

## OPTICAL PROPERTIES OF $\text{Cr}^{3+}$ IN $\text{MgAl}_2\text{O}_4$ SPINEL

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Absorption and luminescence spectra of  $\text{Cr}^{3+}$  in the disordered synthetic  $\text{MgAl}_2\text{O}_4$  spinel are reported. The splitting of the  ${}^4\text{T}_2$  absorption band and the excitation wavelength dependence of luminescence indicate the presence of two different  $\text{Cr}^{3+}$  sites in this crystal. An excitation of  $\text{Cr}^{3+}$  in site A leads to broad band fluorescence whereas an excitation of the B site leads to the narrow band luminescence similar to that of the natural spinel. The nature of luminescence is discussed.

### 1. Introduction

The luminescence properties of the  $\text{Cr}^{3+}$  ion depend to a great extent on the ligand field strength. It is well-known that for low ligand field materials [1] where  $Dq/B < 2.3$  the  $\text{Cr}^{3+}$  luminescence originates from the lowest excited state  ${}^4\text{T}_2$ . Since this state is strongly distorted such materials exhibit broad band fluorescence. In high ligand field compounds, like for instance ruby where  $Dq/B > 2.3$ , the lowest excited state is  ${}^2\text{E}_g$ . This state is practically undistorted and the resulting luminescence is the narrow band phosphorescence.

The discovery of room temperature laser operation for  $\text{Cr}^{3+}$  in low ligand field crystals like alexandrite [2], emerald [3] and fluorine-perovskite  $\text{KZnF}_3$  [4] has focused attention on new insulating  $\text{Cr}^{3+}$ -doped crystals having the low ligand field condition appropriate for tunable solid state laser.

The  $\text{Cr}^{3+}$ -doped  $\text{MgAl}_2\text{O}_4$  spinel exhibits interesting optical properties. The optical spectra for natural spinel were reported a long time ago by Wood et al. [5]. They have found that natural spinel shows a typical phosphorescence behaviour – two sharp  $\text{R}_1$  and  $\text{R}_2$  lines accompanied by many sidebands. They have also noticed that the luminescence spectra for synthetic spinel were characterized by diffuse bands. This strange behaviour was attributed to the irreversible order-disorder transition occurring in this crystal

above  $750^\circ\text{C}$  [6].

This transition is connected with an irregular distribution of the cations in the  $\text{MgAl}_2\text{O}_4$  crystals. In natural spinels, assumed to be normal,  $\text{Cr}^{3+}$  may be substituted for  $\text{Al}^{3+}$ . For annealed or synthetic spinel the cation distribution is partially inverse [7].

The luminescence spectra of synthetic  $\text{Cr}^{3+}$ -doped  $\text{MgAl}_2\text{O}_4$  spinels were investigated by Van den Boom et al. [8]. They have found that the spectral character of the luminescence changed greatly with increasing  $\text{Cr}^{3+}$  concentration. For low concentration the spectrum was similar to that reported by Wood et al. [5] while for higher concentration it was broadened into the red, showing many new features. The present authors have attributed the observed luminescence behaviour to the existence of two  $\text{Cr}^{3+}$  sites in the spinel.

In this paper we report absorption, luminescence and decay time measurements of  $\text{Cr}^{3+}$  in synthetic  $\text{MgAl}_2\text{O}_4$  spinel. It is found that the luminescence depends on the excitation wavelength. The origin of the luminescence in  $\text{Cr}^{3+}$ -doped spinel is discussed.

### 2. Experimental

The crystals of  $\text{Cr}^{3+}$ -doped  $\text{MgAl}_2\text{O}_4$  were grown according to the Verneuil method in the

Skawina Metallurgy Works. The concentration of  $\text{Cr}^{3+}$  ions was about 0.05 atomic percent.

The powder X-ray investigation of the crystal, performed on a Quinier camera, revealed a cubic system with a lattice parameter equal to 7.973 Å.

The absorption spectrum at room temperature was measured on a Cary-Varian and a Specord (C. Zeiss, Jena) spectrophotometer.

The fluorescence spectra were measured with an experimental set-up consisting of a GDM-1000 monochromator (C. Zeiss, Jena), an S-20 photomultiplier or a Boxcar BCI (ZWG, Berlin) connected with the steering circuit of the monochromator. An argon laser ILA 120 (C. Zeiss, Jena) or a dye laser FSL 100 (ZWG, Berlin) were used as excitation sources.

The decay times were measured using the chopped argon laser beam. The temperature of the illuminated sample was checked by means of a thermocouple. The luminescence measurements at elevated temperatures up to 600 K were performed in a sample holder with a cartridge heater.

### 3. Results

#### 3.1. Absorption spectrum

The room temperature absorption spectrum of  $\text{Cr}^{3+}$  in  $\text{MgAl}_2\text{O}_4$  is shown in fig. 1. It was recorded from a crystal of thickness 36 mm. In the visible range it consists of two bands centered at 17 400 and 23 500  $\text{cm}^{-1}$ , corresponding to the spin-allowed  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$  and  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$  transitions, respectively. At the edge of the  ${}^4\text{T}_{2g}$  band at 14 536  $\text{cm}^{-1}$ , the peak attributed to the spin-forbidden  ${}^4\text{A}_{2g} \rightarrow {}^2\text{E}_g$  transition is located. The principal feature of spin-allowed bands is inhomogeneous broadening. We have resolved the observed bands, using the computer program MOP-George-3 for deconvolution of the spectrum into Gaussian curves [10].

The results of this deconvolution are shown in the figure (dashed lines). The observed peak positions are given in the second column of table I, while the wavenumbers of the peaks of the Gaussian components are given in the third col-

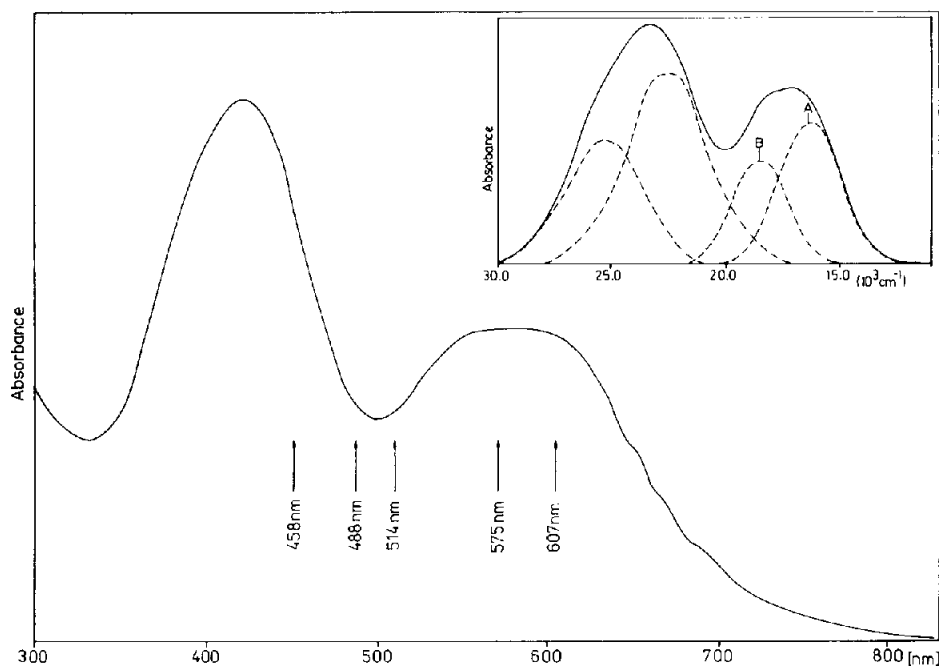


Fig. 1. Absorption spectrum of  $\text{Cr}^{3+}$  in  $\text{MgAl}_2\text{O}_4$  spinel; pumping lines are indicated by arrows. At the upper right-hand corner Gaussian deconvolution is displayed.

Table I  
Excited levels and transitions of  $\text{Cr}^{3+}$  in  $\text{MgAl}_2\text{O}_4$  spinel.

Upper level	Band position observed ( $\text{cm}^{-1}$ )	Peak of Gaussian curves resulting from the deconvolution ( $\text{cm}^{-1}$ )	Level values from ref. [5] ( $\text{cm}^{-1}$ )
${}^2\text{E}_g$	14 536	–	14 653.5
		–	14 660
${}^2\text{T}_{1g}$	–	–	14 812
	14 970	–	15 069
	15 310	–	15 228
${}^4\text{T}_{2g}$	17 400	A 16 240	18 500
		B 18 430	
${}^2\text{T}_{2g}$	21 800	–	22 100
${}^4\text{T}_{1g}$	23 500	22 650	24 100
		25 325	25 800

Crystal field parameters:

$D_q^A = 1624 \text{ cm}^{-1}$	$D_q^B = 1843 \text{ cm}^{-1}$
$B^A = 758 \text{ cm}^{-1}$	$B^B = 698 \text{ cm}^{-1}$
$D_q^A/B^A = 2.14$	$D_q^B/B^B = 2.64$

umn. The first column shows the excited states of  $\text{Cr}^{3+}$  in the  $\text{MgAl}_2\text{O}_4$  spinel. The corresponding level values for natural spinel, as reported by Wood et al. [5], are entered in the fourth column. It is important to note that the peaks found for the  ${}^4\text{T}_{1g}$  band coincide with the values reported by Wood, whereas a remarkable difference occurs in the  ${}^4\text{T}_{2g}$  band. The distance between the maxima of the two constituent curves, denoted by A and B, is equal to  $2190 \text{ cm}^{-1}$ . For natural spinel such a splitting was not observed. Moreover, the crystal field calculations performed for the  $D_{3d}$  symmetry of the  $\text{Cr}^{3+}$  ion in natural spinel [5] exclude a large splitting of the  ${}^4\text{T}_{2g}$  band. In our opinion the splitting of the  ${}^4\text{T}_{2g}$  state indicates the presence of different  $\text{Cr}^{3+}$  sites in  $\text{MgAl}_2\text{O}_4$ . We have determined the crystal field parameter values for both sites assuming the cubic-field approximation; these values are given at the bottom of table I.

### 3.2. Luminescence spectra

The luminescence spectra of  $\text{Cr}^{3+}$  in  $\text{MgAl}_2\text{O}_4$  spinel were measured at different excitation

wavelengths in the range  $13\,000\text{--}15\,000 \text{ cm}^{-1}$  at various temperatures up to 600 K. The luminescence spectrum of  $\text{Cr}^{3+}$  in  $\text{MgAl}_2\text{O}_4$  is characterized by a diffuse line structure depending on temperature. The spectra measured at different temperatures and excitation wavelengths are presented in fig. 2. The excitation wavelengths are indicated by arrows in the absorption spectrum of  $\text{Cr}^{3+}$ :  $\text{MgAl}_2\text{O}_4$  in fig. 1. It is seen that a dramatic change in the luminescence spectrum takes place between the excitation wavelengths 607 and 514 nm. The spectrum excited by the 514 nm radiation is similar to that reported by Mikenda and Preisinger [6] for annealed natural spinel. The maximum intensity peak corresponds to their  $N_3$  line. The sharp lines  $R_1$  and  $R_2$  of the spin-forbidden phosphorescence of the ideal by coordinated  $\text{Cr}^{3+}$  ions, were not observed, but a small hump at  $14\,536 \text{ cm}^{-1}$  could be a trace of the R-line. The spectrum excited by the 607 nm radiation is completely different from the former one. It is characterized by a broad band luminescence centered at  $13\,800 \text{ cm}^{-1}$ . The maximum intensity is remarkably shifted to the red in comparison to the spectrum produced at the

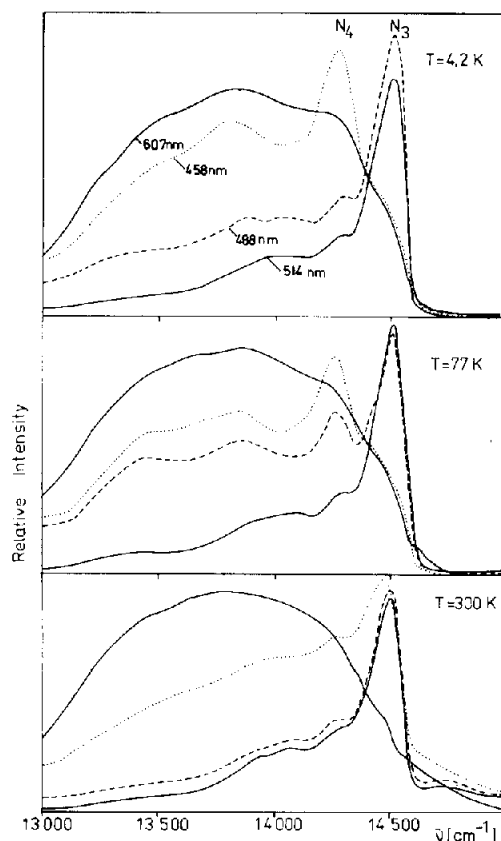


Fig. 2. Luminescence spectra of  $\text{Cr}^{3+}$  in  $\text{MgAl}_2\text{O}_4$  at different excitation wavelengths. The labels  $N$  denote the lines due to the  $\text{Cr}^{3+}$  pairs following ref. [6].

514 nm excitation wavelength. Obviously the origin of the broad band luminescence is associated with the direct excitation of site A (see fig. 1). The luminescence excited by the 514 nm radiation is ascribed to the site B.

The temperature dependence of the luminescence spectrum is noteworthy. The intensity of the overall band increases regularly with increasing temperature. This is shown in fig. 3 in a larger temperature range, for the luminescence spectrum excited by the 488 nm radiation. Consequently, the peak at  $14\,500\text{ cm}^{-1}$  becomes less significant with respect to the broad band luminescence part at the centre of the spectrum. The temperature increase also results in a significant shift of this peak towards the red. In fig. 4 the position in  $\text{cm}^{-1}$  is plotted against the temperature.

The luminescence decay curves were also measured as a function of temperature at different wavelengths near the peak. The decay is nonexponential, but the longest decay times involved were evaluated from the curves and plotted in fig. 5. It is seen from this figure that the decay times are nearly 3–4 times longer at  $14\,500\text{ cm}^{-1}$ , which confirms the phosphorescence behaviour of the band around  $14\,500\text{ cm}^{-1}$ .

The thermalization effect is quite pronounced. The ratio of the intensity of the broad band part

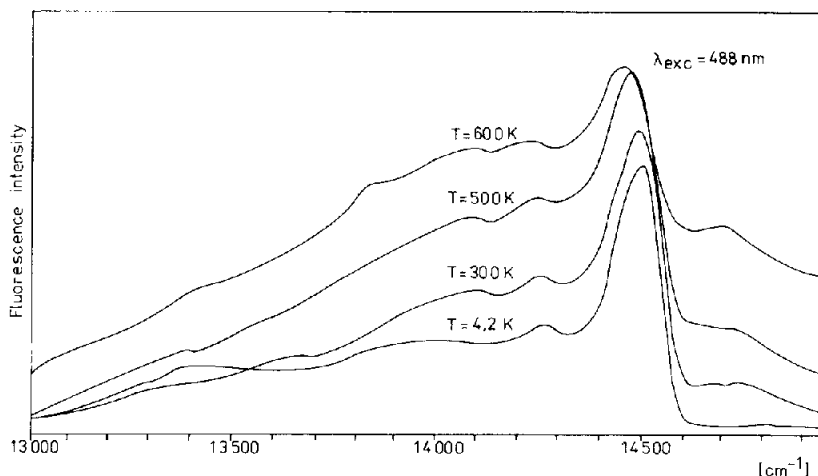
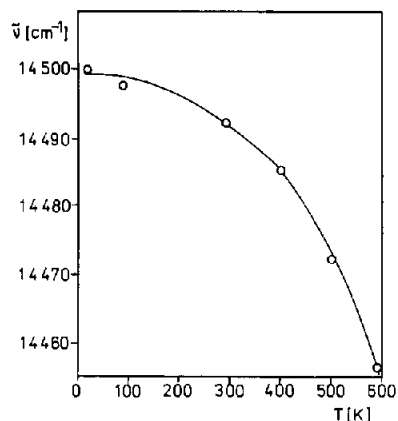
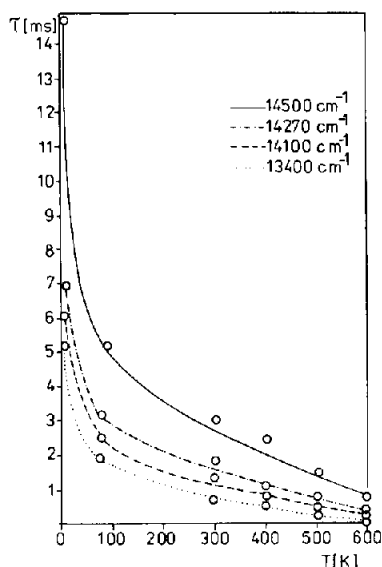


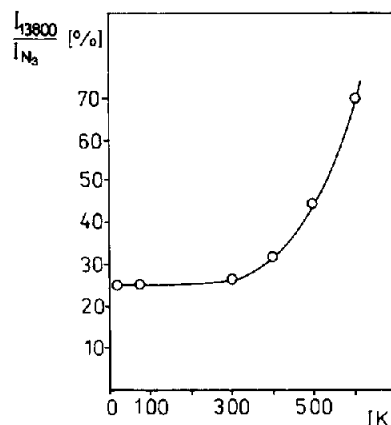
Fig. 3. Temperature dependence of luminescence of  $\text{Cr}^{3+}$  in  $\text{MgAl}_2\text{O}_4$  for  $\lambda_{\text{exc}} = 488\text{ nm}$ .

Fig. 4. Temperature shift of the peak at  $14500\text{ cm}^{-1}$ .Fig. 5. Temperature dependence of the luminescence decay times of  $\text{Cr}^{3+}$  in  $\text{MgAl}_2\text{O}_4$ .

of the spectrum to the intensity of the  $N_3$  peak is 70% at 600 K, whereas at 4.2 K it is less than 30% as shown in fig. 6.

#### 4. Conclusions

The absorption spectra of  $\text{Cr}^{3+}$  in the synthetic  $\text{MgAl}_2\text{O}_4$  spinel are different from those reported by Wood et al. [5] for natural spinel. We have observed a characteristic splitting of the

Fig. 6. Temperature dependence of the ratio of the intensities near  $13800\text{ cm}^{-1}$  and in the  $N_3$  peak.

${}^4T_{2g}$  absorption band which we attribute to the presence of two  $\text{Cr}^{3+}$  sites in the synthetic spinel. The band position associated with site B coincides with the data reported by Wood for natural spinel, while the second site A produces a remarkable shift to the red. The spectra observed are characterized by a more diffuse band structure than that reported by Van den Boom et al. [8]. This is probably due to the difference in the preparation of the crystals.

The spectra measured with the excitation wavelengths of 514 and 488 nm lines are similar to those reported by Van den Boom for the low concentration spinel  $\text{MgAl}_{1.99}\text{Cr}_{0.01}\text{O}_4$ , while for 607 nm there are significant differences. The striking new feature is a large broadening with an approximate bandwidth of about  $1500\text{ cm}^{-1}$ , the maximum intensity of the band shifting to the red, around  $13800\text{ cm}^{-1}$ . The broad band behaviour of this luminescence suggests its attribution to the spin-allowed fluorescence  ${}^4T_2 \rightarrow {}^4A_2$ . Inspection of fig. 1 allows us to conclude that the luminescence spectra measured for  $\lambda_{\text{exc}} = 607\text{ nm}$  correspond to the emission from the A site while the spectra excited by 514 nm correspond to the B sites.

It is interesting to note that for the luminescence excited by 488 nm, the two sites give a comparable contribution at 77 K.

The B site characterizes the high ligand field, with  $Dq/B = 2.64$ , which favours phosphorescence behaviour. The low value of  $Dq/B = 2.14$

for the A site indicates a low ligand field character, in accordance with the fluorescence transitions  ${}^4\text{T}_{2g} \rightarrow {}^4\text{A}_{2g}$ . Such a behaviour was recently reported by Bouderbala et al. [9] for  $\text{Cr}^{3+}$ -doped spinel-type-glasses.

In summary, the results presented indicate that in the synthetic  $\text{MgAl}_2\text{O}_4$  spinel two different  $\text{Cr}^{3+}$  sites contribute to the optical properties of the crystal. We found that  $\text{Cr}^{3+}$  ions in the B sites exhibit spectroscopic properties similar to those observed in annealed natural spinel. Due to the ligand field connected with the B sites the corresponding features have phosphorescence character and are associated with the N lines [6]. The zero-phonon  ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$  transition is much weaker than observed in natural spinel.

The  $\text{Cr}^{3+}$  ions in the A sites are subject to a lower ligand field which promotes fluorescence behaviour. The  ${}^4\text{T}_{2g} \rightarrow {}^4\text{A}_{2g}$  broad band fluorescence becomes dominant especially when the red wing of  ${}^4\text{T}_{2g}$  band is excited.

In view of the current interest in  $\text{Cr}^{3+}$ -doped crystals the  $\text{MgAl}_2\text{O}_4$  synthetic spinel represents

an attractive material for tunable laser operation.

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