

Spectroscopic Investigation of $\text{Na}_{0.4}\text{R}_{0.6}\text{F}_{2.2}$ (R-Y, Lu) and $\text{Na}_{0.4}(\text{Y}, \text{TR}^{3+})_{0.6}\text{F}_{2.2}$ ($\text{TR}^{3+} = \text{Er}^{3+}, \text{Tm}^{3+}$) Crystals in UV and VUV Regions

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Abstract – Spectroscopic investigation of broad band fluoride crystals was carried out in ultraviolet and vacuum ultraviolet region. Transmission, absorption, reflection and TSL spectra of fluorides crystals was obtained and discussed.

1. Introduction Details

Short wavelength radiation of UV and VUV region is necessary to resolve many problems in science and technics. It associated with that energies of many chemical bondings including energies of fotoionization and photodissociation, energies of electronic excitation of atoms and molecules are related to this regions. In order to work with short wavelength radiation are necessary transparent mediums (optic elements) and doped mediums for creation of phosphors, scintillators and active laser mediums in UV and VUV regions. Luminescent materials for VUV excitation are necessary for plasmatic panels and mercury free lamps. For these applications the intraconfigurational $4f^n$ transitions in ions of lanthanides are necessary. The others applications of VUV spectroscopy of lanthanide ions are scintillators and VUV lasers. The $4f^{n-1}5d-4f^n$ transitions in lanthanide ions can be applied here.

2. Experimental

The experiment was carried out with vacuum monochromator VMR-2 with inverse linear dispersion 1.66 nm/mm, and as source of irradiation the home-made hydrogen lamp with MgF_2 window was used. The investigated samples are plates with diameter about 10 mm and thickness from about 0.5 mm to 10 mm. In reflection spectra investigations the wedge-shaped sample is used. Investigated crystals are $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$, $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}$; $\text{Na}_{0.4}(\text{Y}, \text{R})_{0.6}\text{F}_{2.2}$, R – Er^{3+} , Tm^{3+} ; $\text{Na}_{0.4}\text{Er}_{0.6}\text{F}_{2.2}$.

3. Results and Discussion

Transmission spectra of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ single crystals for various thicknesses are shown in Fig. 1. The broad bands of absorption from approx 180 nm to 275 nm for some samples can be explained by various purities of initial reagents. Crystals that are obtained from re-

agents of high chemical purity exhibit high level of transmission (see curve 1). As it seen from Fig. 1 short wavelength transition edge of the $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ single crystal (curve 1) is about 128 nm at the level of transmittance of 1 percent. In transmission spectrum of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ was found absorption band at 140 nm. Its origination associated with uncontrolled impurities.

The transmission edge of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ single crystals that are obtained from reagents of chemical purity, is significantly shifted to long wavelength region (see e.g. curve 4) and is equal to 160 nm. Absorption in this region is usually attributed to oxygen-containing impurities. Moreover, in spectrum is a number of broad bands with maxima about 250, 210 and 202 nm. These bands associated with presence of Ce^{3+} ions.

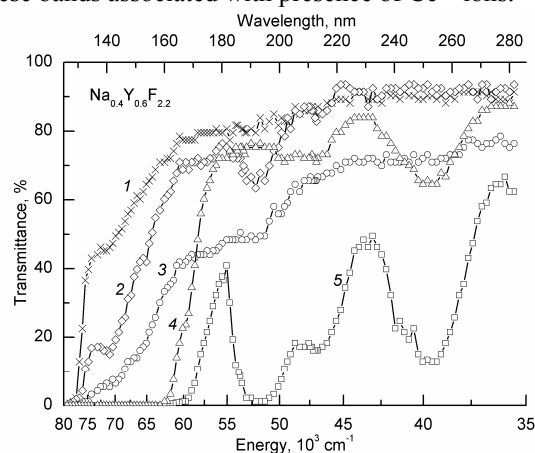


Fig. 1. Transmission spectra of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$. Thicknesses of the samples 1 – 0.8 mm, 2 – 2.86 mm, 3 – 9.63 mm, 4 – 0.6 mm, 5 – 3.4 mm

In spite of observed impurity absorption, crystals $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ compare well with such traditional material for VUV region like CaF_2 and LaF_3 in transparency, but greatly exceed them in isomorphic capacity relative to rare earth ions TR^{3+} . Thus, $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ crystals are perspective for applications in optics in UV and VUV regions, because of high transparency in these regions, radiation hardness, high solidity and nonhygroscopicity.

Absorption spectra of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ doped with trivalent ions of erbium (concentration of Er^{3+} is about

0.02% (curve 1), 0.05% (2)) and absorption spectra of $\text{Na}_{0.4}\text{Er}_{0.6}\text{F}_{2.2}$ (curve 3) are shown in Fig. 2. One can find out three bands in $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}:\text{Er}^{3+}$ spectra. These bands characterized by following positions of maximums λ_{max} : 1 – $\lambda_{\text{max}}=164$ nm; 2 – $\lambda_{\text{max}}=154$ nm; 3 – $\lambda_{\text{max}}=144,4$ nm. It is impossible to say about other absorption bands near to absorption edge of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ host crystal because of abrupt increase of absorption. The large values of half-widths, large values of absorption factors in these bands permit to identify these bands as transitions from $^4I_{15/2}$ ground state of Er^{3+} ion to spread (due to electron-phonon interaction and partially disordered host crystal structure) $4f^{10}5d$ levels of Er^{3+} . It can be noted that in comparison with theoretical evaluation of $5d$ edge configuration of free Er^{3+} ion [1], the location of the first maximum of Er^{3+} d-configuration in $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ crystal is decreased at about 14500 cm^{-1} .

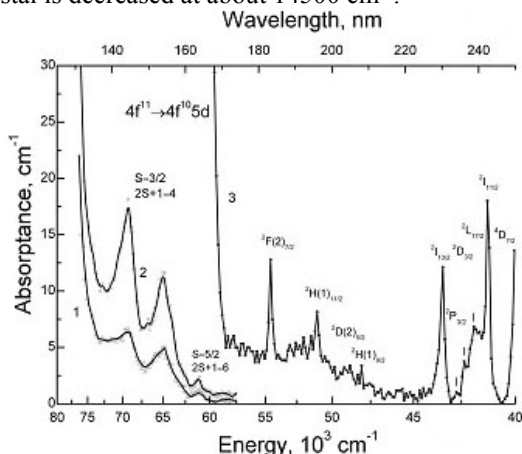


Fig. 2. Absorption spectrum of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}:\text{Er}^{3+}$ and $\text{Na}_{0.4}\text{Er}_{0.6}\text{F}_{2.2}$

There is a weak long-wave band at 164 nm in absorption spectrum of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ doped with trivalent ions of erbium. The nature of weak bands origination in absorption and excitation spectra associated with different spin configuration in excited $4f^{n-1}5d$ level of rare earth elements [2,3]. Let us consider spin configurations of ground state and possible states of excited state in Er^{3+} (number of electrons in $4f$ shell is 11). The maximal number of unpaired electrons in ground state of $4f^{11}$ configuration of Er^{3+} is 3. The spin quantum number S is equal to $3/2$ and spin multiplicity is $2S+1=4$. There are two ways of electron spin orientation in excited $4f^{10}5d$ level of Er^{3+} . The first way is parallel orientation of spin electron to 4 residual electrons in $4f$ shell that leads to high spin state with $S = 5/2$ and $2S+1=6$. And the second one is antiparallel spin orientation of electron to residual electrons. There is low spin state in this case with $S = 3/2$ and $2S+1=4$. In accordance with Hund's rule, high spin state must be less energetic and must be located in long wave region. Thus, transitions from ground state

to the lowest $4f^{10}5d$ level are spin forbidden and therefore are relatively weak. It should be noted that $4f^n - 4f^{n-1}5d$ spin forbidden transitions can be expected for all rare earth ions with $n > 7$.

There is a number of sharp and narrow peaks with half-width $0.7\text{ nm} - 1\text{ nm}$ in absorption spectra of $\text{Na}_{0.4}\text{Er}_{0.6}\text{F}_{2.2}$ crystal. These peaks are attributed to intraconfigurational transitions in $4f$ shell in Er^{3+} ions. The narrowness of the peaks is caused by parity forbidden of transitions and screening of $4f$ shell. Relational big intensity of absorption bands is caused by large (total-lot) concentration of activator. Absorption is slowly arises while moving to short wavelength region and has magnitude 5 cm^{-1} at the wavelength 171 nm. And then it rapidly arises to value that is equal to 30 cm^{-1} . It was impossible to investigate absorptance at shorter wavelength because of the rapid increase of absorptance. Thus, absorption for wavelengths that are shorter than 171 nm is attributed to interconfigurational $4f-5d$ transitions in Er^{3+} ion.

Absorption spectra of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ doped with trivalent ions of thulium (concentration of Tm^{3+} is about 0.05% (dot line)) and $\text{Na}_{0.4}\text{Tm}_{0.6}\text{F}_{2.2}$ (circles + solid) are shown in Fig. 3. There are two absorption bands recognized in spectra of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}:\text{Tm}^{3+}$. These bands is attributed to $4f^{12}-f^{11}5d$ transitions in Tm^{3+} ions and characterized by following positions of maximums λ_{max} : 1 – 155 nm, 2 – 142 nm. The lowest level of $5d$ configuration of Tm^{3+} ion is decreased at the value about 10^4 cm^{-1} in comparison with free ion [4].

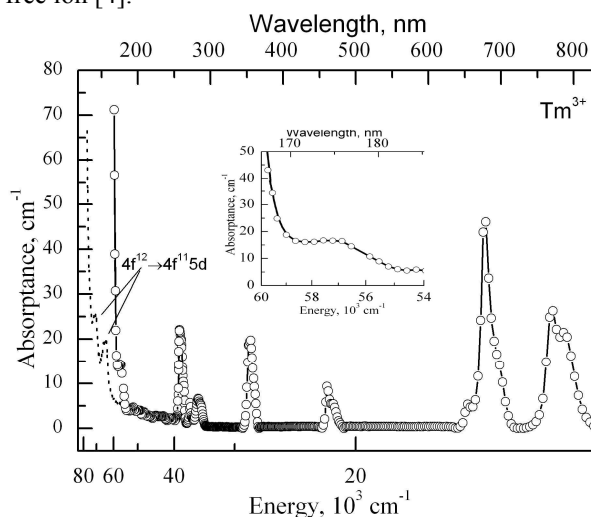


Fig. 3. Absorption spectra of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}:\text{Tm}^{3+}$ (dot) and $\text{Na}_{0.4}\text{Tm}_{0.6}\text{F}_{2.2}$ (circle + solid). Inset: band at about 175 nm in absorption spectra of $\text{Na}_{0.4}\text{Tm}_{0.6}\text{F}_{2.2}$ crystal.

From absorption spectra of $\text{Na}_{0.4}\text{Tm}_{0.6}\text{F}_{2.2}$ in the region from about 830 to 200 nm one can see intraconfigurational transitions $4f$ shell in Tm^{3+} ions. The presence of weak band at about 175 nm (see inset for

$\text{Na}_{0.4}\text{Tm}_{0.6}\text{F}_{2.2}$ absorption spectra from about 166 to 185 nm) in these spectra is under discussion now.

Reflection spectra of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ crystal for different angles of sample reflection surface orientation are shown in Fig. 4. From these spectra it is seen the slowly increasing of reflectance towards to short wavelengths and then more rapid increasing of the reflectance since about 160 nm.

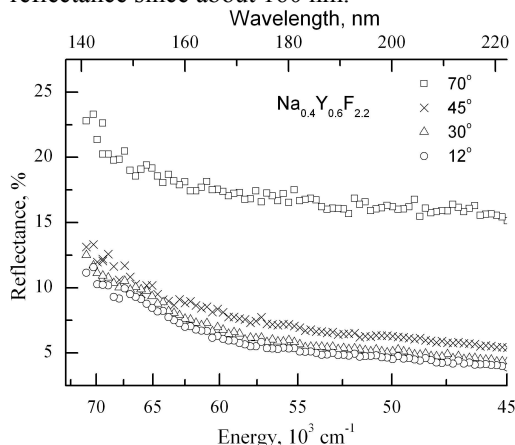


Fig. 4. Reflection spectra of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$

In Fig. 5 luminescence spectrum of $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ crystal at liquid nitrogen temperature is shown. Spectrum consists of one broad band (maximum at 340 nm (3.64 eV) and half-width about 110 nm (1.35 eV)) and long-wave tail.

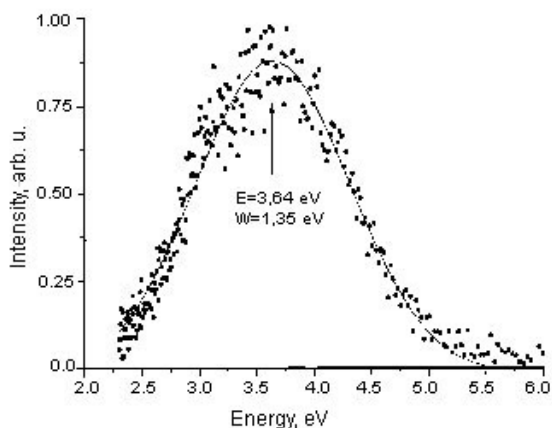


Fig. 5. Luminescence spectrum of the $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$ host crystal. Excitation by X-ray radiation at 1 KeV (Temperature $T=77\text{K}$).

E – position of the maximum of the band
W – half-width of the band

This luminescence is situated at near UV region and is typical for a number of broad band crystals (LiF , CaF_2 , LaF_3 etc.) (see, e.g. [5]). The nature of low-temperature peaks is in need of additional investigation. In [6, 7] TSL of polycrystalline powders in the high temperature region was investigated. It was

found there were two intensive peaks with the maxima at 393 and 508 K. Authors associate the nature of observed traps with the recombination of electrons trapped at various levels and anionic vacancies.

Thermostimulation luminescent (TSL) spectra upon X-ray excitation in the temperature range from about 100 to 400 K were investigated in order to find out lattice defective state of $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}$ crystal. In Fig. 6 TSL spectrum of $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}$ host crystal is shown. There are two bands in this spectrum at 174 and 332 K. Dominant light value come from low-temperature peak.

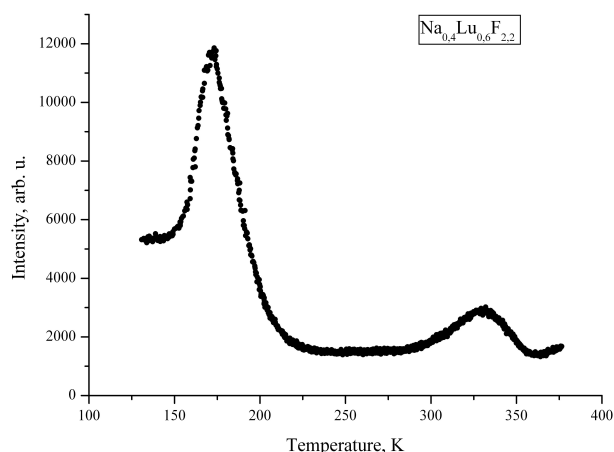


Fig. 6. Deexcitation curve of $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}$ host crystal

Estimation of the depth of occurrence of revealed electron traps was carried out by means of Urbach formula, (1) [8].

$$E(\text{eV}) = \frac{T_m}{500}, \quad (1)$$

where T_m – is maximum temperature in luminescence curve in K.

In the case of $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}$ the depths of occurrence of electron traps are 0.35 and 0.66 eV.

The nature of observed low-temperature peaks is probably associated with creation of exciton type states with long life time and it can be interpreted as a result of electron-hole recombination.

4. Conclusion

The absorbance, reflectance and transmittance investigations of broad band fluoride crystals doped with rare earth elements were carried out in UV and VUV region. TSL spectra of $\text{Na}_{0.4}\text{Lu}_{0.6}\text{F}_{2.2}$ were carried out. It was shown that crystals of that type are transparent in VUV region. Carried out investigations permit to conclude that these crystals can be used as optics elements that are transparent in UV and VUV regions, and to dope host crystals with rare earth ions in order to using its as a phosphors.

References

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