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Abstract. Absorption, emission and excitation spectra of LiF single crystals doped with LiOH have been measured in the UV and VUV regions of the spectrum. An absorption band at 137 nm has been identified as the UV absorption of OH⁻ ions, while bands at 172, 200 and 280 nm are assigned to defects caused by other impurities accidentally contained in the crystals. Only one emission band at 409 nm, assigned to O²⁻ centres, has been observed at all temperatures under excitation in the various absorptions belonging to different defects. As a consequence, an energy transfer mechanism between different centres is suggested. A weak luminescence at 255 nm, excited only in the fundamental absorption, is proposed as an intrinsic emission of LiF.

1. Introduction

The OH⁻ molecular ion, substitutionally introduced at the halide ion position in alkali halide crystals, has optical excitations in the ultraviolet, near-infrared and far-infrared spectral ranges resulting from electronic and vibrational and librational transitions [1–5].

Most of the available information on the electronic spectra has been collected through investigation of OH⁻-doped KCl, KBr and KI crystals, even though the importance of alkali fluorides in different fields (such as quantum electronics or radiation dosimetry) has been widely recognized and has made research on the optical properties of these materials a timely issue.

The main reasons for such a lack of information in LiF and NaF crystals is the spectral position of the electronic absorption bands, which lie on the tail of the absorption edge of the host material [6, 7] and therefore are studied with some difficulty [8, 9]. In particular, to the best of our knowledge, there are no reliable data concerning the optical behaviour of OH⁻ ions in crystals of LiF. In this case the problem of impurities is relevant not only to fundamental studies but also to technological applications (such as optical components for experiments in the ultraviolet range or dosemeters for ionizing radiations). Indeed, no conclusive results concerning OH⁻ impurities were reported in old investigations aiming to identify, through absorption spectra, the defects responsible for thermoluminescence [10, 11]. An unambiguous interpretation of the data was hindered by the lack of a definite correlation between the infrared absorption, which has been proved to be due to OH⁻ stretching modes, and the ultraviolet absorption possibly attributed to OH⁻ centres. This was presumably a consequence of the quality of the crystals studied, which were never intentionally doped, and therefore contained hydroxyl ions just because of hydrolysis of

the LiF powder before or during the crystal growth [10]. On the other hand, it is well known that various kinds of impurity are normally found in nominally pure LiF crystals, depending on the quality of the starting powder and on the procedure of purification and growth. Magnesium and oxygen-related centres are the most common foreign species, and often originate complex defects via association and aggregation processes: among them OH^- embedded in different Mg complexes gives rise to a rich vibrational spectrum in the infrared [10, 12, 13].

In this work, single crystals of LiF are intentionally doped with alkali hydroxides, in order to identify the OH^- absorption and to determine its temperature dependence. Moreover, photoluminescence from $LiF:OH^-$ crystals is carefully investigated for the first time under systematic optical excitation in each of the absorption bands and in the region close to the fundamental absorption of the host crystal. The results are compared with those obtained for samples containing other impurities and OH^- ions introduced by means of oxygen diffusion processes.

2. Experimental procedure

Single crystals of LiF were home grown from the melt by the Kyropoulos method. The starting powder, purchased from Fluka Chemie AG (Switzerland), had purity higher than 99% and was dehydrated under vacuum at 150 °C for several hours. OH^--doped crystals were obtained by adding to the melt 1 mol% of LiOH or KOH. Every growth process was carried out in an open chamber under a continuous flow of nitrogen gas in order to reduce as much as possible contact with moisture or oxygen. Quantitative analysis by atomic absorption spectroscopy shows that the concentration of Mg impurities is 0.2 ppm in the starting powder, 0.3 ppm in the undoped crystals, and 0.1–0.15 ppm in the crystals doped with hydroxyl ions. In the last case the presence of Mg–OH complexes is monitored by the presence of narrow absorption lines in the infrared [12, 13] (see below). Therefore, the Mg content is practically constant in all samples and should not originate appreciable variations in the optical spectra of different crystals.

In some cases samples were cleaved from crystals grown in inert (Ar) atmosphere by means of a vertical zone technique at the Laboratory for Crystal Physics in Budapest (Hungary) and intentionally Ti doped by adding to the melt 10^{-4} mole fraction of Li_2TiF_6. In these samples the doping with hydroxyl ions (particularly OD^-) was obtained by heating the samples at a temperature (about 800 °C), close to the melting point of LiF, in dry nitrogen flowing through D_2O. Samples used in the optical measurements showed typical dimensions of $5 \times 5 \times 0.5$ mm^3.

Optical spectra in the visible and ultraviolet regions were measured using the synchrotron radiation available at the optical spectroscopy beamline of the PULS Laboratory in Frascati, Italy. The temperature of the samples could be changed in the range 20–300 K by means of a closed-cycle He cryostat. The synchrotron light, dispersed and selected in the range 4–12.5 eV by a modified 1 m normal-incidence Hilger–Watts monochromator, was focused on the sample by suitable mirrors.

Absorption spectra were derived from transmittance measurements, after appropriate correction for the wavelength-dependent intensity of the incident beam. The intensity of the transmitted light was measured by taking advantage of the fluorescence of sodium salicilate, which is practically independent of the wavelength of the impinging radiation in all ultraviolet and vacuum–ultraviolet regions [14]. Every spectrum was corrected by subtracting a suitable background in order to compensate for the light scattering.

The luminescence signal, collected at a right angle with respect to the exciting beam, was analysed by an H10 UV-VIS Jobin–Yvon monochromator, revealed by an EMI 9893QB photomultiplier, and properly corrected for the response of the detection system.

The infrared absorption spectra were measured at room temperature by means of a Bomem DA8 FTIR spectrophotometer, equipped with a microscope, and operating in the range 4000–500 cm^{-1} with a resolution as good as 4×10^{-2} cm^{-1}.

3. Results and discussion

3.1. Absorption

Figure 1 shows the low-temperature absorption spectra of two different LiF crystals, the first undoped and the second doped with LiOH. Both spectra exhibit bands at 137 nm (halfwidth at low temperature HW = 0.81 eV), 172 nm (HW = 0.78 eV), 200 nm (HW = 0.70 eV) and 280 nm (HW = 0.58 eV), and all absorptions grow passing from the undoped sample to that doped with LiOH. However, in the last system the 137 nm band shows a dramatic increase and becomes the dominant absorption.

Similar spectra, consisting of several bands in the region 170–220 nm, were observed in previous works for crystals of LiF containing Mg or Ti and oxygen-related impurities [10, 11, 15–18]. The absorption coefficient at the maximum of the 200 nm band in LiF was found to be proportional to the Ti concentration [19], but the role played by OH⁻ and/or O^{2-} is not yet clear [16, 17]. The attribution of the 137 nm band to OH⁻ ions [20] has not so far been confirmed by measurements in the infrared region [10]. The present results, in particular the pronounced increase of the 137 nm absorption in the LiF crystal doped with LiOH, and the negligible variations for the other bands in spite of the doping, allow for a conclusive identification of the 137 nm band with the absorption caused by electronic excitation of OH⁻ ions. A much weaker absorption at 137 nm (not reported in figure 1) was obtained in a LiF crystal doped with KOH. However, the difference between the melting points of LiOH (450 °C) and of KOH (360 °C) must be taken into account: at the growth temperature of LiF crystals (840 °C), KOH turns out to be much more volatile than LiOH, and its large degree of evaporation explains quite well why appreciable dopant levels cannot be achieved, causing a weak 137 nm band in the absorption spectrum. Further support for the attribution of such a band to OH⁻ ions is the good agreement (figure 2) of its peak position with that predicted by the Mollwo–Ivey law [21]. Moreover, its temperature dependence is very similar to that observed for the OH⁻ absorption in other alkali halides: when the crystal is warmed up to room temperature, the peak position is slightly shifted towards longer wavelengths, the halfwidth increases to 0.93 eV and the intensity decreases by about 20%. In contrast, the other bands at 172 and 200 nm do not show appreciable changes with temperature, whereas the 280 nm band seems to be thermally enhanced.

The same conclusions are reached from studies on the absorption spectra of LiF crystals exposed to the above quoted hydrothermal treatment in order to allow for an appreciable diffusion of hydroxyl ions (in the present case OD⁻) at least in the surface layer of the samples [22]. Figure 3 shows the comparison of the absorption spectra of a LiF crystal, containing Ti impurities, before and after the OD⁻ doping: the pronounced increase of the 137 nm band, at odds with the lack of changes in the 200 nm absorption, confirms the above interpretation. The presence of hydroxyl ions in the sample after the hydrothermal treatment is supported by the vibrational spectrum in the infrared (see the inset in figure 3). The broad absorption at about 2745 cm^{-1} is due to the OD⁻ stretching absorption, while the other
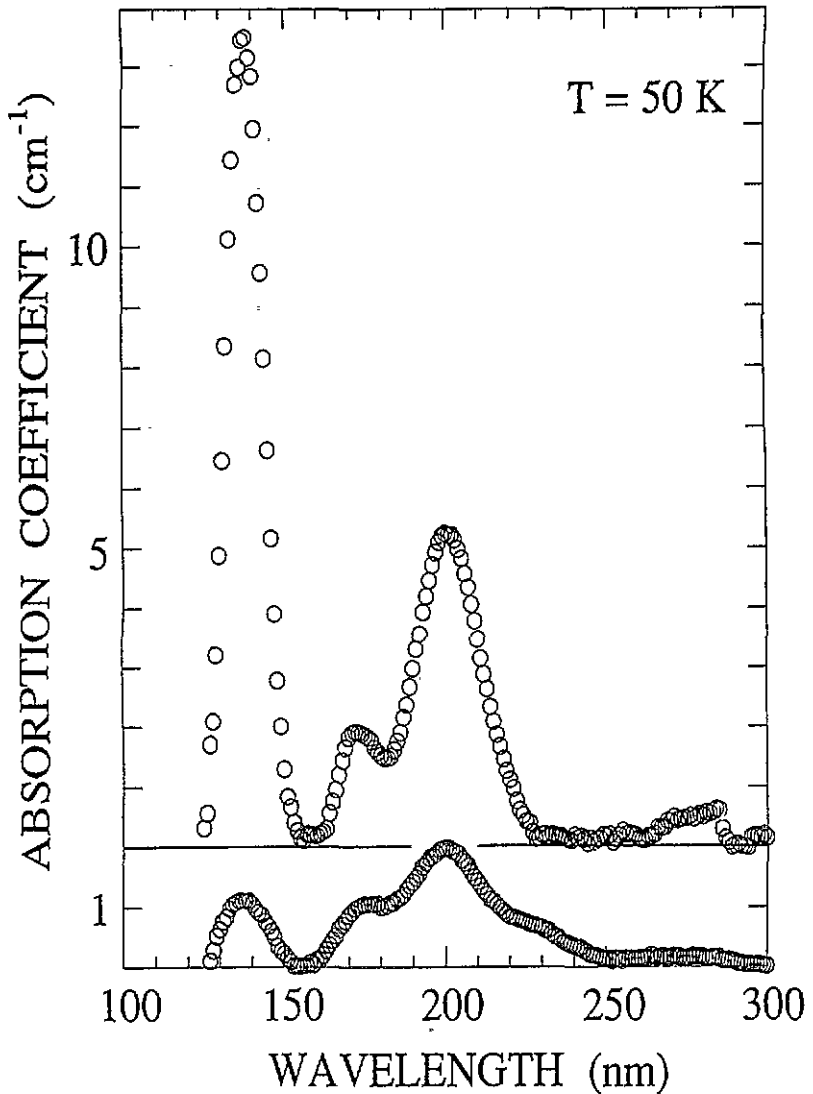
Figure 1. VUV absorption spectra at 50 K of an undoped LiF crystal (below) and of a LiF crystal doped with 1 mol% of LiOH in the melt (above).

narrow lines are due to the OD⁻ stretching modes perturbed by impurity-induced defects: particularly, the line at 2575 cm⁻¹ is related to Ti [22] and the other lines to residual Mg impurities [13]. Such a complex IR spectrum was absent before the thermal treatment. It is worthwhile noticing that the OD⁻ doping causes the increase of the same VUV band at 137 nm as the OH⁻ does, since OH⁻ and OD⁻ have the same electronic configuration, while it *shifts the vibrational spectrum towards lower wavenumbers, since the OD⁻ reduced mass is larger than that of OH⁻.*

The problem of the attribution of the other weak bands at 172 and 280 nm is still unsolved. Whether or not such absorptions are related to the same point defects as are responsible for the 200 nm band can be clarified by luminescence experiments, which also
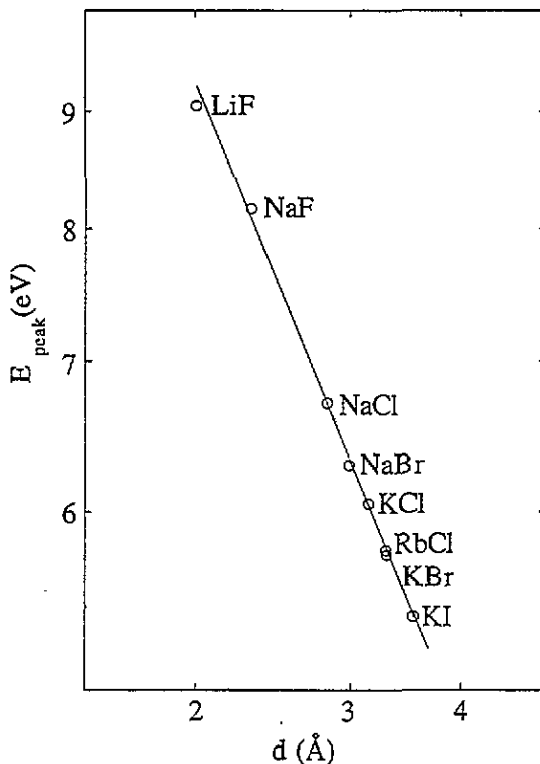
Figure 2. A Mollwo–Ivey plot for the absorption bands of OH⁻ ions in alkali halides.

point to an identification of possible photostimulated emission of OH⁻ centres.

3.2. Emission

Luminescence of LiF:OH⁻ crystals has been excited by optical pumping in each one of the absorption bands and also in the spectral region close to the absorption edge of LiF (lying at about 105 nm). Figure 4 shows the emission spectrum at low temperature under excitation at 135 nm, namely in the OH⁻ absorption: only one band, with a peak position at 409 nm and a halfwidth of 0.73 eV, is observed. Exactly the same result is found in the cases of spectra excited at 175, 200 and 275 nm, which differ only as regards the values of the signal intensity. Under excitation at around 110 nm, the 409 nm emission is accompanied by a weak band peaking at about 255 nm (halfwidth of 1.56 eV and intensity about 5% with respect to that of the other band). The emission spectrum measured for an undoped LiF crystal under the same excitation at 105 nm (figure 5) shows again the two bands at 255 and 409 nm, but in this case the intensity of the latter decreases by one order of magnitude. To the best of our knowledge, luminescence at 255 nm has never been reported in LiF, whereas an emission band with the peak position at about 420 nm and a halfwidth of 0.8 eV was detected at low temperature in LiF crystals doped with Li$_2$O under excitation at 113 and 200 nm. Moreover, the emission in the region 400–420 nm is the most relevant contribution to the thermoluminescence spectrum of LiF(Mg, Ti, OH) [23, 24] and is also present in the photoluminescence spectrum of LiF:Ti (grown in air) under excitation in the 200 nm band [25, 26]. The defect responsible for this emission was identified as the
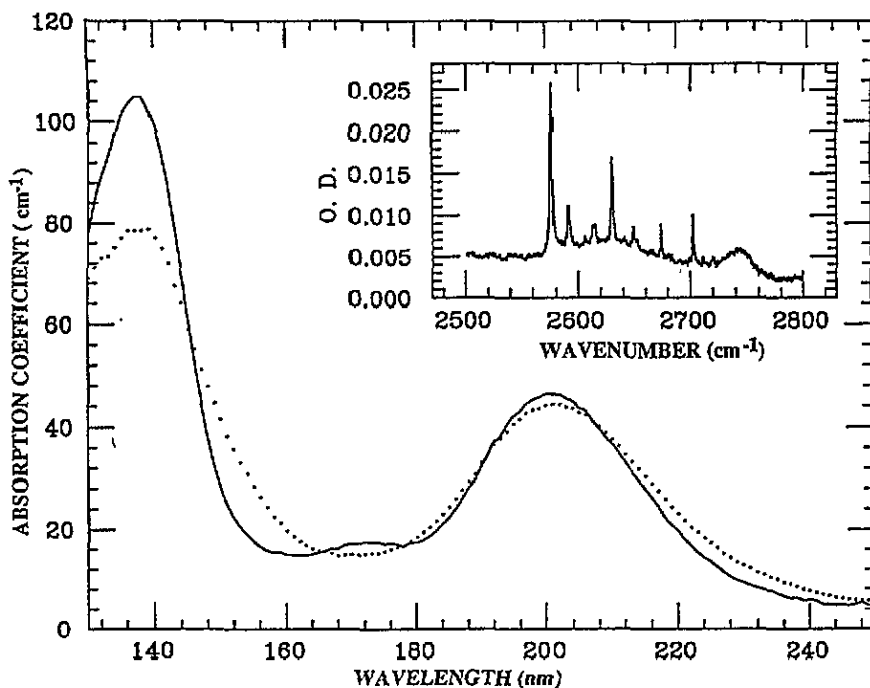
Figure 3. VUV absorption spectra at room temperature of a LiF crystal doped with 10^{-4} mole fraction of Li_2TiF_6: as-grown crystal (dotted curve); sample treated at about 800 °C with dry N_2 flowing in D_2O (continuous curve). Inset: the IR absorption spectrum at room temperature of a thin slice of the above sample after the hydrothermal treatment.

recombination centre active in the thermoluminescence process of LiF(Mg, Ti, OH) [23, 24]. Therefore some authors [16, 18] suggest that this defect is formed by O^{2-} ions with charge-compensating anion vacancies. It is very likely that in the present case the 409 nm emission band is related to O^{2-} ions, contained as impurities in the LiF powder used for the crystal production or formed during the growth because of hydrolysis processes, which are locally associated with anion vacancies or divalent impurities for charge compensation. Such a broad luminescence does not turn out to be formed by overlapping emission bands, because its excitation spectrum does not show any variation if measured in correspondence with the peak or on both sides of the band. A typical example of such a spectrum is displayed in figure 6. The most striking feature of the 409 nm emission is its excitation in all bands found in the absorption spectrum, namely at 137, 172, 200 and 280 nm: this demonstrates that the same kinds of oxygen-related defect are presumably responsible for all three long-wavelength bands, but is in apparent contradiction with the assignment of the 137 nm absorption to OH^- centres, which are expected to originate a different emission. A rough evaluation of the predicted spectral position of the OH^- luminescence in LiF can be attempted on the basis of the few data available in the literature for other alkali halides, namely KI, KBr, KCl, RbCl [9]. According to the general trend of the OH^- luminescence, obtained from such data, the emission band in LiF should occur in the spectral region 170–190 nm, exactly where the absorption bands due to the oxygen-related centres lie. Therefore, taking into account that the OH^- luminescence is generally weak, it is reasonable to assume that all of the emitted light is absorbed by the oxygen-related centres, which are optically
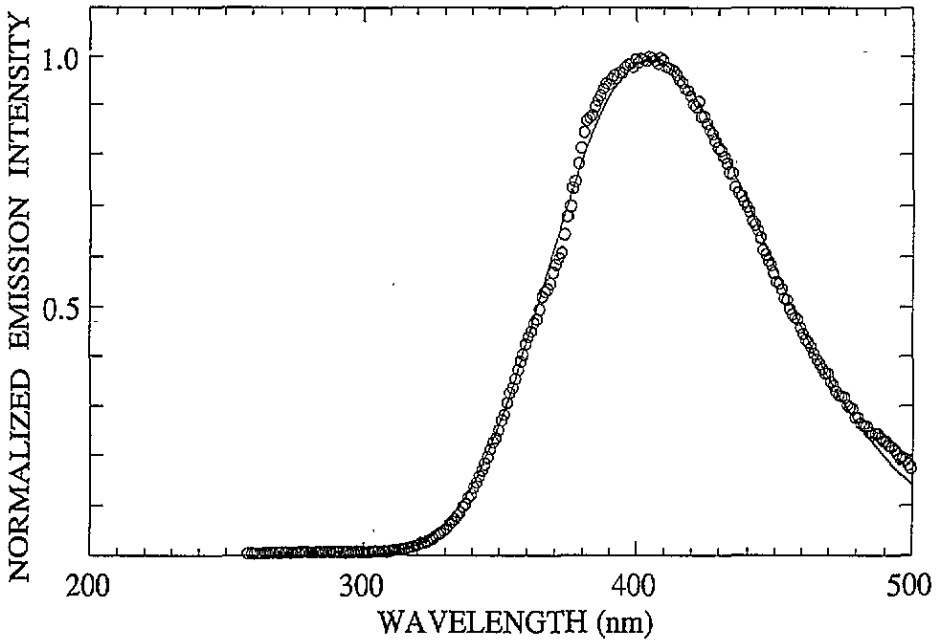
Figure 4. The emission spectrum at 15 K of LiF:OH⁻ excited at 135 nm (the continuous curve is the best fit of data with a Gaussian curve).
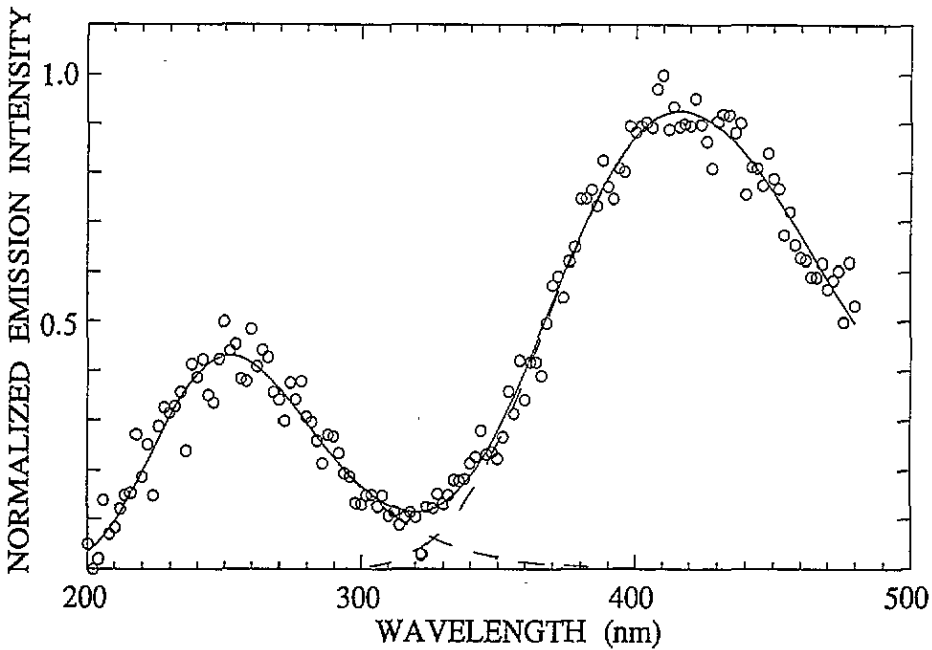

Figure 5. The emission spectrum at 50 K of an undoped crystal of LiF under excitation at 105 nm, fitted with two Gaussian curves.
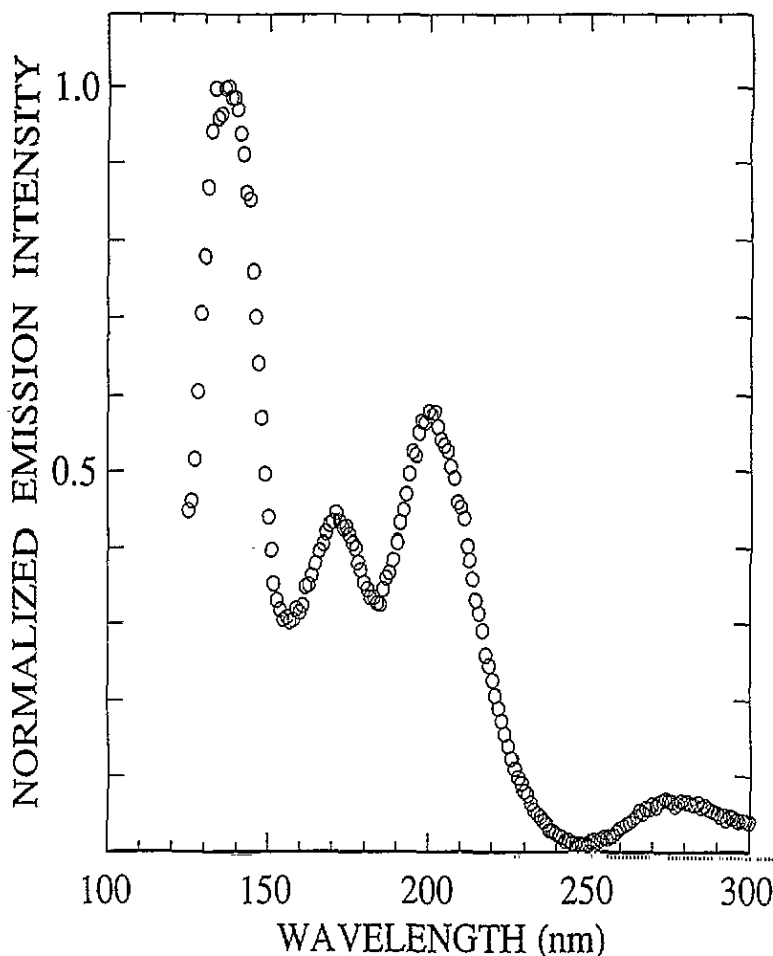
Figure 6. The excitation spectrum at 15 K of the 409 nm luminescence in LiF:OH⁻.

excited and consequently emit their own luminescence. This satisfactorily explains why the 137 nm peak is found in the excitation spectrum of the 409 nm emission. It is also important to note that the direct measurement of the OH⁻ photoluminescence would be particularly delicate even without problems due to self-absorption phenomena, because of the well known absorptions of oxygen and water in the 170–190 nm range, which prevent detection of weak signals in such a region without an evacuable emission set-up.

The luminescence at 255 nm exhibits features, such as excitation only in the proximity of the LiF absorption edge and a higher relative intensity in the undoped crystals, which are not typical of an impurity and therefore might suggest its identification with an intrinsic emission in LiF.

The temperature dependence of the emission spectrum excited at 113 nm, reported in figure 7, is quite interesting. The intensity of the band at 255 nm decreases with increasing temperature and cannot be measured above 200 K. The 409 nm emission, which normally broadens with increasing temperature (HW = 0.82 eV at room temperature), is on the contrary thermally enhanced and exhibits a small but appreciable shift towards shorter wavelengths (400 nm at 300 K). Such anomalous behaviour of the latter luminescence is also observed
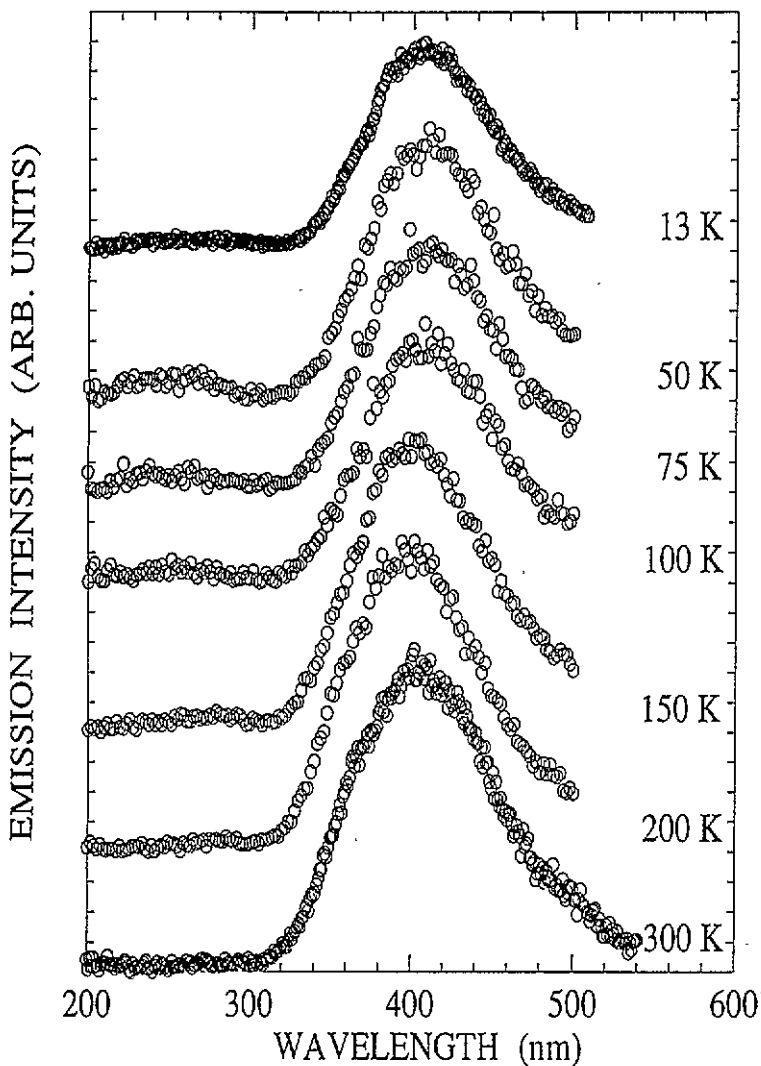
Figure 7. The emission spectra at various temperatures of LiF:OH⁻ under excitation at 113 nm.

under excitation in the absorption bands of the complex centres, for example at 175 nm. The lack of any thermal deactivation of the 409 nm emission can be explained recalling that all absorption bands at 172, 200 and 280 nm are practically independent of temperature (which indicates that the associated centres are insensitive to lattice vibrations, and that non-radiative de-excitations are not competitive with luminescent decays). The reasons for the unusual shift towards higher energies when the crystal is warmed up are unknown at present.

4. Conclusions

Spectroscopic studies on oxygen-related impurities in LiF crystals, performed for the first

time at various temperatures on samples intentionally doped with OH$^-$ ions, allowed for some new and interesting results. The data reported in the literature on the absorption of O^{2-} ions, possibly associated with metal impurities such as Mg or Ti, were confirmed and new bands at 172 and 280 nm were measured. The luminescence of such defects was carefully investigated as a function of the excitation wavelength and of temperature: surprising effects, like a thermal activation of the emission efficiency and a shift of the peak towards shorter wavelengths at high temperature, were detected and are under consideration. The absorption of OH$^-$ defects was identified as the 137 nm peak, in agreement with the prediction of the Mollwo–Ivey plot. Its temperature dependence was determined and found to be similar to that observed in other alkali halides. The luminescence of OH$^-$ centres could not be directly observed, because it should lie between 170 and 190 nm and, therefore, besides typical experimental difficulties of measurements in such a spectral range, reabsorption phenomena due to oxygen defects occur. A new luminescence at 255 nm, excited only in the region of the absorption edge, was studied as a function of temperature and is tentatively identified as the intrinsic emission of LiF crystals.

Acknowledgments

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