

PREPARATION AND PHOTOLUMINESCENCE OF ZnGa₂O₄:Co

V. Zhitar¹, V. Ursaki¹, G. Volodina¹, S. Muntean², T. Shemyakova¹

¹*Institute of Applied Physics, Academy of Sciences of Moldova, 5, Academiei str., MD-2028, Chisinau, Republic of Moldova*

²*Institute of Electronic Engineering and Industrial Technologies (IEEIT), Academy of Sciences of Moldova, 3/3, Academiei str., MD - 2028, Chisinau, Republic of Moldova*

(Received 5 March 2007)

Ceramic samples of ZnGa₂O₄ doped with Co have been prepared. Their photoluminescence spectra measured at laser excitation ($\lambda = 351$ nm) and various temperatures (10 – 300 K) contain a wide band, centered at 2.8 eV (10 K) with its halfwidth ~ 0.5 eV, induced by the recombination of donor-acceptor pairs. The subsequent thermal annealing leads to its concentration quenching.

Introduction

Oxide compounds ZnO, In₂O₃, CuO are intensively investigated owing to their unique physical properties being promising for wide application in various fields of engineering [1-4]. This also relates to the A^{II}B^{III}₂C^{VI}₄ dioxides. For example, ZnGa₂O₄ possesses a wide forbidden gap ($E_g \approx 3.0$ eV, $T = 295$ K). This compound grown at ~ 1300 °C doped with Eu and F may be used as a luminophore in the red spectral range [5]. We obtained this material previously at 900 °C using ceramic sintering method [6]. Unlike results presented in [5], the photoluminescence (PL) spectra contain narrow bands; that is, the spectra are practically linear. It would be expedient to enhance the photoluminescence intensity. With this aim it is necessary to choose a proper doping impurity and its concentration. We have chosen doping with Co because in this kind of crystals stimulated radiation was registered [7]. In this paper we describe results obtained at various temperatures.

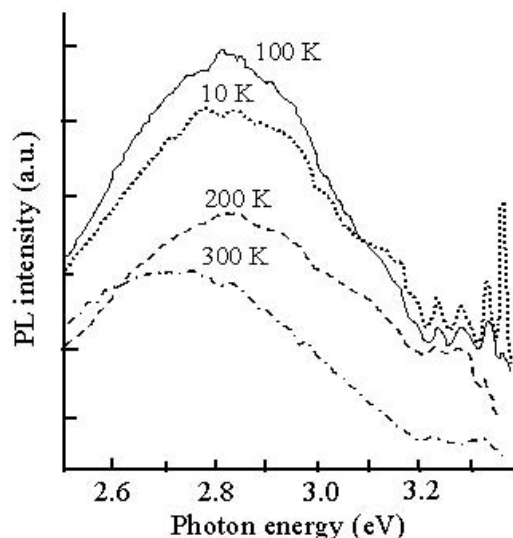
Sample preparation and experimental data

The method of sample preparation has been described in [6]. ZnO, Ga₂O₃, and CoO powders were weighed in the stoichiometric proportion that corresponds the Zn_{1-x}Co_xGa₂O₄ composition, $x = 0.05$. After sintering the pellets of blue colour were obtained. As determined by diffraction X-ray analysis the main composition corresponds to ZnGa₂O₄:Co. ZnO was registered as impurity. Additional annealing during 24 hours at 900 °C did not change the composition of material. PL spectra were measured similar to [4] at laser excitation ($\lambda = 351$ nm) at $T = 10, 100, 200$ and 300 K.

Results and discussion

The PL spectra measured at various temperatures are shown in Fig. 1. Their main feature is a wide band centered at $E_1 \approx 2.8$ eV with its halfwidth $\Delta h\nu \approx 0.5$ eV ($T = 10$ K) and temperature coefficient $dE/dT \approx 1.6 \cdot 10^{-4}$ eV/K. Similar to ZnIn₂S₄ [8] it is generated due to

recombination of donor-acceptor pairs. One of the reasons in favour of this idea is that the peak of the X-ray induced luminescence shifts in the higher energy direction, when the voltage and excitation current increase [9]. There are some peculiarities in the range $3.2 \div 3.4$ eV



that are linked with recombination in ZnO that involves excitons [1]. In [7] the spectrum of stimulated radiation in $\text{ZnGa}_2\text{O}_4:\text{Co}$ single crystals has been shown with peak at ~ 650 nm. $\text{ZnGa}_2\text{O}_4:\text{Co}$ single crystals were grown by the Czochralsky method from nonstoichiometric melt with MgO and ZrO_2 addition. Co^{2+} concentration in the melt was 0.01 wt. %. The interpretation was given in terms of T_d symmetry as transitions from the Co^{2+} upper excited state to the ground state.

Fig. 1. PL spectrum of $\text{ZnGa}_2\text{O}_4:\text{Co}$ ceramic. $T = 10, 100, 200$ and 300 K.

The X-ray diffraction patterns show that at additional annealing (900°C) with the aim to homogenize the samples they retain their initial composition. The PL spectra of samples after annealing measured under the same conditions are shown in Fig. 2.

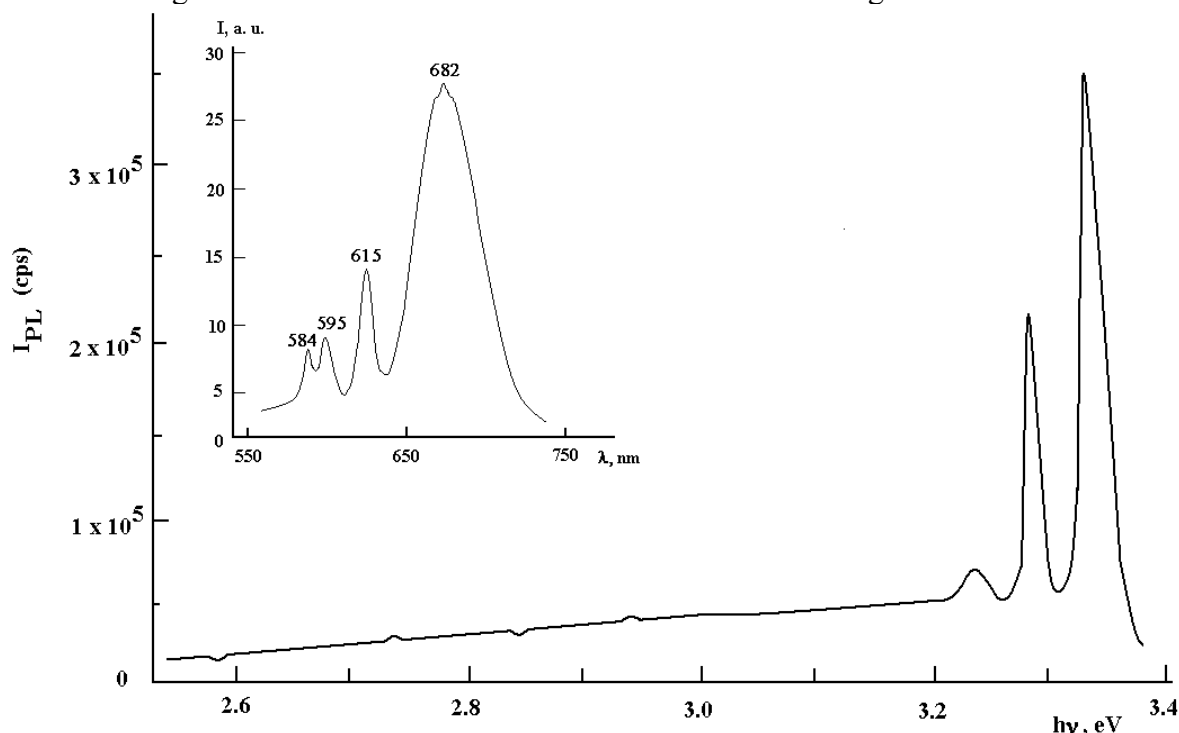


Fig. 2. PL spectrum (10 K) of $\text{ZnGa}_2\text{O}_4:\text{Co}$ after additional annealing. Insert: PL spectrum of $\text{ZnGa}_2\text{O}_4:\text{Eu, F}$ (300 K).

Practically they exhibit peculiarities of radiative recombination similar to that in ZnO that involves excitons. Here the insert shows the PL spectrum of the $\text{ZnGa}_2\text{O}_4:\text{Eu, F}$ sample grown according to [5] with addition of 2 mol. % of EuF_3 . The main band has its maximum at

682 nm and narrow peaks at 584, 595 and 615 nm. As reported in [6] the PL spectrum of the ceramic sample contains a set of sharp peaks in the 650 – 710 nm range, namely at 687, 695, 708 and 714 nm. Comparing our experimental data with results presented in [5-7] we may note that doping with Co using its concentration mentioned above significantly changes the PL spectrum. Instead of previously reported linear spectrum [6] we have a wide band shifted in the energy range. After the thermal treatment the PL disappears. This obviously may be linked with the concentration quenching of the radiation. We may conclude that during recent years the interest has increased in the investigations of dioxide compounds. In particular, the study of nanometer $ZnAl_2O_4$ powder that was obtained using two microemulsion techniques is described in [10]. Earlier the same material was grown using heterometal alcoxide $ZnAl_x(OR)_8$ [11].

Conclusion

In conclusion note that $ZnGa_2O_4$ ceramics doped with Co was obtained. The PL spectra of the material containing a wide band that appears due to the recombination of donor-acceptor pairs were measured. The thermal treatment leads to its concentration quenching.

References

- [1] V.V. Ursaki, I.M. Tiginyanu, V.F. Zhitar et al., *Phys. Stat. Sol. (c)*, 3, 8, 2754, (2006).
- [2] Yu.P. Sukhorukov, B.A. Gijevskii, E.V. Mostovshchikova et al., *Nanocrystalline CuO*, *ZhTP Letters*, 32, 81, (2006).
- [3] A.N. Georgobiani, M.B. Kotlyarevskii and A.V. Marakhovskii, *Izvestia RAN, Neorganicheskie materialy*, 41, 6, 696, (2005).
- [4] A.N. Gruzintsev and E.E. Yakimov, *Izvestia RAN, Neorganicheskie materialy*, 41, 7, 808, (2005).
- [5] V.G. Tagiev, G.G. Guseinov, R.B. Dzhahbarov et al., *Izvestia RAN, Neorganicheskie materialy*, 36, 12, 1415, (2000).
- [6] V.F. Zhitar, V.V., Ursaki, S.P. Munteanu et al., *Mold. J. Phys. Sci.*, 4, 4, 412, (2005).
- [7] N.V. Kuleshov, V.G. Shcherbitskii, V.P. Mikhailov et al., *Optics and Spectroscopy*, 87, 1, 76, (1999).
- [8] V.F. Zhitar, V.I. Raulyan and S.I. Radautsan, *Nuovo cimento D2*, 6, 1919, (1983).
- [9] G.F. Volodina, S.P. Munteanu, V.F. Zhitar et al., *Mold. J. Phys. Sci.*, 1, 1, 73, (2002).
- [10] V. Ciupina, I. Carazeanu and G. Prodan, *J. Optoelectronics and Advanced Materials*, 5, 4, 1317, (2004).
- [11] S. Mahur, M. Veith and H. Shen, *Int. Semicond. Conf. CAS, Sinaya*, 1, 147, (2002).