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THE OPTICAL SPECTRA OF Co^{2+} IN MgAl_2O_4 SPINEL

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Abstract. The spectroscopic properties of MgAl_2O_4 spinel doped by Co^{2+} ions are characterized by low ligand fields strength. In result the broad fluorescence band was observed in visible region.

1. Introduction

The spin-allowed d-d luminescence transitions in transition metal doped crystals are characterized by the broad band offering a practical utilization for tunable laser operation. The room temperature laser operation in visible range was observed for Cr^{3+} [1] and Ti^{3+} ions [2].

Cobalt(II) ion is a counter partner to Cr^{3+} ion, so their energy level schemes are similar. The principal difference is associated with much weaker ligand field strength observed for Co^{2+} ion. In result the emission arising from the first excited state ${}^4\text{T}_2$ is observed in the infrared. The laser operations for Co^{2+} has been reported for a number of crystals but only at lowered temperature and for infrared region [3]. The broad band luminescence in the visible region was recently reported for Co^{2+} doped LiGa_5O_8 [4].

In this paper we present the results of spectroscopic measurements of Co^{2+} doped MgAl_2O_4 spinel. This system exhibits a visible luminescence in room temperature.

2. Results

The absorption spectrum of $\text{MgAl}_2\text{O}_4 : \text{Co}^{2+}$ was first reported by Drifford [5]. The results of our investigation are shown in Figure 1.

Table I. Energy levels of Co^{2+} in spinel MgAl_2O_4

Level	Energy [cm ⁻¹]	Rel. inten- sity [%]	
⁴ T ₂ (⁴ F)	G	4058	1
	E _{1/2}	4174	2
	G	4223	4
		4366	5
	E _{5/2}	4826	5
⁴ T ₁ (⁴ F)	G, E _{1/2}	6452	25
	G	7300	23
	E _{5/2}	8026	18
⁴ T ₁ (⁴ P)	G, E _{5/2}	14960	1
	G	15725	73
	E _{1/2}	15974	84
	2T ₁ (² G)	16835	87
	2E(² G)	17212	100
² T ₂ (² G)	G	17870	67
		18349	55
	E _{5/2}	19198	21
² T ₁ (² H)		20758	4
		22075	0.7
² T ₁ (² P)		24570	0.6
² T ₂ (² D ₁)		27550	0.1
² T ₁ (² F)		36530	0.8

The absorption spectra were measured at 3.8 K. The absorption bands extend from far infrared to ultra-violet. The assignments of energy transitions as well as relative intensity of each line are shown in Table 1. Two first bands are assigned to ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}(\text{F})$ and ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ transition. The splitting of this bands is caused by presence of spin-orbit coupling. The strongest band centered at 17200 cm^{-1} was assigned to the ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ transition and to the transitions from the ground level ${}^4\text{A}_2(\text{F})$ to levels from ${}^2\text{G}$ term. The intensities of other bands are much weaker relatively to the strongest band (see Tab I). The luminescence spectra of $\text{MgAl}_2\text{O}_4 : \text{Co}^{2+}$ were observed in 77 K and room temperature. The luminescence measured in 77 K is shown in Figure 2. The band in visible region is assigned to the ${}^4\text{T}_1(\text{P}) \rightarrow {}^4\text{A}_2(\text{F})$ transition, the band in infrared is assigned to the ${}^4\text{T}_1(\text{P}) \rightarrow {}^4\text{A}_2(\text{F})$ transition. Red band, centered at 14550 cm^{-1} is structureless in room temperature, but for 514.5 nm excitation a small hump is appear in 15128 cm^{-1} . At 77 K the transition exhibits two strong maxima at 14550 cm^{-1} and 15128 cm^{-1} . The infrared band has two maxima (at 10880 cm^{-1} and at 11580 cm^{-1}) in both temperatures.

Fig. 1. Absorption spectra of $\text{MgAl}_2\text{O}_4:\text{Co}^{2+}$ at 3.8 K.

The decay time was measured only in visible region. The observed decay curve was exponential. The decay time in liquid nitrogen temperature was about 220 ns, and 155 ns in room temperature.

Fig. 2. Fluorescence of $\text{MgAl}_2\text{O}_4:\text{Co}^{2+}$ for two excitation at 77 K.

Figure 3 shows the temperature dependence of luminescence intensity for both bands. Figure 4 presents the temperature dependence of intensity of visible band to intensity of infrared band. Both dependencies have this same feature. It is an inflexion point at temperature about 350 K.

3. Discussion

The results of absorption measurements were used for calculation the crystal field, Racah's parameters and spin-orbit coupling constant.

We have obtained $Dq = 402 \text{ cm}^{-1}$, $B = 815 \text{ cm}^{-1}$, $C = 3266 \text{ cm}^{-1}$ and $|\lambda| = 275 \text{ cm}^{-1}$. The small value of Dq parameter pointed on the tetrahedral symmetry of Co^{2+} ions in MgAl_2O_4 . The parameter $|\lambda|$ is higher then for free ion ($|\lambda|_{\text{free ion}} = 178 \text{ cm}^{-1}$). It may be explained by the presence of local deformation disturbing the positions of multiplets ${}^4T_1(F)$ [5].

Fig. 3. Temperature dependence of fluorescence intensity.

The value $Dq/B = 0.5$ plays this same role for tetrahedral configuration d^7 ions as $Dq/B = 2.3$ for d^3 ions for octahedral coordination. In these points the 2E term cross the terms ${}^4T_1({}^4P)$ and ${}^4T_1({}^4F)$.

If $Dq/B < 0.5$ the ${}^4T_1(P)$ lies below the 2E level giving broad band emission with a short lifetime (the weak field case), while for the strong field case ($Dq/B > 0.5$) the term 2E is lowest giving a narrow emission with longer lifetime. In $\text{MgAl}_2\text{O}_4:\text{Co}^{2+}$ $Dq/B = 0.493$ it's a low field case.

The band maximum in the visible range is located at 14550 cm^{-1} . In perature 77 K this band is more structured. The position of the peak assigned to the ${}^4T_1(F) \rightarrow {}^4A_2(F)$ transition was not changed. The second strong peak, which dominates for 514.5 nm excitation, was identified with the transition ${}^2T_2 \rightarrow {}^4A_2(F)$.

Two maxima of infrared emission were simply identified with the transition to $E_{5/2}$ and $E_{1/2}$ fine levels of ${}^4T_2(F)$ term.

A fast radiative decay rate confirms allowed electric-dipole character of these transitions.

Fig. 4. The relatively temperature dependence.

4. Conclusion

The Co^{2+} ions exhibits a strong preference to the location in tetrahedral symmetry. Such symmetry was reported in many hosts [6], [7]. An octahedral symmetry was reported only in a few cases [8]. The Co^{2+} in MgAl_2O_4 spinel is characterized, as we shown, by tetrahedral symmetry. This assignment is confirmed by small value of Dq parameter.

The visible broad band emission due to the low ligand field ($Dq/B < 0.5$) was observed to be efficient at room temperature. It may be utilized for tunable laser operation.

References:

1. P.T.Kenyon, L.Andrews, B.McCollum and A.Lempicki, IEEE J.Quant.Elect., QE18,(1982)1189.
2. F.Multon, Laser Focus (1983)83.
3. A.A.Kaminskii, Laser Crystals, Springer Verlag (1981).
4. J.F.Donegan, F.J.Bergin and G.F.Imbush, J.Lumin. 31/32 (1984)278
5. M.Drifford et P.Rigny C,R.Acad.Sc, Paris, t. 263, série B (1966)180.
6. R.Pappalaardo, D.L.Wood and R.C.Linores Jr. ,J.Chem. Phys. 35 (1961) 2041.
7. D.L.Wood and J.P.Remeika, J.Chem.Phys., 46 (1967)3595.
8. L.F.Johnson, R.E.Dietz and H.J.Guggenheim Appl.Phys.Let, 5 (1964)21.