ABOUT THE GREEN BAND NATURE IN THE PL SPECTRA OF ZnS:Al CRYSTALS ANNEALED IN Bi AND Pb BASED MELTS

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Abstract. The photoluminescence at 77K of ZnS and ZnS:Al single crystals annealed in the Pb, Pb+0,2wt% $PbCl_2$, and Bi+1,5·10^{-3}wt% Al melts was investigated.

It is shown that during the annealing process in the near the surface region of the crystal a layer or a new phase inclusions could be formed near the ZnS lattice distortions. The green radiation with the maximum close to 530…540nm in the PL spectra of ZnS:Al crystals annealed in Bi or Pb containing melts is stipulated by aluminum presence in the ZnS crystals.

Key words: zinc sulfide, bismuth, lead, aluminum, photoluminescence. ***UDC 535.37***

INTRODUCTION

In the PL spectra of ZnS crystals the radiation bands in the green region of spectrum are observed quite often, The radiation centers on the base of oxygen (λ=520nm) [1], copper (λ=500...510nm) [2], double charged sulfur vacancies (λ=520nm) [3] could be responsible for the appearance of these bands. The results of PL studies of ZnS crystals annealed in Bi based melts are brought in paper [4]. Authors supposed, that intracentred transitions in the complex center of ($V_{Zn}^{/}$-Bi*)^{x} type, or DX^{-} centers with bismuth participation are responsible for the band with the maximum close to 530nm appearing at the excitation of the near to surface region. Later it was observed, that the analogous band appears also sometime in the PL spectrum of ZnS:Al crystals annealed in the vacuum or in the sulfur atmosphere. For to find out the nature of the radiation centers responsible for the green band in ZnS:Al crystals, the results of PL studies of ZnS and ZnS:Al crystals annealed in the lead melts and lead with $PbCl_2$ salt additions.

EXPERIMENTAL

The samples for the annealing were cleaved from the same ZnS or ZnS:Al bulk. The doping was carried out during the annealing process in the melts: Pb, Pb+0,2wt% $PbCl_2$, and Bi+1,5·10^{-3}wt%Al at the temperature of 1200K during 100hrs then the crystals were cleared of the melt and cooled outside the furnace in the air. The luminescence was studied at the excitation of the near to surface and inner regions (volume) of the crystal after the cleaving. The PL spectra (77K) were

studied at the luminescence excitation by N_2 laser (λ=337,1nm) and recorded by synchronous detecting method.

RESULTS AND DISCUSSION

The PL spectrum (77K) of the starting ZnS (Fig.1, curve 1) consist of the band with the maximum close 400nm which is stipulated by the presence of the single charged sulfur vacancy V_S^x [5] and of a weak band centered close to 650nm formed, probably, at the holes capture on the acceptor level of Fe^{+2} [6]. After the crystals annealing in Pb melt the luminescence intensity sharply decreases (more then by two orders of magnitude) (Fig.1, curve 2). At that the PL radiation spectra are practically the same independently of the excitation place. The sharp intensity decrease is also observed at these crystals annealing in Bi melt.

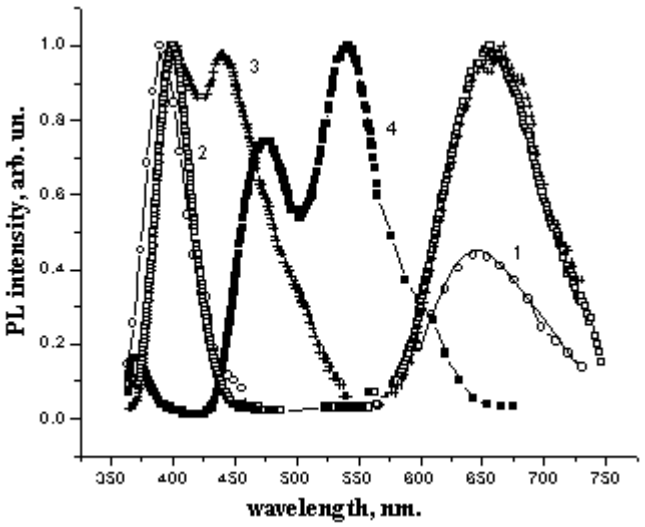

Fig.1. The PL spectra of ZnS crystals at 77K.
1- starting; annealed in the melts: 2- Pb; 3- Pb with addition of $PbCl_2$; 4- Bi with addition of Al. Curves 2 and 3 are increased in 100 times.

At PL excitation in the cleavage middle of the ZnS sample annealed in Pb melt with $PbCl_2$ additions the luminescence intensity also sharply decreases (Fig.1, curve 3). At that in the spectrum a complex band with the maximum at 440nm which is gently sloping in the long wavelength region appears. The PL spectra structure is analogous both in the near to surface region as well as in the bulk volume.

From the analysis of the above given PL spectra one can see, the chlorine presents in the Pb melt leads to the appearance of a radiation in the blue-green region of spectrum close to 440nm. In none of these samples the radiation with the maximum close to 530nm was observed.

A different picture is observed at the annealing in the same media of Zns crystals containing Al impurity. The PL (77K) spectrum of the starting ZnS:Al crystal is given in Fig.2, curve 1. The predominant luminescence band has maximum close to 400nm. On its long wavelength slope the

peculiarities at 435nm, 460nm and relatively weak radiation in the green region of spectrum are observed. The sulfur vacancy V_S 405nm [5] and Al based radiation centers 435nm [7] and 460nm [6] besides the red band with the maximum close to 650nm is present.

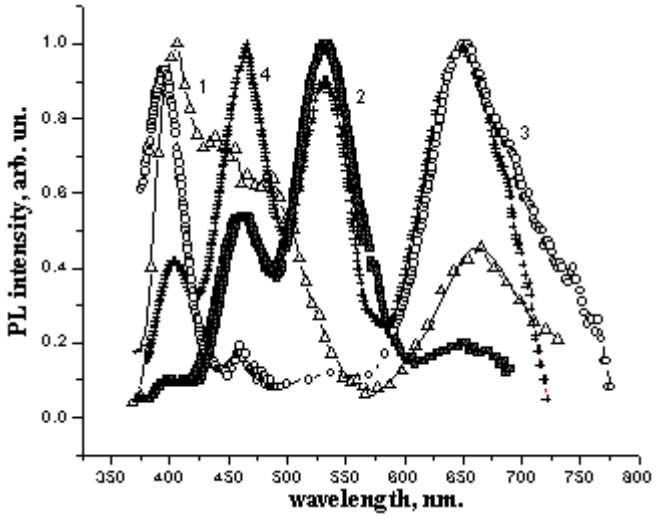

Fig.2. The PL spectra of ZnS:Al crystals at 77K.
1- starting; annealed in the melts: 2- Pb (crystal volume); 3- Pb (subsurface region); 4- Pb with addition of $PbCl_2$. Curves 2, 3 and 4 are increased in 1000 times.

After ZnS:Al crystal annealing in the Pb melt the position of the radiation bands maxima from the bulk volume do not change. But the luminescence intensity sharply decreases (by about 3 orders of magnitude) (Fig.2, curve 2). At the excitation of the near surface region in the PL spectrum a weak radiation bands with the maxima close to 400nm, 460nm and 650nm are also observed (Fig.2, curve 3).However the predominant band with the maximum at 530nm appears. ZnS;Al sample annealing in the Pb ($PbCl_2$) melt leads to the appearance in he PL spectrum pf a band centered at 530nm. The predominant band in this case became the band with the maximum at 460nm ((Fig.2, curve 4).

The radiation quenching in the blue-green region of spectrum indicates that at ZnS:Al crystal annealing in Pb ($PbCl_2$), apparently, the extraction occurs of the aluminum occupying the zinc knots from the bulk volume in the near to surface region. At the same time from the near to surface region to the crystal volume a flux of the zinc atoms is moving, and are completing the freed of Al zinc vacancies. The Zns crystal annealing in the Bi melt containing aluminum also leads to the occurs of the radiation band with the maximum close to 530nm in the PL spectrum (77K) (Fig.1, curve 4). In the paper [8] it was shown that the predominant radiation band in the PL spectrum at 77K in the polycrystalline α-$ZnAl_2S_4$ the band with the maximum close to 540nm is predominant. Therefore, one can assume, that during the above named annealing processes in the near to surface region of the samples a layer or inclusions of a new phase can be formed close to the ZnS lattice distortions.

CONCLUSIONS

The analysis of the given results allows making a conclusion that the green radiation with the maximum close to 530nm in the PL spectrum of ZnS crystal can appear in the places enriched by Al impurity.

Thus, on the bases of the carried out studies one can make a conclusion that the green radiation with the maximum close to 530…540nm in the PL spectra (77K) of ZnS:Al crystals annealed in Bi and Pb based melts is stipulated by the aluminum presents in ZnS crystals. No radiation bands that could be related to the lead based radiation centers was observed.

REFERENCES

1. Морозова Н.К., Кузнецов В.А.; 1987, Сульфид цинка. Получение и оптические свойства.; Наука; М; 200с:
2. Кюри Д., Пренер Д.С.;1970, Люминесценция, связанная с глубокими уровнями; Под ред. Медведева С.А.; Физика и химия соединений A_2B_6.;Мир; М.; 624:
3. Георгобиани А.Н., Варламов И.В.; (1993); Неорганические материалы; 28; No 10; 1362-1366;
4. Коротков В.А., Брук Л.И., Соболевская Р.Л., Сушкевич К.Д..; (2002); ЖПС; 69; No 2; 225-228;
5. Туницкая В.Ф., Филина Т.Ф., Панасюк Е.И., Илюхина З.П..; (1971); ЖПС; 14; No 2; 239-245;
6. Берлов П.А., Буланый М.Ф., Коваленко А.В., Коджесекиров Ф.Ф.. Якунин А.Л.; (1985); 21; No 9; 1453-1456;
7. Abdel-Kader A., Farag H.G.; (1988); J. Mater. Science; 23; 2382-2386;
8. KAI Tetsuya, KAFUKU Masakazu, AKSENOV Igor and SATO Katsuaki.; (1995); Jap.J. Appl. Phys.; 34; No9A; 3073-3074;