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Optical properties of Ag^+ impurities in $KMgF_3$ crystals

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Abstract. The optical properties of Ag^+ impurities in single crystals of the perovskite-like $KMgF_3$ are studied. The optical absorption spectra consist of two bands at 192 and 213 nm, which are attributed to parity-forbidden $4d^{10} \rightarrow 4d^95s$ transitions by analogy with the alkali halides. Under optical excitation in each of the absorptions, only one photoluminescence band is observed at 243 nm, which is thermally enhanced. The temperature dependence of its decay time is similar to that found for alkali halides, and therefore its behaviour is analogously attributed to two emitting levels, the lowest one being metastable. Measurements of the thermally stimulated luminescence, and of its spectral distribution show that for $KMgF_3$:Ag^+ two kinds of emission mechanism coexist, one due to the deexcitation of Ag^+ ions, and the second caused by intrinsic deexcitation of the host lattice. The features of the optical behaviour of Ag^+ in $KMgF_3$ crystals are compared with those known of for Ag^+ in other systems.

1. Introduction

Spectroscopic studies on the optical properties of metal ions showing an $(nd)^{10}$ electronic configuration in their ground state (such as Ag^+, Cu^+, and Au^+) have been carried out on crystals of several alkali halides [1]. In the particular case of Ag^+ ions, substitutionally introduced into the lattices of alkali halides, their absorption in the ultraviolet region of the electromagnetic spectrum has been measured in detail as a function of the dopant level and of the temperature [2–5]. The results clearly showed that in all of the systems the majority of the absorption bands, which are relatively weak and thermally enhanced, must be assigned to $4d^{10} \rightarrow 4d^95s$ transitions, which are parity forbidden, and allowed by lattice vibrations. Such a conclusion is in agreement with theoretical predictions [6], and a model taking into account the spin–orbit interaction in the free ion and the cubic symmetry of the crystal field [7]. The alternative possibility of $4d^{10} \rightarrow 4d^95p$ allowed transitions [8] was ruled out because of the too large energy difference (about 10 eV) between the excited and ground states, which turns out to be incompatible with the data. Up to eight different energy levels are predicted by the above model, and this explains the relative abundance of peaks in the absorption spectra. In contrast, the emission spectra of Ag^+-doped alkali halides exhibit only two bands: one of them, peaking in the ultraviolet, is the only luminescence

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due to isolated Ag^+ impurity ions, and the other, lying at higher wavelengths, is attributed to dimers [3].

Such a considerable level of knowledge of the optical features of Ag^+ ions is not available for many ternary compounds, where the impurity can be accommodated in different non-equivalent positions in the host lattice. The recent discoveries of good performances in solid-state lasers [9, 10] and in radiation dosimetry [11, 12] of crystals of $KMgF_3$, a compound belonging to the group of fluoroperovskites, doped with suitable metal impurities, made it worthwhile to investigate the optical behaviour of $KMgF_3$:Ag^+ crystals. The aim of this work is to fully characterize such a system, and to compare its properties with those known of for other materials, by taking into account the peculiar cubic symmetry of the fluoroperovskite lattice.

2. Experimental procedure

Single crystals of $KMgF_3$ were home grown by the Kyropoulos method from the melt. The initial charge was formed of a stoichiometric mixture of pure (99.9%) powders of KF and MgF_2 purchased from Merck, Germany, and carefully dried at 250 °C under a vacuum supplied by a rotary pump for 24 hours. The growth processes were carried out by using platinum crucibles in a closed chamber filled with argon. Typical dimensions of the crystalline boules were 3–3.5 cm diameter and 3–4 cm length. Doping was achieved by adding to the initial charge a very large amount (about 10 mol%) of AgI. The choice of such a silver salt and of its high initial concentration in the melt was made in order to compensate for the losses due to the dopant evaporation during the growth: among the silver halides, AgI shows the highest melting point (558 °C), and therefore it has the best probability of being incorporated in the host crystals of $KMgF_3$ at their growth temperature (1040 °C). In spite of these extreme doping conditions, the crystalline boules contained no more than 0.1 mol% of the impurity, as roughly estimated by atomic absorption spectrometry, which indicates that both evaporation and possible segregation phenomena strongly reduce the dopant level in the solid phase. The samples used in the measurements were thin slabs, cleaved or sawed from the boules, with typical dimensions of $5 \times 5 \times 1$ mm^3.

Optical absorption was measured by means of a Varian 2300 Spectrophotometer, at various temperatures between 77 and 300 K. Photoluminescence was excited by the light of a deuterium lamp filtered by a Minuteman 305-M monochromator, analysed by a Jobin–Yvon H 10 monochromator, and detected by a RCA C31034A photomultiplier. Alternatively, emission measurements were carried out by taking advantage of the synchrotron radiation at the SUPERLUMI beamline of HASYLAB at DESY, Hamburg, Germany. In this case, the exciting light was selected by means of a normal-incidence McPherson monochromator, and the luminescence was collected at a right angle to the exciting synchrotron radiation beam, analysed by a Czerny–Turner monochromator coupled to appropriate filters, and revealed by a position-sensitive detector (IPDM18 ITL/Photek). The decay times of the photoluminescence were measured between 30 and 300 K by using a Perkin–Elmer LS-50 Fluorimeter suitable for operating between 200 and 850 nm in the range 10 μs to 1 s. The thermoluminescence (TL) was measured for samples irradiated at room temperature using a ^{90}Sr–^{90}Y β-source (activity: 1.5×10^9 Bq). The measurements were carried out using a home-made high-sensitivity TL spectrometer [13], able to record TL intensity as a function of both temperature and emission wavelength, operating between room temperature and 500 °C in the spectral range 200–800 nm.

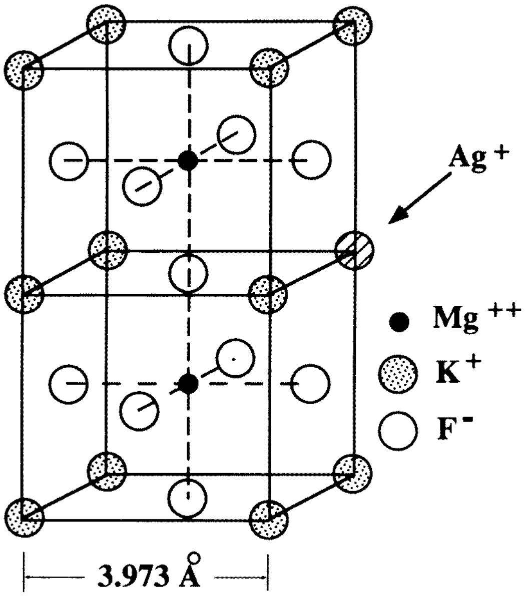

Figure 1. The perovskite-like lattice of KMgF$_3$, with the substitutional site for the Ag$^+$ impurity.

3. Results and discussion

In the cubic lattice of KMgF$_3$, shown in figure 1 [14], a substitutional Ag$^+$ impurity can in principle replace one of the two cations of the host system, namely the K$^+$ and Mg^{2+} ions. However, the substitution in the K$^+$ site is highly favoured from the point of view of two different physical parameters: the electric charges are identical, which implies no need for compensating cation vacancies, and the values of the ionic radii are very similar (1.26 Å and 1.33 Å for free Ag$^+$ and K$^+$ ions, respectively, while the ionic radius of the free Mg^{2+} ion is 0.66 Å [15]), which implies minimization of the lattice distortion caused by the dopant ion. Incidentally, it should be pointed out that, even if the absolute value of the radius of a substitutional ion is somewhat different in a crystal, its relative size with respect to the ions in the host lattice does not change dramatically. As a consequence, it can reasonably be assumed that the Ag$^+$ impurity, replacing a K$^+$ ion, is surrounded by 12 nearest-neighbour F$^-$ ions (figure 1), at variance with the case for alkali halides, in which six anions are included in the first shell around the monovalent foreign ion. The possible influence of such a different symmetry on the spectroscopic behaviour of Ag$^+$ ions in KMgF$_3$ will be studied in detail. The possibility of formation of impurity dimers or clusters seems to be ruled out by the very low Ag$^+$ concentration found in the crystals.

3.1. Optical absorption measurements

Optical absorption spectra of KMgF$_3$:Ag$^+$ crystals in the ultraviolet region, measured as functions of the temperature, are shown in figure 2. Two evident bands, peaking at about 192 and 213 nm at 77 K, are observed together with a weaker band at about 202 nm. With increasing temperature, the peak positions of the two main absorptions shift slightly toward longer wavelengths, and their intensities appreciably increase, whereas the band at

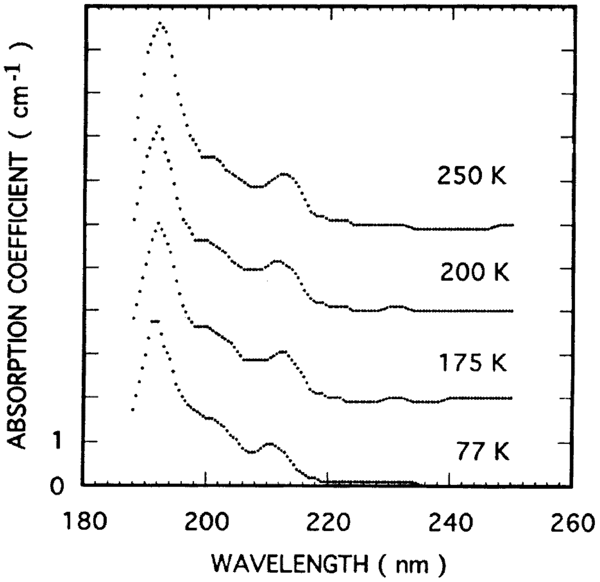

Figure 2. Absorption spectra at various temperatures of a $KMgF_3$:Ag^+ crystal (dopant concentration in the melt: about 10 mol%).

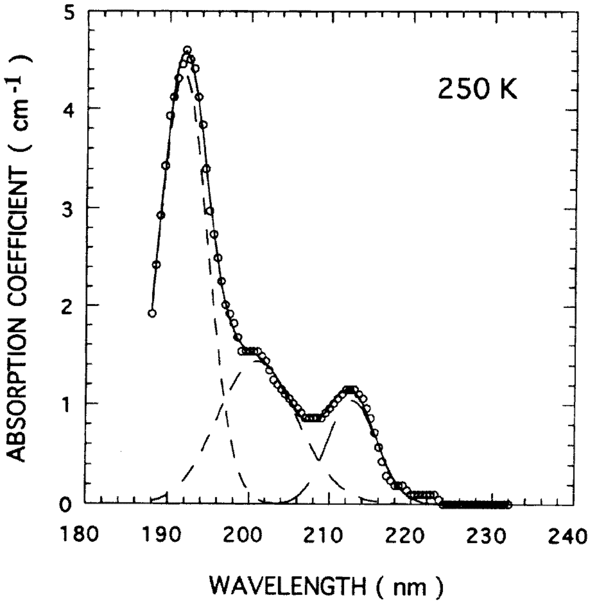

Figure 3. The computer resolution of the absorption spectrum at 250 K of $KMgF_3$:Ag^+. The experimental data (dots) are fitted with a sum (continuous line) of Gaussian curves (dashed lines).

202 nm looks to be practically unchanged. Such an absorption has already been detected in $KMgF_3$ crystals containing oxygen-related impurities, for example in $KMgF_3$ doped with

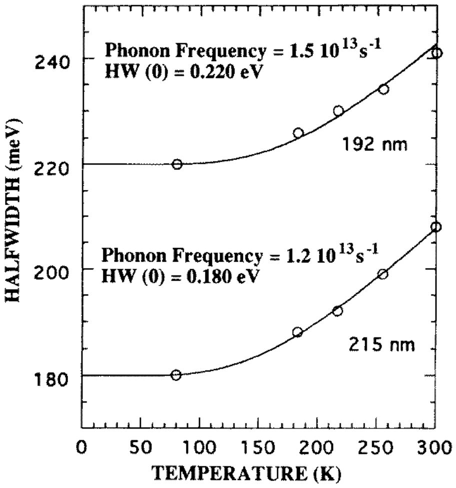

Figure 4. The temperature dependence of the halfwidths of the absorption bands of Ag$^+$ impurities in KMgF$_3$ crystals.

OH$^-$ ions [16], and the suggestion has been advanced of attributing it to complex oxygen defects. Its weak intensity in the specimens used in this work indicates a low concentration of oxygen-related species, presumably contained in the starting powders used for the growth and not completely removed by the heating and pumping procedure. It is worth noticing that no absorption rise appears below 190 nm, which means that hydroxyl ions, whose typical band peaks for KMgF$_3$ at 187 nm [16], do not appreciably contaminate crystals grown in an inert atmosphere. In contrast, KMgF$_3$:Ag$^+$ samples grown in air or in a nitrogen atmosphere show a very intense OH$^-$ absorption band, overlapping the 192 nm band due to the Ag$^+$ ions, and exhibit phenomena of energy transfer between the two impurities [17]. As a consequence, it is possible to conclude that Ag$^+$ ions are responsible only for the two absorption bands at 192 and 213 nm in the spectral region investigated. Such a conclusion is strongly supported by the thermal enhancement of both bands, which is expected for forbidden electronic transitions of Ag$^+$ impurities in analogy with the above-quoted results for alkali halides.

This allows an attempt to be made at identification of the two Ag$^+$ bands at 213 and 192 nm, which could be assigned to transitions toward ^{3}D energy levels according to the theoretical model [7]. However, the number of observed bands is much smaller than that found for alkali halides (two as opposed to five). This behaviour can be attributed to the much lower crystal field of the cubo-octahedral symmetry in the present case with respect to that of the octahedral symmetry of alkali halides. The splitting of the ^{3}D levels is thus smaller, so the two observed bands might be due to transitions toward several close-lying energy levels. This interpretation is further confirmed by recent results [18] found for SrF$_2$:Ag$^+$, where, in a cubic symmetry with eight nearest-neighbouring ions for the impurity, the absorption spectrum again exhibits only two bands, whose spectral positions and intensity ratio are very similar to those for KMgF$_3$:Ag$^+$. In any case, it is reasonable to predict, again on the basis of the data known for potassium halides, the occurrence of other absorption bands at higher energies, which will be investigated in the future. Computer resolution of the absorption spectra of KMgF$_3$:Ag$^+$ into Gaussian curves (a typical example is displayed in figure 3) shows that both Ag$^+$ bands broaden

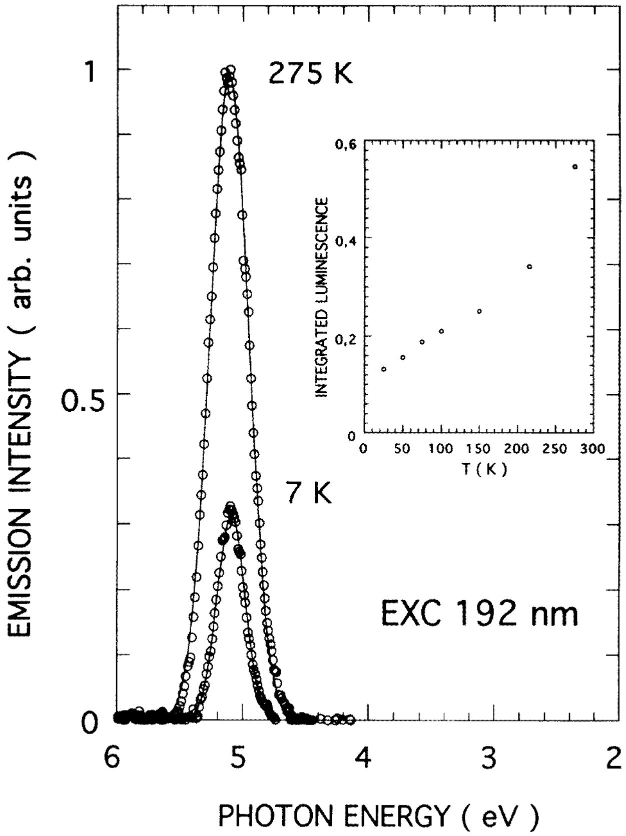

Figure 5. Emission spectra at two different temperatures of KMgF$_3$:Ag$^+$ excited at 192 nm. The inset shows the increase with temperature of the integrated photoluminescence signal.

with increasing temperature, in agreement with the usual $[\coth(\hbar\omega/kT)]^{1/2}$ dependence, as displayed in figure 4.

3.2. Photoluminescence measurements

The emission spectra of KMgF$_3$:Ag$^+$ have been measured at various temperatures under excitation in the region of the 192 nm absorption band, and figure 5 shows the curves recorded at 7 and 275 K. Only one band is detected, at about 242 nm, whose intensity (the inset in figure 5) and halfwidth (figure 6) steadily increase with temperature. No appreciable shift of the peak position is observed over the whole temperature range. Identical features are found in the emission spectra excited in the range of the 213 nm absorption band. Such results allow for the identification of the 242 nm emission as the Ag$^+$ luminescence, and give experimental evidence of a strict analogy with alkali halides, where only one emission band is found under excitation in the different absorptions of isolated Ag$^+$ ions. The thermally activated increase of the emission intensity, analogous to and perhaps more evident than (see the inset in figure 5) that observed in the absorption spectra, lends further support to the attribution of the optical bands to forbidden electronic transitions of Ag$^+$ ions in KMgF$_3$. No weak emission bands possibly caused by dimers were detected. The

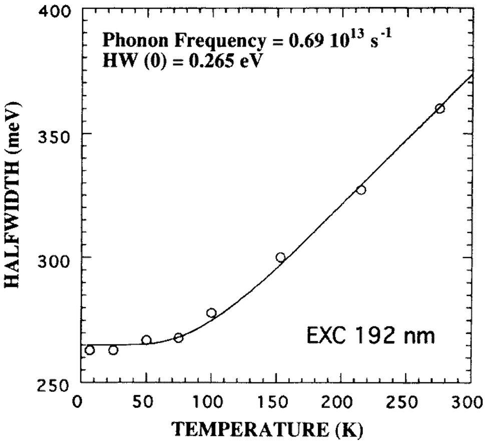

Figure 6. The temperature dependence of the halfwidth of the emission band of Ag$^+$ impurities in KMgF$_3$ crystals.

excitation spectrum of the 242 nm luminescence, measured at room temperature (figure 7), exhibits two bands at 192 and 213 nm in perfect agreement with the absorption spectrum, confirming that the two absorptions are caused by the same defect.

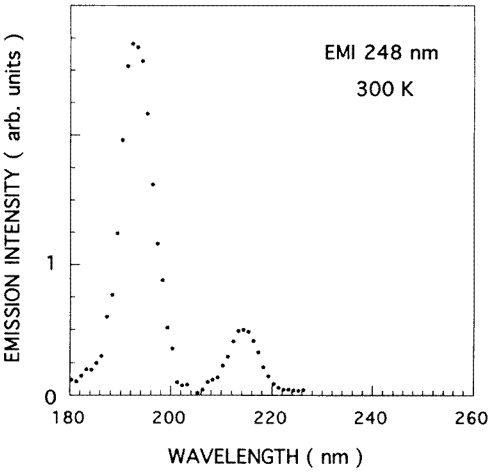

Figure 7. The excitation spectrum at room temperature of the 242 nm luminescence in KMgF$_3$:Ag$^+$.

3.3. Luminescence decay measurements

The decay times of the 242 nm photoluminescence, measured as functions of the temperature in the range 30–300 K, are listed in detail in table 1. All of the values are in the range of μs, and a decrease of about one order of magnitude is observed passing from low to room temperature. Such a behaviour turns out to be very similar to that previously reported for Ag$^+$ impurities in alkali halides [19], and to those recently found in the case of Cu$^+$ ions

Table 1. Experimental values at different temperatures of the decay time of the 242 nm emission in $KMgF_3:Ag^+$ excited at 215 nm.

Temperature (K)	Decay time τ (μs)
29.98	348
33.00	220
36.60	215
40.13	195
44.85	132
50.03	95.8
60.22	74.4
70.48	57.9
80.97	46.8
101.3	33.4
151.0	22.3
201.0	19.7
250.6	18.4
300.9	17.6

in certain similar systems [20], so the experimental data are by analogy explained with a model which takes into account two different emitting levels, whose energy separation is Δ, the lowest one being metastable. If A_m and A_2 are the transition rates from the metastable and the normal level, respectively, to the ground state, then the temperature dependence of the decay time τ is described by the following equation:

$$1/\tau = [A_m + A_2 \exp(-\Delta/kT)]/[1 + \exp(-\Delta/kT)]. \qquad (1)$$

This implies that at low temperature the metastable level at lower energy is preferentially populated, and so the transition lifetime is relatively long. With increasing temperature, the higher normal level becomes more and more thermally populated at the expense of the metastable level, and the emission lifetime turns out to be an average between the times typical of the two single levels. As a consequence, when the crystal is warmed up, the influence of the fast component due to the stable level increases, and the emission lifetime becomes shorter and shorter. The contributions of the ionization processes are in general neglected for alkali halides, due to the high energy required to reach the conduction level. Based on such a model, detailed calculations were performed on the energy levels of Cu^+ and Ag^+ impurities in alkali halides [21, 22].

If it is now assumed that the validity of such a model can be extended to the case of $KMgF_3:Ag^+$ crystals, then a fit of the experimental data with equation (1) can be attempted. The result, displayed in figure 8, is more than satisfactory, again indicating substantial analogies in the optical behaviours of Ag^+ ions in both alkali halide and fluoroperovskite cubic lattices. The following values of the parameters contained in equation (1) are deduced from the best fit:

$$A_m = 2100\ \mathrm{s}^{-1}$$
$$A_2 = 149\,800\ \mathrm{s}^{-1}$$
$$\Delta = 12.7\ \mathrm{meV}.$$

Such a result for Δ is only slightly larger than those found for $NaCl:Ag^+$ (6 meV) and for $LiCl:Ag^+$ (8 meV) [19].

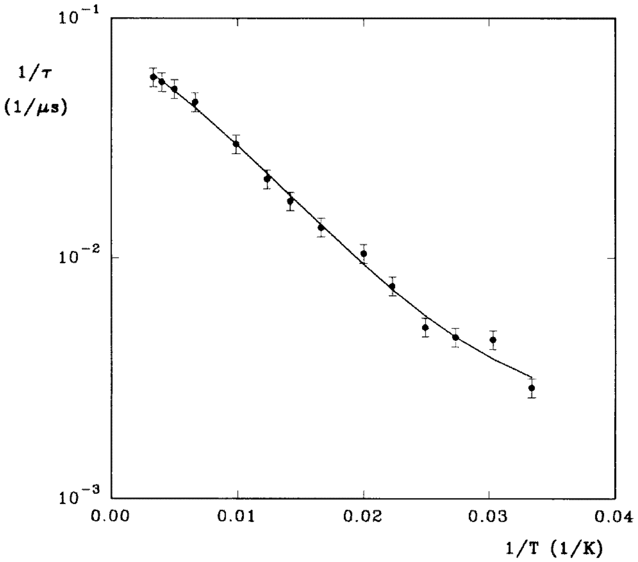

Figure 8. The temperature dependence of the decay time of the 242 nm emission in $KMgF_3$:Ag^+ under excitation at 215 nm. The experimental data (dots) are fitted (continuous line) with equation (1) (see the text).

3.4. Thermoluminescence measurements

The thermally stimulated luminescence (TSL), already studied for β-irradiated crystals of $KMgF_3$:Ag^+ grown in air [12], was carefully measured for the crystals grown in inert atmospheres as a function of temperature and of wavelength, with a heating rate of 1 °C s^{-1}. Figure 9 shows the 3D plot of the TSL in the range 40–500 °C for the spectral region 200–350 nm. TSL peaks are found at about 80, 150, and 175 °C, in perfect agreement with the previous data, but a new very intense peak, never observed before, was found at about 400 °C. The most striking feature is that all of the TSL peaks are found in the spectral range 247–250 nm, with the only exception being that at 150 °C, in which such a main emission is accompanied by a shoulder at about 277 nm, as is shown better in figure 10, where the spectra measured at various temperatures are computer resolved into Gaussian bands. Leaving aside for the moment the weak 277 nm emission, the most obvious conclusion would be that thermal stimulation leads to all of the recombination processes involving the same emitting centres, which could be the Ag^+ impurity ions (the small shift in the spectral position from 242 to 250 nm being fully justified by the higher temperatures of the samples in the TSL measurements). However, previous experiments on a different system, namely a crystal of $KMgF_3$:Tl^+, supplied results on the TSL [23] and on the photoluminescence [24] which seem to point toward a different conclusion. Emission at about 242 nm, found by measuring both the spectrally resolved thermoluminescence of β-irradiated samples and the photoluminescence under excitation in the fundamental absorption of the host material (at about 120 nm), was interpreted as an intrinsic feature of the $KMgF_3$ fluoroperovskite. As a consequence, it is possible that in $KMgF_3$:Ag^+ crystals two different emission mechanisms coexist: (i) the normal excitation leading to the photoluminescence of the Ag^+ ions, which is consistently enhanced by increasing temperature, and (ii) the fundamental excitation of the host $KMgF_3$, which would release

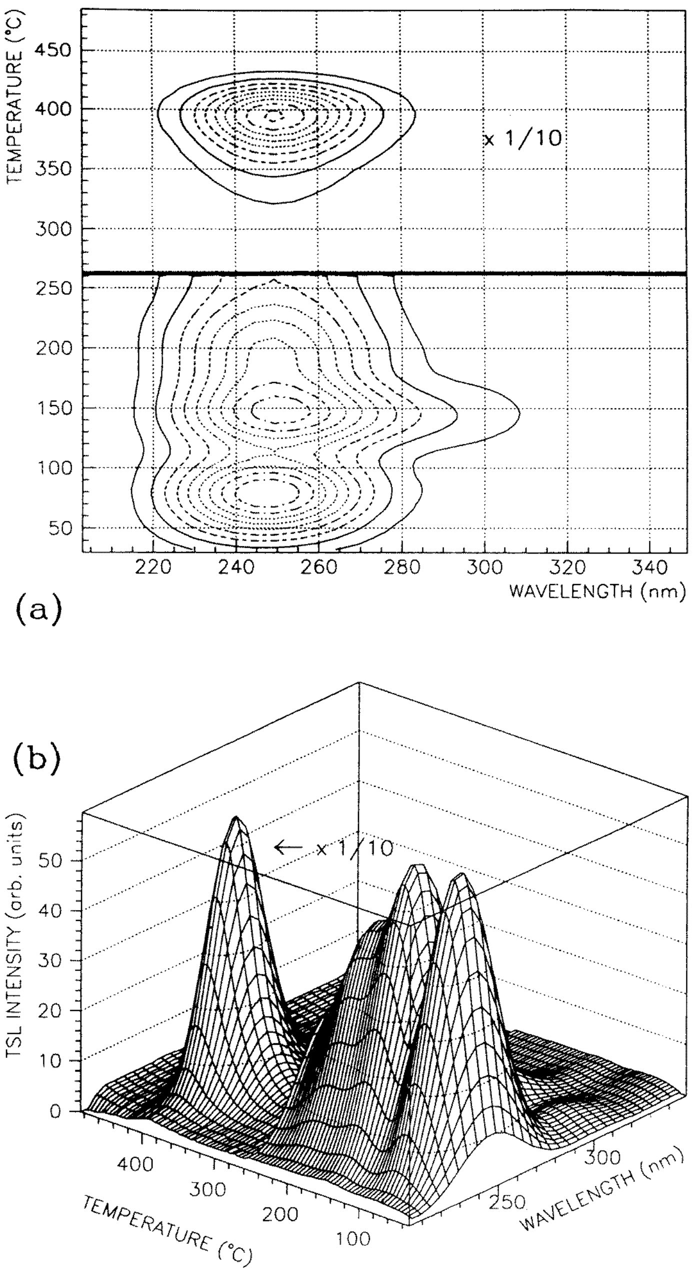

Figure 9. The thermally stimulated luminescence of β-irradiated $KMgF_3$:Ag^+ measured as a function of temperature and wavelength: (a) contour plot; (b) 3D representation.

its own emission, independently of the doping. Attempts to discriminate between these two alternatives were unsuccessful, because the spectral positions and halfwidths of the TSL peaks in the two systems are perfectly comparable. Therefore, this point requires further investigation, which could be carried out by studying the spectral features of the

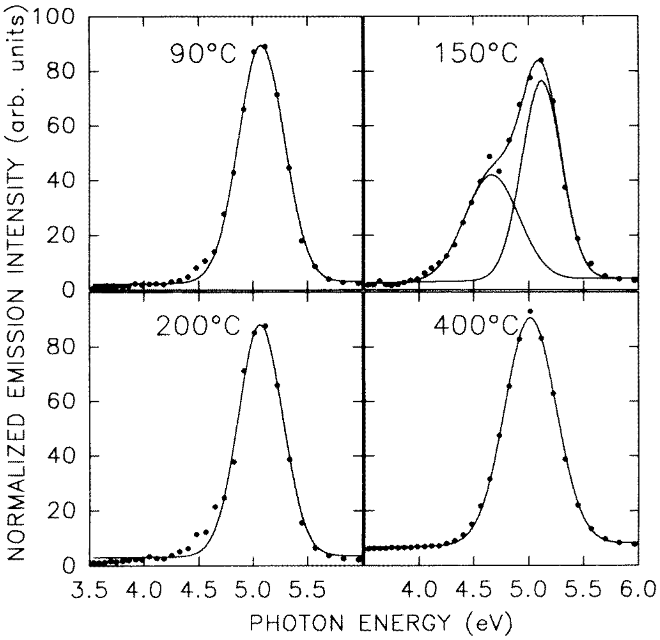

Figure 10. The computer resolution of the thermally stimulated emission in KMgF$_3$:Ag$^+$. The experimental data (dots) are fitted with the sum of two Gaussian curves (continuous lines).

photoluminescence under VUV excitation. As far as the 277 nm emission is concerned, the dependence of its intensity on the dopant concentration in KMgF$_3$:Ag$^+$ crystals could clarify a possible attribution to dimer centres.

4. Conclusions

From the results and considerations reported above, a clear picture of the optical behaviour of Ag$^+$ impurity ions in crystals of KMgF$_3$ can be deduced. In general, passing from the fcc lattices of alkali halides to the typical symmetry of the perovskite-like lattice, the optical spectra of Ag$^+$ point defects seem to be partially modified. Both optical absorption and emission show several features which recall those already known of for alkali halides, such as there being more than one absorption band, only one photoluminescence, thermal enhancement of the optical bands, and a temperature dependence of the luminescence decay time. However, the change in the crystal field results, as expected, in a less resolved degeneracy of the energy levels, and therefore in a smaller number of transitions detected in the absorption measurements. Moreover, in the particular case of KMgF$_3$:Ag$^+$ an interesting problem is raised by the possible simultaneous occurrence of two different emissions, both found in the same spectral region, and more exactly at 245 nm. Such radiative deexcitations would concern the isolated impurity ions and the host lattice at the same time. This suggests the need to carry out further experiments, possibly involving a deeper use of synchrotron radiation, in order to discriminate between two such emitting channels, and to identify possible interactions, such as energy-transfer processes, between the matrix and the impurity ions.

From the point of view of possible applications, it is worth noticing that for KMgF$_3$:Ag$^+$

the intensity of the emission at 242 nm is appreciably increasing with temperature. This means that there is some chance of obtaining a sufficiently intense emission at room temperature, provided that an intense pumping source is available, suitable for use in a solid-state laser in the UV region. Good performances could also be obtained in radiation dosimetry, by making use of the particularly intense TSL peak at about 400 °C, which should be studied in detail for this purpose, mostly because of its expected resistance to any fading effect. Moreover, the possibility of interactions of Ag^+ ions in $KMgF_3$ with other dopant species, such as OH^- impurities [17], opens up a new area of investigation into the modifications of the optical behaviour in codoped crystals.

Acknowledgments

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