

Investigation of Solid's Surfaces by Radical Recombination Luminescence

Yu.I. Tyurin, V.D. Khoruzhii, Yu.A. Sivov, S.H. Shigalugov

Tomsk polytechnic university, Lenin avenue 30, Tomsk, Russia, 3822 563-437, E-mail: tyurin@fmsm.tpu.edu.ru
Norilek. Industrial Institute, Norilsk, Russia

Abstract – The crystal phosphor radical recombination luminescence (RRL) spectra excited by heat energy atoms (hydrogen or oxygen) are investigated. It has been shown that in RRL spectra of crystal phosphor activated by manganese, there is a red band, which is absent in photo luminescence (PL) spectra. The origin of red centers and the mechanism of transmitting them energy liberated while the adsorption and recombination of the crystal phosphor surface atoms is discussed.

1. Introduction

A radical recombination luminescence (RRL) of crystal phosphors is due to the recombination of free atoms and radicals on the surface of solids [1].

The surface excitation is specific in comparison with photo excitation. It is clearly seen in the RRL spectra. For example, in RRL spectra of ZnS-Mn phosphors, a red band is found which is not present in photo luminescence spectra [2].

Its intensity depends on RRL excitation, sample preparation, and manganese concentration. In this work we have studied the RRL red band of phosphors: Zn_2SiO_4 -Mn, $CaSO_4$ -Mn, $Zn_3(PO_4)_2$ -Mn (K-59), AlN-Mn and GFK – Sb, Mn – Toshiba.

2. Research methods

RRL is excited by hydrogen and oxygen atoms generated by the HF non electrode discharge in a molecular gas. Hydrogen is produced by the electrolytic method. It is cleansed from impurities by passing through a heated palladium membrane. Oxygen is produced by thermic decomposition of chemically clean $KMnO_4$ with subsequent incandescence in vacuum upon a molecular 13X sieve.

A spectrograph ISP-51 controls the luminescence spectra. The spectrograph is equipped with a photoelectric prefix FEP-1 and the plotter potentiometer PS1-02. A secondary emission photocell FEU-79 is used as a receiver. The luminescence spectra are corrected on spectral sensibility and normalized. The PL is excited by DRT-220 lamp with a 313 nm line.

3. Experimental results and discussion

Fig. 1–2 show the PL and RRL spectra of Zn_2SiO_4 -Mn and $CaSO_4$ -Mn crystal phosphors. The PL spectra of Zn_2SiO_4 -Mn and $CaSO_4$ -Mn include a green line with $\lambda_{max}=520$ nm (Fig. 1, curves 1 and 2) and a blue line with $\lambda_{max}=500$ nm (Fig. 2, curve 3). The PL AlN-Mn spectra have orange band with $\lambda_{max}=600$ nm (Fig. 3,

curve 3). The PL spectra of GFK-Sb, Mn have two bands: the blue one with $\lambda_{max}=480$ nm and the orange band with $\lambda_{max}=580$ nm (Fig. 4, curve 2). For all phosphors, there is practically no radiation in the red region while photo excited. Unlike, the RRL_H spectra of these phosphors include mainly a red band with $\lambda_{max}=660-680$ nm (Fig. 1 – Fig. 4).

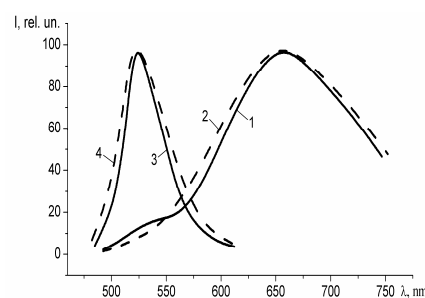


Fig. 1. RRL_H (1, 2) and PL (3, 4) Zn_2SiO_4 -Mn spectra at 295 K (1, 3), 390 K (2), and 450 K (4)

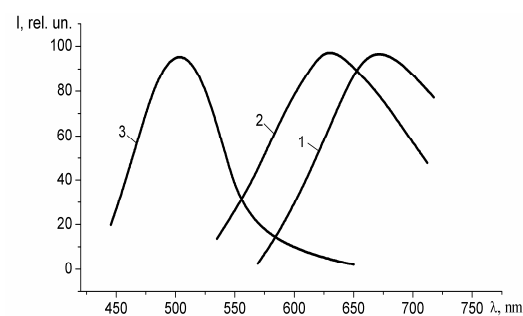


Fig. 2. RRL_H (1, 2) and PL (3) $CaSO_4$ -Mn spectra at 295 K (1, 3) and 470 K (2)

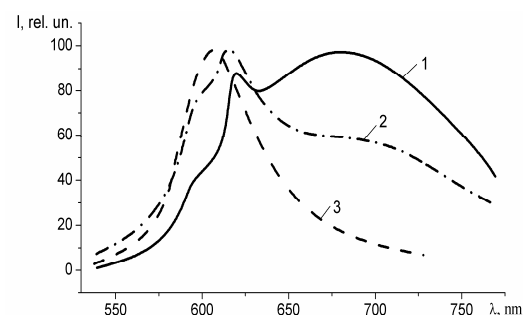


Fig. 3. RRL_H (1, 2) and PL (3) AlN-Mn spectra at 295 K (1, 3) and 370 K (2)

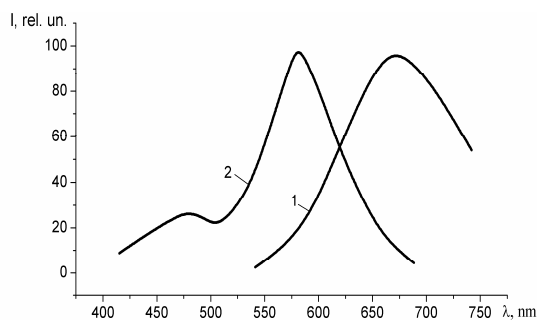


Fig. 4. RRL_H (1) and PL (2) GFK-Sb, Mn (Toshiba) spectra at 295 K (1).

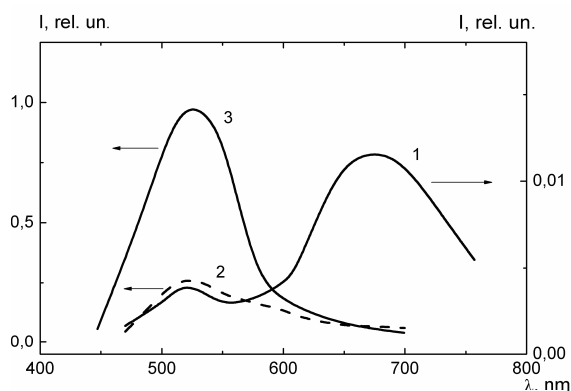


Fig. 5. RRL_O Zn₂SiO₄-Mn spectra at 295 K (1, 3), 450 K (2), and 550 K (3)

A red band with $\lambda_{\max} = 660$ nm [3, 4], is absent in PL spectra. However, it is found in RRL spectra of crystal phosphor Zn₂SiO₄-Mn, excited by the oxygen atoms (Fig. 5).

We have not found like change in crystal phosphors activated (in nitrogen) by manganese. It is due to the fact, that Mn²⁺ ion almost does not adsorb nitrogen.

Photo excitation of crystal phosphors is volumetric [5], and penetrates in crystal at a distance about 1 micron. Absence of the red band proves that there are no red centers, or their quantity is negligible in comparison with that of orange, blue, and green centers. However, the red centers concentration is sufficient to be excited by hydrogen atoms. We assume that the red centers are located in a thin surface layer of a thickness not more than 2–3 lattice constants.

Generation and origin of the ZnS-Mn red centers are widely discussed in literature. Generation of the red band is supposed to be due [6, 7] to a phosphor synthesis techniques. When crystal is grown up from Te-solution in melt, the PL spectra include the red band with $\lambda_{\max} = 650$ nm. However, when growing by a gas transport reaction method (the manganese concentration is the same) there is no the red band [6]. In accordance with [7], the red band appears only in thermo unstable systems [7].

Obviously, near the surface, conditions for the red centers generation are preferable. While synthesizing

ZnS-Mn, the temperature and incandescence time can provide a non-uniform manganese depth concentration. Thus, in the surface layers, a thermodynamically non-equilibrium imbalance activator concentration is produced. Superfluous manganese in a surface layer can be stabilized in accordance with a volumetric compensation principle [8].

Stabilization can also happen on the surfaces of phosphors synthesized in a neutral medium. At that, the process takes place after the synthesis, due to the adsorption of ambient air oxygen on the surface of a phosphor produced.

While interaction between hydrogen and ZnS-Mn [9], the manganese ions migrate from the crystal depth to its surface. Thus, the surface concentration increases, which leads [6, 10] to extinguishing of orange band suppress the red band generation.

Double and triple associates of Mn²⁺ are supposed to be responsible for the red band [10, 11]. In [6], the manganese center radiation is believed to be caused by a coordinate group build by Mn²⁺ and surrounding anions. The red centers [6] are associated with Mn²⁺ in octahedral or mixed tetrahedron position. The octahedron surrounding of Mn²⁺ [6] leads to a greater level splitting of Mn²⁺ than octahedral surrounding, the d-d optical transition energy being changed.

The RRL band (Fig. 1–4) is very wide. Its half width is about 150 nm for Zn₂SiO₄-Mn, Zn₃(PO₄)₂-Mn, CaSO₄-Mn, ALN-Mn; and about 140 nm for GFK – Sb,Mn, which confirms its complexity. We assume that two or even three center types are responsible: the octahedral red centers generate the short wave band, the long wave band being caused mainly [10, 11] by double and triple Mn²⁺ associates.

We also assume that the probability of the recombination energy transmission in the crystal volume is negligible. In RRL, the recombination energy transmission to the volumetric light centers is possible only while the hole migration. Thus, while exciting the red band, a direct red band excitation mechanism through neutral form of chemisorption dominates.

The red band excitation is due to a strike recombination with adsorbed neutral atoms producing oscillate excited H₂ and O₂ molecules. The oscillation energy transmission to the light centers is in accordance with a multi quanta oscillation transmission [3]. When the multi quanta excitation mechanism is true, relaxation of luminescence of the oscillate excited molecule (dipole or quadruple) can be accompanied by an electron transition in the light center caused by the absorption of oscillate quanta energy. This transition is possible in the first order decomposition of the multi pole bond moment through the inter nuclear displacements according the enharmonic oscillation [3].

In spite of the orange band weakness, we assume that partial excitation of the red band is a result of adsorption and recombination on the orange centers of hydrogen and oxygen with formation of excited mole-

cules H_2 and O_2 with following energy transmission to the red centers. The coincidence of the red and orange bands of PL ZnS-Mn confirms it [12].

4. Conclusion

The red band light centers are located in a thin surface layer. The associates Mn^{2+} represent these centers because the surface impurity concentration is greater than the volumetric one. It is possible that the red centers generation is due to withdrawal of manganese ions while interactions with hydrogen. The red band excitation is caused by the strike recombination with neutral atoms. The excited molecule oscillation energy is transmitted to the light centers in accordance with oscillation multi quantum mechanism [3].

References

- [1] Volkenshtein F.F., Gorban A.N., Sokolov V.A., *Radical recombination luminescence of crystal phosphors*, M., Science, 1978. P. 376.
- [2] Khoruzhii V.D., Sivov Yu. A., Tyurin Yu.I., *Surface*. 1988. N2. P.115–120.
- [3] Tyurin Yu. *Chemical excitation of solids surfaces*, Tomsk; TSU edition, 2001. P. 622.
- [4] Shigalugov S.H., Investigation of interaction nonequilibrium oxygen – containing gas fluids with solids states by of luminescent methods, *Dis...doct. phys. – mathematic scienc. Tomsk*. 2005. P.173.
- [5] Grigoriev N.N., Fok M.V., *FIAN USSR Works*. 1973. V.68. P.111–146.
- [6] D.Thong, W.Heimbrodt, D. Hommeland, O.Goede, *Phys.Stat.sol. (a)*.1984.V.81. N2. P.695–700.
- [7] Osiko V.V., *Optiks and spectroscopy*. 1963. V.1. P. 244.
- [8] Gurvish A.M., *Introduction at chemistry physic of crystallophosphors*, M.: "High. Sci.", 1982. P. 376.
- [9] Izmailov Sh.L., Styrov V.V., *GPS* 1978. V. XXVIII. Tap. 3. P.448–453.
- [10] Benoit J., Bonnalloul P., Geoffrov A., *Phys. stat. sol. (a)*. 1984.V81. P.661–667.
- [11] Vlasenko N.A., *Izv. AN SSSR (ser.phys.)*. 1985. V. 49. N10. P.1909–1929.
- [12] R. Mach and G.Muller., *Phys.Stat.sol. (a)*.1982.V. 69. N1. P.11–66.