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Photoluminescence spectra and unusual temperature shift of zero-phonon emission line of V^{3+} in $SrTiO_3$

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The paper presents the first observation of photoluminescence spectra of V^{3+} impurity in $SrTiO_3$. The broad band of the observed emission is located in the near IR region and at low temperatures consists of a pronounced zero-phonon line (ZPL) with a maximum at 1157.1 nm (8642 cm^{-1}) at 77 K and developed vibronic sidebands extending to 1450 nm. The observed ZPL is associated with an intracenter ${}^1T_{2g} \rightarrow {}^3T_{1g}$ or a closely located ${}^1E_g \rightarrow {}^3T_{1g}$ emission transition in V^{3+} ($3d^2$) ions replacing Ti^{4+} ions. It was found that the temperature shift of zero-phonon line is unusually large and its frequency decreases upon lowering the temperature. The local configuration instability of V^{3+} ions in the ${}^3T_{1g}$ ground state caused by soft TO_1 temperature-dependent phonon mode present in $SrTiO_3$ is considered as a possible source of the observed unusual temperature shift.

Keywords: ABO_3 incipient ferroelectrics, impurity ions of transition metals, luminescence, zero-phonon lines.

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1. Introduction

A model representative of the ABO_3 family of highly polarizable strontium titanate oxides ($SrTiO_3$, STO) is the object of increased attention of academic and applied research. Possessing a relatively simple cubic perofskite-like structure, at $T = 105$ K STO undergoes a model O_h^1–D_{4h}^{18} antiferrodistoric (AFD) second-order phase transition with R_{25} phonon mode condensation at the boundary of the Brillouin zone. With a further decrease in temperature, the permittivity, accompanied by a softening of the Slater polar soft TO $_1$ phonon mode, increases (virtual ferroelectricity), but in the area of dominant quantum statistics, the growing instability and the tendency to ferroelectric ordering are suppressed (quantum paraelectricity). It is the presence of soft TO $_1$ modes and high susceptibility that determine the richness and variety of STO properties, among which doping effects and various phase transitions caused by impurities occupy a prominent place.

In turn, the unusual properties of quantum paraelectrics and the presence of temperature-dependent soft phonon modes significantly affect the structure and properties of impurity centers. In this connection, the temperature shift of the zero-phonon R-luminescence lines of $3d^3$transition metal ions Cr $^{3+}$ and Mn $^{4+}$ in $SrTiO_3$and $KTaO_3$ [1–3] should be specially noted associated with the local configurational instability of degenerate excited states of impurity centers due to the quadratic multimode Jahn-Teller effect on the soft polar TO_1mode [3]. It is extremely surprising that an unusually large, much larger than usually observed in the spectra of $f - f$-luminescence of triply charged rare-earth ions, the temperature shift of zero-phonon emission lines was also recently observed in the photoluminescence spectra of Er^{3+} ($4f^{11}$) ions in the related quantum paraelectric $KTaO_3$ [4].

In this paper, the results of the first studies of the luminescence of vanadium-doped STO single-crystals are presented in order to obtain information on the temperature behavior of the ZPL luminescence of impurity d^2 ions V^{3+} in a quantum paraelectric.

2. Samples and experimental procedure

The STO : V single-crystals lightly doped with vanadium (36.8 ± 0.6 ppm) grown by the Verneuil method were applied in the paper. Experimental samples were made in the form of rectangular$4 \times 3 \times 1$ mm parallelepipeds with polished edges oriented normally to the $\langle 001 \rangle$ cubic axes. X-ray analysis (XRD Brucker D8 advance X-ray diffractometer) showed the single-phase perofskite-like O_h^1 cubic structure of the grown single-crystals.

Analysis of the composition, performed by the PIXE method (Proton-Induced X-ray Emission), also showed the presence of impurities in the amount of Cu — 35 ppm, Cr — 10 ppm, Mn — 5 ppm and Fe — 40 ppm. Let us note that Mn and Fe impurities are often present in the noted amounts in undoped STO, and Cr is an

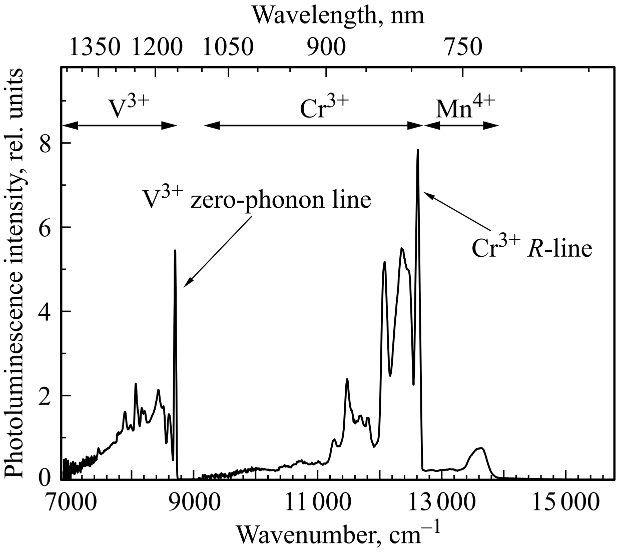

Figure 1. Overview photoluminescence spectrum of a single-crystal $SrTiO_3:V$ ($T = 5$ K). Excitation at a wavelength of 514.5 nm, emission lines of an Ar–Kr laser.

unremovable impurity in it [5]. The content of vanadium was determined in [6] by the method of neutron spectrometry with discrimination of the γbackground (INAA Instrumental Neutron Activation Analysis with discriminating gamma-ray spectrometry).

Photoluminescence spectra were measured at temperatures of 5–300 K on samples attached to a copper holder of a closed-cycle helium refrigerator on a setup assembled on the basis of a Jarrell Ash grating monochromator with a focal length of 1 m. The intensity of photoluminescence generated by the emission lines of the Ar^+–Kr^+ laser was recorded in 350–850 nm area in the photon counting mode using a cooled RCA 31034 photomultiplier (GaAs photocathode). For registration in the spectral area 800–1600 nm, a Ge detector cooled in liquid nitrogen was used. All the emission spectra were corrected for the spectral dependence of the equipment response.

3. Results and Discussion

The ratio between the sizes of the effective radii of the $3d^2$ ions V^{3+} and Ti^{4+}ions located in the oxygen octahedron (0.64 and 0.605 Å respectively [7]) suggests that impurity vanadium ions in STO can replace titanium ions, which, in particular, agrees with the data [8]. Meanwhile, local and nonlocal charge compensation can lead to both noncentral and central positions of the V^{3+} ions in the oxygen octahedron, which is typical, in particular, for impurity Cr^{3+} ($r = 0.615$ Å) ions in STO.

Fig. 1 shows an overview photoluminescence spectrum of $SrTiO_3$:V single-crystals obtained at $T = 5$ K and excitation by the 514.5 nm line of the Ar–Kr laser, which clearly shows the zero-phonon lines and vibronic luminescence spectra of random impurities Cr^{3+} and Mn^{4+}, as well as the luminescence spectrum, which is associated with emission transitions in the V^{3+} ions located in the oxygen octahedron. It can be seen that the luminescence spectrum of vanadium consists of a narrow zero-phonon line with a maximum in the vicinity of 1155 nm and a well-developed vibronic spectrum extending up to 1450 nm. The well-pronounced ZPL of the luminescence, which is associated with the ${}^1T_{2g} \to {}^3T_{1g}$ or closely lying ${}^1E_g \to {}^3T_{1g}$ transitions in impurity V^{3+} ions, is well resolved below 140 K. Fig. 2 shows the Tanabe – Sugano diagram of the d^2-configuration levels in the octahedral field and the obtained luminescence emission spectra of V^{3+} centers in the ZPL spectral area at temperatures ≤ 140 K.

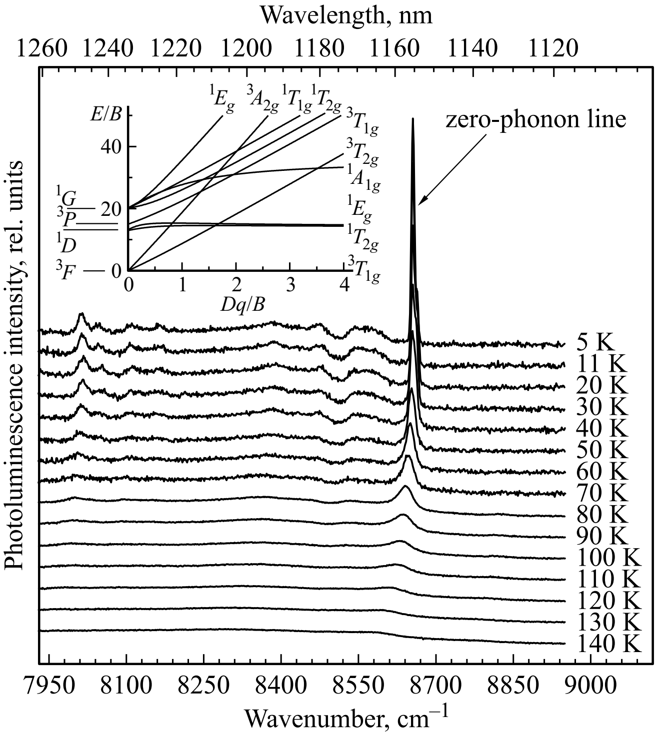

Figure 2. Photoluminescence spectra in the ZPL area of V^{3+} in $SrTiO_3$ at $T < 140$ K. Excitation at a wavelength of 647 nm, emission lines of an Ar–Kr laser. Registration of the spectrum with a resolution of 0.8 nm. The insert shows the Tanabe – Sugano diagram of the positions of the levels of the d^2 configuration in the octahedral field.

The ZPL is asymmetric below 50 K, and at very low temperatures the presence of a ratio arm is clearly visible on its high-energy side. As the temperature increases, the intensity of the ratio arm relative to the ZPL maximum increases, and its asymmetry decreases. This behavior indicates that the ZPL consists of at least two components, the intensity ratio of which depends on temperature.

Fig. 3 shows the temperature dependence of the energy of the ZPL luminescence maximum of V^{3+} ions, and the table shows — the ZPL shifts in some ionic crystals and in quantum paraelectrics. As follows from the table, the temperature shift of the ZPL of the V^{3+} luminescence turns

Temperature ZPL shift of the luminescence of impurity centers in ionic crystals (cm^{-1})

$MgO:Cr_{3+}$	$Al_2O_3:Cr^{3+}$	$SrTiO_3:Cr^{3+}$		$SrTiO_3:Mn^{4+}$	$KTaO_3:Cr^{3+}$
4.2 → 200 K	4.2 → 200 K	4.2 → 200 K	4.2 → 77 K	4.2 → 77 K	4.2 → 77 K
−8.4 [9]	−6.6 [10]	+45 [1]	+8.2	−10 [1,2]	+4 [3]

$SrTiO_3$	
5 → 77 K	5 → 130 K
−13	−69

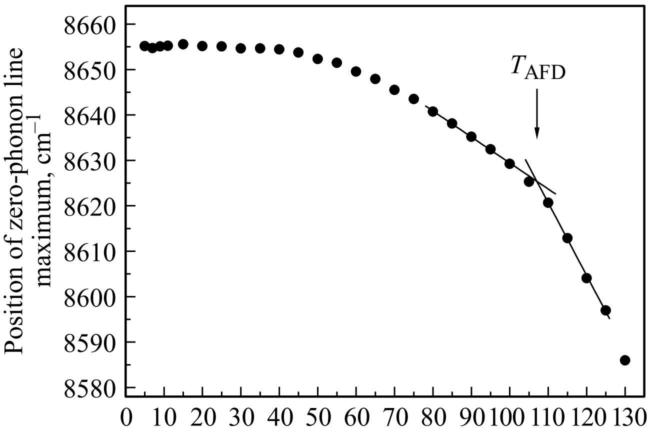

Figure 3. Temperature dependence of the maximum energy of the zero-phonon luminescence V^{3+} line of $SrTiO_3$:V single-crystals (circles) and its linear approximations below and over the temperature of the structural phase transition T_{AFD} (solid lines).

out to be significantly larger than the shift of the *R*-line of Cr^{3+} in MgO or Al_2O_3 and, which is especially important, than in STO. Meanwhile, the sign of the shift is opposite to that observed in STO:Cr^{3+} and coincides with the shift in STO:Mn^{4+}.

4. Conclusions

In this paper, the detection of photoluminescence associated with impurities of $3d^2$ ions V^{3+}, which replace Ti^{4+} ions in an octahedral environment, in a quantum paraelectric $SrTiO_3$ has been reported for the first time. The actual emission consists of a zero-phonon line located in the near-IR area with an emission maximum at 1157.1 nm, (8642 cm^{-1}) at 77 K, corresponding to the $^1T_{2g} \rightarrow ^3 T_{1g}$- or close-lying $^1E_g \rightarrow ^3 T_{1g}$-transition, and is accompanied by a developed vibronic spectrum.

Meanwhile, the temperature shift of the zero-phonon luminescence line turns out to be much larger than the shifts characteristic of the optical spectra of d^3 ions impurities in model ionic crystals and observed in STO. It is believed that the observed phenomenon is due to the presence of the temperature-dependent soft polar TO_1 phonon mode and the specific features of the impurity-lattice interaction, which are characteristic of quantum paraelectrics. Clarification of the physical mechanism of the observed phenomenon requires specification of the structure, symmetry, methods of charge compensation of V^{3+} centers and a detailed theoretical analysis. Since the luminescence spectra reflect the structure of the ground state at low temperatures, the opportunity of local configurational instability of V^{3+} ions should be considered as a potential cause of the phenomenon. In this case, in contrast to the properties of Cr^{3+} in STO, the implementation of the quadratic multimode Jahn–Teller effect on the soft TO_1 mode turns out to be possible in the main $^3T_{1g}$ state, which determines both the unusual value and the sign of the observed temperature shift of the zero-phonon luminescence line.

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Conflict of interest

The authors declare that they have no conflict of interest.

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