Opto-structural study of $A_2BMF_6$: Cr$^{3+}$ elpasolite crystals. Variation of the $(CrF_6)^{3-}$-complex optical properties with Cr-F bond distance, hydrostatic pressure and excited-state crossover

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Abstract. This work investigates the optical properties of the Cr$^{3+}$-doped and Cr$^{3+}$-pure elpasolites $A_2BMF_6$ along compound series and as a function of pressure. We are interested in establishing structural correlations between the electronic structure and the actual Cr-F distance, $R_{Cr-F}$, from which we have been able to reveal the local structure around the Cr$^{3+}$ impurity. As salient features, we show, firstly, a weak dependence of the first excitation band energy, $E_1$, usually identified as $10Dq$, with $R_{Cr-F}$ as $E_1 = K R_{Cr-F}^{-3.3}$, and, secondly, an increase of the Stokes shift upon $R_{Cr-F}$ reduction or with increasing pressure. We associate this unusual behavior with the existence of Fano resonance in the first excitation band of Cr$^{3+}$. High-pressure experiments performed on Rb$_2$KCrF$_6$ indicate that the excited-state spin crossover, $^2E_g(G) \leftrightarrow ^4T_{2g}(F)$, takes place around 7 GPa. Short lived broad-band luminescence changes into long-lived ruby-like narrow lines. The reported results point out the suitability of the selected $A_2BMF_6$: Cr$^{3+}$ elpasolites to establish structural correlations between PL and $R_{Cr-F}$.

1. Introduction

Elpasolites have received particular attention due to their simple cubic structure and the isolated character of $(CrF_6)^{3-}$ complexes, which do not share any common F ligand in the elpasolite structure [1]. Fluorides are usually employed as ideal host lattices for accommodating di- and trivalent cations in perfect octahedral sites (M) due to the large variety of cubic crystals with the perovskite (AMF$_3$) and elpasolite ($A_2BMF_6$) structures, respectively. But such correlation is hard to establish in impurity systems, due to difficulty in determining precisely the actual Cr-F distance, $R_{Cr-F}$. This feature makes pure $A_2BCrF_6$ attractive systems to establish correlations between the optical properties and the structure, what is crucial for a microscopic understanding of the PL properties.

2. Experimental

Single crystal elpasolites of K$_2$NaGaF$_6$, Rb$_2$KGaF$_6$ and Rb$_2$KInF$_6$ doped with 1 mol% of Cr as well as single crystals of Rb$_2$KCrF$_6$ and Tl$_2$KCrF$_6$ were grown [1]. The elpasolite structure ($Fm\bar{3}m$) of the crystals at ambient conditions was checked by X-ray diffraction (XRD) and Raman. Spectroscopic measurements were done as described elsewhere [2].
3. Results and discussion

The excitation and corresponding PL spectra at room temperature for the investigated \(A_2\)BMF_{6}:Cr^{3+} crystals are shown in Figure 1.

![Figure 1](image1.png)

**Figure 1.** Emission, and excitation/absorption of the \(A_2\)BMF_{6}:Cr^{3+} crystals. The bands are assigned according to the Tanabe-Sugano diagram for a d^{3} ion (Figure 2). Note the presence of components in the first excitation band (see text).

The bands are assigned to electronic crystal-field (CF) transitions within \(O_h\) symmetry \(\text{CrF}_6^{3-}\), according to the Tanabe-Sugano diagram for d^{3} ions (Figure 2). It is worth noting the triplet structure exhibited by the first band in the OA spectrum, which is associated with Fano resonance among the \(4T_{2g}(F), 2E_g(G)\) and \(2T_{1g}(G)\) states. The CF parameter, \(10Dq\), obtained from the OA spectrum is close to the excited-state crossover (ESCO) point, \((10Dq/B)_{\text{ESCO}} = 22\), and thus these states are significantly coupled by the spin-orbit interaction.

**Figure 2.** Tanabe-Sugano diagram for a d^{3} ion. Notation corresponds to \(O_h\) symmetry. The arrows represent luminescence in weak and strong crystal fields, respectively.

Figure 3 plots the variation of \(10Dq\) obtained by fitting the energies of the absorption bands \((E_1 \approx 4T_{2g}(F), 2E_g(G)\) and \(2T_{1g}(G), E_2 = 4T_{1g}(F))\) versus \(R_{Cr-F}\) for the Cr^{3+}-pure elpasolites. \(R_{Cr-F}\) for the Cr-pure elpasolites has been obtained from the a_{1g} vibrational breathing mode of the \((\text{CrF}_6)^{3-}\) complex frequency, measured by Raman spectroscopy [2]. The results are compared with \(R_{Cr-F}\) dependences of 10Dq given by

\[
10Dq \propto R_{Cr-F}^{-n} \tag{1}
\]

for \(n = 5\) and \(n = 3.3\). The exponent \(n = 3.3\) provides a more realistic account for the observed variation than \(n = 5\). Besides accidental coincidence with the point-charge CF model, \(n\) exponents around 5 have been obtained in different transition metal oxide complexes from high-pressure experiments [3]. We associate such different behavior \((n = 3.3\) instead of \(n = 5\)) as due to the Fano resonance of the first transition energy \(E_1\) around ESCO. We must take into account that, although the CF parameter 10Dq can be derived from the first excitation energy, \(E_1 = 10Dq\), its variation with \(R_{Cr-F}\)
is not the same as \(10D_q\): \(\frac{\partial E_j}{\partial R_{Cr-F}} \neq \frac{\partial 10D_q}{\partial R_{Cr-F}}\). The reason of this inequality lies on the \(10D_q\)-dependence of the centroid \(E_1\). According to the Tanabe-Sugano diagram (Figure 2), it is expected to vary as \(E_1 = 10D_q\) for CF values far from the ESCO. On the other hand, near the ESCO, \(E_1\) behaves somewhat intermediate between \(10D_q\) and the constant value \(22B\) corresponding to the \(^2E_g(G)\) energy. Depending on the orbital mixing induced by the spin-orbit coupling, \(\frac{\partial E_j}{\partial 10D_q}\) has values between 1 and 0, and thus \(\frac{\partial E_j}{\partial R_{Cr-F}}\) exhibits an intermediate behavior between \(\frac{\partial 10D_q}{\partial R_{Cr-F}}\) and 0 [2, 4].

The structural effects on the optical properties in the series (chemical pressure) are evidenced through the slight band shifts observed on passing from \(K_2NaAlF_6:Cr^{3+}\) to \(Rb_2KlnF_6:Cr^{3+}\). \(10D_q\) varies only 0.09 eV for \(\Delta R_{M-F} = 0.22\) Å. Such a distance variation would induce a larger shift if the variation of the host M-F distance were the same as the impurity Cr-F distance. This is well illustrated in the Cr-pure elpasolite series, whose \(10D_q\) varies from 2.00 eV in \(Rb_2KcrF_6\) \((R_{Cr-F} = 1.88\) Å) to 1.91 eV in \(Tl_2KcrF_6\) \((R_{Cr-F} = 1.94\) Å). This difference can be concealed with variations as a function of \(R_{M-F}\) if we consider lattice relaxation effects around \(Cr^{3+}\) in impurity systems. These results show that the impurity Cr-F distance and the host M-F distance are different, \(R_{Cr-F} \neq R_{M-F}\). The optical excitation data of Figure 1 provide essential information on the real Cr-F distance for impurity systems if we compare them with pure compounds. We can estimate \(R_{Cr-F}\) from \(10D_q\) through Eq. 1. The so-obtained \(R_{Cr-F}\) values for the impurity systems are very similar irrespective of the choice \(n = 3.3\) or \(n = 5\) (Figure 4). This is related to the fact that \(R_{Cr-F}\) along the series slightly deviates from the equilibrium Cr-F distance. As Figure 4 shows, the actual \(R_{Cr-F}\) derived from Eq.(1) deviates from \(R_{M-F}\) in the \(A_2BMF_6:Cr^{3+}\) series as: \((R_{Cr-F} - R_0) = f (R_{M-F} - R_0)\). We obtain values of \(R_0 = 1.908\) and 1.907 Å, and \(f = \) 0.06 and 0.09, for \(n = 3.3\) and 5, respectively. In either case, we conclude that there is an important lattice relaxation around \(Cr^{3+}\). Since \(R_{Cr-F}\) deviates from the equilibrium Cr-F distance, \(R_0 = 1.908\) Å, only the 6% the difference \(R_{M-F} - R_{Cr-F}\), confirming the stiffness of the Cr-F bond in comparison to the more ionic M-F bond.

**Figure 3.** \(10D_q\) derived from the excitation spectra as a function of \(R_{Cr-F}\) for the Cr-pure compounds of the series. The lines correspond to fits to the given expressions (see text).

**Figure 4.** Cr-F versus M-F distances in impurity systems. \(R_{M-F}\) has been derived from XRD, and \(R_{Cr-F}\) from \(10D_q\) using two different exponents in Eq. 1. Linear fits are given as a function of \(f\) and \(R_0\) (see text).
For all investigated compounds, the PL spectra consist of a single broad emission band peaking around 1.6 eV, which is related to the $^4T_{2g}(F) \rightarrow ^4A_{2g}(F)$ transition. $10Dq$ lies close but below the ESCO ($^4T_{2g} \leftrightarrow ^2E_g$) and thus, broad-band PL occurs instead of narrow R-line emission. Nevertheless it must be noted that the actual CF governing the PL crossover is given by the excited-state equilibrium Cr-F distance, $R_{Cr-F}^{exc}$. As Figure 2 shows, $\frac{\partial E_i}{\partial 10Dq} > 0$, then the linear electron-lattice coupling associated with this transition is negative, $\frac{\partial E_i}{\partial R_{Cr-F}^{exc}} < 0$, and thus $R_{Cr-F}^{exc} > R_{Cr-F}^{ESCO}$ for Cr$^{3+}$. This means that broad PL band can be observed even if the ground-state CF verifies $10Dq < 10Dq_{ESCO}$.

A puzzling result concerns the unexpected behavior of the PL Stokes shift, $E_S = E_i - E_{PL}$, with $R_{M,F}$. $E_S$ increases upon $R_{Cr-F}$ (or $R_{Cr-F}^{exc}$) reduction shows an opposite variation of $E_S$ with $R$ observed for Cr$^{3+}$ in chloroelpasolites and Mn$^{2+}$ in chloro- and fluoroperovskites. This different behavior is explained on the basis of electron-phonon couplings within the complex (MF$_6$) taking into account contributions from the stronger coupled modes: $a_{1g}$ and the Jahn-Teller $e_g$ mode [4].

High-pressure experiments carried out on Rb$_2$KCrF$_6$ provide additional knowledge on the interplay of the structural and vibrational properties and electronic configuration of these systems.

**Figure 5.** Configuration diagram of the $^2E_g$, $^4T_{2g}$ (excited) and $^4A_{2g}$ (ground) states. The excited state equilibrium coordinate $Q_0$ (with respect to the ground state coordinate) is associated with a bigger $R_{Cr-F}$ due to negative electron-phonon coupling coefficient (see figure 2 and text). The dotted lines represent the situation after the ESCO. $E_{em}^T$ is the $^4T_{2g}$ emission energy of state. Note that the ESCO occurs when the zero phonon lines ($E_{ZPL}^T$ and $E_{ZPL}^E$), respectively coincide. The oscillator strenght of the spin allowed $^4T_{2g} \rightarrow ^4A_{eg}$ transition is about an order of magnitude bigger. As a consequence, broad-band emission will be observed after ESCO.

**Figure 6.** Variation of photoluminescence with pressure. Note the presence of sharp features as a consequence of the pressure-induced $^2E_g \leftrightarrow ^4T_{2g}$ excited-state crossover (ESCO) at 7 GPa. The three sharp lines correspond to the $^2E_g \rightarrow ^4A_{2g}$ transition, and Stokes and antiStokes vibronic replicae.
The PL band (figure 6) experiences a blueshift of 0.09 eV with increasing pressure in the 0 – 7 GPa range, in agreement with the increase of $10Dq$ upon $R_{Cr-F}$ reduction. Above this pressure, sharp features appear corresponding to the mainly $^2E_g(G) \rightarrow ^4A_{2g}(F)$ zero-phonon line (ZPL), and the Stokes and anti-Stokes phonon replicas associated with the $\delta_{2u}$ vibrational mode [5].

PL lifetime increases with pressure from $\tau = 45 \mu$s (ambient pressure) to $\tau = 1.0$ ms (16.5 GPa). This variation confirms the occurrence of the ESCO phenomenon. According to the normal-coordinate configuration diagram of Figure 5, it actually takes place when the ZPL energy of $^4T_{2g}$ and $^2E_g$ coincides: $E_{ZPL}(^4T_{2g}) = E_{ZPL}(^2E_g)$. From the estimated ZPL for $^4T_{2g}$ and the observed band shifts [2], the variation of the ZPL-energy difference with pressure is given by $\Delta(E) = E_{ZPL}(^4T_{2g}) - E_{ZPL}(^2E_g) = 0.013 P - 0.065$, and thus the ESCO takes place at 7 GPa. It is worth noting the presence of broadband emission above the ESCO pressure at 7 GPa, reflecting the thermal population of the $^4T_{2g}(F)$ state. The oscillator strength for the spin-allowed $^1A_{2g}(F) \rightarrow ^4T_{2g}(F)$ transition is about an order of magnitude greater than the spin-forbidden $^2E_g(G) \rightarrow ^4A_{2g}(F)$ one, and therefore the broad band emission still dominates the PL spectrum at the ESCO pressure and even at higher pressures.

As it was observed along the fluoroelpasolite series upon decreasing $R_{Cr-F}$, the emission blueshift induced by pressure is smaller than the excitation blueshift ($\delta_{E_{ZPL}} > \delta_{E_{2g}}$), foreseeing an increase of the Stokes shift. Therefore the pressure results confirm that the PL properties and main spectral features of Cr$^{3+}$-doped elpasolites can be explained on the basis of a (CrF$_6$)$^{3-}$ complex, the variation of which is governed by the actual Cr-F bond distance imposed by the host crystal.

4. Conclusions
Throughout this work we show 1) the local structure around the impurity in Cr$^{3+}$-doped elpasolites can be derived from the corresponding optical spectra after structural correlation established in Cr$^{3+}$-pure elpasolite series. 2) The $R$-dependences of $10Dq$ and the Stokes shift exhibit anomalous deviations with respect to CF model expectations, due to the Fano resonance of the first absorption band of Cr$^{3+}$. 3) The PL properties along the elpasolite series or as a function of pressure can be understood on the basis of the (CrF$_6$)$^{3-}$ complex, whose actual Cr-F distance is mainly governed by either the host crystal or the external pressure. There is a strong lattice relaxation around Cr$^{3+}$ in Cr-doped elpasolites yielding either an inward or an outward relaxation of the fluorine octahedron depending on whether the host M-F distance is longer or shorter than $R_{Cr-F} = 1.903$ Å. 4) The $^2E_g(G) \rightarrow ^4T_{2g}(F)$ excited-state crossover takes place in the Cr-pure Rb$_2$KCrF$_5$ around 7 GPa. However this effect is not evidenced by the presence of sharp features at 7 GPa but about 12 GPa at room temperature. This pressure provides enough energy separation between $^4T_{2g}(F)$ and $^2E_g(G)$ to increase the population of the long-lived $^2E_g(G)$ state with respect to short-lived $^4T_{2g}(F)$ state at room temperature.

The present results point out that the selected A$_2$BMF$_6$: Cr$^{3+}$ crystals are suitable systems to establish structural correlations between optical properties and $R_{Cr-F}$.

Acknowledgements
The authors thank the Spanish Ministerio de Educación y Ciencia (Project No MAT2005-00099) and the Research Intensification program (I3) of the University of Cantabria.

References

[1] Guengard H 1994 PhD thesis (University of Bordeaux 1)
[2] Hernández I 2006 PhD thesis (University of Cantabria)
[3] Drickarmer H G and Frank C W 1973 Electronic transitions and the high pressure chemistry and physics of solids (London: Chapman & Hall)
[4] Hernández I, Rodríguez F and Tressaud A 2007 submitted
[5] Dolan J F, Kappes L A and Bartram R H 1986 Phys. Rev. B 33 7339.