

## Effect of $\text{Cr}^{3+}$ concentration on structural and optical properties of $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$

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**Abstract.**  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$  powders with  $\text{Cr}^{3+}$  contents ranging from  $x = 0.005$  to  $0.3$  have been synthesized by sol-gel method using the following precursors: zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), aluminium nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), chrome nitrate ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), and citric acid. The effect of the  $\text{Cr}^{3+}$  concentration on structural and optical properties of the synthesized samples has been studied. For the samples with low  $\text{Cr}^{3+}$ -dopant concentrations, the photoluminescent (PL) spectra consist of sharp lines assigned to the  ${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$  transition of ions  $\text{Cr}^{3+}$  in strong octahedral field. But for the samples with high  $\text{Cr}^{3+}$ -dopant concentrations, the PL spectra consist of a broad band centered at longer wavelengths assigned to the  ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$  transition of ions  $\text{Cr}^{3+}$  in weak octahedral field.

### 1. Introduction

The optical properties of  $\text{Cr}^{3+}$  ion located in octahedral coordination of materials such as ruby and spinel was extensively studied for several decades and these studies played an important role in the development of ligand-field theory. For the weak ligand-field, the lowest excited state is the  ${}^4\text{T}_2({}^2\text{g}^2, \text{e}_g^1)$  state having the same spin multiplicity as the  ${}^4\text{A}_2({}^2\text{g}^3)$  ground state, meanwhile for the strong ligand-field the lowest excited state is the  ${}^2\text{E}({}^2\text{g}^3)$  state having a different spin multiplicity, but the same orbital occupancy as the  ${}^4\text{A}_2({}^2\text{g}^3)$  ground state [1]. The optical properties of  $\text{Cr}^{3+}$ -doped spinel  $\text{ZnAl}_2\text{O}_4$  were studied by Luc et al. [2], Wood et al. [3], Mikenda et al. [4], Nie et al. [5]. They found that the optical properties of the  $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$  were characterized by sharp emission lines associated with the  ${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$  transitions of different  $\text{Cr}^{3+}$  sites in the strong ligand-field. However, the broad luminescence band characterizing the  ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$  transitions of the  $\text{Cr}^{3+}$  ions in the low ligand-field has not been reported up to now.

In the present work we report the optical properties of  $\text{Cr}^{3+}$ -doped  $\text{ZnAl}_2\text{O}_4$  spinel. In particular, the effect of  $\text{Cr}^{3+}$  concentration on the structural and luminescence properties of  $\text{ZnAl}_2\text{O}_4:\text{Cr}^{3+}$  was investigated.

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## 2. Experimental

The  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$  powders with various  $\text{Cr}^{3+}$  contents  $x = 0.005, 0.01, 0.10$  and  $0.30$  have been prepared by a sol-gel method. The powders were prepared from  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and citric acid. The aqueous solutions of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were mixed with the  $\text{Zn}^{2+} : \text{Al}^{3+} : \text{Cr}^{3+}$  mole ratios of  $1 : 2(1-x) : 2x$ . Citric acid solution was added to the above solution. The final mixed solution was kept constant at a temperature of  $70^\circ\text{C}$  until a highly viscous gel was formed. After drying in air at  $120^\circ\text{C}$  for 24 h, the gel was converted to a xerogel more opaque and dense. The xerogel was annealed at a temperature of  $1050^\circ\text{C}$  in air for 3 h.

The crystal structure of the samples was characterized by a Siemens D5005 X-ray diffraction (XRD) diffractometer. In order to determine the elemental composition of the samples, the energy dispersive spectra (EDS) were recorded by means of an equipment JSM5410 LV & ISIS 300 JEOL Japan. PL spectra and photoluminescence excitation (PLE) spectra were measured at room temperature using a Fluorolog FL3-22 spectrofluorometer with a xenon lamp of 450 W being used as an excitation source.

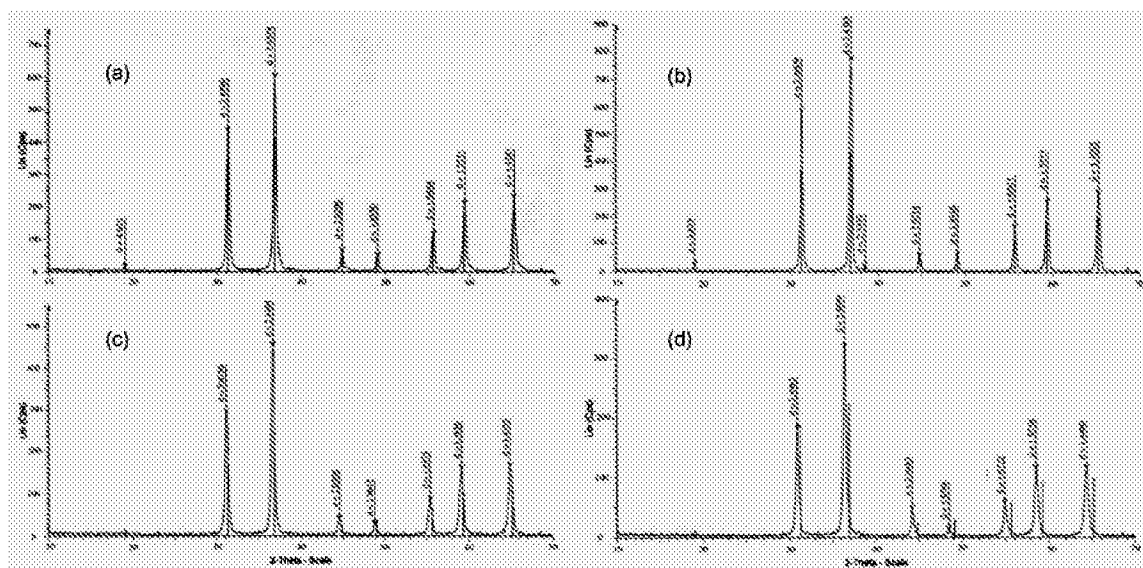


Fig. 1. The XRD patterns of the  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$  spinel with different mole fraction  $x$  (a)  $x = 0.005$ , (b)  $x = 0.01$ , (c)  $x = 0.10$  and (d)  $x = 0.30$ .

## 3. Results and discussion

XRD analysis was performed for the  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$  spinel xerogel with  $x = 0.005 - 0.3$  annealed at a temperature of  $1050^\circ\text{C}$  for 4 h. In figure 1 XRD patterns of the spinel xerogel doped with  $x = 0.005, 0.01, 0.10$  and  $0.30$  are represented. As evident from the figure, the samples are single-phase material with good crystallinity and all the peaks can be assigned to the spinel  $\text{ZnAl}_2\text{O}_4$  phase. No characteristic peaks of impurity phase have been observed. It can be noticed that with increasing the mole fraction  $x$ , the position of the diffraction peaks shifted towards the small-theta

Table 1. The dependence of  $d_{hkl}$  and lattice constants on the mole fraction  $x$  of the  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$ .

$x$	$d_{220}(\text{nm})$	$d_{311}(\text{nm})$	$d_{422}(\text{nm})$	$d_{511}(\text{nm})$	$d_{440}(\text{nm})$	$a(\text{nm})$
0.005	0.2859	0.2438	0.1648	0.1555	0.1428	$0.8081 \pm 0.0003$
0.01	0.2861	0.2439	0.1650	0.1556	0.1429	$0.8086 \pm 0.0003$
0.10	0.2875	0.2449	0.1657	0.1562	0.1436	$0.8122 \pm 0.0005$
0.30	0.2896	0.2470	0.1672	0.1576	0.1446	$0.8189 \pm 0.0004$

side, which is associated with an increase in the  $d_{hkl}$  and the lattice constants. With increasing the lattice constants the  $\text{Zn}^{2+} - \text{O}^{2-}$ ,  $\text{Al}^{3+} - \text{O}^{2-}$ ,  $\text{Cr}^{3+} - \text{O}^{2-}$  distances increase. The result is that the ligand-field influenced  $\text{Cr}^{3+}$  ion is decreased. The values of  $d_{hkl}$  and lattice constants of the samples calculated from the XRD patterns are shown in table 1.

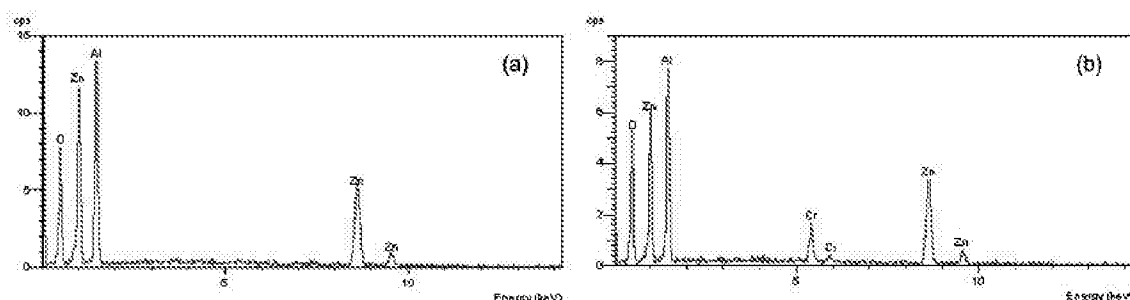


Fig. 2. The energy dispersive spectra of the  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$  spinel with different mole fraction  $x$ . (a)  $x = 0.005$  and (b)  $x = 0.10$ .

Figure 2 shows the EDS of the  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$  spinel with  $x = 0.005$  and  $0.10$ , in which some characteristic X-ray peaks originating from Zn, Al, O and Cr are observed. However, Cr element is only detected with sample  $x = 0.10$ . In sample  $x = 0.005$ , Cr element is not detected due to a relatively low dopant concentration.

Figure 3 shows the PL spectra of the  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$  with  $x = 0.005$  at  $12$  and  $300$  K excited by  $390$  nm wavelength. In the spectrum at  $12$  K is observed a very distinct zero-phonon R-line

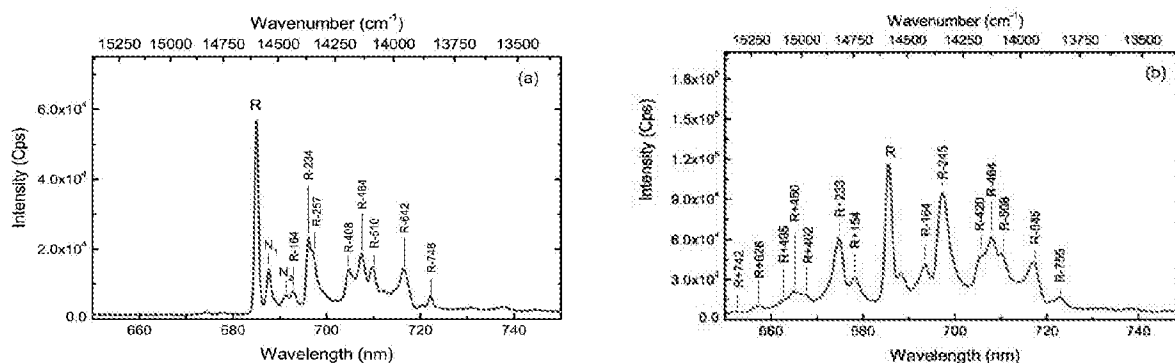


Fig. 3. The PL spectra excited by  $390$  nm wavelength of the  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$  with  $x = 0.005$  at different temperatures. (a)  $12$  K and (b)  $300$  K. The phonon-sideband of R-line is denoted by  $\text{R} \pm 250$ , where  $250$  is energy (in  $\text{cm}^{-1}$ ) of the phonon, the sign  $(-)$  corresponds to the emission of phonon, the sign  $(+)$  to the absorption of phonon.

at 685.5 nm corresponding to the  ${}^2E({}^2G) \rightarrow {}^4A_2({}^4F)$  transition. In addition, there are found many phonon-sidebands (PSBs) of R-line (Stokes' lines) as shown in figure 3(a). Whereas in the spectrum at 300 K depicted in figure 3(b) on the shorter-wavelength side of R-line appear many anti-Stokes' lines originated from the  ${}^2E({}^2G) \rightarrow {}^4A_2({}^4F)$  transitions accompanying an absorption of the phonons. From figure 3 it is noticed that the two emission lines  $N_1$  (687.6 nm) and  $N_2$  (691.3 nm) do not relate to the R-line and the phonon-sidebands of the R-line (R-PSB) because the corresponding anti-Stokes' lines are absent in the spectrum at room temperature. Therefore, the  $N_1$ - and  $N_2$ -lines must arise from other emission centers than the R-line and R-PSB.

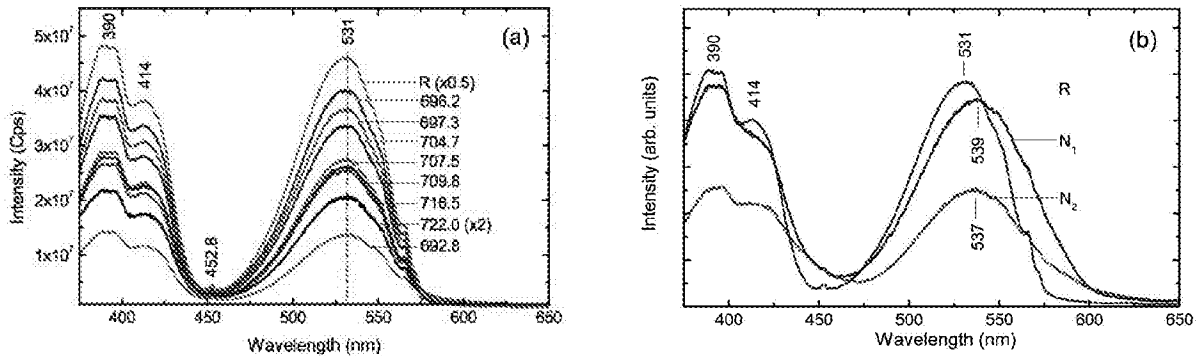


Fig. 4. The PLE spectra at 12 K of  $Zn(Al_{1-x}Cr_x)_2O_4$  with  $x = 0.005$  recorded at different emission lines: (a) at R-line (685.5 nm) and R-PSBs (692.8, 696.2, 697.3, 704.7, 707.5, 709.8, 716.5 and 722.0 nm); (b) at the R-line and the  $N_1$ -,  $N_2$ -lines.

In order to confirm the above-mentioned interpretation, the measurements of PLE spectra were performed. The results showed that the PLE spectra monitored at the R-PSBs: R-164 (692.8 nm), R-234 (696.2 nm), R-257 (697.3 nm), R-408 (704.7 nm), R-464 (707.5 nm), R-510 (709.8 nm), R-642 (716.5 nm) and R-748 (722.0 nm) are similar to those recorded at R-line at 685.5 nm (figure 4(a)). The PLE spectra consisted of two strong broad bands. The broad band centered at 531 nm corresponds to  ${}^4A_2({}^4F) \rightarrow {}^4T_2({}^4F)$  transitions, meanwhile two bands centered at 390 and 414 nm correspond to  ${}^4A_2({}^4F) \rightarrow {}^4T_1({}^4F)$  transitions. It is noticed that in the trigonal crystal field and under the spin-orbit effect the  ${}^4T_1({}^4F)$  level is split into two levels  ${}^4E({}^4T_1({}^4F))$  and  ${}^4A_2({}^4T_1({}^4F))$  [5]. Thus, the band at 390 nm is attributed to the  ${}^4A_2({}^4F) \rightarrow {}^4E({}^4T_1({}^4F))$  transition and the band at 414 nm to  ${}^4A_2({}^4F) \rightarrow {}^4A_2({}^4T_1({}^4F))$  transition. The above results prove that the R-line and R-PSB lines arise from the same optical center. It can be seen from Fig. 4b that the broad excitation bands centered at 539 and 537 nm corresponding to  ${}^4A_2({}^4F) \rightarrow {}^4T_2({}^4F)$  transitions in the PLE spectra monitored at the  $N_1$ - and  $N_2$ -lines are shifted towards the longer-wavelength side in comparison with those of R-line and R-PSB lines. This proves that the  $N_1$ - and  $N_2$ -lines arise from other centers than R-line and R-PSB lines. According to authors [6], the N-lines maybe arise from different classes of  $Cr^{3+}$  ions with different, more or less perturbed short range orders.

The PL spectra excited by 531 nm at 300 and 12 K of the  $Zn(Al_{1-x}Cr_x)_2O_4$  with different mole fraction  $x$  are presented figure 5. The results showed that the intensity ratio of the 706.0, 722.8, 740.0, 745.7 and 754.0 nm lines to 685.5 nm line at 300 K (figure 5(a)) increases with increasing mole fraction  $x$  in ranging from  $x = 0.005$  to 0.04. The increase of the intensity ratio of the 704.5, 727, 730, 737, 745 and 754 nm lines to 685 nm line with increasing mole fraction  $x$  was more clearly observed

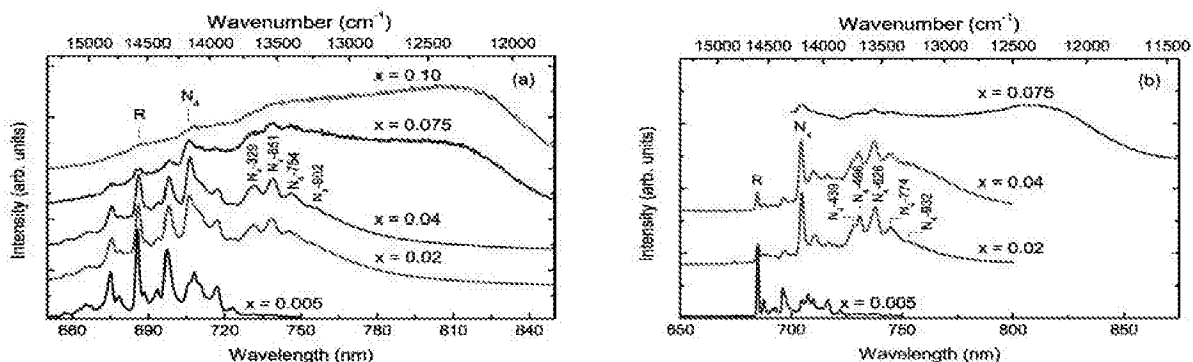


Fig. 5. The PL spectra excited by 531 nm at (a) 300 K and (b) 12 K of the  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$  with different mole fraction  $x$ .

at 12 K (figure 5(b)). In order to find out about the origin of the emission lines, PLE spectra at 12 K were measured. It can be seen from figure 6(a), the PLE spectra monitored at emission wavelengths 727, 730, 737, 745 and 754 nm lines are similar to that recorded at 704.5 nm line. It is well known that in the samples with the enough high  $\text{Cr}^{3+}$ -concentrations, the  $\text{Cr}^{3+}$  ions have the possibility of pairing. Therefore, like the previous reports [2, 4, 5], the 704.5 nm line (denoted by  $\text{N}_4$ ) in the PL spectrum measured at 12 K is interpreted to arise from  $\text{Cr}^{3+}$  -  $\text{Cr}^{3+}$  pairs and 727, 730, 737, 745 and 754 nm lines are the phonon-sidebands of  $\text{N}_4$ -line:  $\text{N}_4$ -439 (727 nm),  $\text{N}_4$ -496 (730 nm),  $\text{N}_4$ -626 (737 nm),  $\text{N}_4$ -774 (745 nm) and  $\text{N}_4$ -932 (754 nm).

In particular, as increasing mole fraction  $x$  up to 0.075 and more, on the long wavelength side of the  $\text{N}_4$ -lines a very broad emission band centered at 813 nm at 300 K (figure 5(a)) or at 810 nm at 12 K (figure 5(b)) appeared. In the PL spectrum of the sample  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$  with  $x = 0.10$  the short-wavelength lines are extremely weak, and the spectrum is dominated by the broad emission band centered at 813 nm.

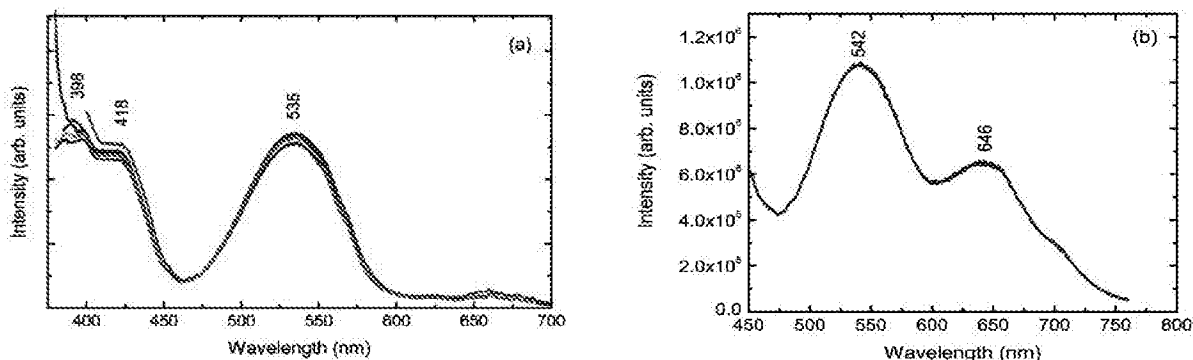


Fig. 6. The PLE spectra at 12 K of the  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$  with  $x = 0.075$  monitored at different emission wavelength: (a)  $\text{N}_4$ -439 (727 nm),  $\text{N}_4$ -496 (730 nm),  $\text{N}_4$ -626 (737 nm),  $\text{N}_4$ -774 (745 nm) and  $\text{N}_4$ -932 (754 nm); (b) 810 nm.

Figure 6(b) shows the PLE spectrum at 12 K of the  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$  with  $x = 0.075$  recorded at 810 nm. Two broad excitation bands are detected. The band at 542 nm corresponds to  $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_1(^4\text{F})$  transitions and the band at 646 nm to  $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_2(^4\text{F})$  transitions [7]. It is seen from figure 6(b) and figure 4(b) that the broad excitation band corresponding to  $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_2(^4\text{F})$  transition in

the PLE spectrum monitored at 810 nm are shifted by 115 nm towards the longer-wavelength side, compared with the PLE spectrum monitored at the R-line. This proves that the  $\text{Cr}^{3+}$  ions in the samples doped with high Cr contents locate in the lower octahedral field than in the samples doped with low Cr contents. This result is in good agreement with the result obtained by XRD analysis, in which the ligand-field influenced  $\text{Cr}^{3+}$  ion is decreased with increasing the mole fraction  $x$ . Therefore, the broad emission bands centered at 813-810 nm can be interpreted as the  ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$  transition of  $\text{Cr}^{3+}$  ions in the low octahedral field.

#### 4. Conclusion

The effect of  $\text{Cr}^{3+}$  dopant concentration on the structural and optical properties of the synthesized samples  $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$  has been studied. With increasing Cr contents, the lattice constants increase and the ligand-field surrounding  $\text{Cr}^{3+}$  ions is decreased. For the samples with low  $\text{Cr}^{3+}$  dopant concentrations, the PL spectra mainly consist of sharp lines (R-line and R-PSB) assigned to the  ${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$  transitions of ions  $\text{Cr}^{3+}$  in strong octahedral field. With increasing  $\text{Cr}^{3+}$  contents the PL spectra exhibit the PL lines ( $\text{N}_4$ -line and  $\text{N}_4$ -PSB) related to the transitions in the  $\text{Cr}^{3+} - \text{Cr}^{3+}$  pairs. Further increasing  $\text{Cr}^{3+}$  dopant concentrations up to an appropriate value, in the PL spectra a broad band centered at 810-813 nm appears. This broad band is assigned to the  ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$  transition of ions  $\text{Cr}^{3+}$  in weak octahedral field.

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