

# NEPHELAUXETIC EFFECT IN LUMINESCENCE OF $\text{Cr}^{3+}$ DOPED LITHIUM NIOBATE AND GARNETS

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The luminescence of  $\text{Cr}^{3+}$  ions in laser materials that experience strong crystal field strength is dominated by relatively sharp luminescence lines associated with the  ${}^2\text{E} \rightarrow {}^4\text{T}_2$  transitions (so called R-lines). Energy of the  ${}^2\text{E}$  level in the  $d^3$  electron system, according to the Tanabe-Sugano theory, increases a little with increase of the strength of the crystal field. The strength of crystal field experienced by the dopand ions can be controlled by application of hydrostatic pressures, which decreases interatomic distances. The high-pressure low-temperature  $\text{Cr}^{3+}$  luminescence experiments in the diamond anvil cell (DAC) show, contrary to the prediction of the Tanabe-Sugano theory, that the energy of the  ${}^2\text{E}$  level of  $\text{Cr}^{3+}$  ions decreases slightly with increase of the crystal field strength. This happens due to so called nephelauxetic effect, i.e. decrease of interelectronic crystal field Racah's repulsion parameters B and C due to covalency of bonds between the central ion and ligands. An enhancement of the nephelauxetic effect, responsible for the red shift of the R-lines, is attributed to greater covalency due to a reduction of bond lengths with pressure.

Although the effect is well understood qualitatively and also applied for pressure calibration in DAC technique (ruby R-line luminescence), its quantitative description is far from completeness and clarity. In this paper we would like to present a new approach to this problem, based on Harrison theory of ionic-covalent bonding, normally considered in the context of band structure. A model is developed for quantitative explanation of the nephelauxetic effect in  $\text{Cr}^{3+}$  ions luminescence, taking into account valence orbitals of nearest and second nearest neighbor atoms. The results are used for description of the effect in chromium doped lithium niobate and garnet crystals, although the model can be also applied for the other systems. The results are in very good agreement with the luminescence experimental data, obtained in the DAC with pressures up to 150 kbar.

## RADIATION DEFECTS CREATION IN $\text{CsI}(\text{Tl})$ CRYSTALS AND THEIR LUMINESCENT PROPERTIES

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Radiation defects creation processes in  $\text{CsI}(\text{Tl})$  crystal have been studied. It was determined, that identical activator electron color center may be formed in two ways: (i) the diffusion of the anionic vacancy to an activator ion, an electron was captured by, and (ii) the diffusion of the F-center to an activator ion. Process (i) is stimulated by the presence of borate ions in  $\text{CsI}(\text{Tl})$  crystals, process (ii) - of carbonate and hydroxyl ions. Irrespective of admixture composition the same bands at 355, 390, 430, 470, 520, 560, 840, 975 nm were observed in absorption spectra of irradiated  $\text{CsI}(\text{Tl})$  crystals. The number of these bands exceeds the number of the bands typical for electronic transitions between the neutral Tl center states. If a  $\text{CsI}(\text{Tl})$  crystal treated by ionizing radiation is illuminated by the mercury lamp emission, break-down of 430, 520, 560, 840, 975 nm bands will be accompanied by the increase in the intensity of 390, 470 nm bands in the absorption spectrum. The model, according to which an electron is captured by the defect being an activator ion close to anionic vacancy, is considered in this paper. It was found that the luminescence can be excited at room temperature in radiation induced at 355, 390, 470 nm bands as well as in the typical for  $\text{CsI}(\text{Tl})$  crystal thallium monomers absorption of 200-300 nm region. The luminescence maximum is shifted to the long-wavelength region compared with the luminescence of non-irradiated crystal. At 80K the emission can be excited in the 500-560 nm region as well. The luminescence spectrum of irradiated crystal consist of several bands. The most long wavelength band with the maximum at 670 nm is typical for irradiated crystals only. Another band with the maximum at 590 nm is also observed in the spectrum of the non-irradiated crystal. The luminescence of thallium monomers also appears in the luminescence spectrum of irradiated crystals. They were considerably distorted by the radiation defects absorption. Probable nature of the luminescence at 670 nm was considered. Research supported by STCU Project No 921.