Cross-luminescence of complex halide crystals

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Abstract. The cross-luminescence (CRL) resulting from radiative electronic transitions from the mainly anion-related valence band to the uppermost cation core band has been studied in a number of complex halides containing CsCl, RbF, KF, and BaF$_2$. The energy of the CRL photons is determined by the energy difference of the two bands, and the shapes of the spectra reflect the grouping of the molecular orbitals in the clusters involving cations with a hole in the core shell and nearest-neighbour halide ions. For crystals with more than one type of cation, the spectrum reveals information about the 'active' cation which contains the core hole and also about the other cations. Correlations have been established between the local symmetry of the clusters in different crystals and the number and position of the subbands in the CRL spectra.

1. Introduction

It is now well established that in a number of simple and complex halides a specific intrinsic luminescence can be observed due to radiative electronic transitions from the mainly halogen-related valence band to the uppermost cation core band (see e.g. [1–5] and references therein). As analogous transitions in x-ray spectroscopy are called 'cross-transitions' the term 'cross-luminescence' (CRL) was proposed for this type of luminescence [2]. It is observed only in materials where the energy differences between the levels involved are too small for non-radiative Auger transitions involving transfer of electrons from the valence band to the conduction band. Therefore the term 'Auger-free luminescence' was independently suggested for the same process [3]. The CRL materials are mainly wide-band-gap fluorides and chlorides containing at least one type of alkaline or alkaline-earth cation with relatively low ionization potentials, i.e. having the corresponding uppermost core bands not far from the valence band. The CRL can only be excited by photons or particles with energy sufficient to create holes in the uppermost core band and therefore the optical excitation spectra have thresholds corresponding to the ionization energies of cations. This peculiarity of the CRL usually serves as the proof for the existence of this type of luminescence.

As a close correlation was established between the CRL and x-ray photoelectron spectroscopy (XPS) data [2], the CRL spectra were explained with the band structure approach in which the emission maxima were ascribed to the density of states maxima

of the valence band. The process itself was regarded as a recombination of quasi-free holes in the core band with valence band electrons. More detailed analysis, taking into account the electronic and vibrational relaxation of the excitations before the phototransition, led to the conclusion that an approach using a cluster model of strongly localized excitations is more appropriate. The results of the first cluster calculations [6–9] are in reasonable agreement with experimental data.

The aim of this study is to present experimental results on CRL in complex halides and to systematize the observed CRL spectra in accordance with the local symmetry of the excitations giving rise to CRL. The peculiarities of the CRL in several perovskite-type crystals with structural phase transitions are discussed, taking into account the recent results of decay kinetics measurements.

2. Experimental details

The spectra and decay kinetics of the CRL were studied under excitation with a 7 keV pulsed electron beam with a current density of about 100 μA cm^2. The experimental set-up based on a Seya–Namioka-type vacuum monochromator with a concave diffraction grating (1200 grooves mm^{-1}) was as described earlier [10]. The spectra were measured in the photon counting regime using an FEU-106 photomultiplier with an MgF$_2$ entrance window. To measure separately the CRL spectra with their nanosecond decay, the photons were counted during the 30 ns immediately after the excitation pulses. The decay kinetics were studied by the correlated photon counting method under excitation with electron pulses about 100 ns long with 2 ns decay time. This was also the limit of the shortest measurable CRL decay times.

For the CRL measurements, small crystal samples of about $1 \times 1 \times 0.5$ mm^3 were attached to the cryostat's cold finger using indium metal. The KF-based complex fluorides were obtained by the method of hydrothermal synthesis in the reaction of solutions of KF with the corresponding oxides. The complex RbF- and BaF$_2$-based fluoride crystals and CsCl-based crystals were obtained by growing from the melt.

3. Results and discussion

3.1. BaF$_2$-based complex fluorides

The CRL of BaF$_2$ crystals has been widely studied, and the calculations on the cluster (Ba^{3+}F$_8$) give an explicit explanation for the observed CRL emission spectrum [7]. The BaF$_2$ CRL emission spectrum with its main maxima at 6.36 and 5.64 eV is shown in figure 1. We have measured the CRL spectra of two complex Ba-containing fluorides and analysed the results taking into account the different crystallographic and electronic structure of the crystals.

LiBaF$_3$ crystals have the antiperovskite-type cubic structure (space group $Pm3n$) with lattice constant $a = 3.988$ Å [11]. The Ba^{2+} ions have 12 nearest-neighbour (NN) F$^-$ ions at a distance of 2.82 Å. The CRL spectrum, shown in figure 1, is wider than that of BaF$_2$ and extends further in the vacuum ultra violet (VUV) region which is in accordance with XPS measurements [12]. The presence of two main maxima in the emission spectrum was also revealed by calculations on the (Ba^{3+}F$_{12}$) cluster

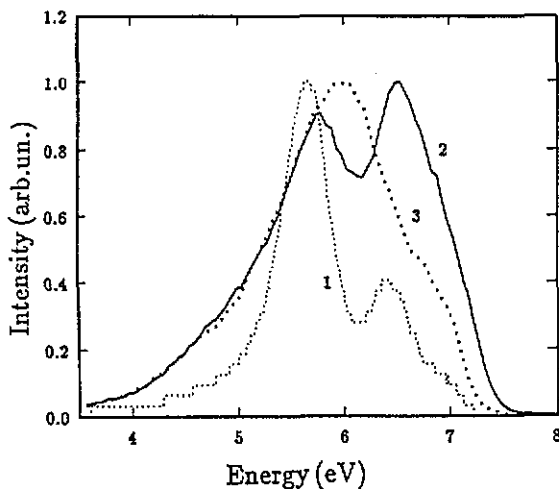**Figure 1.** Cross-luminescence spectra at 300 K. The spectra are normalized to 1 at the maximal emission intensity. (1) BaF_2; (2) $LiBaF_3$; (3)$BaMgF_4$.

[9], and are directly related to the so-called bonding and antibonding groups of the neighbouring 36 fluorine p orbitals.

$BaMgF_4$ has the orthorhombic $BaFeF_4$ type lattice where the Ba^{2+} ions are surrounded by six F^- ions at the apices of a distorted trigonal prism with two more F^- ions located in the equatorial plane through the rectangular prism faces [13]. Consequently, the coordination number of Ba is eight as in BaF_2, but the local symmetry of the (BaF_8) cluster is much lower. One broad maximum is observed in the CRL spectrum with, except for a shoulder at the high-energy side of the emission spectrum, no pronounced structure. Detailed theoretical analysis of the molecular orbital (MO) structure of clusters with such a low symmetry has not yet been carried out. However the theoretical work on the low-symmetry case K_2LiGaF_6, described in [9], is consistent with the observed spectrum.

3.2. KF-based complex fluorides

Because of the relatively high ionization energy of the K^+ 3p shell and the correspondingly large energy separation between the valence band and the core band, the CRL of KF-based compounds is observed mainly in the VUV region. Having studied the CRL spectra of various KF-containing complex fluorides with different crystallographic structures, we can now try to analyse the shapes of the CRL spectra from a common standpoint.

In the simplest case of KF, the theory predicts one main emission band [6–8] corresponding to the $a_g \rightarrow t_{1u}$ and $e_g \rightarrow t_{1u}$ transitions in the (KF_6) clusters. Experimentally observed spectra of this [14], see figure 2 and other octahedral clusters like (RbF_6) [2] in RbF see figure 8 and ($CsCl_6$) in Cs-doped KCl [15], contain besides the main maximum a small additional one at higher energy. The origin of it is not yet clarified. We have not studied compounds containing (KF_8) clusters with cubic symmetry. The $KMgF_3$ perovskite crystals have (KF_{12}) clusters with nearly perfect cubic symmetry. In accordance with the analysis described for the analogous clusters (BaF_{12}) we again obtain two main bands with nearly equal intensity [9].

The structure of $KCaF_3$ can be represented as slightly distorted perovskite. As a result, the CRL spectrum at 80 K is rather similar to that of $KMgF_3$ [14]. At
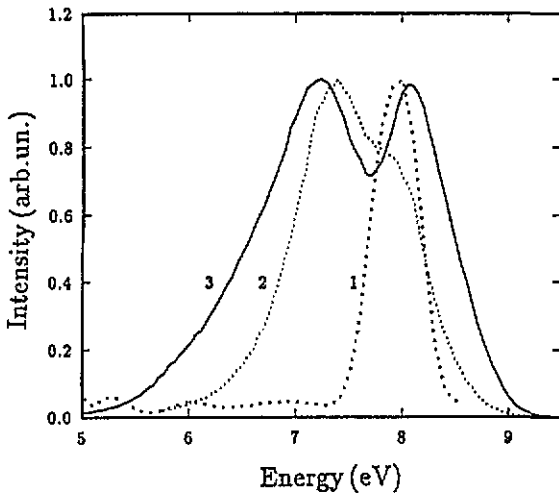
Figure 2. Normalized CRL spectra. (1) KF at 80 K; (2) $KCaF_3$ at 300 K; (3) $KMgF_3$ at 300 K.

room temperature, the double peak structure is not resolved clearly (see figure 2). Evidently the insignificant deviations from the cubic symmetry of the (KF_{12}) cluster do not cause substantial changes in the structure of MOs.
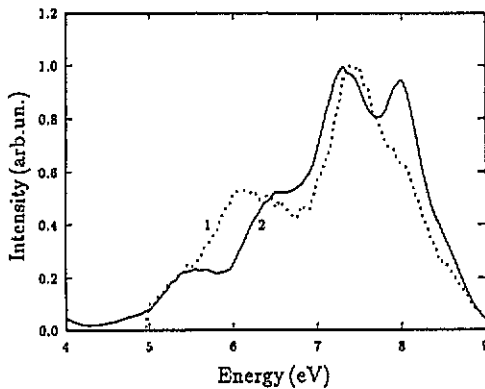

Figure 3. Normalized CRL spectra. (1) K_2LiGaF_6 at 80 K; (2) K_2NaAlF_6 at 300 K.
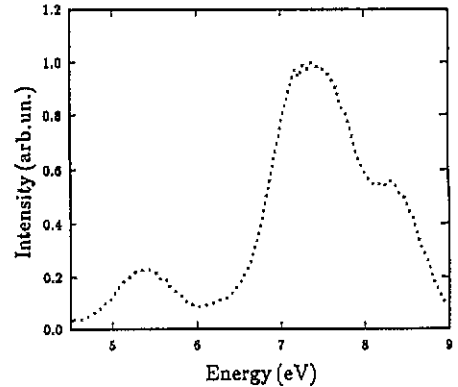
Figure 4. Normalized CRL spectra of K_2SiF_6 at 300 K.

A very 'rich' structure of CRL spectra is observed in the elpasolites K_2LiGaF_6 and K_2NaAlF_6 (see figure 3). In these crystals, the local symmetry (C_3) of the (KF_{12}) cluster is rather low [16], and as a result the MOs are spread over a wide range of energy. Calculations on the (KF_{12}) cluster revealed also the 'rich' structure extending over a wide energy range [9]. It was found that the Al^{3+} ions cause an energy lowering of a certain group of the 36 p orbitals belonging to the 12 fluorine ions surrounding the K^+ ion. This group of orbitals explains the structure in the CRL spectrum in the 5–7 eV region. XPS measurements give a valence band width of about 8 eV [12]. As the result of the relatively low energy resolution and sensitivity of the method, it is difficult to determine with certainty the existence and the width of the gap between the valence band and the core band.

Still stronger deviation from the cubic symmetry field around K^+ ions is observed in K_2SiF_6. This material is also cubic elpasolite at high temperatures but changes into the hexagonal structure below 350 °C [17]. The CRL spectrum (see figure 4) shows a transition in the 5-6 eV region separated by a deep minimum from the main transitions at high energies. This is anticipated to be the result of fluorine subbands lowered in energy due to interactions with the Si cations.

In a number of complex fluorides such as K_2YF_5 and KYF_4, the symmetry of K^+ ions is very low. The K_2YF_5 crystals can be represented as parallel infinite chains of (YF_7) polyhedra linked by edges. The K^+ ions are positioned between the chains and have eight NN F^- ions at different distances. The CRL spectra of such fluorides have one wide asymmetric maximum (see figure 5).
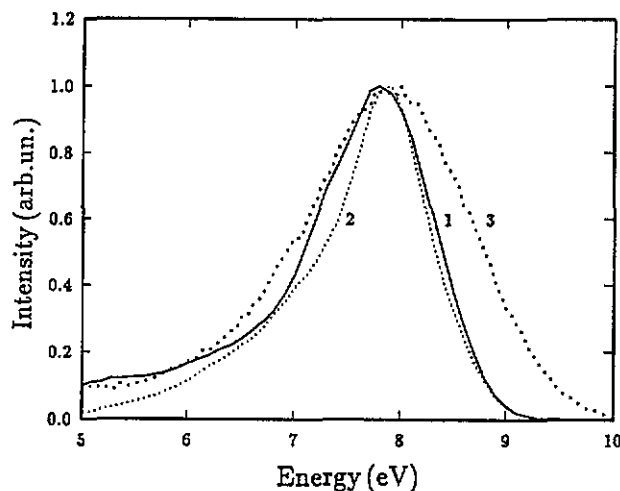

Figure 5. Normalized CRL spectra. (1) K_2YF_5 at 300 K; (2) KYF_4 at 300 K; (3) K-Be-fluoride glass at 300 K.

CRL is observed also in disordered fluorides, e.g. in potassium–beryllium fluoride glass [18] (see figure 5). The structure of this glass can be represented as a network of corner-linked BeF_4 tetrahedra with K^+ ions distributed between them. The CRL spectrum is similar to that of low-symmetry crystals with the peculiarity that it is wider and extends further to the high-energy side.

Summarizing the data on CRL in complex KF-containing fluorides, we can conclude that radiative core–valence transitions can be observed in various materials with different local symmetry of K^+ ions. The width of the CRL spectrum reflects the width of the valence band and the cluster approach allows us to describe, at least qualitatively, the shape of the observed spectra.

Although the main CRL emission in all cases is above 4–5 eV, in elpasolites a weak emission with a fast decay is observed at lower energies where it overlaps with other types of emission. To get a full picture on the CRL spectrum, time-resolved spectral measurements are necessary in the visible spectral region down to 1–2 eV energies.

3.3. The peculiarities of CRL in crystals with structural phase transitions (SPT)

The first observation of the dependence of CRL spectra on the structure of the material dates back to 1977 when Ackerman *et al* observed a significant difference in the electron-beam-induced luminescence spectrum below and above the SPT temperature

in CsCl at 733 K [19]. Below the SPT temperature, a spectrum with two maxima located at 5.2 and 4.6 eV was observed. Calculations on the (CsF_8) cluster also showed, similarly to the (BaF_8) cluster in BaF_2 crystals, two main maxima [7,8]. A spectrum with one dominating maximum was observed experimentally at higher temperatures. Such a spectrum is typical for crystals with a face-centered cubic structure such as KF and RbF.

The first attempts to observe the influence of the SPT on the CRL spectra in perovskite-type crystals gave seemingly negative results. There were no abrupt changes at the phase transition temperature in the CRL spectra of $CsCaCl_3$ at 95 K and in $CsSrCl_3$ at 362 and 380 K [20]. Nevertheless, a very significant shift in the CRL spectrum at the high-energy side was observed over the whole temperature region together with some change in the shape of the spectrum. This can be observed for $CsCaCl_3$ in figure 6 and for $CsSrCl_3$ in figure 7. The same pattern, a gradual change of the spectrum, is observed in $RbCaF_3$, having a cubic to tetrahedral phase transition at 195 K [21] (see figure 8). At higher temperatures, the spectrum is in general similar to that of $KMgF_3$, having two maxima of nearly equal intensity located near 5.2 and 4.5 eV. With decreasing temperature, an additional maximum appears near 6 eV already well above the SPT temperature and grows gradually up to 80 K.
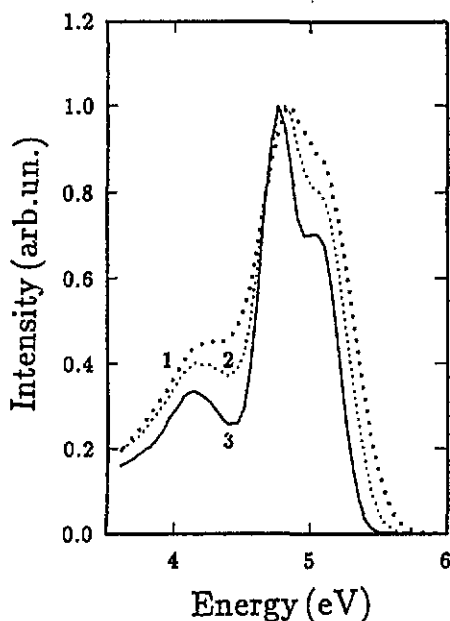

Figure 6. Normalized CRL spectra of $CsCaCl_3$. (1) 300 K; (2) 200 K; (3) 105 K.
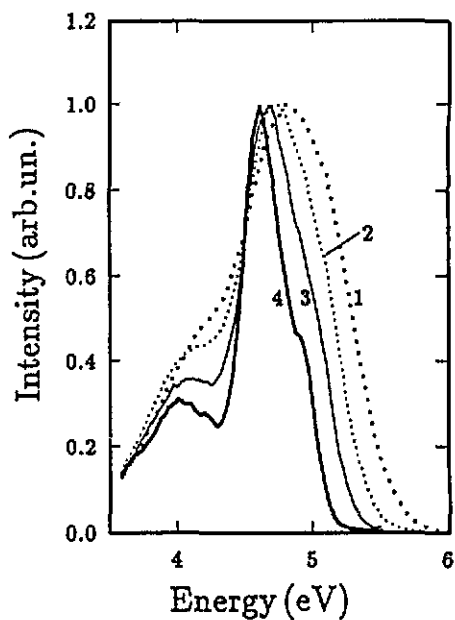
Figure 7. Normalized CRL spectra of $CsSrCl_3$. (1) 400 K; (2) 300 K; (3) 200 K; (4) 80 K.

Our working hypothesis for the interpretation of these effects is based on the analysis of the relaxation of the cluster with a core hole. The results of previous calculations showed considerable inward relaxations of the NN anions surrounding the cation with the core hole in simple halides [6–9]. These relaxations are usually greater than the changes of lattice constant when going from 300 K to 4 K. Nevertheless no
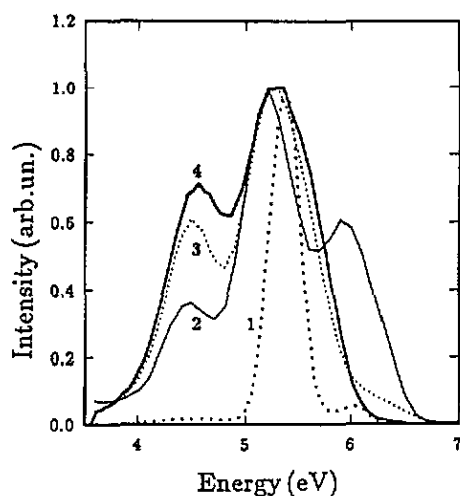
Figure 8. Normalized CRL spectra. (1) RbF at 80 K; (2) RbCaF$_3$ at 80 K; (3) RbCaF$_3$ at 200 K; (4) RbCaF$_3$ at 300 K.

strong changes of CRL spectra are observed in simple halides, which indicates that the local symmetry of the relevant cluster remains the same.

The situation is different in perovskites with SPTs where the relatively rigid octahedra (MeX$_6$), with alkaline-earth ions surrounding the alkali ion, have several degrees of freedom. In RbCaF$_3$, the coordinated rotations of these octahedra lead to the macroscopic phase transition at 195 K [21]. It can be assumed that analogous local rearrangements of octahedra surrounding the alkali cation can take place when the core hole is created, even above the SPT temperature.

In a recent work by Kamenskikh *et al*, two different decay times were observed in the CRL of RbCaF$_3$, CsCaCl$_3$, and CsSrCl$_3$ [5]. Unfortunately the authors could not measure separately the decay times for the individual bands of the CRL spectra. Therefore, we can only guess that the growing intensity of the fastest-decay component in RbCaF$_3$ is connected mainly with the high-energy component in the CRL spectrum which grows also at lower temperatures (see figure 8). Time-resolved spectra are necessary to make a final conclusion.

One more general point deserves discussion here. As has been stated earlier [2], only one decay pattern can be observed for various CRL bands if there is only one type of cluster with a core hole. In such a case the decay of all bands reflects the lifetime of the holes which in turn is determined by the sum of transition probabilities of all possible transitions. So the observed decay time is shorter than the individual decay would be, even for the 'fastest' transition. The existence of two different decay components [5] can only be explained if we assume that two different types of relaxed cluster exist with different symmetry and consequently different transition probabilities and hole lifetimes. Within each cluster, the decay time can depend on temperature in an individual way.

We have no experimental data on the symmetry of the relaxed clusters, e.g. in RbCaF$_3$, but the very existence of the cubic and tetragonal phases and the presence of soft vibrational modes allows us to suggest as the simplest choice that there are at least two minima on the potential surface which can be reached from the unrelaxed 'as-created' hole state. The probability that the lower-symmetry cluster will be formed gradually increases as the temperature decreases, but there is no abrupt change at the SPT temperature. This can be understood because the hole in the uppermost cation

core shell causes strong perturbation of the electronic and ionic subsystems of the crystal which is largely independent of the macroscopic symmetry of the crystal.

4. Summary

The general concept of CRL—radiative electronic transitions from the valence band to the cation core states—has been established now in a large number of halide materials. In many cases detailed understanding of the nature of these transitions can be reached by analysing the structure of MO of clusters centered on cations with core holes. The reasonable correlation between the experimentally determined and 'simulated' CRL spectra demonstrates the usefulness of such an approach. The next step would be to solve the reciprocal problem: the reconstruction of the electronic structure of the valence states of unexcited crystals from the CRL spectra. The high-energy resolution of the CRL spectra gives rather detailed information about the relaxed clusters' electronic energy structure. On the other hand, the XPS spectra reflecting the structure of unrelaxed electronic systems have much lower resolution and accuracy because of a lower signal to noise ratio.

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