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Luminescence of CsTaF$_6$ studied by VUV spectroscopy

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Abstract

Broad-band luminescence with maximum at 3.35 eV has been revealed from new luminescence material CsTaF$_6$ under VUV excitation. This luminescence was interpreted as emission of molecular type self-trapped excitons localized at the $[TaF_6]^-$ complexes. The energy of effective vibrational mode responsible for exciton-lattice coupling was determined to be equal to 45 meV (363 cm^{-1}), which does not correspond to the energy of breathing mode of $[TaF_6]^-$ complex vibrations. The observed luminescence possesses thermal quenching with activation energy ~58 meV.

Keywords: Luminscence; self-trapped exciton; exciton-lattice coupling; thermal quenching; CsTaF$_6$

1. Introduction

Luminescence of CsTaF$_6$ is an interesting subject for investigation as crystals based on complexes of transition metal ions with empty *d*-shell (such as, e.g., tungstates $[WO_4]^{2-}$ or molibdates $[MoO_4]^{2-}$) often show an intense broad-band emission with large Stokes shift. Crystals of CsTaF$_6$ are known to have unimolecular rhombohedral cell of a shape that makes them slightly distorted CsCl arrangement of Cs^+ and $[TaF_6]^-$ ions (Landolt-Börnstein, 1973). The $[TaF_6]^-$ complex possesses distorted O_h symmetry (octahedron). An essential feature of this crystal is very high electron affinity for the $[TaF_6]^-$ complex, namely 8.4 eV (Gutsev and Boldyrev, 1983), and this molecular ion is

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considered as 'superhalogen' (*e.g.* for F^- the electron affinity is 3.4 eV). In the present work the luminescence properties of $CsTaF_6$ were studied using excitation by vacuum ultraviolet (VUV) synchrotron radiation.

2. Experimental details

The measurements were performed at station 3.1 of synchrotron radiation source (SRS) at Daresbury Laboratory (Cernik, 1994). using 1-meter Seya-Namioka monochromator for excitation in the spectral range 4-30 eV. Emission spectra were recorded using a home-made visible/UV monochromator with a resolution of 5 nm and a photomultiplier tube XP2020Q. $CsTaF_6$ powder samples were synthesized by S.S. Galaktionov at D. Mendeleev University of Chemical Technology of Russia.

3. Results and discussion

The measurements have revealed the presence in $CsTaF_6$ of a broad Gaussian-like emission band with maximum at 3.35 eV and FWHM = 0.74 eV at $T = 90$ K (see insertion of Fig. 1), which is typical for crystals with a complex anion. As is also typical for such kind of crystals this luminescence possesses thermal quenching. The temperature dependence of intensity of this luminescence band $I(T)$ is plotted in Fig. 1 and was fitted by the well-known Mott relation:

$$I(T) = I(0)/(1+A\exp(-\varepsilon/k_BT)), \qquad (1)$$

with an activation energy of thermal quenching $\varepsilon = 58$ meV, k_B is Boltzmann constant.

The temperature dependence of emission bandwidth $W(T)$ (shown in the same Figure) can be rather well approximated by the well-known formula for phonon broadening in the limit of strong interaction of the optical center with the lattice:

$$W(T) = W(0)[\coth(\hbar\omega/2k_BT)]^{1/2}, \qquad (2)$$
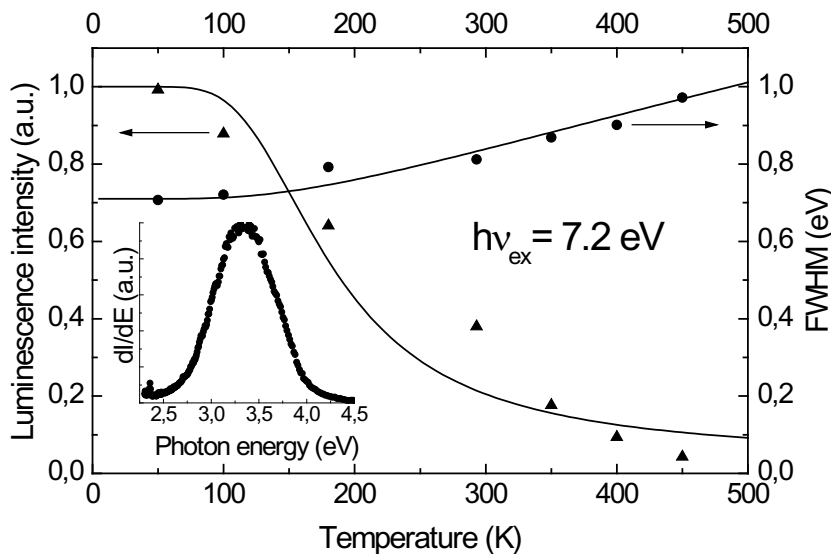

Fig. 1. Temperature dependencies of luminescence intensity and bandwidth (FWHM) for $CsTaF_6$ (dots – experimental data; lines – fitting). In the inset, luminescence spectrum of $CsTaF_6$ at 90 K is shown. Excitation energy was 7.2 eV.

where $\hbar\omega$ is the energy of efficient vibrational mode of lattice vibrations, $W(0)$ is bandwidth at $T = 0$ K (Henderson and Imbusch, 1989). Thus we have obtained $\hbar\omega = 45$ meV (363 cm^{-1}). According to data on infrared spectra of solid CsTaF$_6$ presented in (Fordyce and Baum, 1966) the phonon energies corresponding to Ta-F stretching modes of vibrations do not correspond to this value. Accordingly, we can conclude that Ta-F stretching modes are not the dominating modes of interaction with the lattice for electronic transitions in CsTaF$_6$ and the phonon energy 45 meV can be considered as some convolution of many modes of host lattice vibrations.

The excitation spectra are shown in Fig. 2 in the region 4-10 eV at T=50 and 293 K, measured with a LiF filter in order to remove the second order of the excitation monochromator, and in Fig. 3 in the region 7-30 eV at T=90 and 300 K. It is easily seen that luminescence excitation starts with energy ~5 eV which well corresponds to the energy gap E_g of CsTaF$_6$ determined by photoemission measurements in (Kamada et al, 1996).
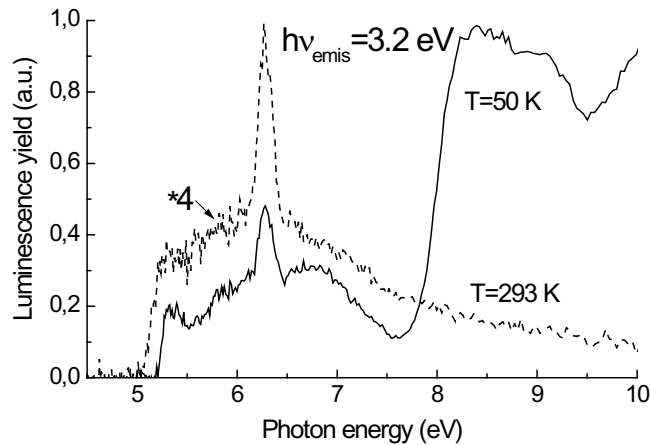
Fig. 2. Excitation spectrum of CsTaF$_6$ at T=293 and 50 K measured with LiF filter in the energy region 4-10 eV.
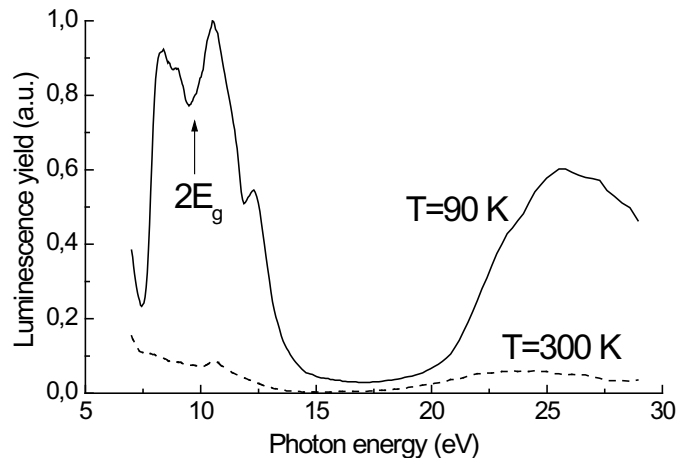
Fig. 3. Excitation spectrum of CsTaF$_6$ at T=300 and 90 K measured in the energy region 7-30 eV.

To the best of our knowledge, there are no any energy band structure calculations in the literature for CsTaF$_6$. Accordingly, we can give only tentative analysis of the observed spectra basing on comparison with optical properties and energy band structure calculations available for other crystals with complex anions containing

transition metal ions with empty *d*-shell, mainly tungstates and molibdates (Zhang et al, 1998; Abraham et al, 2000; Nagirnyi et al, 2003; Kotlov et al, 2005).

By analogy with other crystals with complex anions of similar nature the low-energy part in the excitation spectrum (~5-8 eV) of $CsTaF_6$ corresponds to electronic transitions from the *F 2p* states in the valence band to *Ta 5d* states in the conduction band, which do not result in the direct creation of excitonic states. However, due to strong coupling to the lattice the created geminate pairs of electrons and holes recombine practically immediately with the creation of self-trapped excitons (STE) localized at the $[TaF_6]^-$ complexes. Thus, luminescence at 3.35 eV can be treated as radiative recombination of these molecular-type STEs, i.e. as charge-transfer (from central Ta^{4+} ion to surrounding fluorines) radiative transitions inside the $[TaF_6]^-$ complex. These transitions take place after lattice relaxation which results in the appearance of the Stokes shift. The value of the Stokes shift (*SS*) can be estimated from relation (Henderson and Imbusch, 1989) $SS = W(0)^2/4\hbar\omega \approx 2.7$ eV, i.e. the Huang-Rhys parameter is $S = SS/2\hbar\omega \approx 30$, which confirms the case of strong interaction with lattice vibrations.

Due to high electron affinity for the complex anion mentioned above the electronic transitions from the valence band composed of electronic states of the $[TaF_6]^-$ complex to the conduction band composed of Cs^+ *5d/6s* states are expected to start at ~8 eV. Indeed at this photon energy a rather strong increase of luminescence intensity is observed at low temperature. This energy well corresponds to the edge of intrinsic absorption in CsF, which results in this host in the appearance of intrinsic luminescence from STEs (Makhov et al, 2005). Such a behavior can indeed be expected if the top of the valence band in $CsTaF_6$ is composed from *F 2p* electronic states. The schematic diagram of energy band structure of $CsTaF_6$ is shown in Fig.4.

Fig. 4. Schematic diagram of energy bands and electronic transitions in $CsTaF_6$.

The host takes part in luminescence process only at low temperature, as efficiency of the luminescence at excitation energy higher than 8 eV is very low at room temperature (see Figs. 2 and 3). This fact might be explained if the electronic transitions from the valence band to Cs^+ *5d/6s* states result in the creation of another type of STEs which have at low temperature a sufficiently long lifetime (with respect to nonradiative decay into electron-hole pairs) for the efficient relaxation into $[TaF_6]^-$-type of STEs. According to this model, the free electrons can be created in Cs^+ *5d/6s* sub-band of the conduction band at photon energies higher than ~9 eV taking into account the expected bound energy ~1 eV for this another type of STEs (by analogy with CsF). When the temperature is higher the lifetime of these STEs decreases and as a result the intensity of 3.35 eV luminescence under excitation at $h\nu > 8$ eV is reduced. On the other hand, the 3.35 eV luminescence has its own thermal quenching mechanism according to temperature behavior described above for the 7.2 eV excitation.

When the energy of exciting photons is higher than 11 eV the intensity of 3.35 eV luminescence decreases rapidly reaching practically zero value at ~15 eV (see Fig. 3). This effect is due to a rather high kinetic energy of electrons and holes created after the photons absorption, which results in a separation of a geminate pair of carriers at a rather large distance. Accordingly, this pair can't recombine into exciton and does not excite luminescence. Starting from energy ~20 eV an enhancement of the quantum yield is observed which is supposed to occur due to the effect of multiplication of electronic excitations (MEE) (Lushchik et al, 1996) when hot photoelectrons (or hot photoholes) have sufficient kinetic energy for the creation of secondary electronic excitations. The energy of 20 eV considerably exceeds the value of $2E_g \sim 10$ eV as well as $(E_g + 9)$ eV. This means that in $CsTaF_6$ the so-called excitonic mechanism of MEE doesn't work, i.e. hot photocarriers cannot directly create secondary excitons (of $[TaF_6]^-$-type), and only creation of secondary separated (free) electrons and holes by fast photocarriers with kinetic energy larger than ~9 eV, i.e. under excitation by photons with the energy exceeding ~18 eV, results in the appearance of secondary STEs.

4. Conclusions

Broad-band luminescence with maximum at 3.35 eV and FWHM = 0.74 eV (at $T = 90$ K) has been revealed from the $CsTaF_6$ powder samples under VUV excitation and interpreted as emission of molecular type STEs localized at the $[TaF_6]^-$ complexes. The energy gap of $CsTaF_6$ was estimated as ~5 eV. The energy of efficient vibrational mode responsible for exciton-lattice coupling was determined from the analysis of thermal broadening of STE emission bandwidth and is equal to 45 meV (363 cm^{-1}). This phonon energy does not correspond to the energy of breathing mode of $[TaF_6]^-$ complex vibrations and can be associated with effective mode of vibrations of the whole crystal lattice. Luminescence of STEs in $CsTaF_6$ is observed only at low temperature and activation energy of its thermal quenching was estimated as ~58 meV.

Acknowledgements

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