OPTICAL PROPERTIES OF Co^{2+} IN SYNTHETIC $ZnAl_2O_4$ SPINEL

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Abstract: The $Zn_{1-x}Co_xAl_2O_4$ (x = 0.005 ÷ 0.300) spinel powders have been synthesized by the sol-gel method. Optical properties of Co^{2+} ion in the synthesized samples were investigated. The dependence of the emission spectrum on the excitation wavelength and temperature was presented. Transitions taking place in the tetrahedral coordinate site were conclusively identified.

1. Introduction

Recently transparent glass-ceramics, as a new kind of materials, have attracted a lot of interests due to their novel thermal and optical properties as well as their relatively low production costs [1]. Extensive studies of transparent glass-ceramics doped with various transition metals and rare-earth elements have been carried out so far [2], [3], [4], [5], [6]. In this report, we present the optical properties of Co^{2+} ion in cobalt-doped zinc aluminate ($ZnAl_2O_4:Co^{2+}$) synthesized by the well-known sol-gel method. The dependence of the photoluminescence spectrum on the excitation wavelength and on the temperature was investigated providing some insight into the actual optical properties of Co^{2+} in the tetrahedral coordinate site.

2. Experimental

The $Zn_{1-x}Co_xAl_2O_4$ spinel was synthesized by the sol-gel method described in detail elsewhere [7]. $Zn(NO_3)_2$, $Co(NO_3)_2$ and $Al(NO_3)_3$ were used as starting materials. The xerogel sample was placed at the center of the horizontal tube furnace. The furnace was then heated up to 1050 ^{0}C at a heating rate of 7 ^{0}C/min and kept for 3 h. After sintering, the sample was left inside the furnace to cool down naturally.

The crystal structure of the synthesized samples was characterized by a Siemens D5005 XRD diffractometer. Photoluminescence (PL) and photoluminescence excitation spectra (PLE) were both measured in the temperature range from 11 to 300 K using a Fluorolog FL3-22 Spectrofluorometer with a Xenon lamp of 450 W as an excitation source.

3. Results and discussion

Figure 1 shows typical XRD pattern of the synthesized sample. All the diffraction peaks closely resembles that of $ZnAl_2O_4$ crystal in the database. No other phases are detected. The strong and sharp diffraction peaks also indicate a remarkable good crystalinity of the synthesized $ZnAl_2O_4$ samples.

The photoluminescence excitation (PLE) spectra of $Zn_{1-x}Co_xAl_2O_4$ (x = 0.005) recorded by monitoring the fluorescence of transitions at two different wavelengths, 643 and 689 nm, are shown in Fig. 2. It is well-known that Co^{2+} ions, having the electronic configuration $3d^7$, often occupy tetrahedral sites as they are doped in $ZnAl_2O_4$. The PLE lines around 404, 424, 475, 545 and 618 nm are indeed due to the characteristic transitions of Co^{2+} ion from the $^4A_2(^4F)$ ground state to the $^2T_2(^2H)$, $^2E(^2H)$, $^2T_1(^2P)$, $^2A_1(^2G)$ and $^4T_1(^4P)$ excited states, respectively. The luminescence excitation lines around 570 and 590 nm are attributed to the vibronic transition from $^4A_2(^4F)$ to $^4T_1(^4P)$ [5].

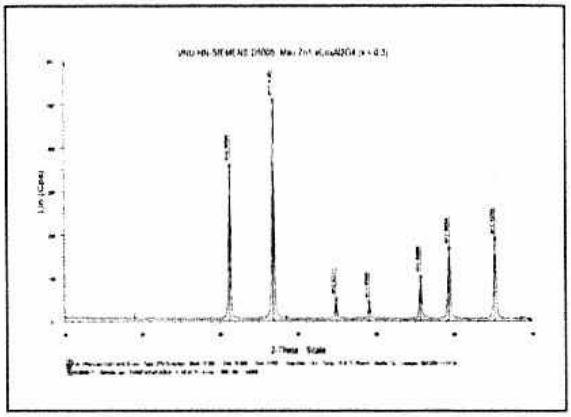

Fig.1. The XRD patterns of the $Zn_{1-x}Co_xAl_2O_4$ spinel with x = 0.300

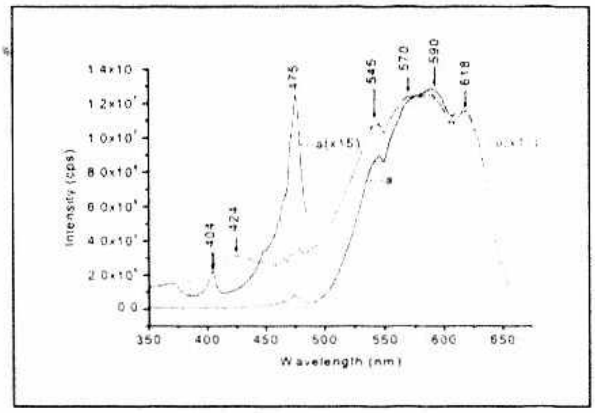

Fig.2. The PLE spectra of $Zn_{1-x}Co_xAl_2O_4$ (x = 0.005) monitored at 643 nm (a), 689 nm (b)

The photoluminescence (PL) spectra of the synthesized $Zn_{1-x}Co_xAl_2O_4$ (x = 0.005) excited at three different excitation wavelengths of 590, 475 and 424 nm are shown in Fig. 3. It is found that the PL spectrum of the sample strongly depends on the excitation wavelength. The PL spectrum excited at 590 nm manifests only a broad band around 643 nm. The origin of this transition has been inconsistently reported elsewhere [2], [3] and the matter would be brought back into discussions later in this report. Under excitation wavelength of 475 nm, the PL consists of a strong broad emission band at 643 nm and a series of weak emission lines locating around 676, 699, 709 and 718 nm (Fig. 3a). The PL spectrum is completely dominated by a series of seven emission lines centered at about 669, 676, 687, 699, 709, 718 and 724 nm (Fig.3b) as the shorter excitation wavelength of 424 nm is employed. Interestingly, this spectrum nearly coincide with that of Cr^{3+} ion in the octahedral coordinate site as depicted also in Fig. 3. It should be noticed here the fact that the energy levels of Cr^{3+} ion ($3d^3$) in octahedral site are similar to those of Co^{2+} ion ($3d^7$) in tetrahedral site [1]. Therefore, the series of sharp emission lines appearing in the range of 650 to 730 nm can be evidently attributed to the transition from $^2E(^2G)$ exited state to the $^4A_2(^4F)$ ground state and its vibronic transitions.

As already mentioned, there have been some conflict results concerning the origin of the broad band around 643 nm. Denisov *et al.* assigned this band to $^4T_1(^4P) \rightarrow {}^4A_2(^4F)$ transition as they observed a broad band at 300 K [2]. Whereas Tanaka *et al.*, having observed it as a series of sharp lines at 4.5 K, concluded that this emission band is due to $^2E(^2G) \rightarrow {}^4A_2(^4F)$ transition [3]. In order to clarify the matter, we examined the dependence

of this band on the temperature. Figure 4 shows the evolution of the concerned emission band as the temperature varies from 13 K to 300 K. It is clear that the broad band around 643 nm at 300 K is split up into several sharp lines at temperature lower than 150 K due to

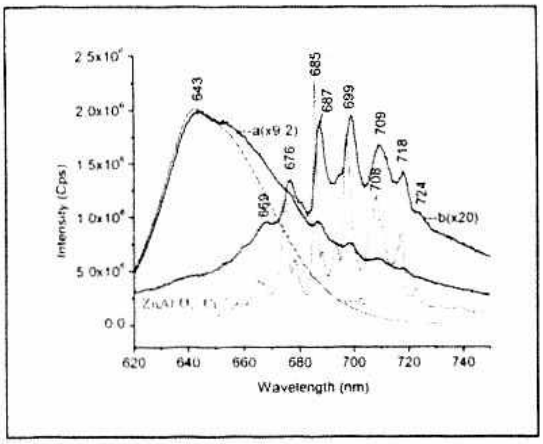

Fig.3. The emission spectra of the $Zn_{1-x}Co_xAl_2O$ with x = 0.005 excited at 476 (a), 424 (b) and 590 nm (c)

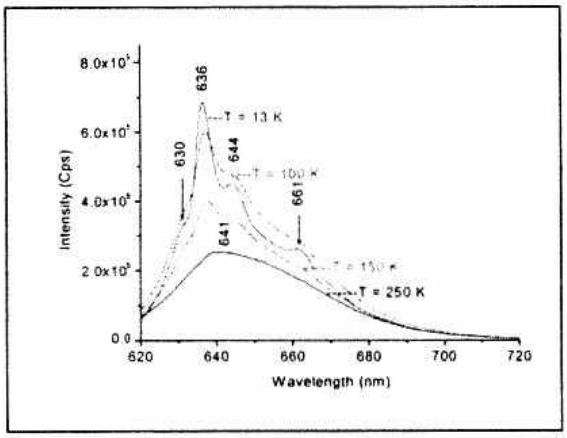

Fig.4. The emission spectra of $Zn_{1-x}Co_xAl_2O_4$ (x = 0.010) excited at 589 nm recorded at different temperature

the strong spin-orbit interaction. Four emission lines at around 630, 636, 644 and 661 nm are clearly identified at 13 K (Fig.4a). They can be assigned to the transitions from $\Gamma_6{}^4T_1({}^4P)$, $\Gamma_8{}^4T_1({}^4P)$, $\Gamma_7{}^4T_1({}^4P)$ and $\Gamma_8{}^4T_1({}^4P)$ states to the ${}^4A_2({}^4F)$ ground state, respectively.

4. Conclusion

The optical properties of Co^{2+} ion synthetic $ZnAl_2O_4{:}Co^{2+}$ was studied. Transitions of Co^{2+} ion taking place in the tetrahedral site were evidently identified. The broad band around 643 nm was attributed to the ${}^4T_1({}^4P) \rightarrow {}^4A_2({}^4F)$ transition, whereas the ${}^2E({}^2G) \rightarrow {}^4A_2({}^4F)$ transition together with its vibronic transitions results in a series of sharp emission lines.

Acknowledgement. The Authors wish to express their sincere gratitude to the Center for Materials Science, University of Science for permission to use equipment.

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