OPTICAL ABSORPTION OF Tl+ IONS IN KMgF₃ CRYSTALS

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Abstract—Absorption spectra of Tl⁺-doped KMgF₃ single crystals have been measured at various temperatures between 9 and 300 K in the V.U.V. region. Three main bands are found, and they are labelled A, B, C in order of increasing energy because of their close similarities to those of Tl⁺ ions in alkali halides. The most striking novelty in KMgF₃: Tl⁺ is given by the clearly resolved structures of the A and C bands, which both exhibit three components at all temperatures. These structures are related to the Jahn–Teller splitting, due to the interaction of the impurity ion with non-cubic lattice vibrations, and to a static distortion of the host lattice.

Keywords: Optical absorption, Tl⁺ ions, fluoroperovskites, KMgF₃.

INTRODUCTION

The optical properties of metal ions with ns² electronic configuration in their ground state, introduced as substitutional impurities in crystals of ionic compounds, are well known in the case of alkali halides [1–3]. The absorption spectra in such host materials, measured on the long wavelength side of the u.v. absorption edge, show the following common features: three absorption bands (labelled A, B, C in order of increasing photon energy), caused by electronic transitions of the impurity ion from the ns² ground state to the nsnp excited state configuration, and from one to three D bands (depending on the particular types of impurity ion and of host crystal lattice) at higher energies, due to charge-transfer transitions. Because of the strong electron–phonon interaction, the A, B, C bands can be split into various components, due to the Jahn–Teller effect on the degenerate electronic states of the ns² configuration.

Excitation into these absorption bands induces optical emission, whose spectral features strongly depend on the crystalline host system, on the type and electric charge of the impurity ion, and on the pumping wavelength. In general, the most studied luminescence is that observed under excitation in the A absorption band. Excitation into the B and C absorption bands causes, besides the above luminescence, the appearance of other emission bands due to radiative transitions from higher excited states. Such an extensive knowledge of the optical behavior of ns² ions, especially of Tl⁺, In⁺, Ga⁺, Sn³⁺ and Pb²⁺, in alkali halides, has so far only been achieved in few other host lattices, mostly because of the difficulties of doping, with volatile impurities, ionic materials with high melting points. The recent interest in the scintillation properties of BaF₂, and of alkaline earth fluorides in general, fostered investigation on activators in such systems: spectroscopic studies on Pb²⁺ ions in CaF₂ [4] and in BaF₂ [5–6], and on Pb²⁺ and Bi³⁺ in various alkaline earth fluorides [7] were reported.

No information is available, to the best of our knowledge, on the optical properties of ns² ions in ternary compounds belonging to the group of the fluoroperovskites. The aim of this paper is to study the spectral features of the absorption of Tl⁺ ions in a particular system, the perovskite-like KMgF₃, which received recent attention for application as an active material in solid state lasers [8] and as a phosphor for ionizing radiation dosimetry [9]. Preliminary results of this investigation were recently reported [10]. In the cubic lattice of the perovskite-like KMgF₃ (Fig. 1), every K⁺ ion is surrounded by 12 nearest neighboring F⁻ ions and by eight next nearest neighboring Mg²⁺ ions. In such a lattice, a substitutional Ti⁺ impurity is expected to replace a K⁺ ion because of both its electric charge and ionic size. Therefore, the Ti⁺ ion experiences a static
The perovskite-like crystal lattice of KMgF$_3$ with substitutional Tl$^+$ impurity.

Fig. 1. The perovskite-like crystal lattice of KMgF$_3$ with substitutional Tl$^+$ impurity.

crystal field which is not that found in alkali halides, where six anions are the nearest neighbors of the defect and there are no other surrounding ionic species. As a consequence, the optical study on KMgF$_3$:Tl$^+$ should clarify the influence of the local field on the physical behavior of the ns$^2$ impurity ion.

EXPERIMENTAL PROCEDURE

All optical experiments were carried out on samples cut from single crystals of KMgF$_3$, grown from the melt by using the Kyropoulos technique [11]. In every growth the starting melt, contained in a platinum crucible, consisted of a stoichiometric mixture (mole ratio 1:1) of pure and dried KF and MgF$_2$, and the whole process was performed under a nitrogen gas atmosphere. Doping was obtained by adding to the melt, just before the beginning of pulling, about 1 mole % of TlCl. This salt has been chosen in the place of TlF because of its higher melting point, which allows for a sufficient dopant level. Typical dimensions of the crystal ingotes were 2–3 cm in diameter and 3–4 cm in length. All samples, sawed from the crystal boules with a typical thickness of 1.5–2.0 mm, were colorless and after polishing optically transparent in the visible spectrum. Spectroscopic measurements showed a very high segregation of the impurity during the growth, which causes large differences in the Tl$^+$ concentration observed at different positions in crystals. For this reason, the actual concentration in the samples can only be estimated to be about 0.1 mole %, and all measurements involving comparison among different spectra were carried out by keeping the position of the sample unchanged with respect to the incident light beam.

Since the fundamental absorption of KMgF$_3$ crystals is reported at about 130 nm [12–13], the absorption bands of Tl$^+$ ions are expected to lie in this material in the near ultraviolet or in the vacuum ultraviolet spectral region. Therefore, absorption measurements were in almost all cases performed by taking advantage of the Synchrotron radiation facility at the ADONE storage ring in Frascati, Italy. The available photon energies were selected between 4 and 10 eV by means of a f/16 Hilger–Watts monochromator coupled to a LiF filter.

Absorption spectra at various temperatures between 9 and 300 K were recorded by collecting the light transmitted through the sample on a film of sodium salicilate, whose luminescence quantum efficiency is known to be constant under excitation in the 4–10 eV energy range [14]. The intensity of the outcoming luminescence signal was measured by a RCA 1P28 photomultiplier. From this signal, suitably normalized to the intensity of the incident light, the absorption coefficient was deduced. The absorption bands of the Tl$^+$ impurities were determined by subtracting from the spectra of doped samples the spectrum of an undoped KMgF$_3$ crystal of similar thickness and surface quality.

RESULTS

The absorption spectrum at 9 K of Tl$^+$ ions in KMgF$_3$:Tl$^+$ (Fig. 2) exhibits the typical A, B, C bands quoted. The A and C bands, peaking at 203 and 150 nm, respectively, clearly show a multiplet structure which will be discussed later. The much weaker B band is found in a spectral position (168 nm) which is in some way unusual for Tl$^+$ impurities in alkali halides, where it normally lies on the long wavelength tail of the C band [15]. A very weak band is observed at about 138 nm as a shoulder over a continuously rising absorption: the experimental difficulties found in the measurements in this spectral region do not allow the possible identification of such a band as the D absorption in KMgF$_3$:Tl$^+$. Another very weak absorption can be observed around 187 nm, where

Fig. 2. Absorption spectrum at 9 K of KMgF$_3$:Tl$^+$. 
previous experiments identified the spectral position of the absorption band of OH⁻ defects in KMgF₃ [16]. In spite of the careful dehydration of the starting powders of the KMgF₃ components and of the inert gas atmosphere used to avoid any moisture or unwanted contamination during the growth, it seems that small amounts of OH⁻ impurities were incorporated in the crystals. At least qualitatively, the absorption of Tl⁺ ions in KMgF₃ is quite similar to that observed in alkali halides, which suggests that the local field has no marked influence on the general optical behavior of the ns⁺ ion, as already found for similar impurities in alkaline earth fluorides [7].

Both A and C absorption bands in KMgF₃:Tl⁺ are clearly structured. Such a feature, already observed in the A band, which was resolved into two [17] or three [18] components in Tl⁺-doped alkali halides, is completely new for the C band of Tl⁺. Indeed such absorption has never, so far, clearly split into three components in alkali halides containing Tl⁺ ions, in contrast with the behavior of crystals doped with Ga⁺, Sn²⁺ or Pb²⁺ ions. Only in the case of KI:Tl⁺ was some multiplet structure reported [19]. In KMgF₃:Tl⁺ the evident triplet structure of the C absorption band is a clear fingerprint of a remarkable Jahn–Teller effect. In order to determine quantitatively the parameters involved in such peculiar behavior, the temperature dependence of the absorption spectrum of KMgF₃:Tl⁺ was systematically investigated and the A and C bands were computer resolved into their components at each temperature.

The A absorption band (experimental dots shown in Fig. 3) exhibits a resolved structure that can be approximately fitted with the sum of two symmetric Gaussian bands with peaks at 204 and 200 nm, respectively. However, the best fit of the data, which is very good at 300 K, is not satisfactory at lower temperatures: the low energy side of the band is not well reproduced by a symmetric Gaussian curve, and also the region between the two peaks, where a bump is observable in the experimental points, is not properly fitted with two bands. For this reason, a resolution with three symmetric Gaussian curves (the third component peaking at about 202 nm, in the region of the above bump) was attempted, and typical results at 9, 100 and 300 K are displayed in Fig. 3 with continuous lines. In this case, the experimental data are all fitted in a very good way, and the temperature behaviors of all spectroscopic parameters of the A₁, A₂, A₃ absorptions are very similar to those observed for alkali halides. The total area of the A absorption at different temperatures is found to be constant within a few per cent. The temperature dependences of the peak positions and of the band halfwidths are shown in Figs 4 and 5, respectively. The spectral positions of all three components shift towards lower energies with increasing temperature, the splittings increase linearly above 100 K with T¹¹², and the band halfwidths agree with the usual [coth(hω/kT)]¹¹ dependence. The splitting of the A absorption into three components in KMgF₃:Tl⁺ confirms theoretical expectation of a triply degenerate energy level for the lowest excited state of the Tl⁺ impurity. The dynamical Jahn–Teller splitting is clearly observable for Tl⁺ ions only in the cases in which the electron–lattice interaction is strong enough, as found for KF:Tl⁺.
Fig. 5. Temperature dependence of the band halfwidths for the three components of the A absorption in KMgF$_3$:Tl$^+$. [17], and this is presumably also the case for KMgF$_3$:Tl$^+$. The C band, measured at 10, 100 and 300 K and computer resolved into three symmetric Gaussians, is shown in Fig. 6. In this case, where the triplet structure is evident at every temperature, the $C_1$, $C_2$, and $C_3$ components are found at low temperature at 152, 149 and 147 nm, respectively. The intensities of the $C_1$ and $C_2$ bands decrease with increasing temperature more than that of the $C_3$ band, so that the absolute maximum of the C band is shifted from the high wavelength peak at 10 K to the central peak at 300 K. The total area of the C absorption decreases slightly with increasing temperature. The temperature dependences of the peak positions and of the band halfwidths are displayed in Figs 7 and 8, respectively.

The intensity of the B band appreciably increases with temperature (so that its total area at 300 K is about 50% bigger than that at 10 K), as expected for an absorption caused by forbidden electronic transitions which are vibronically allowed. No fine structure was evident in this band, and therefore it was not studied in detail.

Fig. 7. Temperature dependence of the peak positions of the three components and of the first moment of the absorption lineshape for the C band in KMgF$_3$:Tl$^+$. C$_1$ components are found at low temperature at 152, 149 and 147 nm, respectively. The intensities of the $C_1$ and $C_2$ bands decrease with increasing temperature more than that of the $C_3$ band, so that the absolute maximum of the C band is shifted from the high wavelength peak at 10 K to the central peak at 300 K. The total area of the C absorption decreases slightly with increasing temperature. The temperature dependences of the peak positions and of the band halfwidths are displayed in Figs 7 and 8, respectively.

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Fig. 8. Temperature dependence of the band halfwidths for the three components of the C absorption in KMgF$_3$:Tl$^+$.
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DISCUSSION AND CONCLUSIONS

The positions of the A, B and C bands in potassium halides follow (Fig. 9) a trend described by the Mollwo-Ivey law [1, 20], if one neglects the data concerning KF:Ti⁺, where all three bands occur at energies smaller than expected [17]. In KMgF₃:Ti⁺ it can be assumed that the cation-anion distance relevant to determine the spectral positions of the Ti⁺ bands must be taken as the K⁺−F⁻ distance (2.81 Å). With this value, the experimental data for Ti⁺ bands in KMgF₃:Ti⁺ are all in reasonable agreement with the expected peak positions.

A semiquantitative check can be attempted by applying to KMgF₃:Ti⁺ the Sugano formula [1] relative to the ratio of the C band dipole strength to the A band dipole strength. By assuming the peak positions for the A, B, C bands to be $E_A = 6.12$ eV, $E_B = 7.38$ eV, $E_C = 8.27$ eV, respectively, so that $x = (E_B - E_A)/(E_C - E_A) = 0.586$, the ratio turns out to be $R = \frac{4 - 2x + (6 - 2(2x - 1))^{1/2}}{2 + 2x - (6 - 2(2x - 1))^{1/2}}$, (1)

obtained. The agreement with the prediction $R = 7.2$ is not excellent, but can be considered quite reasonable, mostly recalling the rough approximation in the estimate of the variation of the unknown refractive index of KMgF₃, and the approximation on the radial wavefunctions.

Detailed experimental and theoretical studies showed that in alkali halides measurements of the peak positions and areas of the A and C bands allow the determination of all parameters needed to explain the features of the singlet and triplet states [15, 21]. In this way, the exchange integral $G$, the spin-orbit splitting $\zeta$, the mixing coefficients $\mu^2$ and $\nu^2$ between singlet and triplet states, and the parameter $\lambda$ which depends on the difference in the radial wavefunctions of the singlet and triplet states, can be calculated. Moreover, the interaction of the ns² localized impurity with the lattice vibrations was described with a model containing three ($a$, $b$, $c$) system-dependent parameters [22]. The $a$ parameter is responsible for the broadening and smoothing of the line shape of the bands. The $b$ and $c$ parameters describe the coupling with tetragonal ($E_g$) and trigonal ($T_{2g}$) lattice vibrations, respectively. The interaction with the $T_{2g}$ lattice mode is responsible for removing the level degeneracy (dynamical Jahn-Teller effect).

<table>
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<tr>
<th>System</th>
<th>$E_A$ (eV)</th>
<th>$E_B$ (eV)</th>
<th>$E_C$ (eV)</th>
<th>$R$</th>
<th>$\mu^2$</th>
<th>$\nu^2$</th>
<th>$G$ (eV)</th>
<th>$\zeta$ (eV)</th>
<th>$\lambda$</th>
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<tr>
<td>KMgF₃:Ti⁺</td>
<td>6.12</td>
<td>7.38</td>
<td>8.27</td>
<td>4.8</td>
<td>0.827</td>
<td>0.173</td>
<td>0.481</td>
<td>0.888</td>
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<td>0.106</td>
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<td>6.36</td>
<td>5.0</td>
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<td>0.166</td>
<td>0.271</td>
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<td>5.33</td>
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<td>0.714</td>
<td>0.286</td>
<td>0.134</td>
<td>0.454</td>
<td>1.287</td>
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The observed value $R_{obs}$ can be determined according to the relation

$$R_{obs} = \frac{n_C}{(n_C^2 + 2)^{1/2}} \frac{(\nu^2 + 2)}{\nu_C} \frac{E_A}{E_C}$$

where $n_C$ and $n_A$ are the values of the refractive index of KMgF₃ at wavelengths corresponding to the maxima of the C and A absorption bands, respectively, $A$ and $C$ are the integrals of the absorption coefficient $\alpha(E)$ defined as

$$A = \int A(E) dE$$
$$C = \int C(E) dE$$

and $E_A$ and $E_C$ are the first moments of the absorption line shape function $\alpha(E)/E$. By assuming a not significant change of the refractive index of the material between 6 and 8 eV, a value $R_{obs} = 4.8$ is obtained. The agreement with the prediction $R = 7.2$ is not excellent, but can be considered quite reasonable, mostly recalling the rough approximation in the estimate of the variation of the unknown refractive index of KMgF₃, and the approximation on the radial wavefunctions.
values of the coupling parameters and those of the quadratic terms in the electron–lattice Hamiltonian $\alpha$, $\beta$, $\gamma$, can be derived from the temperature dependence of the moments of the absorption lineshape [21]. Such analysis was applied to the case of NaBr:Ti$^+$, deriving the numerical values of the parameters in good agreement with those known for other alkali halides [23]. Here an extension of the model to the case of KMgF$_3$:Ti$^+$ is attempted, in order to identify analogies and discrepancies among systems in which the lattice symmetry is always of Oh type, but the electron–lattice interaction can be different because of the different crystal structure. Figures 4 and 7 show the temperature dependence of the first moments of the line shape function for the $A$ and $C$ bands in KMgF$_3$:Ti$^+$: the values extrapolated to 0 K, together with that obtained for the $B$ band, are reported in Table 1. From them, and from the value $R_{\text{morf}} = 4.8$, it is possible to calculate the parameters $\mu^2$, $\nu^2$, $G$, $\zeta$, $\lambda$ [21], which are also listed in Table 1. A comparison with typical values for potassium halides shows similarities for $\mu^2$, $\nu^2$, $\lambda$, while the values of $G$ and $\zeta$ in KMgF$_3$:Ti$^+$ are similar to those of KF and somewhat larger than in the other potassium halides, where such parameters decrease with increasing anion radius.

The temperature dependence of the second moments of the line shape function for the $A$ and $C$ bands is shown in Fig. 10. From the slopes of the high temperature behaviors of the first and second moments of the absorption bands in Figs 4, 7 and 10, the values of $2b^2 + 3c^2$, $\alpha + 2\beta + 3\gamma$ can be derived according to very simple equations [21], and the results are summarized in Table 2, together with those found for Ti$^+$-doped potassium halides. These coefficients show a large spread in the various measurements. However, the trend of the values of $2b^2 + 3c^2$ is to decrease with increasing anion radius, and the value found for KMgF$_3$ is close to that of KCl. According to the model of the electron–lattice coupling, one would expect a much larger value of $2b^2 + 3c^2$ in those systems where the splittings of the $A$ and $C$ absorption bands is more pronounced. Therefore, the similarity of the parameters describing such coupling does not give a definite clue for the interpretation of the spectra observed for KMgF$_3$:Ti$^+$, which are much more resolved and structured than those of KCl:Ti$^+$. Then, we have further analyzed the temperature dependence of the second moments of the $A$ and $C$ bands, that above 100 K can be described as

$\langle E^2 \rangle = A_{1A} + A_{2A}kT$ and $\langle E^2 \rangle = A_{1C} + A_{2C}kT$ (4)

where the constants $A_{1A}$ and $A_{2A}$ reflect the contribution to the band width due to the dynamical electron–phonon interaction, as described above, while the constants $A_{1C}$ and $A_{2C}$ indicate the presence of an additional perturbation such as a static crystal field with symmetry lower than cubic [3]. From the data of Fig. 10 it is evident that the temperature independent contribution is a sizeable portion of the second moment at every temperature. In the study of Sn$^{2+}$ ions in alkali halides, the temperature independent perturbation has been associated with the lowering of the lattice symmetry due to the presence of a nearby charge-compensating cation vacancy. These vacancies can be excluded in the case of KMgF$_3$, where the Ti$^+$ impurities replace K$^+$ ions, but an analogous symmetry lowering perturbation can be given by a static lattice distortion around the impurity ion. Indeed some experiments point toward the existence in KMgF$_3$ of a monoclinic sublattice, which could originate from such distortion [27, 28].

Further investigation on the optical behavior of other ns$^{2}$ ions in the same host material or in analogous systems is planned in order to test the above hypothesis of static lattice distortion.

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<table>
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<th>System</th>
<th>$\sigma^2$ (eV)</th>
<th>$2b^2 + 3c^2$ (eV)</th>
<th>$\alpha + 2\beta + 3\gamma$</th>
<th>Reference</th>
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<tr>
<td>KMgF$_3$:Ti$^+$</td>
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<td>3.12</td>
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<td>This paper</td>
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<tr>
<td>KF:Ti$^+$</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>KCl:Ti$^+$</td>
<td>0.26</td>
<td>3.72</td>
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<td>KBr:Ti$^+$</td>
<td>0.31</td>
<td>3.15</td>
<td>4.53</td>
<td>24</td>
</tr>
<tr>
<td>KI:Ti$^+$</td>
<td>0.085</td>
<td>1.20</td>
<td>—</td>
<td>24</td>
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</table>

Fig. 10. Temperature dependence of the second moments of the absorption lineshape for $A$ and $C$ bands in KMgF$_3$:Ti$^+$.  

Table 2. Experimental values of the electron–lattice coupling coefficients for Ti$^+$ ion in KMgF$_3$ and in potassium halides.  

$\langle E^2 \rangle = A_{1A} + A_{2A}kT$ and $\langle E^2 \rangle = A_{1C} + A_{2C}kT$ (4)  

The constants $A_{1A}$ and $A_{2A}$ reflect the contribution to the band width due to the dynamical electron–phonon interaction, as described above, while the constants $A_{1C}$ and $A_{2C}$ indicate the presence of an additional perturbation such as a static crystal field with symmetry lower than cubic [3]. From the data of Fig. 10 it is evident that the temperature independent contribution is a sizeable portion of the second moment at every temperature. In the study of Sn$^{2+}$ ions in alkali halides, the temperature independent perturbation has been associated with the lowering of the lattice symmetry due to the presence of a nearby charge-compensating cation vacancy. These vacancies can be excluded in the case of KMgF$_3$, where the Ti$^+$ impurities replace K$^+$ ions, but an analogous symmetry lowering perturbation can be given by a static lattice distortion around the impurity ion. Indeed some experiments point toward the existence in KMgF$_3$ of a monoclinic sublattice, which could originate from such distortion [27, 28].
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