Mechanisms of Impact Ionization of Manganese in Zn_2GeO_4:Mn at Photo- and Electroluminescence

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The luminescence emission mechanisms in oxide phosphors can be described quite well by intrinsic center recombination as well as by charge transfer luminescence. However, there is a lack of data indicating on the existence of efficient energy transfer mechanisms in oxide-based electro- and cathodoluminescent phosphors, which together with high crystallization temperature substantially limits their usage in electroluminescent and field-emission display applications.

It was found that both by efficiency and technological parameters as a prospective one can be considered one of related to $(Zn,Me)_2GeO_4$ compounds. The willemite-type structure Zn_2GeO_4:Mn shows the existence of two spectral regions of excitation of luminescence at 535 nm (corresponding to $^4T_1(^4G)$-$^6A_1(^6S)$ transitions in Mn^{2+} ions in tetrahedral neighborhood) and photoconductivity: band-to-band (260 nm) and near-bandgap (360 nm); the two temperature quenching processes, and correlated behavior of photoconductivity temperature quenching. It should be noted that the temperature dependencies of luminescence do not differ substantially dependent of the excitation region. This makes it possible to propose such type of excitation mechanism in Zn_2GeO_4:Mn: band-to-band excitation energy transfer to the nonradiative recombination center, which in turn transfers energy to Mn^{2+}-center in a resonance way (Fig.1). In the region of 250 to 280 K the temperature quenching is caused by the quenching of excitation process, which can be approved by the correlation between the luminescence (0.20 eV) and photoconductivity (0.19 eV) thermal quenching energies. The high-temperature ($T > 280$ K) quenching (0.40 eV) is caused by intrinsic quenching in Mn^{2+} ion. It is in agreement with the values of luminescence quenching energy for Mn^{2+} in Zn_2SiO_4:Mn (0.36 eV), which has the same crystal structure and Mn^{2+} ion neighborhood.

Similar mechanisms of energy transfer have been observed in Zn_2GeO_4:Mn-based electroluminescent structures as well, which reveals in: existence in Mn^{2+} luminescence kinetics of emission peaks both at rise and fall edges of excitation pulses; singularities in B-V and Q-V curves and influence of UV illumination on them; existence of peaks in emission waves and active current both at maximal and minimal field strengths, decreasing of EL quenching rate with increasing of excitation level.

This behavior of EL in Zn_2GeO_4:Mn can be explained with the existence of two EL mechanisms: direct impact excitation of Mn^{2+} ion and resonant energy transfer to Mn^{2+} ion from primarily ionized by the electric field sensitizing center followed by recombination with trapped electron.

Mechanism of direct impact excitation in observed Zn_2GeO_4:Mn EL structures is dominating in the region of voltages higher than the threshold of sharp increasing of EL intensity and is revealed in maxima of emission waves correlated in time with the peaks of active current and peaks of hot-carriers emission. It also approves by the increasing of direct excitation fraction as well as emission excitation under polarization field.

Mechanism of EL based on the ionization of sensitizing defect followed by resonant excitation of Mn^{2+} is accompanied by formation of space charge and field redistribution in the active layer. In Zn_2GeO_4:Mn it reveals in: delayed recombination which results in emission at the moment of decreasing of voltage or changing polarity; complex shape of Q-V curves with characteristic region of space charge generation; substantial (10^2 times) increasing of charge stimulated by UV-illumination.

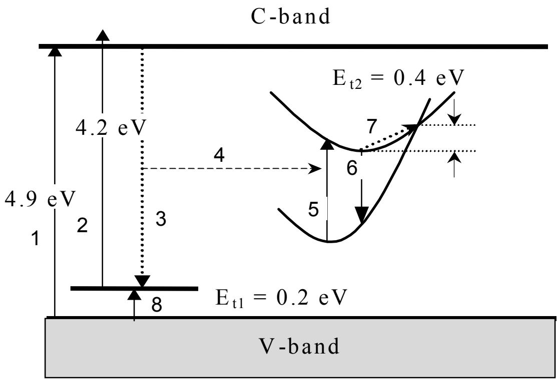

Fig. 1. Energy band diagram of Zn_2GeO_4:Mn phosphor
1 - band-to-band excitation,
2 - nonradiative center excitation with creation of free carriers,
3 - nonradiative transition,
4 - energy transfer of nonradiative recombination to Mn^{2+},
5 - Mn^{2+}-center excitation,
6 - Mn^{2+}-center emission,
7 - Mn^{2+}-center thermal quenching,
8 - nonradiative center thermal quenching.

Thereby, based on obtained results, it is shown for the first time that in Zn_2GeO_4:Mn electroluminescence excitation of Mn^{2+} ions takes place by the ionization with the electric field of sensitizing defect followed by resonant energy transfer to manganese ions.

The complex mechanism of EL found is prospective for practical applications because it includes the simultaneous action of two mechanisms which separately have been observed in the best EL phosphors: ZnS:Mn - impact excitation, and SrS:Ce - ionization with space charge generation.