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Electrical properties of GaSe doped with Er

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Measurements of the Hall effect and Er-related luminescence were made on Er-doped GaSe. Deep-level transient spectroscopy (DLTS) was also performed. Hall measurements show that hole concentrations of 0.2%, 0.5%, and 1% Er-doped GaSe samples are 1.5×10^{17} – 6×10^{17} cm⁻³ at room temperature, and that the mobility of these holes is in the range 22–34 cm²/Vs. The temperature dependence of the hole concentration is explained using the two-acceptor model, in which one acceptor level is at around 65 meV above the valence band and the other one is at ~ 158 meV. The DLTS measurements yield similar results. Furthermore, the shallow acceptor impurities contribute free hole carriers and act as radiative centers; the deep acceptor impurities are nonradiative centers, which are responsible for the quenching behavior of Er-related luminescence. The temperature dependence of the hole mobility can be understood as the combined scatterings of homopolar optical phonons and ionized impurities. © 2004 American Institute of Physics. [DOI: 10.1063/1.1760238]

I. INTRODUCTION

Gallium selenide (GaSe) exhibits large optical nonlinearity and is transparent to a wide range of wavelengths, whose properties make it highly promising for use in nonlinear optics.¹ Moreover, GaSe is a native *p*-type semiconductor that belongs to the III-VI layered semiconductor family. It has a relatively large band gap energy of ~ 2.0 eV, so impurity doping in GaSe has attracted much interest because of its potential applications to photoelectric devices that operate in the visible region.² Many researchers have reported the electrical and optical characteristics of GaSe doped with elements in groups I, II, IV, and VII.^{3–7} Hole concentrations of the order of 10^{15} – 10^{16} cm⁻³ at room temperature have been obtained by doping with Cd, Zn, Cu, and Ag.

The doping of semiconductors with rare earth (RE) elements has also attracted significant attention. RE elements have partially filled *4f* shells, which are well screened by the outer closed orbitals of *5s*² and *5p*⁶. The intracenter transitions of *4f* electrons in various host materials give rise to sharp, atomlike, and emission spectra that are independent of temperature. Recently, the erbium ion, when incorporated into a semiconductor such as Si (Ref. 8) or GaN (Ref. 9), has been shown to exhibit an intra-*4f* transition at a wavelength of 1.54 μ m, whose transition is important as a source of light in optical communication technology. Only a few research groups have investigated the erbium-doped GaSe crystal (Er:GaSe). Lee *et al.*¹⁰ and Tagiev *et al.*¹¹ reported the optical absorption and luminescence excitation spectra of the Er:GaSe crystal, respectively. The recombination mecha-

nisms of radiative centers in Er:GaSe crystal have already been obtained from measurements of photoluminescence (PL).¹² One important 2.064 eV emission band has been found, and attributed to the transition between the conduction band and the acceptor level at around 64 meV above the valence band. However, the electrical behavior of Er impurities as dopants in GaSe has not yet been investigated. This study concentrates on the Hall effect, the deep-level transient spectra (DLTS), and free carrier related luminescence measurements of the Er:GaSe crystal. The activation energies of acceptor impurity levels are determined from the temperature dependence of the hole concentrations, DLTS, and measurements of Er-related luminescence. Moreover, the role of Er as a doping agent in GaSe is discussed. The scattering-dependent hole mobility in Er:GaSe at various temperatures is also analyzed.

II. EXPERIMENTAL PROCEDURE

The *p*-type Er:GaSe crystals used in this study were obtained by the Bridgmann method. Er with a purity of 99.95% was added, at 0.2, 0.5–1 at. %, to a stoichiometric melt of GaSe. Raw materials were enclosed in a well-cleaned quartz tube at 10^{-6} Torr. Growth proceeded with a thermal gradient of 30 °C/cm and a growth rate of 2 cm/day. After growth, square samples with faces perpendicular to the *c* axis were prepared using a razor blade; their typical dimensions were $4 \times 4 \times 0.3$ mm³.

The Hall coefficients were made using a four-point direct current Van der Pauw configuration at temperatures between 80 and 300 K to obtain the effects of temperature on the concentration and mobility of carriers. The current was made to flow in the surface planes and a magnetic field (~ 0.5 T) was applied perpendicular to these planes. The

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TABLE I. The results of Hall effect measurement.

Initial Er concentration (at. %)	Hole concentration (cm^{-3})	Mobility ($\text{cm}^2/\text{V s}$)	Resistivity ($\Omega \text{ cm}$)
Undoped GaSe	1.058×10^{15}	56.76	104
0.2% GaSe:Er	1.529×10^{17}	34.073	1.199
0.5% GaSe:Er	2.084×10^{17}	23.358	1.283
1.0% GaSe:Er	4.132×10^{17}	22.44	0.784

ohmic contacts were soldered using high-purity indium and then all samples were heated to 600 K for 10 min at 10^{-6} Torr to improve the ohmicity of the contact.

The DLTS measurements were made on the Schottky barriers diode, which was formed by thermally evaporating Au onto a *c* surface plane.¹³ The pattern of the Schottky contact was a circle with a diameter of ≈ 1 mm. The ohmic contact was formed on the same side by soldering high-purity indium. The Au/*p*-GaSe Schottky diodes exhibited good rectification characteristics when forward biased. Each diode had an effective barrier height of 0.68 eV and forward characteristics with an ideality factor of $n = 1.79$ at room temperature. This high ideality factor may be partially related to the defects, caused by the preparing of the surface of the semiconductor. DLTS measurements were made at a bias of -1 V, pulsed periodically to 0 V to fill the traps. Transient capacitance signals were obtained using a test ac signal at 1 KHz with an amplitude of 100 mV at temperatures from 130 to 380 K. The error in the measured temperature was estimated to be under 1 K when the measurement was made.

Samples were cooled in a variable-temperature cryostat to make PL measurements. The samples were excited using a 488 nm line output from an argon laser at an intensity of ≈ 10 W/cm². Luminescence was collected and dispersed with an HR 1000 Jobin-Yvon monochromator. An InGaAs detector was used under cooling condition to measure the PL spectra.

III. RESULTS AND DISCUSSION

The hole concentration was determined from the Hall measurements by assuming a unit Hall factor.¹⁴ Table I lists the typical resistivity, hole mobility, and hole concentration of three different Er:GaSe samples at room temperature. The values are compared with those of the undoped GaSe, which was grown under the same conditions. The estimated hole concentration increased from $\sim 1.5 \times 10^{17}$ to $\sim 6 \times 10^{17} \text{ cm}^{-3}$ in samples as the concentration of dopants increased from 0.2 to 1 at.%; these values are one order of magnitude higher than those obtained with other dopants, as reported in GaSe.¹⁵ Figure 1 plots the temperature-dependent hole concentration of three different Er:GaSe samples. Throughout the range of temperatures, the hole concentration in Er:GaSe samples increases with temperature. The temperature dependence of the carrier concentration can be interpreted by assuming that the semiconductor contains two acceptor levels, with ionization energies of E_{a1} and E_{a2} , respectively. The following cubic equation for hole concen-

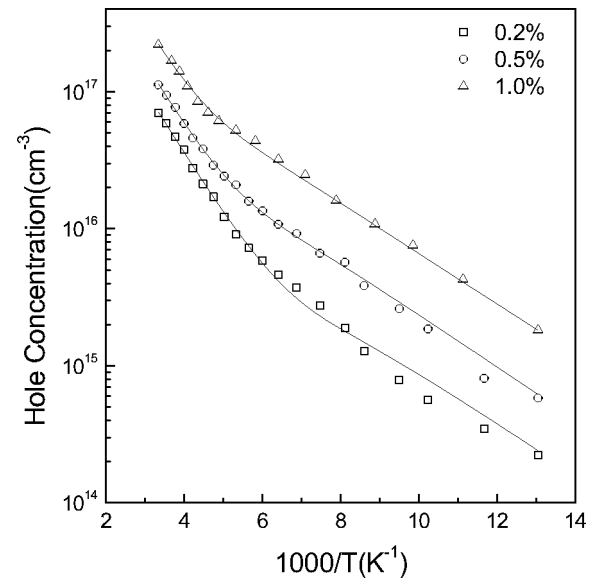


FIG. 1. Hole concentrations as a function of reciprocal temperature in Er:GaSe samples. The solid lines show the calculated hole concentrations from Eq. (1).

tration can be easily obtained by applying the neutrality condition under the nondegenerate assumption:¹⁶

$$p = \frac{N_{a1}}{1 + \frac{\beta p}{N_v} \exp\left(\frac{E_{a1}}{k_B T}\right)} + \frac{N_{a2}}{1 + \frac{\beta p}{N_v} \exp\left(\frac{E_{a2}}{k_B T}\right)}, \quad (1)$$

where p represents the hole concentration, T is the absolute temperature, N_{a1} and N_{a2} are the doping concentrations of the acceptor impurities, k_B is the Boltzmann constant, and β is the degeneracy factor, which is taken to be 2 in this calculation. In Eq. (1), the density of states, N_v , and the effective mass m_v^* of the valence band are $N_v = 4.83 \times 10^{15} T^{3/2} (m_v^*/m_0)^{3/2}$ and $m_v^* = (m_{h\perp}^* m_{h\parallel}^*)^{1/3}$, respectively, where m_0 , $m_{h\perp}^*$, and $m_{h\parallel}^*$ are the free electron mass, the effective hole mass perpendicular to the (100) plane, and that parallel to the (100) plane, respectively. Here, the effective hole masses $m_{h\perp}^* = 0.8m_0$ and $m_{h\parallel}^* = 0.2m_0$, such that $m_v^* = 0.5m_0$, are used in Eq. (1). The best fitting curves for the concentrations of holes in the three different samples are quite close to the experimental results and are represented by the solid lines in Fig. 1. Table II lists values of N_{a1} , N_{a2} , E_{a1} , and E_{a2} obtained from various samples. The deep and shallow acceptor energy levels are located at around 158 ± 3 and 65 ± 3 meV above the top of the valence band. The concentration increased with increasing erbium concentra-

TABLE II. The parameters of fitting results from temperature dependence of Hall effect measurement.

Initial Er concentration (at. %)	N_{a1} (cm^{-3})	N_{a2} (cm^{-3})	E_{a1} (meV)	E_{a2} (meV)
0.2% GaSe:Er	3.116×10^{15}	5.549×10^{17}	67.76	156.94
0.5% GaSe:Er	1.791×10^{16}	1.291×10^{18}	67.13	158
1.0% GaSe:Er	8.504×10^{16}	4.506×10^{18}	63.26	160.75

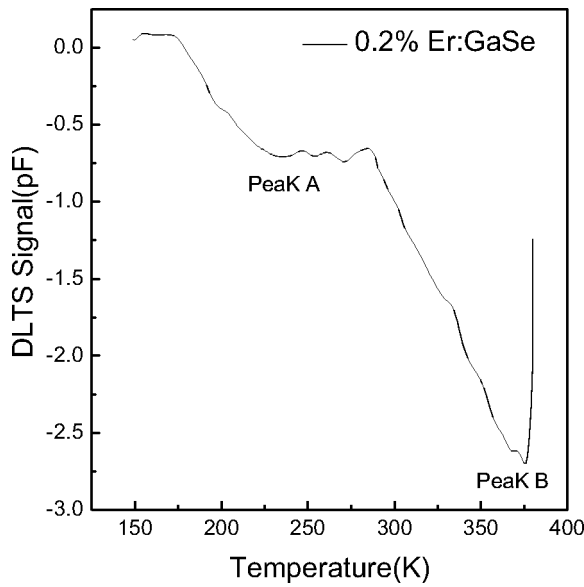


FIG. 2. DLTS spectrum of 0.2% Er:GaSe.

tion in all Er:GaSe samples, at all levels of impurities. A comparison of the impurity level at an ionization energy of 65 meV obtained from Hall measurements with that obtained by PL measurement¹² revealed that this acceptor state was not only a radiative center but also electrically active.

DLTS spectra were measured to obtain more information about the impurity level in Er:GaSe. Figure 2 displays the DLTS spectra from a 0.2% Er:GaSe sample. The applied pulse bias did not exceed the dc bias throughout the experiments, so only the impurity levels of majority carrier (hole) traps were determined. Two peaks A and B were obtained at temperatures of about 240 and 370 K. The thermal emission rate e_p was related to the activation energy of the trap level, E_t , and the hole capture cross section σ_p by the well-known equation¹⁷

$$e_p = \sigma_p v_p N_v \exp(-E_t/k_B T_M), \quad (2)$$

where v_p is the average thermal velocity of holes and T_M is the peak temperature of the DLTS signal. v_p is assumed to vary as $T^{1/2}$, and N_v as $T^{3/2}$. The activation at a given trap level can be determined from the slope of $\ln(e_p/T_M^2)$ vs $1/T_M$. Figures 3(a) and 3(b) present the Arrhenius plots that correspond to peaks A and B, respectively. The solid lines represent least-square fits and the activation energies of both acceptors are 65 meV and 158 meV. Moreover, the energies 65 meV and 158 meV are quite close to the activation energies of the acceptor levels obtained by measuring the concentration of holes. The trap level, corresponding to peak B detected by DLTS, at around 158 meV was not obtained by PL measurement in Ref. 12, suggesting that the trap state acceptor acts as a nonradiative center.

As measurements of the electric characteristics of Er:GaSe, measurements of Er-related luminescence due to carrier transitions yield more information about the level of impurities. The 4f-shell luminescence is involved in transferring energy from the semiconductor host to the Er 4f core via Er-related defects, so luminescence associated with 4f-shell transition can be observed. Figure 4 shows the PL

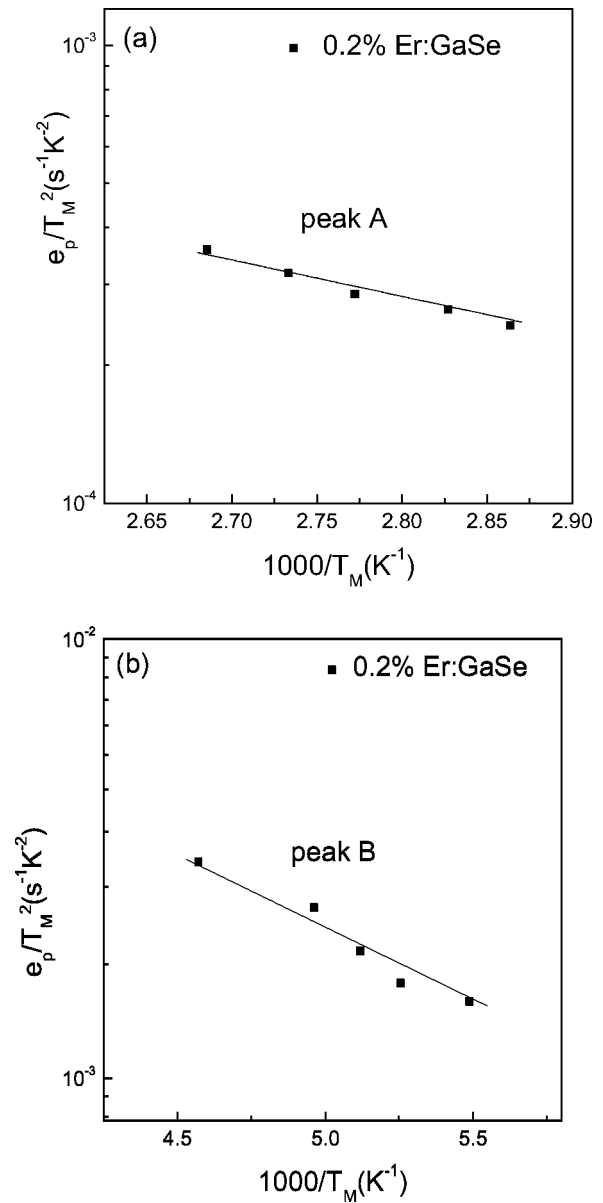


FIG. 3. Arrhenius plot of e_p/T_M^2 vs $1/T_M$ in peaks A and B.

spectra of Er-related intra-4f-shell luminescence from a 0.5% Er:GaSe sample at 35 K and at room temperature (300 K). The peak wavelength at around 1.54 μm is associated with a transition from two spin-orbit interacting related manifolds ($4I_{13/2} \rightarrow 4I_{15/2}$). Apart from the peak at a wavelength of 1.54 μm , various additional peaks appeared at shorter wavelengths ($\sim 1.52 \mu\text{m}$) as the temperature increased to 300 K. The additional peaks of Er correspond to the splitting patterns of the ground manifold ($4I_{15/2}$) due to the surrounding crystal field caused by host atoms that surround Er. The main peaks ($\sim 1.54 \mu\text{m}$) do not shift to longer wavelength over this wide range of temperatures because the intra-4f transitions are shielded by the outer closed orbits. However, the integrated intensity is quenched by a factor of ≈ 5 as the temperature is increased to 300 K. Figure 5 displays the Arrhenius plot of the thermal quenching of the integrated intensity. At high temperature, the intensity is reduced with an activation energy of about 162 meV. This

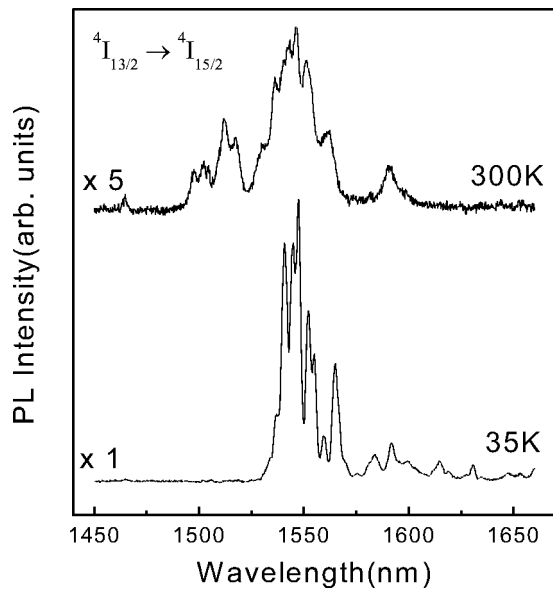


FIG. 4. Er-related luminescence around 1.54 μm in 0.5% Er:GaSe at 35 K and room temperature.

value is almost the same as that of the deep acceptor level revealed by DLTS measurements. A similar behavior has also been reported to be exhibited by Er-doped GaAs and Yb-doped InP,¹⁸ whose excitation mechanisms have been comprehensively studied. Hence, the corresponding quenching mechanism in this case is believed to involve the back transfer of energy. This mechanism is simply the reverse of Er^{3+} excitation; the excited Er^{3+} ion decays by capturing electrons and transfers its energy back to fill the deep acceptor state from the conduction band via a nonradiative process.

The doping of GaSe with erbium is now considered. Before the acceptor configuration can be explained with reference to the impurity Er in GaSe, the reader should be aware that similar RE elements, such as gadolinium (Gd),

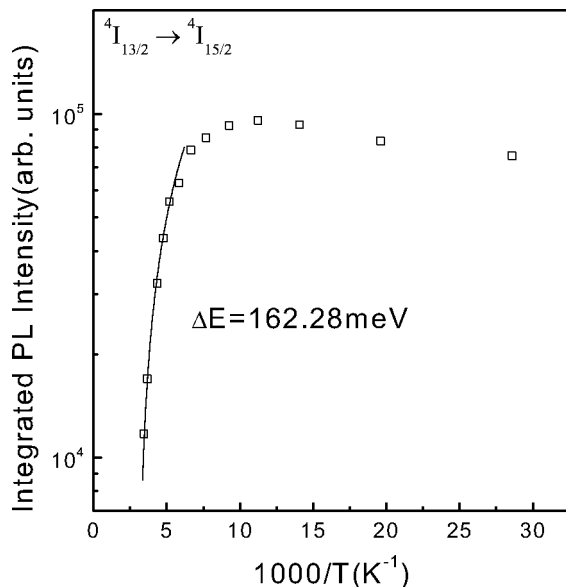


FIG. 5. Temperature dependence of the integrated intensity for $4I_{13/2} \rightarrow 4I_{15/2}$ emission.

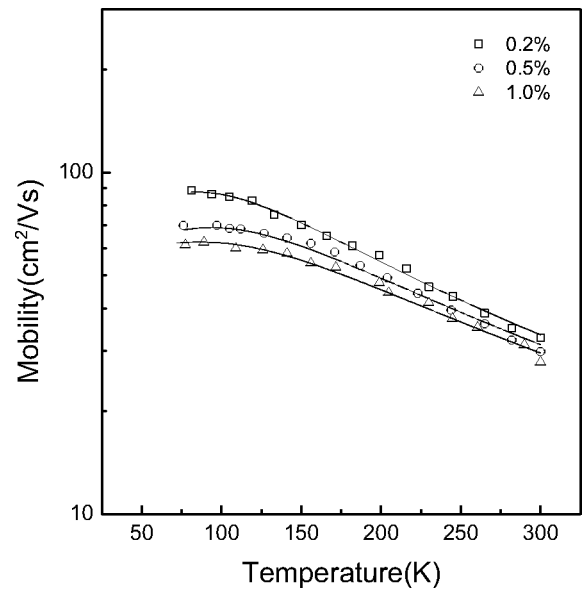


FIG. 6. Hole mobility as a function of temperature in Er:GaSe samples.

doped in GaSe have been examined by electron paramagnetic resonance spectroscopy.¹⁹ The doping process has been established to involve the replacement of one covalent-bound pair of gallium Ga_2^+ atoms with one Gd^{3+} atom, which acts as an acceptor. The configuration of acceptors in GaSe has been speculated to be determined by the substitution of one Er^{3+} atom for one pair of Ga^{2+} atoms. In another possible model, Er^{3+} ions are interstitial at interlayer sites, corresponding to sites in between two layers of Se atoms, and bond with Se atoms in the octahedral configuration.¹⁵ This configuration will yield a Ga vacancy, which contributes to the character of the acceptor. Therefore, two acceptor levels are probably associated with Er atoms that are involved in the substitutional and interstitial processes in GaSe.

Figure 6 plots the temperature dependence of the hole mobility in Er:GaSe samples. The Hall mobility in Er:GaSe samples decreases as the temperature increases in the range 80–300 K. The hole mobility was determined by considering the mechanisms of scattering from both homopolar optical phonon and ionized impurities.

(i) Scattering due to 16.7 meV A_1' homopolar optical phonon can be described using the Fivaz-Schmid relaxation time²⁰

$$\tau = \frac{\hbar(\hbar\omega)^{1/2}}{3\sqrt{\pi}g^2(k_B T)^{3/2}}, \quad (3)$$

where g is a coupling constant for intraband interactions between three-dimensional carriers and the homopolar optical branch, and $\hbar\omega$ is the energy of the optical phonon.

(ii) Scattering due to ionized impurities is accounted for in the relaxation time approximation according to the known Brooks-Herring formula,²¹

$$\tau_{ion} = \frac{2^{7/2}m^{1/2}(4\pi\epsilon)^2(k_B T)^{3/2}}{\pi^{3/2}e^4 Z^2 N_i \left[\ln(1+\beta) - \frac{\beta}{1+\beta} \right]} \quad (4)$$

where $\beta = (24m\epsilon/n)(k_B T/e\hbar)^2$; N_i and eZ represent the concentration of ionized impurity and the ionic charge of the impurity, respectively.

The solid lines in Fig. 6 represent the results of this calculation. The theoretical behavior is experimentally supported at various doping concentrations in Er:GaSe samples over the whole range of temperatures. The hole-phonon coupling constant g^2 was determined to be 0.235, 0.243, and 0.252 at 0.2%, 0.5%, and 1.0% Er:GaSe, respectively. At low temperatures, the Hall mobility is limited by ionized impurity scattering, while at higher temperatures, the mobility of hole carriers is probably limited by the short-range interaction with homopolar optical phonons, polarized normally to the layers. The mechanism by which neutral impurities are scattered has not yet been elucidated. The Erginsoy relaxation time²² of neutral impurities indicates that the mobility of holes can be affected when it is in the order of 10^4 cm²/Vs at 300 K, which greatly exceeds the values measured herein; therefore, the neutral scattering mechanism is negligible herein.

IV. CONCLUSIONS

The electrical characteristics and Er-related luminescence of Er:GaSe samples were studied using Hall, DLTS, and PL measurements. The temperature dependence of carrier concentration reveals that erbium introduced two acceptor levels with ionization energies of $E_a \sim 65$ and 158 meV. The measurements of DLTS and of the temperature dependence of Er-related luminescence indicate that the moderately deep acceptor level of 158 meV is importantly involved in the thermal quenching mechanism, which is associated with the energy back transfer process. Additionally, these acceptor levels could be associated with the substitution of two Ga²⁺ atoms by one Er³⁺ atom or are related to a Ga vacancy via the interstratifying of an Er³⁺ ion at the inter-layer site. The temperature dependence of hole mobility was also analyzed by scattering from homopolar optical phonons and ionized impurities.

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