1. INTRODUCTION

Recent investigations have revealed that optical spectra of lithium niobate exhibit specific features at temperatures of 90 and 120–125 °C due to the rearrangement of the electronic subsystem [1]. Lithium tantalate is isomorphous with lithium niobate. In this respect, it would be of interest to elucidate whether lithium tantalate undergoes a phase transition in the temperature range 20–200 °C.

2. OBJECTS OF INVESTIGATION AND EXPERIMENTAL TECHNIQUE

The objects of our investigation were commercial lithium tantalate single-crystal plates cut out parallel (the YZ cut) and perpendicular (the XY cut) to the ferroelectric axis with thicknesses of 0.187 and 0.153 cm, respectively. The absorption spectra were recorded on an SF-14 spectrophotometer in the visible range (400–750 nm) and on an IKS-14A IR spectrophotometer in the near-IR range (3700–14100 cm⁻¹) at temperatures varying from 20 to 220 °C. The temperature was controlled with a VRT-3 heat regulator to an accuracy of 0.1 °C.

3. ABSORPTION SPECTRUM OF LITHIUM TANTALATE IN THE VISIBLE RANGE AND THE LUMINESCENCE SPECTRUM

The absorption spectra of the YZ and XY cuts of the lithium tantalate single crystal in the visible range contain absorption bands with maxima at wavelengths of 440 and 400 nm, respectively. These bands can be assigned to a charge-transfer vibronic exciton [2], because the absorption edge of lithium tantalate lies in the ultraviolet spectral range [3] and green luminescence is observed for lithium tantalate. The long-wavelength edge of these absorption bands obeys the Urbach rule. The parameter σ of the Urbach rule, which determines the slope of the linear dependence of the logarithm of the absorption coefficient ln[K] on the energy of the incident light, has resonance minima for the YZ cut at temperatures of 120 and 180 °C (Fig. 1) and for the XY cut at 120 and 160 °C. The energies corresponding
to the absorption edge at a constant absorption coefficient $\ln K = 0.4$ for the YZ cut at temperatures close to 120 and 180°C decrease by 0.3 and 0.1 eV, respectively (Fig. 1). Since the minimum of the parameter $\sigma$ corresponds to the most disordered state of the material, we can assume that the rearrangement of the electronic subsystem or the isostructural phase transition occurs at temperatures of 120 and 160–180°C. All the parameters of the Urbach rule contribute to the change in the energy position of the long-wavelength edge of the absorption bands with maxima at wavelengths of 440 and 400 nm for the YZ and XY cuts of the lithium tantalate single crystal, respectively. For example, for the YZ cut of the lithium tantalate crystal at a temperature of 120°C for $\ln K = 0.4$, the contributions from the anomalies of the parameters $E_0$, $K_0$, and $\sigma$ are numerically equal to $-0.026$, $0.253$, and $-0.028$ eV, respectively. At 180°C, the contributions from the anomalies of the parameters $E_0$, $K_0$, and $\sigma$ are equal to $-0.100$, $0.126$, and $-0.080$ eV, respectively.

The electron–phonon interaction constant $g$ was determined according to the formula $g = 2/3\sigma_0^{-1}$, where the value of $\sigma_0$ was determined from the dependence of the parameter $\sigma$ on $1/(kT)^2$. The energy of the effective phonon was determined from the formula $\sqrt{(\sigma_0 - \sigma)}\sigma_0^{-1}12(0K)^2$. The energy of the effective phonon for the YZ cut of the lithium tantalate single crystal is equal to 467 cm⁻¹ at temperatures below 120°C, 262 cm⁻¹ in the range 120–180°C, and 522 cm⁻¹ at temperatures above 180°C. The electron–phonon interaction constant $g$ for the XY cut of the lithium tantalate single crystal is determined to be 33 below 120°C, 29 in the range 120–160°C, and 25 above 160°C. The energy of the effective phonon for the XY cut of the lithium tantalate single crystal is equal to 375 cm⁻¹ at temperatures below 120°C, 423 cm⁻¹ in the range 120–160°C, and 311 cm⁻¹ above 160°C. These values are in agreement with the phonon spectrum of lithium tantalate [4].

The luminescence spectrum of the YZ cut of the lithium tantalate single crystal at a temperature of 24°C exhibits a band with a maximum at a wavelength of 495 nm, a half-width of 0.508 eV, and a Stokes shift of 0.595 eV. The observed spectrum can be interpreted as a superposition of vibronic transitions, because the profile of the luminescence band involves a purely electronic transition and four combinations with an effective phonon energy of 1270 cm⁻¹ at 24°C. The energy of the effective phonon was calculated from the formula $h\omega_{\text{eff}} = 0.363AE_i^2/\Delta E_{\text{St}}$, where $\Delta E_i$ is the half-width of the luminescence band and $\Delta E_{\text{St}}$ is the Stokes shift. The electron–phonon interaction force was calculated according to the formula $F_{\text{eff}} = \Delta E_i\sqrt{2m_0\hbar\omega/0.357c}$ and amounted to 1.14 eV/Å at 24°C. The exciton–phonon interaction forces reach maxima of 1.52 and 1.58 eV/Å at temperatures of 120 and 180°C, respectively. The degree of polarization of the luminescence bands has minimum values at 120 and 180°C. Since the minimum degree of polarization corresponds to the most disordered state of the material, the hypothetical phase transitions should occur at temperatures of 120 and 180°C.

4. ABSORPTION SPECTRUM OF LITHIUM TANTALATE IN THE NEAR-IR RANGE

The absorption spectrum of the XY cut of the lithium tantalate single crystal in the near-IR range exhibits a band with a maximum at a frequency of ~12200 cm⁻¹.

![Fig. 2. (a) Absorption spectra in the near-IR range for (1–3) the XY cut of the lithium tantalate single crystal at temperatures of (1) 180°C, (2) 200°C, and (3) 220°C and (4) the YZ cut of the crystal at 40°C. (b) Temperature dependences of the integrated intensity of the absorption bands in the near-IR range for (1) the XY cut and (2) the YZ cut of the lithium tantalate single crystal.](image-url)