
Luminescence Spectra of $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ Spinel Nanopowders

H.H. LUC^{a,*}, T.K. NGUYEN^a, V.M. NGUYEN^a, A. SUCHOCKI^b,
A. KAMIŃSKA^b, V.K. LE^b, V.H. NGUYEN^a AND T.T. LUONG^a

^aFaculty of Physics, Hanoi University of Education
136 Xuan Thuy, Cau Giay, Hanoi, Vietnam

^bInstitute of Physics, Polish Academy of Sciences
al. Lotników 32/46, 02-668 Warsaw, Poland

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The synthetic ZnAl_2O_4 spinels doped with Cr^{3+} ions are prepared from ZnSO_4 , $\text{Al}_2(\text{SO}_4)_3$, and $\text{Cr}_2(\text{SO}_4)_3$. The spinel single phase is detected from X-ray diffraction. Luminescence properties of Cr^{3+} in ZnAl_2O_4 were studied by low temperature luminescence and decay measurements. Four luminescence lines at 14570, 14520, 14460, and 14330 cm^{-1} were found to originate from structure distortion and the line at 14175 cm^{-1} — from chromium pairs. The broad emission band at about 13540 cm^{-1} is considered to arise from a new Cr^{3+} center in ZnCr_2O_4 .

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1. Introduction

The study of luminescence properties of Cr^{3+} doped both natural and synthetic spinel has been reported in several publications [1–3]. Due to the possible application as a tunable solid state laser material, it is important to understand clearly optical properties of active ions in spinel. Since the spectra characteristic of transition metal ions are strongly dependent on the local environment, the optical properties may give interesting information about the crystal sites occupied by the Cr^{3+} ions [2, 4, 5]. In previous papers [1, 2, 4–6], the ${}^2E \rightarrow {}^4A_2$ emission lines of Cr^{3+} in spinel structure are denoted as R and N lines. R line is due to class

*corresponding author; e-mail: hoanglhsp@yahoo.com

of Cr^{3+} centers located in ideal crystal sites. Two kinds of N lines exist: the lines which depend on the lattice structure are called “structure dependent lines” and those, which are chromium concentration dependent — “ Cr^{3+} pair lines” [2, 7–9]. Some papers on $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ [10–12] present partly differing results on the N lines. Therefore, the question of the nature of the Cr^{3+} fluorescent centers in both polycrystalline and single crystals of $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$ is still open.

In this paper, the result of preparing synthetic ZnAl_2O_4 powder spinel doped with Cr^{3+} ions is presented. The grain size and polycrystalline properties of those samples were investigated by AFM and X-ray diffraction measurements. The different sites of Cr^{3+} in ZnAl_2O_4 spinel are determined by using luminescence and luminescence decay measurements. The Cr^{3+} pair lines and their side band were found and discussed.

2. Experiment

The initial materials used for fabricating spinel powder were: $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (99, 5%), and $\text{Cr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. They were dissolved in distilled water to concentration of 0.5 M, then mixed in a proportion to get final composition of ZnAl_2O_4 doped with 0.5, 0.7, 1, and 2% Cr^{3+} ions. Ammonia solution was added drop by drop into the mixed sulfate solution, which was stirred with a magnetic stirrer until the gel became fully viscous. The gel was then annealed at 750°C in 1 hour at heating rate of $1^\circ\text{C}/\text{min}$. The grain size of 80–90 nm of the powder spinel sample was indicated from AFM image. The X-ray diffraction measurement was taken on a D5000 Siemens system. The luminescence spectra were obtained by using GDM 1000 double grating monochromator equipped with a liquid nitrogen cooled photomultiplier EMI 9684B and an SR 530 lock-in amplifier. Low temperature measurements was performed in an Oxford 1204 cryostat with temperature controller. Decay kinetics of luminescence were obtained by using a SR 430 Multichannel Scaler. The Ar laser line of 514.5 nm was used as an excitation source.

3. Results and discussions

The X-ray diffraction spectrum of ZnAl_2O_4 spinel doped with 0.5% Cr^{3+} is presented in Fig. 1. This shows that this powdered sample possesses single-phase spinel structure.

The luminescence spectra of ZnAl_2O_4 doped with 0.5% mol Cr^{3+} at different temperatures are shown in Fig. 2.

It can be seen that all the luminescence lines are shifted to higher wave numbers with decreasing temperature. The splitting of R line into two components can be clearly observed at 20 K, however only the low-energy component can be seen at 10 K. The disappearance of the R line high-energy component at low temperature can be interpreted by the effect of energy level occupation. The

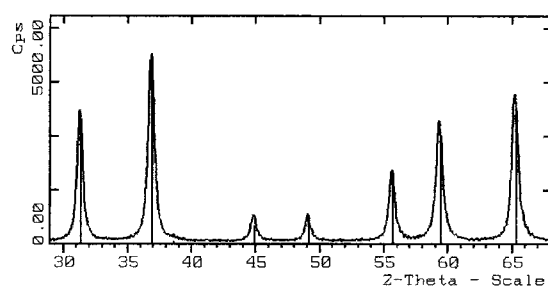


Fig. 1. X-ray diffraction spectrum of ZnAl_2O_4 spinel powder.

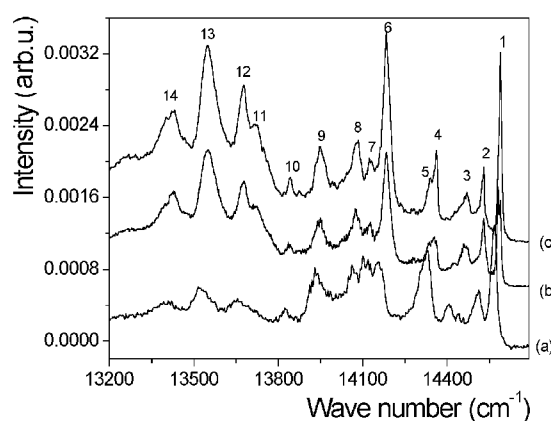


Fig. 2. Luminescence of $\text{ZnAl}_2\text{O}_4:0.5\%\text{Cr}^{3+}$ at different temperatures: 300 K (a), 20 K (b) and 10 K (c).

separation of R lines at 20 K gives directly the splitting of the lowest excited state E_{2g} , which is caused by trigonal distortion and spin-orbit interaction. The energy levels calculation for a Cr^{3+} ion in a trigonally distorted octahedral site, taking into account the spin-orbit coupling, were described by Macfarlane [8, 9]. This type of calculation was applied by Wood and Imbusch [10] to the case of ZnAl_2O_4 and MgAl_2O_4 spinels.

The decays of the luminescence lines of ZnAl_2O_4 doped with 0.5% Cr^{3+} are measured at 10 K. The lifetimes of different lines are obtained by fitting the decay kinetics with one or two exponential curves. Table I shows the fitting results for the lifetime of the lines together with their identification.

The R luminescence line has a long lifetime of 32.7 ms. This is consistent with a line arising from an electric dipole forbidden transition. The lines number 4, 7, 8, 9, and 10 have the same lifetime as that of R line. Therefore it is natural to assign these lines to phonon-assisted side lines of the R line. The remaining lines have shorter lifetimes. This suggests that they all arise from centers with lower sites symmetry. They can be divided into four groups: (i) line number 2 with

TABLE I
Lifetime of luminescence lines of ZnAl_2O_4 doped 0.5% Cr^{3+} at 10 K and their identification.

Peaks number	Positions [cm^{-1}]	Lifetime τ [ms]	Identification
1	14578	32.7	R line
2	14520	20.0	N2
3	14460	13.0	N3
4	14352	32.5	R side band
5	14330	$\tau_1 = 8.0, \tau_2 = 33.0$	N ₄ and R side band
6	14175	4.0	N5
7	14120	32.5	R side band
8	14073	32.5	R side band
9	13940	32.5	R side band
10	13830	32.5	R side band
11	13715	4.0	N5 side band
12	13665	4.2	N5 side band
13	13540	4.1	N5 side band
14	13415	4.0	N5 side band

lifetime $\tau = 20$ ms, (ii) line number 3 with $\tau = 13$ ms, (iii) line number 5 with $\tau = 8$ ms and 33 ms; (iv) lines number 11, 12, 13, and 14 with $\tau = 4$ ms. In order to determine which of those N lines are Cr^{3+} pair lines, samples of ZnAl_2O_4 doped with different Cr^{3+} concentrations are used. The luminescence spectra of ZnAl_2O_4 containing 0.5%, 0.7%, 1%, and 2% of Cr^{3+} are presented in Fig. 3.

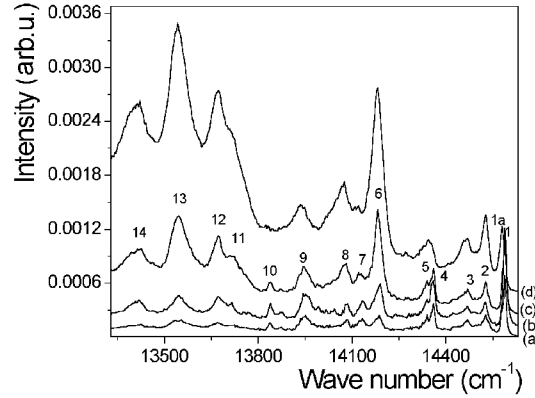


Fig. 3. Luminescence spectra of ZnAl_2O_4 doped with 0.5% Cr^{3+} (a), 0.7% (b), 1% (c), and 2% (d) at temperature $T = 10$ K.

The luminescence decay measurements have been performed for all lines in each sample. It turns out that the decay times of luminescence lines in samples doped with 0.5% (a), 0.7% (b) and 1% (c) of Cr^{3+} do not depend on Cr^{3+} concentration.

It can be seen from the spectra (a), (b) and (c) that the relative intensity of lines number 6, 11, 12, 13, and 14 increases with increasing Cr^{3+} concentration, while no such dependence is observed for the lines number 2, 3, and 5. Therefore the lines number 6, 11, 12, 13, and 14 may originate from Cr^{3+} pairs. Moreover, these lines have the same lifetime of about 4 ms, then we assume that line number 6 is the zero phonon line and the lines 11, 12, 13, and 14 are its phonon replicas. There is additional evidence for this interpretation if we notice that the distances between the lines number 11, 12, 13, 14, and line number 6 (N5 line) are very similar to the spectral distances of particular lines in the side band of the R line in Table II.

TABLE II
Vibronic side bands positions of the R and N_5 luminescence lines.

Position of R side band [cm^{-1}]	Line number	Position of N_5 side band [cm^{-1}]	Line number
-226	4		
-458	7	-460	11
-505	8	-490	12
-638	9	-635	13
-748	10	-760	14

The spectrum (d) in Fig. 3 shows that, with increase in Cr^{3+} concentration to 2%, the 1a line at 14570 cm^{-1} dominates. Moreover, there is a significant change of intensity of the N_5 and its side lines (line 11, 12, 13, and 14). The fluorescence decay of 2% Cr^{3+} doped ZnAl_2O_4 were recorded and the results are presented in Table III. The appearance of the 1a lines, having lifetime of 15.5 ms, gives evidence for the existence of new class of centers in highly doped sample. The presence of 1a line, the increasing background, and the broadening of the luminescence lines in this sample indicate the increase in the lattice disorder. It is interesting to note that the fluorescence decays for some lines (number 11, 12, 13, and 14) are not exponential. The decay times of 0.5 ms and 4 ms of those lines were obtained by fitting the decay kinetics with two exponential curves. The nonexponentiality of those luminescence decays may be explained by the existence of the broad emission band centered at about 13540 cm^{-1} , which have lifetime of 0.5 ms (N6 band). Following [11], the existence of ZnCr_2O_4 in high Cr^{3+} concentration doped sample is considered as one of the origins of this broad emission band.

TABLE III

Lifetime of luminescence lines of ZnAl_2O_4 doped with 2% Cr^{3+} at 10 K and their identification.

Peak number	Positions [cm^{-1}]	Lifetime τ [ms]	Identification
1a	14570	$\tau_1 = 15.5, \tau_2 = 33.0$	N1 and R
2	14520	20.0	N2
3	14460	13.0	N3
5	14330	$\tau_1 = 8.0, \tau_2 = 33.0$	N4
6	14175	4.0	N5
8	14073	32.5	R side band
9	13940	32.5	R side band
11	13715	$\tau = 0.5, \tau_2 = 4.0$	N5 side band broad emission
12	13665	$\tau_1 = 0.5, \tau_2 = 4.0$	N5 side band band (N6) with
13	13540	$\tau_1 = 0.5, \tau_2 = 4.0$	N5 side band lifetime
14	13415	$\tau_1 = 0.5, \tau_2 = 4.0$	N5 side band of 0.5 ms

4. Conclusions

The synthetic powder spinels ZnAl_2O_4 doped with Cr^{3+} ions were prepared. The luminescence and luminescence decay properties of Cr^{3+} in ZnAl_2O_4 were studied at low temperature. The splitting of the lowest excited state is observed at 20 K. Evidence is found of the existence of five distinct classes of Cr^{3+} associated with lowering of the symmetry, that is by two classes more than in previous publications [11, 12]. Among those, the class which gives rise to N_5 line and its phonon side bands is found to be the class of first nearest neighbor Cr^{3+} pairs.

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