluminescence (PL) for CaS:Eu single crystals obtained by the FZ technique, at 20 K and at room temperature. Moreover, we obtained MCD absorption (MCDA) and MCD photoluminescence (MCDPL) spectra to obtain further insight into the localized electronic structure.

2. Experiment

The single crystal of CaS:Eu (0.1 mol%) was grown by the FZ technique using a Xe-arc image furnace at University of Tokyo. The crystal was grown along one of the ⟨100⟩ axis of the FCC structure. The sample was cut along one of the {100} planes of the crystal. The sample size was about 5 mm in diameter and about 2–3 mm in thickness.

The sample was attached to the cold finger of the He-refrigerator cryostat which was set between the pole-pieces of an electromagnet with a perforation at the center of the pole-pieces (JASCO MCD-1BS type) and cooled down to 20 K. One of the ⟨100⟩ axis of the sample was set along the optical path and the magnetic field was applied parallel to the optical path. The maximum field applied was 1.2 T.

For ABS and MCDA measurements, the light from a Xe-lamp (150 W) was dispersed by a JASCO CT-50C monochromator (focal length of 50 cm) with a 1200 groove/mm grating blazed at 500 nm and focused on the crystal. The transmitted light was detected by a Hamamatsu R636 photomultiplier. For PL and MCDPL measurements, the sample attached on the cryostat was irradiated at 514 nm using an Ar^+ ion laser (100 mW) as an excitation source. The emitted light was dispersed by the JASCO CT-50C monochromator, and was detected by the Hamamatsu R636 photomultiplier. The resolution of MCD measurements was approximately 0.3 meV.

For MCD measurements the polarization of light was modulated by using a photoelastic modulator (PEM) (Hinds International PEM-CF3). Details of MCDA and MCDPL measurements are described in ref. [10].

3. Results and discussions

Optical absorption (ABS) spectra at room temperature and at 20 K are shown in fig. 1. At room temperature, no fine structure was observed, whereas, at 20 K, a fine structure appeared on the ABS spectrum. This band has been assigned to the absorption due to the f–d transition from the ground state $4f^7(^8S_{7/2})$ to the excited state $4f^6(^7F_J)5d$ of the Eu^{2+} ion. The strongest line is observed at 1.9808 eV (labeled as "3" in fig. 1 and table 1), which will be assigned to the zero-phonon line (ZPL) of the f–d electronic transition based on the photoluminescence spectra.

MCDA measurements were carried out for three magnitudes of the applied field, 0.5, 1.0 and 1.2 T. The intensity of MCDA peak was found to be approximately proportional to the applied field and the profile was almost unchanged for different fields. Fig. 2 shows the MCD spectrum of absorption (MCDA) at 20 K in the magnetic field of 1.2 T. Fine structure was observed on the absorption band corresponding to the f–d transition of Eu^{2+} ion. The MCDA line shape for each absorption line was of the dispersion-type with an asymmetrical line shape. Each line consists of a negative peak (absolute value I_-) and a positive peak (absolute value I_+) with an energy separation of nearly 1 meV. The ratio of I_+/I_- deviates from unity. Especially, the strongest signal due to the ZPL at

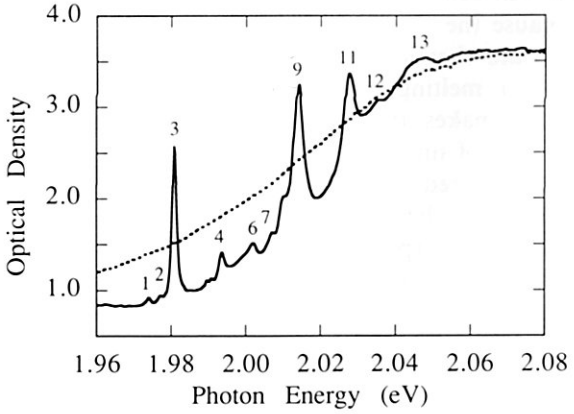

Fig. 1. Optical absorption spectra for Eu-doped CaS, at 20 K (solid line) and at room temperature (broken line).

Table 1
Energies of emission and absorption lines related to the f–d transition of Eu^{2+} ion in CaS. Underlined values represent strong absorption and emission lines. Asterisks (*) represent weak lines observed in MCDA and MCDPL spectra, the energies being determined from those of positive peaks of MCDA and MCDPL with an uncertainty of ± 0.15 meV

	Emitted line [eV]	Energy difference [meV]		Absorption line [eV]	Energy difference [meV]	
N	1.8737					
M	1.8937					
L	1.9118		62.7			
K	1.9192 *	58.5				
J	1.9261	54.7				
I	(1.94)		(34.5)			
H	1.9430	34.7				
G	1.9466	34.2				
F	1.9528 *		21.7			
E	1.9561 *	21.6				
D	1.9595	21.3				
C	1.9745 *		0	1 1.9739		0
B	1.9777 *	0		2 1.9774	0	
A	1.9808	0		3 1.9808	0	
				4 1.9936		19.7
				5 (2.00)	(22)	
				6 2.0019	21.1	
				7 2.0071		33.2
				8 2.0110*	33.6	
				9 2.0140	33.2	
				10 2.0275*		53.6
				11 2.0295	52.1	
				12 2.0361	55.3	
				13 2.0479	67.1	

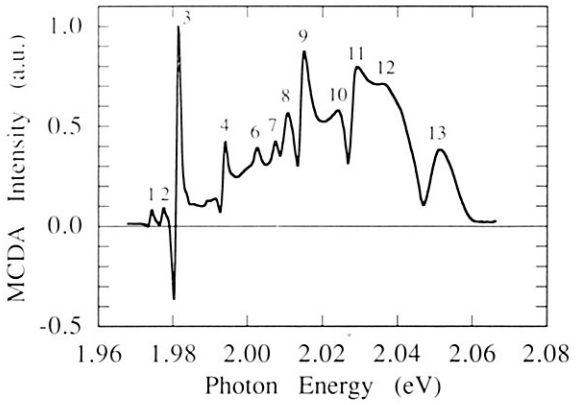

Fig. 2. Magnetic circular dichroism spectrum of absorption for Eu-doped CaS at 20 K in the magnetic field of 1.2 T.

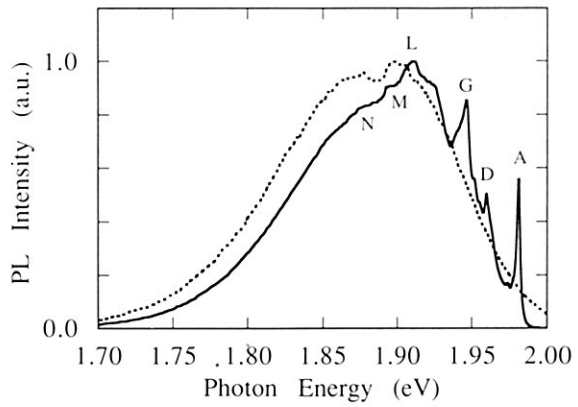

Fig. 3. Photoluminescence spectra for Eu-doped CaS, at 20 K (solid line) and at room temperature (broken line).

1.9808 eV has a prominent zero-crossing dispersion line shape with $I_+/I_- = 8/3$. The dominance of the transition for right circular polarization (RCP) was observed over the entire absorption band of f–d transition. Weak lines at 1.9739, 1.9774 and 2.0110 eV (denoted as 1, 2 and 8, respectively, in fig. 2), which are difficult to resolve in usual absorption measurements due to overlap of strong neighboring lines, become clearly observed in the MCDA spectrum.

Photoluminescence (PL) spectra at room temperature and at 20 K are shown in fig. 3. At room temperature, the PL spectrum is composed of a broad band peaking at about 1.90 eV. This band has been assigned to the d–f transition from the excited state $4f^6(^7F_J)5d$ to the ground state $4f^7(^8S_{7/2})$ of the Eu^{2+} ion. At 20 K, the peak position moves to higher energies by nearly 14 meV, and several emission lines appear on the broad emission band, with peak positions at 1.9808, 1.9595, 1.9466 and 1.9118 eV (denoted as A, D, G and L, respectively, in fig. 3 and table 1). The line A can be assigned to the ZPL, since it is observed at the same energy position as line 3 in the absorption spectrum.

Fig. 4 shows the MCD spectrum of photoluminescence (MCDPL) at 20 K in the magnetic

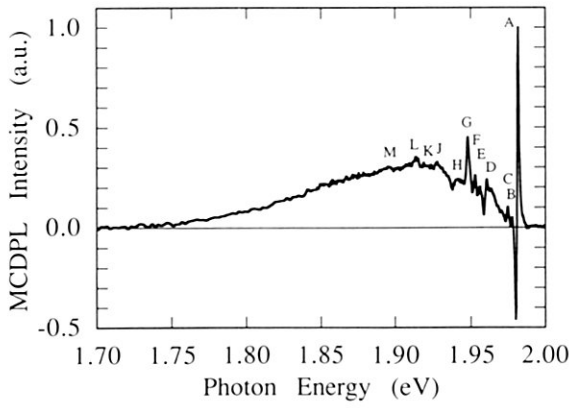

Fig. 4. Magnetic circular dichroism spectrum of photoluminescence for Eu-doped CaS at 20 K in the magnetic field of 1.2 T.

field of 1.2 T. The MCDPL intensity was approximately proportional to the applied field, and no change in the line shape was observed. A fine structure was observed on MCDPL spectrum associated with the broad emission band due to the d–f transition. The strong signal of the ZPL at 1.9808 eV showed an asymmetrical zero-crossing dispersion line shape with $I_+/I_- = 6.5/3$. On the PL spectrum (fig. 3), only a few strong lines were observed, whereas on the MCDPL spectrum, additional lines at 1.9777, 1.9745, 1.9581 and 1.9528 eV (denoted as B, C, E and F, respectively, in fig. 4 and table 1) became clearly observed. It is thus clear that MCDPL is far more sensitive for studies of fine structure than the usual PL, since it shows the difference between photoluminescence for RCP and left circular polarization (LCP), making this technique a form of "derivative" spectroscopy.

Putting all the results of MCDA and MCDPL measurements together with ABS and PL, energies of emission and absorption lines are listed in table 1. The line A in PL and 3 in ABS can be assigned to the ZPL of the f–d transition in Eu^{2+} ion as described above, because the positions of these lines (1.9808 eV) are identical. The two lines at 1.9777 eV (B) and 1.9745 eV (C) in the MCDPL spectrum can also be assigned to ZPLs because these positions show a good correspondence with the absorption lines of 1.9774 eV (2) and 1.9739 eV (1), respectively. Since no such correspondence can be seen for the other lines, they can be regarded as phonon side lines. The energy differences between these positions and the three ZPLs are also listed in table 1. The phonon energies appearing in absorption are 20.9 eV and 33.3 meV on the average, whereas those associated with emission are 21.5 meV and 34.5 meV on the average. The phonon energies obtained are slightly different from the bulk phonon energies of 28.4 meV (TO-mode) and 42.4 meV (LO-mode) determined by Kaneko et al. [4]. We ascribe them to the pseudolocalized phonons in the vicinity of Eu^{2+} ion in the CaS host, after the analyses for the fine structure in $CaS:Eu^{2+}$ by Nakao [6] and for that in $CaS:Ce^{3+}$ by Yokono et al [13].

In order to approximately evaluate the pseudolocalized phonon energies in the vicinity of Eu^{2+} ion in CaS, we utilize the formula for a linear diatomic chain given by

$$\hbar\omega \propto \sqrt{\frac{1}{M_1} + \frac{1}{M_2}}, \tag{1}$$

where M_1 and M_2 are masses of two atoms, by neglecting the effect of the force constant between atoms. The ratio of phonon energies in the linear chain of Ca–S to Eu–S can be calculated using the atomic masses, $M_{Ca} = 40$, $M_S = 32$, $M_{Eu} = 152$, in eq. (1). Thus we have

$$\sqrt{\frac{1}{M_{Eu}} + \frac{1}{M_S}} \Big/ \sqrt{\frac{1}{M_{Ca}} + \frac{1}{M_S}} = 0.82. \tag{2}$$

Using this value and the bulk phonon energies of CaS determined by Kaneko et al. [4], phonon energies in EuS are estimated as 23.3 and 34.8 meV. These values are close to the experimental values obtained in the present work.

We provide a brief discussion on the asymmetrical dispersion-type line shape of ZPL in MCDA and MCDPL spectra. Experimental MCDA spectra and their theoretical analyses of Eu^{2+} ion in CaF_2 were reported by Weakliem [12]. He observed complete dominance of RCP transitions over LCP in both experimental results ($T = 2$ K and $H = 2.9$ T) and theoretical calculation for f–d transition in Eu^{2+} ion. Although our situation is slightly different from the case of

CaF_2 : Eu (different in the symmetry around Eu^{2+}), we expect similar results for CaS : Eu. Theoretical calculations in the framework of the ligand-field theory are now proceeding.

Acknowledgement

This work has been supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

[1] S. Tanaka, Y. Mikami, J. Nishiura, S. Ohshio, H. Yoshiyama and H. Kobayashi, 1987 SID Int. Symp., Digest of Technical Papers (1987) p. 234.

[2] H. Yoshiyama, S.H. Shon, S. Tanaka and H. Kobayashi, Electroluminescence, ed. S. Shionoya and H. Kobayashi, (Springer-Verlag, Berlin, Heidelberg, 1989) p. 48.

[3] K. Realo, Trudy Instituta Fiz., Akad. Nauk Est. SSR 43 (1975) 260.

[4] Y. Kaneko, K. Morimoto and T. Koda, J. Phys. Soc. Jpn. 51 (1982) 2247.

[5] M. Drofenik and A. Azman, J. Phys. Chem. Sol. 33 (1972) 761.

[6] Y. Nakao, J. Phys. Soc. Jpn. 48 (1980) 534.

[7] Y. Kaneko, K. Morimoto and T. Koda, Oyo Buturi 50 (1981) 289 (in Japanese).

[8] A.N. Gruzintsev, S.V. Demishev and T.V. Nikiforova, Phys. Stat. Sol. (b) 161 (1990) 705.

[9] B.K. Meyer, J.M. Spaeth and M. Scheffler, Phys. Rev. Lett. 52 (1984) 851.

[10] K. Sato, M. Hirai and T. Tamaki, J. Phys. Soc. Jpn. 61 (1992) 3803.

[11] F.J. Ahlers, F. Lohse and J.M. Spaeth, Phys. Rev. B 28 (1983) 1249.

[12] H.A. Weakliem, Phys. Rev. B 6 (1972) 2743.

[13] S. Yokono, T. Abe and T. Hoshina, J. Phys. Soc. Jpn. 46 (1979) 351.