

Exciton Emission in LaF₃ Crystals

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Abstract

The ultraviolet photoluminescence at 4.1 eV was found in all LaF₃ samples, with near 100% quantum yield at 78 K. Emission excited near interband transitions (peak at 10.5 eV). Decay time of 4.1 eV emission increased continuously from 6 μs at 290 K up to 600 μs at 12 K. All these features allow us to assign this 4.1 eV band to the emission of triplet self-trapped excitons in LaF₃ crystals.

Introduction

In spite of chemical simplicity the properties of excitons in lanthanide trifluoride crystals are still almost unknown. For many ionic crystals the self trapping of excitons is accompanied by self trapping of holes. The self-trapped holes were found recently in LaF₃ crystals [1].

The broad band centered at 3.65 eV (340 nm) was suggested to be self-trapped exciton luminescence [2]. This band was observed in pure crystals of different quality excited by the X-ray and 20 eV photons [1, 2]. At the temperatures below 200 K, the spectrum of X-ray excited luminescence is dominated by the band at 4.3 eV (290 nm), which is attributed to 5d-4f transitions of Ce impurity [1].

In early optical investigations of LaF₃ crystals using synchrotron source the reflectance peak that may belong to excitons was not observed [3]. The reflectance spectra show strong interband transitions in the 10-15 eV region, presumably from the F 2p valence band to lanthanide 5d and 6s conduction band [3]. All the peculiarities of the 10-15 eV reflectance peaks with polarized light were interpreted in terms of band to band transitions [3].

The absence of strong exciton absorption bands was observed also in the LaCl₃, LaBr₃ thin films, although a weak band with absorption coefficient close to 10⁵ cm⁻¹ is observed in chloride at liquid nitrogen temperature [4]. The broadness of the observed spectra suggests that the continuum of band-to-band transition predominates over the exciton absorption [4].

Usually the excitons absorb light with the energy close to the band to band transitions, for lanthanide trifluorides it is about 10.5 eV. Therefore we try to study the intrinsic LaF₃ emission under excitation near interband transitions in the vacuum ultraviolet (VUV) region 9-12 eV.

Experimental

LaF₃ and CeF₃ crystals were grown by the Stockbarger method. The purification from oxygen was obtained by the addition of PbF₂ to the extent of about 1-3 wt. %. The mixture is slowly heated under vacuum up to the melting point. Crystals are grown under vacuum 10⁻³ - 10⁻⁴ torr. The transmission in vacuum ultraviolet region was the test oxygen absence. The crystals with the best transparency in VUV region were grown from LaF₃ prepared by Angarsk Electrochemical Company. The another LaF₃ crystal with similar good VUV transparency was kindly loaned by Williams R.T. His crystals was grown at Optovac from LaF₃ prepared from 99.999% pure La oxide [2]. Both crystals show 4.1 eV emission band excited above 10 eV, but different sharp line spectra excited at lower energies are observed as well. Obviously these emission lines belong to transitions of some rare-earth ions with estimated concentration of few ppm.

Results

The wide band close to 4.1 eV was observed at 78 K in all the LaF₃ crystals when excited into 9.8-11 eV region (excitation peak 10.5 eV). At 16 K the maximum is found at 4.2 eV (Fig.1). The emission at 4.1 eV is slightly asymmetric.

Below 9.8 eV the sharp line spectra were observed. These spectra depend on purity of the material and it belongs to the trace of some rare-earth impurity. In the lower purity crystal there is anticorrelation between impurity excitation spectrum and 4.1 eV spectrum at 9-10.5 eV region.

The absorption spectrum of LaF₃ crystals at room temperature shows the strong edge above 10 eV (see Fig.1). Our purest crystals and crystal loaned by Williams R.T. have similar absorption spectra. The excitation spectrum for 4.1 eV band shows the well-defined band with maximum at 10.5 eV and halfwidth 0.6 eV at 78 K (see Fig.1). The halfwidth of excitation band is unusually narrow. Near to 11 eV the excitation drop significantly. Usually excitation spectrum has a long tail above the first exciton peak [5] and promotes to band-to-band region.

Due to the decreasing temperature from room temperature to 78 K the intensity of ultraviolet band was increased several times with shifting maximum by 0.15 eV, the excitation band was shifted to high energy side by 0.1 eV. No other emission was observed up to 9 eV with the X-ray excitation at room temperature and 80 K.

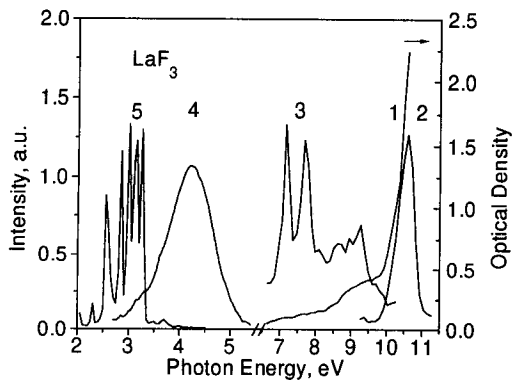


Fig. 1 Absorption (1), excitation (2,3) and emission (4,5) spectra of LaF₃. Spectra were measured at 295 K (1), 78 K (3,5) and 16 K (2,4). Absorption spectrum was measured for the sample of 1 mm thickness.

decreases.

Discussion

X-ray excited luminescence

Let us compare the difference in the temperature dependence of luminescence spectra of LaF₃ under vacuum ultraviolet and x-ray excitations. The most intense part of X-ray excited spectrum within 4.0-4.4 eV was attributed to the (unresolved) spin orbit splitted 5d-4f transition on the dilute Ce impurity [1]. On the other side with decreasing temperature the emission band at 4.3 eV (290 nm) is relatively increased with respect to the other bands close to 3.4 eV (360 nm) and 2.53 eV (490 nm) [1]. The later band possibly belong to praseodymium impurity. This behavior correlates with the exciton luminescence in many crystals, which is the most intensive at low temperatures. Then at high temperature the exciton energy transfer to the impurities or nonradiative quenching take place [5]. So we believe this band belongs to the excitons rather than to Ce impurity.

Decay time of the 4.1 eV band consists of one or two components in micro- millisecond time range (Fig.2). No shorter components were observed. The decay time of 4.1 eV emission increased continuously from 6 μ s at 290 K up to 600 μ s at 12 K. Two decay components were observed at temperatures 80-150 K. The decay time was independent of photon energy of excited light. Emission spectra of stationary emission and emission in both components are the same. The decay times are not changed within emission band.

The rise time about one microsecond of 4.1 eV luminescence decay was observed in LaF₃ crystal (the inset in Fig.2). The rise time not depend on the temperature at least in 78-140K range while decay time decreases from 15 to 9 μ s. Above 140K the rise time also decreases.

The 4.3 eV (290 nm) emission is completely quenched at room temperature and then dramatically increases as temperature is lowered, peaking at 150 K. The maximum luminescence temperature corresponds to the largest of two thermoluminescence glow curve peaks [1]. Obviously the thermoluminescence and X-ray luminescence peaks caused by detrapping of charge carriers (possibly holes). The 4.1 eV photoluminescence intensity increased continuously from 290 K down to 78 K. It means that free electrons and holes are much less effectively created at 10-11 eV photo-excitation with respect to the 4.1 eV excitons.

Rise of emission

Usually the occupation of exciton luminescent states is very fast processes in subpicosecond time scale. Nevertheless, in certain cases the rise time can be long enough to be observed. We observed a long rise stage of exciton photoluminescence in BaFBr crystals also [0].

Generally the emission kinetic can be described in terms of exponential rise and decay stages. With some minimal assumptions for one rise and one decay time the kinetic equation is:

$$I = I_1 \cdot \exp(-t/\tau_{\text{decay}}) \cdot [1 - I_2 \cdot \exp(-t/\tau_{\text{rise}})] \quad (1)$$

where I_1, I_2 - some initial intensities. The calculated curves fit the experimental data reasonably well with I_2 near 0.3 (see Fig.2).

The absence of temperature dependence of τ_{rise} at low temperatures might be attributed to the tunnel transitions and the τ_{rise} decrease above 140K can be attributed to the over-barrier transitions. The physical nature of such a barrier is not clear.

Urbach edge

In many materials the low energy tail of first exciton absorption band is exponential in photon energy [5]. The straight line on the semilogarithmic plot fit the Urbach-Toezawa rule:

$$\alpha(E) = \alpha_0 \exp(-\sigma(E_0 - E)/kT) \quad (2)$$

The family of straight lines intersected in one point of exciton peak energy E_0 . The σ

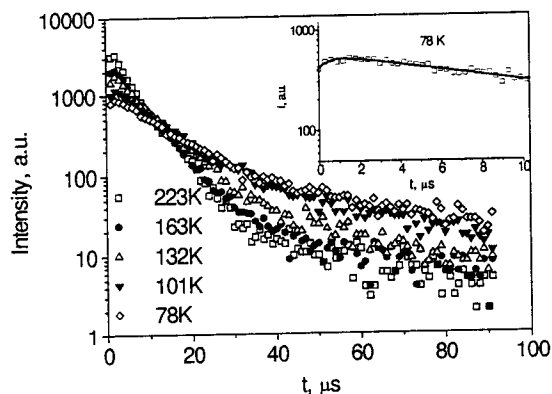


Fig. 2 Decay of exciton emission (4.1 eV band) in LaF_3 with 10.5 eV excitation. Inset-curve was fitted by rise and decay stage using equation (1).

empirical slope coefficient is the important characteristic of exciton-phonon coupling. Thus a small σ_0 (a high temperature limit of σ) is the evidence of the exciton self-trapping [5]. This rule also holds for Ag halides, where due to indirect transitions there are no strong exciton peaks at the absorption edge. The absorption edge of some wide-gap glasses obeys to modified Urbach rule [6]:

$$\alpha(E) = \alpha_0 \exp(AE + T/T_1) \quad (3)$$

where A - slope constant, T_1 - some temperature. The main difference from equation (2) is that the slope of lines at different temperatures is the same. The slope of absorption line in semilogarithmic plot is several times less than for relevant crystals (with exception of SiO_2 glass). The constant A is in range of $5-6 \text{ eV}^{-1}$, T_1 is in range of 200-250 K [6].

The LaF_3 shows unusually broadened absorption edge (Fig.3). The edge consists of two areas; the first one is temperature independent with slope $A=3 \text{ eV}^{-1}$. The second one is described as 'glassy' type edge (equation (3)) with parameters: $A=5.4 \text{ eV}^{-1}$ and $T_1=256 \text{ K}$.

It might be that such 'glassy' type absorption edge arises because of flexibility of the fluorine sublattice in LaF_3 . The extrinsic fluorine vacancies have a very low migration energy 0.1-0.2 eV that is directly connected with superionic properties. Both LaF_3 and CeF_3 show an unusual large anion vacancy concentration [8]. Below 415 K the extrinsic anion vacancy exist mainly in the mixed La-F layers, whereas above 415 K, vacancies populate the pure fluorine layers [8]. The NMR studies point on high mobility of fluorine in mixed layers at 273K. The transformation of NMR spectra due to high mobility of fluorines from pure layers was observed since 420 K [7].

Obviously the observed absorption edge of LaF_3 is not related to exciton transitions. The exciton transitions at energies up to 10.3 eV are in the range of the interband transitions.

Conclusion

The following properties support the self-trapped exciton nature of 4.1 eV emission in LaF_3 :

- The emission was found in all the LaF_3 crystals studied. This fact point that it is rather intrinsic emission than that of an impurity center.
- The emission is excited by photons of energy close to the band-to-band transitions similar to known exciton emissions.
- The decay time is in micro-millisecond region. This is typical for triplet excitons. The temperature dependence is similar to that of excitons in alkaline-fluoride crystals.

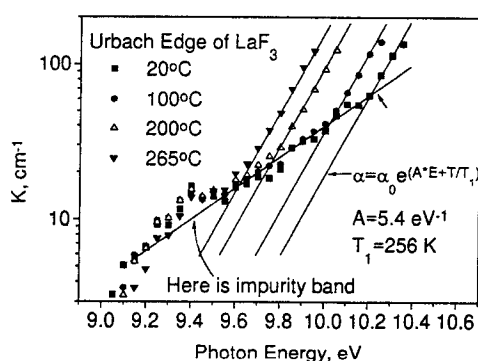


Fig.3 Absorption edge of LaF_3 crystal.

The exciton bands were evidenced only in the emission (or excitation) spectra. In vacuum ultraviolet absorption and reflectivity spectra they are overlapped by the interband transitions.

Acknowledgments

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References

- [1]Thoma E.D., Shields H.W., Zhang Y., McCollum B.C. and Williams R.T., *Proceedings of International Conference Inorganic Scintillators and Their Applications SCINT95, Delft, The Netherlands, Delft University Press* 1995 193-195
- [2]Moses W.W., Derenzo S.E., Weber M.J., Ray-Chaudhuri A.K., Cerrina F. *J. of Luminescence* **59** 89-93 (1994)
- [3]Olson C.G., Piacentini M. and Lynch D.W. *Phys Rev B.* **18** 5740-5749 (1978)
- [4]Sato S. *J.Phys.Soc.Japan* **41** 913-920 (1976)
- [5]Song, Williams R.T. *Self Trapped Excitons* - Berlin, Heidelberg,N.Y.: Springer-Verlag -1993 404 p
- [6]Trukhin A.N. *J.Non-Crystalline Solids* **189** 1-15 (1995)
- [7]Habuda S.P., Gagarinsky Yu.W., Polyshchuk S.A. *NMR in inorganic fluorides* (in Russian), Moscow, Atomizdat, 1978, 208 p.
- [8]Aalders A.F., Arts A.F.M., de Wijn H.W. *Phys.Rev. B* **32** 5412 (1985)

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