

Temperature behavior of the zero-phonon line of vanadium photoluminescence in SrTiO₃:V crystal

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Strontium titanate (SrTiO₃) is a model ABO₃ perovskite-type oxide with highly polarizable structure and soft TO phonon modes. However, SrTiO₃ crystals remain in paraelectric phase down to the lowest temperatures because transition to ferroelectric phase is suppressed by quantum effects. Very unusual and large temperature shift of the zero-phonon R-line was observed in the emission spectra of photoluminescence of Cr³⁺ and Mn⁴⁺ impurity ions (3d³ electron configuration) substituted for octahedral coordinated Ti⁴⁺ ions in SrTiO₃:Cr and SrTiO₃:Mn crystals, respectively [1, 2]. Besides, this temperature shift was found to be proportional to the reciprocal permittivity of SrTiO₃ crystals and to the square of temperature-dependent TO₁ soft phonon mode frequency below the temperature of structural phase transition from the cubic to tetragonal phase in the vicinity of 105 K. At the same time, the R-line temperature shift occurs in the case of Cr³⁺ and Mn⁴⁺ ions in the opposite direction. Better understanding of these effects that are very unusual in the spectroscopy of transition metal impurity ions in ionic crystals requires an analysis of temperature behavior of zero-phonon emission lines for other impurity ions with different 3dⁿ electron configuration in SrTiO₃ crystals.

Recently we have found structured photoluminescence in the near infrared spectral region in the slightly vanadium doped SrTiO₃ single crystals that at low temperatures consisted of a pronounced zero-phonon line near 1157 nm accompanied by well developed vibrational sidebands. We suppose that this photoluminescence originates from V³⁺ ions (3d² electron configuration) substituted for Ti⁴⁺ ions in SrTiO₃:V crystal. Present detailed analysis of emission spectra at temperatures between 4.2 and 300 K showed an unusually large temperature shift of the zero-phonon line for studied photoluminescence of SrTiO₃:V crystal as well. The origin of the observed line shift to lower energy side with increasing temperature will be discussed taking into consideration structure of vanadium impurity center in SrTiO₃:V crystal and the specificity of impurity-lattice interaction in ABO₃ perovskite-type oxides with soft TO phonon modes.

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