Functional Materials 20, No.4 (2013) 

# Peculiarities of electron-phonon interaction in $Pr^{3+}$ centers of $SrCl_2$:Pr single crystals

***O.T.Antonyak, A.S.Voloshinovskii, V.V.Vistovskyy, Ya.M.Chornodolskyy***

I.Franko National University of Lviv,
8 Kyrylo and Mefodiy Str., 79005 L'viv, Ukraine

*Received July 4, 2013*

The luminescence excitation and emission spectra of $SrCl_2$:Pr single crystals containing 0.2 mol. % Pr were investigated at $T = 10$ K using vacuum ultraviolet synchrotron radiation. From analysis of the fine structure of the low-energy excitation band of an activator, the following main frequencies associated with the local structure of the activator centers were found in the phonon spectrum of $SrCl_2$:Pr crystal: 194; 210; 266 and 298 $cm^{-1}$.

При температуре 10 К исследован спектр возбуждения активаторной люминесценции монокристаллов $SrCl_2$:Pr (0,2 М %) под воздействием синхротронного излучения в области вакуумного ультрафиолета. Посредством анализа тонкой структуры низкоэнергетической полосы активаторного возбуждения найдены следующие главные частоты фононного спектра кристалла $SrCl_2$:Pr: 194; 210; 266 и 298 $см^{-1}$, которые связаны с локальной структурой активаторних центров.

***Особливості електрон-фононної взаємодії в $Pr^{3+}$ центрах монокристалів $SrCl_2$:Pr***. *О.Т.Антоняк, А.С.Волошиновський, В.В.Вістовський, Я.М.Чорнодольський.*
За температури 10 К досліджено спектр збудження активаторної люмінесценції монокристалів $SrCl_2$:Pr (0,2 М %) під впливом синхротронного випромінювання в області вакуумного ультрафіолету. З аналізу тонкої структури низькоенергетичної смуги активаторного збудження знайдено такі головні частоти фононного спектра кристала $SrCl_2$:Pr: 194, 210, 266; та 298 $см^{-1}$, що пов'язані з локальною структурою активаторних центрів.

## *1. Introduction*

$SrCl_2$ single crystal belongs to the cubic fluorite-type structure [1] and turns out to be a suitable crystalline matrix for modelling the electron structure of rare-earth activator centers. The activator trivalent lanthanide ions ($Ln^{3+}$) replace $Sr^{2+}$ cations in regular sites of a crystal lattice. The introduction of trivalent lanthanide ions into the $SrCl_2$ crystal lattice leads to formation of activator centers with different local structures which depend on the mechanism of excess charge compensation and concentration of impurities [2, 3]. In particular, the tetragonal ($C_{4v}$) $Ce^{3+}$-centers are the major centers in $SrCl_2$:Ce single crystals with small concentrations of the activator ($2.0 \cdot 10^{-4} \le C_{Ce} \le 1.2 \cdot 10^{-3}$ mol.%) [4]. For these centers, the fine electron-phonon structure of the absorption and luminescence spectra caused by both crystalline and pseudolocal vibrations was revealed in $SrCl_2$:Ce crystals [4]. An increase of cerium concentrations leads to formation of rhombic ($C_{2v}$) and more complex cluster centers of the activator in $SrCl_2$:Ce ($C_{Ce} \ge 1.5 \cdot 10^{-1}$ mol.%) crystals, which is accompanied with increase of the electron-phonon interaction and with complication of the phonon spectrum [5]. Thus, there is a correlation between the local structure and the activator

center frequencies of pseudolocal and local vibrations of the matrix in vicinity of the activator ions. Therefore, we have conducted the detailed analysis of the fine structure of luminescence excitation spectrum of $SrCl_2$:Pr ($C_{Pr}$ = 0.2 mol.%) crystals characterized by intense activator luminescence [6], trying to connect the frequencies of phonon spectrum with the local structure of the activator centers in $SrCl_2$ matrix.

## 2. Experimental

$SrCl_2$:Pr ($C_{Pr}$ = 0.2 mol. %) single crystal was grown in the evacuated and pre-graphitized quartz ampoules using Bridgman-Stockbarger method. Raw materials were purified from oxygen-containing impurities using treatment of the melt by $CCl_4$ [7]. Pr impurity was added to the crystal composition in the form of $PrCl_3$ compound. Measurements of luminescence excitation and emission spectra of $SrCl_2$:Pr (0.2 mol. %) crystals were performed using the equipment of SUPERLUMI Laboratory (HASYLAB, DESY, Hamburg) [8]. Temperature measurements at 10 K were carried out in the helium cryostat. The luminescence spectrum was measured in 200–550 nm spectral range with resolution of 1 nm using a monochromator-spectrograph ARS "Spectra Pro 308" with a focal length of 30 cm, equipped with a CCD detector and HAMAMATSU R6358P photomultiplier. The luminescence excitation spectrum was measured in 5–22 eV range using a monochromator with a focal length of 2 m and resolution of 4.0 Å. The luminescence excitation spectrum was corrected on the intensity of the incident photon flux.

## 3. Results and discussion

*Luminescence of $SrCl_2$:Pr crystals excited by synchrotron radiation at 10 K*

The luminescence spectrum of $SrCl_2$:Pr ($C_{Pr}$ = 0.2 mol. %) crystal obtained under excitation by a quanta $h\nu_{ex}$ = 5.7 eV at 10 K, consists of two main groups of emission bands: a short-wave group in the UV region and a long-wave group in 480–500 nm spectral range (Fig. 1). The short-wave group contains two pairs of close emission bands having peaks at 248.5 nm and 261 nm, 283 nm and 295 nm, and one separate band with a maximum at 325 nm. Among the observed emission bands, the band at 248.5 nm was the most intensive, whereas the band having a peak at 325 nm was the weakest. The group of the long-wave bands has peaks at 488 nm and 495 nm, the first of which dominates at 10 K. One can notice that the short-wave luminescence bands are characterized by a half-width ~ 0.2 eV, that is one order greater than the half-width of the long-wave bands (~ 0.03–0.04 eV). Location of these luminescence spectrum bands is, in general, in a good agreement with the data of [6]. The bands correspond to the following transitions in $Pr^{3+}$-centers: $4f^15d \rightarrow {}^3H_4$ (248.5 nm); $4f^15d \rightarrow {}^3H_5$ (261 nm); $4f^15d \rightarrow {}^3H_6$ (283 nm); $4f^15d \rightarrow {}^3F_3$ (295 nm); $4f^15d \rightarrow {}^1G_4$ (325 nm); ${}^3P_2 \rightarrow {}^3H_4$ (488 nm) and ${}^3P_{0,1} \rightarrow {}^3H_4$ (495 nm).

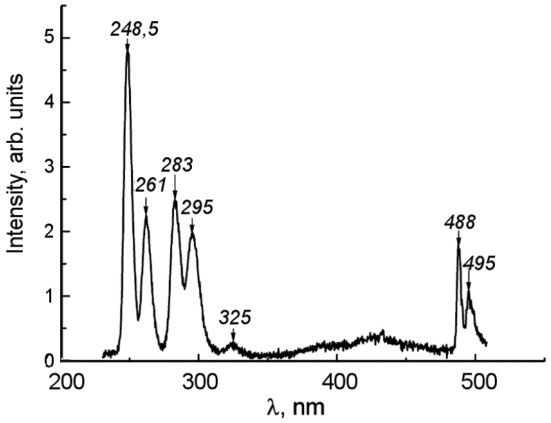


Fig. 1. Luminescence spectrum of $SrCl_2$:Pr (0.2 mol. %) crystal excited with $h\nu_{ex}$ = 5.7 eV synchrotron radiation at 10 K.

These data well coincide with the results of [6], obtained for polycrystalline $SrCl_2$:Pr (0.5 %) samples, except of $4f^15d \rightarrow {}^3H_6$ (283 nm) band, fixed by us for better separation of the luminescence spectrum in the single crystals.

Narrow (~ 0.03 eV) band at 488 nm of the long-wave part of the luminescence spectrum is obviously responsible for intra-configuration transition between $4f^2$ configuration levels, the provisions of which are consistent with described in other crystals doped with praseodymium, in particular, in [6]. This leads us to referring this band to ${}^3P_2 \rightarrow {}^3H_4$ transition. Complex luminescence band of 495 nm obviously corresponds to ${}^3P_{0,1} \rightarrow {}^3H_4$ transitions.

The identified experimental luminescence transitions were used in constructing an energetic scheme of the lower levels of $Pr^{3+}$ ions (i.e., $4f^2$ configuration) in the $SrCl_2$ crystal lattice (Fig. 2).

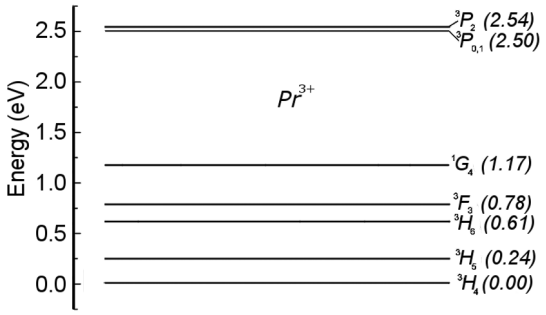


Fig. 2. Energetic scheme of the lower $4f^2$ configuration $Pr^{3+}$ levels in $SrCl_2$ crystal lattice.

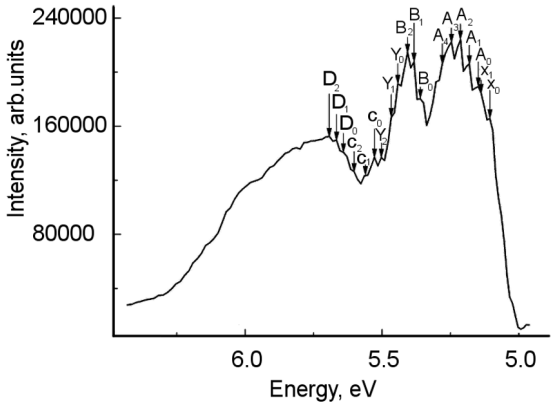


Fig. 3. Fine structure of the low-energy $f$–$d$ band of the excitation spectrum for emission band peaked at 291 nm in $SrCl_2$:Pr (0.2 mol. %) crystal at 10 K.

Phonon structure of the luminescence excitation spectrum of $SrCl_2$:Pr ($C_{Pr}$ = 0.2 mol. %) crystal under synchrotron emission excitation in the region of 5–22 eV at 10 K is only revealed for the low-energy region (5–6.5 eV), which corresponds to $4f^2$–$4f5d$ absorption of the activator centers (Fig. 3).

Detailed consideration of the luminescence excitation bands for the low-energy region shows that they contain several zero-phonon lines corresponding to electron ($f$–$d$) transitions accompanied with vibrational repetitions (i.e., phonon sidebands) (Fig. 2). The analysis of this region of the luminescence excitation spectrum reveals several series of vibrational replicas with different frequencies of phonons. The following main phonon series in the low-energy range can be distinguished: 1) zero-phonon line $A_0$ (5.147 eV) with its four vibrational replicas: $A_1$ (5.180 eV), $A_2$ (5.213 eV), $A_3$ (5.246 eV) and $A_4$ (5.279 eV) — with phonon energy $h\nu_{1ph}$ = 0.033 eV (266 $cm^{-1}$); 2) zero-phonon line $B_0$ (5.358 eV) with two vibrational replicas $B_1$ (5.382 eV) and $B_2$ (5.406 eV) with $h\nu_{2ph}$ = 0.024 eV (194 $cm^{-1}$); 3) zero-phonon line $C_0$ (5.527 eV) with two vibrational replicas: $C_1$ (5.564 eV) and $C_2$ (5.601 eV) — with $h\nu_{3ph}$ = 0.037 eV (298 $cm^{-1}$); and 4) zero-phonon line $D_0$ (5.640 eV) with two vibrational replicas: $D_1$ (5.666 eV) and $D_2$ (5.692 eV) — with $h\nu_{4ph}$ = 0.026 eV (210 $cm^{-1}$). The above mentioned electron-vibrational bands in the low-energy region of the luminescence excitation spectrum can be ascribed to vibration of the $Pr^{3+}$ activator centers in the regular positions of the lattice. Moreover, in the considered region of the luminescence excitation spectrum there were observed additional weak bands denoted as $X_0$ (5.105 eV) with one vibrational repetition $X_1$ (5.137 eV) ($\nu_{1ph}$ = 258 $cm^{-1}$) and $Y_0$ (5.442 eV) with two vibrational repetitions: $Y_1$ (5.465 eV) ($\nu_{2ph}$ = 185 $cm^{-1}$) and $Y_2$ (5.502 eV) ($\nu_{ph} = \nu_{2ph} + \nu_{3ph}$ = 185 $cm^{-1}$ + 299 $cm^{-1}$)). These additional X and Y weak series can be assigned to the vibrations of $Pr^{3+}$ ions located in crystallographic inequivalent positions of $SrCl_2$:Pr crystal lattice.

The spectral parameters of vibrational structure of the low-energy $f$–$d$ band in the luminescence excitation spectrum of the centers of $Pr^{3+}$ in $SrCl_2$:Pr crystals are collected in Table. Among the four observed main phonon frequencies (194 $cm^{-1}$, 210 $cm^{-1}$, 266 $cm^{-1}$, and 298 $cm^{-1}$) in the luminescence excitation spectrum of $SrCl_2$:Pr crystal, one of them (210 $cm^{-1}$) is close to $A_{1g}$ frequency of the fully symmetric vibration of the crystal lattice forming the vibrational structure of absorption and luminescence spectra in $SrCl_2$:$Yb^{2+}$ (209 $cm^{-1}$ [9], 210 $cm^{-1}$ [10]), in $SrCl_2$:$Sm^{2+}$ (213 $cm^{-1}$ [11]), in $SrCl_2$:$Eu^{2+}$ (210 $cm^{-1}$ [12]), and in $SrCl_2$:$Tm^{2+}$ (212 $cm^{-1}$ [13]) crystals, where $Ln^{2+}$ lanthanide ions are located in the cubic crystal field. Therefore, it was logical to suppose that the phonons with frequency $\nu_{4ph}$ = 210 $cm^{-1}$ can occur in the cubic ($O_h$) $Pr^{3+}$ centers with non-local compensation of the excess charge in $SrCl_2$:$Pr^{3+}$ crystal.

Four vibrational repetitions of $A_0$ (5.147 eV) zero-phonon line are caused by the phonon with frequency $\nu_{1ph}$ = 266 $cm^{-1}$, which is close to the phonon frequency 242 $cm^{-1}$ detected in $SrCl_2$:$Ce^{3+}$ crystal [4] and attributed to the pseudolocal vibrations of $Cl^-$ compensator in the structure of tetragonal $C_{4v}$-centers. This result indicates the presence of $C_{4v}$-centers with local compen-

Table. Vibrational structure of the low energy $f$–$d$ excitation band of $Pr^{3+}$ centers in $SrCl_2$:Pr (0.2 mol. %) crystals at 10 K ($\nu_0$ — frequency of the electronic transition)

| Excitation band | $E_i$, eV | $\nu_i$, $cm^{-1}$ | $\Delta\nu_{i0} = \nu_i - \nu_0$, $cm^{-1}$ | Excitation band | $E_i$, eV | $\nu_i$, $cm^{-1}$ | $\Delta\nu_{i0} = \nu_i - \nu_0$, $cm^{-1}$ |
|---|---|---|---|---|---|---|---|
| $A_0$ | 5.147 | 41511 | 0 | $C_0$ | 5.527 | 44575 | 0 |
| $A_1$ | 5.180 | 41777 | $\nu 0 + 266$ | $C_1$ | 5.564 | 44874 | $\nu 0 + 299$ |
| $A_2$ | 5.213 | 42043 | $\nu_1 + 266$ | $C_2$ | 5.601 | 45172 | $\nu_1 + 298$ |
| $A_3$ | 5.246 | 42309 | $\nu_2 + 266$ | $D_0$ | 5.640 | 45486 | 0 |
| $A_4$ | 5.279 | 42575 | $\nu_3 + 266$ | $D_1$ | 5.666 | 45696 | $\nu_0 + 210$ |
| $B_0$ | 5.358 | 43212 | 0 | $D_2$ | 5.692 | 45906 | $\nu_1 + 210$ |
| $B_1$ | 5.382 | 43406 | $\nu_0 + 194$ | $Y_0$ | 5.442 | 43890 | 0 |
| $B_2$ | 5.406 | 43599 | $\nu 1 + 193$ | $Y_1$ | 5.465 | 44075 | $\nu 0 + 299$ |
| $X_0$ | 5.105 | 41172 | 0 | $Y_2$ | 5.502 | 44374 | $\nu_1 + 299$ |
| $X_1$ | 5.137 | 41430 | $\nu_0 + 258$ | | | | |

sation of $Pr^{3+}$ excess charge by $Cl^-$ anions located in the neighboring interstitial sites of the $SrCl_2$:Pr (0.2 mol. %) crystal lattice.

Phonons with frequencies $\nu_{2ph} = 194$ $cm^{-1}$ and $\nu_{3ph} = 298$ $cm^{-1}$ were not observed earlier in pure and activated $SrCl_2$ crystals. These phonons can be attributed to the local vibrations of anionic environment of $Pr^{3+}$ centers including $Pr^{3+}$ clusters in $SrCl_2$:Pr (0.2 mol. %) crystal. Using the analogy with $SrCl_2$:$Ce^{3+}$ crystals containing 0.15 mol. % Ce, which show the presence of $Ce^{3+}$ tetragonal centers (local symmetry — $C_{4v}$) and complex clusters of $Ce^{3+}$ centers with the local symmetry $C_{2v}$ and more complex clusters [5], it was supposed that in $SrCl_2$:Pr (0.2 mol. %) crystal there are single (i.e. isolated) $Pr^{3+}$ centers and complex clusters of $Pr^{3+}$ centers. Using site-selective laser spectroscopy in $CaF_2$:$Pr^{3+}$ crystals, which are isostructural to $SrCl_2$ crystals, there were registered 10 main types of $Pr^{3+}$ centers including clusters containing two or more $Pr^{3+}$ ions [14]. Recently, having analyzed the luminescence and luminescence excitation spectra, there were found three types of $Pr^{3+}$-centers with different local symmetry in $CaF_2$:$Pr^{3+}$ crystals [15, 16].

Thus, we can argue that the fine structure of the low-energy region of luminescence excitation spectra in $SrCl_2$:Pr (0.2 mol. %) crystal is formed by zero-phonon lines corresponding to $4f^2 \rightarrow 4f5d$ transitions of the single and complex $Pr^{3+}$ centers with different local structure and by their vibration replicas.

## 4. Conclusions

The fine structure of the luminescence excitation band of $Pr^{3+}$ in $SrCl_2$:Pr (0.2 mol.%) single crystals formed by zero-phonon transitions and its vibrational replicas in $Pr^{3+}$ centers was revealed at 10 K. After analysis of the fine structure, the following main phonon frequencies were found: 194 $cm^{-1}$, 210 $cm^{-1}$, 266 $cm^{-1}$ and 298 $cm^{-1}$. Two of these frequencies (210 $cm^{-1}$ and 266 $cm^{-1}$) were attributed to pseudolocal vibrations that occur within cubic ($O_h$) and tetragonal ($C_{4v}$) centers of $Pr^{3+}$, respectively, the other two frequencies (194 $cm^{-1}$ and 298 $cm^{-1}$) were attributed to the local vibrations in the cluster praseodymium centers.

## References


1. R.W.G.Wyckoff, Crystal Structures, v.1, Interscience Publishers, New York (1963).
2. W.W.Osiko, *Fiz. Tverd. Tela*, **7**, 1294 (1965).
3. W.J.Mantey, *Phys. Rev. B*, **8**, 4086 (1973).
4. O.T.Antonyak, I.V.Kityk, M.S.Pidzyrailo, *Opt. Spectrosc.*, **63**, 529 (1987).
5. O.T.Antonyak, I.V.Kityk, M.S.Pidzyrailo, *Opt. Spectrosc.*, **69**, 606 (1990).
6. A.Zych, A.L.op Reinink, K.van der Eerden et al., *J. Alloy Compd.*, **509**, 4445 (2011).
7. R.Voshka, I.Tarjan, L.Berkes et al., *Kristall und Technik*, **1**, 423 (1966).
8. G.Zimmerer, *Radiat. Meas.*, **42**, 859 (2007).
9. Z.Pan, C.Duan, P.A.Tanner, *Phys. Rev. B*, **77**, 085114 (2008).
10. A.A.Kaplyanskii, P.L.Smolyanskii, *Opt. Spectrosc.*, **40**, 528 (1976).
11. M.Karbowiak, A.Urbanowisz, M.F.Reid, *Phys. Rev. B*, **76**, 115125 (2007).

12. Z.Pan, L.Ning, B.M.Cheng et al., *Chem.Phys. Lett.*, **428**, 78 (2006).
13. J.Grimm, O.S.Wenger, K.W.Kramer et al., *J. Luminescence*, **126**, 590 (2007).
14. A.Lezama, M.Oria, C.B.de Araujo, *Phys.Rev. B*, **33**, 4493 (1986).
15. K.D.Oskam, A.J.Houtepen, A.Meijerink, *J. Luminescence*, **97**, 107 (2002).
16. I.A.Boiaryntseva, N.V.Shiran, A.V.Gektin et al., *Functional Materials*, **19**, 192 (2012).