Study of zero-phonon line splitting in the emission spectrum of vanadium photoluminescence in $SrTiO_3$:V crystal

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Strontium titanate ($SrTiO_3$) is a model ABO_3 perovskite-type oxide with highly polarizable structure and soft TO phonon modes. However, $SrTiO_3$ crystals remain in paraelectric phase down to the lowest temperatures and only structural phase transition from the cubic to tetragonal phase occurs near 105 K. Recently we have found structured photoluminescence in the near infrared spectral region in vanadium doped $SrTiO_3$ crystals that at low temperatures consisted of a pronounced zero-phonon line near 1157 nm accompanied by well developed vibrational sidebands. We suppose that it originates from V^{3+} ions ($3d^2$ configuration) substituted for octahedral coordinated Ti^{4+} ions. The zero-phonon line shows a surprisingly large shift to lower energy side with increasing temperature. This very unusual effect in the spectroscopy of transition metal impurity ions in ionic crystals seems to be inherent to luminescence centers in $SrTiO_3$ with specific properties of energy levels involved in emission transition because very similar temperature shift of the zero-phonon R-line has been observed earlier in the emission spectra of photoluminescence of Cr^{3+} and Mn^{4+} impurity ions ($3d^3$ configuration) substituted for Ti^{4+} ions in $SrTiO_3$:Cr and $SrTiO_3$:Mn crystals, respectively [1, 2]. However, while the R-line of Cr^{3+} and Mn^{4+} emission shifts with increasing temperature monotonically to higher and lover energy side, respectively, a temperature behavior of position of the zero-phonon line near 1157 nm observed below 30 K is rather complex.

Present study of emission spectra of V^{3+} photoluminescence in $SrTiO_3$:V crystal at high spectral resolution and temperatures between 4.2 and 140 K proved splitting of the zero-phonon line near 1157 nm into four components at low temperatures resulting from the splitting of both ground $^3T_{1g}$ and excited $^1T_{2g}$ states of V^{3+} ions. Consequently, complex temperature behavior of the zero-phonon line position originally observed below 30 K under unresolved line structure is related to the changes of relative intensities of the line components owing to the alteration of thermal population of the higher energy sublevel of the $^1T_{2g}$ excited state. An origin of the ground $^3T_{1g}$ and excited $^1T_{2g}$ state splitting in V^{3+} impurity center in $SrTiO_3$:V crystal will be discussed taking into consideration structural phase transition in $SrTiO_3$ crystal, spin-orbit coupling, and possible action of the Jahn-Teller effect.

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