

Relative halide-concentration dependence of the F-centre optical absorption properties in $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystals: influence of Eu^{2+} -cation vacancy dipoles

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The influence of Eu^{2+} -cation vacancy ($I-V$) dipoles on the relative halide-concentration dependence of the F-centre optical absorption properties in $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystals has been investigated. These crystals are made of a single mixed face-centred cubic (FCC)-phase whose unit-cell size a_0 obeys the Vegard's rule, and their optical absorption spectrum consists of a single F-band whose spectral width depends on x , reaching 0.414 ± 0.006 eV at $x = 0.5$, and whose spectral frequency ν_m and equivalent energy ε_m satisfy the equations $\nu_m a_0^{2.24 \pm 0.09} = 26 \pm 2$ and ε_m (eV) = $(0.06 \pm 0.01)x^2 + (0.16 \pm 0.01)x + (1.98 \pm 0.01)$. Comparison with the F-centre optical absorption properties reported elsewhere for pure FCC alkali-halide and $\text{KCl}_x\text{Br}_{(1-x)}$ crystals showed that in $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystals, the alkali and halide ion sizes drive mainly the F-band spectral position, and also that this position is more sensitive to changes in a_0 in $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystals than in pure FCC alkali-halides. This is due to the crystalline electric field distortion caused locally at the F-centre by the mixed halide surroundings. This distortion affected the F-band spectral position in $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystals to a lesser extent than it did in $\text{KCl}_x\text{Br}_{(1-x)}$ crystals. This might be due to the presence of $I-V$ dipoles.

Keywords: F-centres; Eu^{2+} -cation vacancy dipoles; Optical properties; Mixed alkali halides; X-ray diffraction

1. Introduction

From a structural point of view, $\text{KCl}_x\text{Br}_{(1-x)}$, where $0 < x < 1$ is the Cl^- -relative halide-concentration, was the first ever studied mixed alkali-halide crystalline system. Currently, it is well known that this system is completely miscible [1] and that it can be described [2–4] by using a face-centred cubic (FCC) crystal lattice whose unit-cell size a_0 can be computed by applying the rule $a_0 = xa_{01} + (1-x)a_{02}$ (known nowadays as the Vegard's rule), where a_{01} and a_{02} are the unit-cell sizes of KCl and KBr, respectively. This knowledge, together

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with the fact that single crystals of the system $\text{KCl}_x\text{Br}_{(1-x)}$ are optically transparent, makes this crystalline system suitable for studying the influence of the x concentration on the optical properties of any optically active singularity within its mixed crystal matrix. In particular, the optical properties of F-centres and Eu^{2+} -ion impurities have been separately investigated to some extent. The F-centre optical absorption band in pure $\text{KCl}_x\text{Br}_{(1-x)}$ crystals, previously grown in a nitrogen atmosphere by a pulling technique and then coloured by irradiating them with 3 MeV electrons, was studied by Smakula *et al.* [5] for $x = 0.75, 0.50$ and 0.25 . They found that the spectral position of this band depends on x in such a way that the band-maximum spectral energy ε_m is not a linear function of x but deviates, in an amount $\Delta\varepsilon_m$, towards lower energy, in relation to an imaginary straight line connecting the band-maximum spectral energies corresponding to KCl and KBr crystals, reaching a maximum $\Delta\varepsilon_m$ value of about 0.03 eV at $x = 0.5$. These results were later confirmed [6] when working with a batch of coloured $\text{KCl}_x\text{Br}_{(1-x)}$ crystals prepared by using a wide variety of x values ($x = 1, 0.98, 0.97, 0.96, 0.94, 0.87, 0.62, 0.46, 0.39, 0.29, 0.15$ and 0) and irradiated with Cu-X-rays, obtaining the additional result that $\Delta\varepsilon_m$ changes quadratically with x . Smakula *et al.* [5] also compared the observed $\Delta\varepsilon_m$ values in crystals of $\text{KCl}_x\text{Br}_{(1-x)}$ with the $\Delta\varepsilon_m$ values, also obtained by the same group, corresponding to crystals of $\text{KCl}_x:\text{RbCl}_{(1-x)}$ and $\text{RbCl}_x:\text{KBr}_{(1-x)}$. They found that the observed band-maximum spectral energy deviation is the same whether cations or anions only, or both simultaneously, are exchanged. Therefore, they concluded that the distortion caused in the crystalline electric field by the substitution of different ions is responsible for the observed deviation in spectral shift. The F-absorption band spectral position data included in the article by Smakula *et al.* [5] obey a relation of the form $\nu_m a_0^N = C$, where ν_m is the F-band maximum spectral frequency and N and C are constants. A relation of this form (known as a Mollwo–Ivey-type relation) was first established theoretically by Fröhlich [8], and then empirically by Mollwo [9, 10] and Ivey [11] for FCC alkali-halide crystals, and the best fit, by using the least squares method, through Mollwo’s experimental data gives [7] an N value of 1.83. The importance of a Mollwo–Ivey-type relation is that it means that the F-centre has been formed within the crystal lattice, otherwise ν_m would not have a simple relation with a_0 . In contrast, the optical properties of Eu^{2+} -ion impurities in non-coloured $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystals have been investigated [12–14] as a function of x for different thermal treatments. The optical emission spectrum of freshly quenched $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ single-crystals consists of a single band which has been ascribed to the presence of isolated Eu^{2+} -cation vacancy dipoles within the mixed crystal matrix, whereas the optical emission spectrum of long-annealed $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ single-crystals consists of two bands which can be deconvoluted in four contributions. One of these contributions has been ascribed to the presence of isolated Eu^{2+} -cation vacancy dipoles and the other three to different metastable secondary mixed Eu^{2+} -dihalide phases. Even when the aggregation–precipitation states of the Eu^{2+} -ion impurity in $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystals is expected to influence the x dependence of the F-centre optical absorption properties, such as it has been observed [15] to occur in $\text{KCl}:\text{Eu}^{2+}$ and $\text{KBr}:\text{Eu}^{2+}$ crystals, no studies have been performed, as far as we are aware, on this matter.

The present work was undertaken to study the influence of the presence of Eu^{2+} -cation vacancy dipoles on the Cl^- -relative halide-concentration dependence of the F-centre optical absorption properties in $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystals. This was done by using optical spectrophotometry to monitor the spectral position and shape of the F-centre absorption band in freshly quenched $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ single-crystals prepared with different values of x for a whole x -range. In parallel, the unit-cell size of these crystals was monitored using powder X-ray diffractometry to investigate the consequences that the existence of these dipoles had on the disordered substitutional solid-solution character of the $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystalline matrix.

2. Experimental details

Transparent $KCl_xBr_{(1-x)}\cdot Eu^{2+}$ single-crystals, pear-like in shape (about 4 cm in length and 2 cm in major diameter), were grown by using the Czochralski method [16] from a melt at 750 °C prepared by mixing different relative molar concentrations of chemically pure KCl and KBr salts ($x = 1, 0.99, 0.95, 0.85, 0.75, 0.60, 0.50, 0.45, 0.30, 0.15, 0.10, 0.05, 0.01$ and 0.0). Chemically pure $EuCl_2$ salt, in a concentration of about 0.1% by weight, was added to the mix in all the cases. A dry argon atmosphere was maintained inside the growth chamber to minimize the contamination by molecules and ions in the air, like H_2O , O_2 and OH^- . The crystals that grew were found to cleave easily along the $\{100\}$ -planes, and, crystal slices of about $0.5\text{ cm} \times 0.5\text{ cm} \times 0.05\text{ cm}$ were cleaved along these planes. The slices were then quenched, by dropping them onto a copper block at room temperature after they had been heated at 500 °C for 45 min, in order to dissociate any europium di-halide aggregates formed within the crystal as a result of the growing process. F-centres were created in the quenched crystal plates by irradiating them in the dark for 20 min at room temperature with unfiltered Cu-X-rays. This was done with the aid of a Philips PW1729 X-ray generator working under operation conditions of 30 kV and 20 mA. Once irradiated, the crystal slices were transported, inside a metallic envelope to prevent undesired effects of bleaching, to a Milton-Roy Spectronic 3000 spectrophotometer, in order to obtain their optical absorption spectra. Some of the quenched crystal slices were ground to powder in an agate mortar and then mixed with a powder of standard silicon (in concentration of about 20% by weight) in order to get suitable specimens for powder X-ray diffractometry. Powder X-ray diffraction analyses were made for phase identification and unit-cell size monitoring purposes with the help of a Siemens D5000 diffractometer equipped with a Cu-anode X-ray tube (working at operation conditions of 35 kV and 25 mA), a primary-arm variable divergence diaphragm and a secondary-arm graphite monochromator. X-ray diffractograms taken for phase identification purposes were recorded from 20° to 100° in twice the Bragg angle (2θ) by using a counting time of 1 s per scanning step of 0.02°. As the 2θ -position of the observed high-angle (600)-reflection was used to monitor the unit-cell size, X-ray diffractograms taken for such a purpose were recorded from 87° to 97° in 2θ , by using a counting time of 2 s per a scanning step of 0.01°. The 2θ -position of this reflection was measured and then corrected for any systematic deviation by using a calibration curve previously built by plotting the differences between the measured and the expected 2θ -positions for the (511) and (422)-reflections from the silicon used as an internal standard against 2θ . From the calibrated 2θ -positions, the corresponding interplanar distances $d_{(600)}$ were obtained by means of the Bragg's law. This was then used to obtain the corresponding unit-cell sizes a_0 with an accuracy of about 0.002 Å.

3. Results

Figure 1 shows the powder X-ray diffractogram of a typical freshly quenched $KCl_{0.5}Br_{0.5}\cdot Eu^{2+}$ crystal. The (hkl)-line patterns of KCl and KBr, as taken from the Powder Diffraction File of the International Centre for Diffraction Data [17], are included in the figure for the sake of comparison. This diffractogram, consisting of a number of well-defined Bragg reflections, each appearing systematically between an (hkl)-line of KBr and the corresponding (hkl)-line of KCl, shows that the sample under study is made of a fully crystallized FCC-phase of a unit-cell size between 6.2917 Å and 6.6005 Å (the unit-cell sizes of KCl and KBr, respectively [18, 19]). Actually, this diffractogram was properly indexed on the basis of an FCC-phase with a unit-cell size of about 6.45 ± 0.01 Å. However, this value was found to change with x .

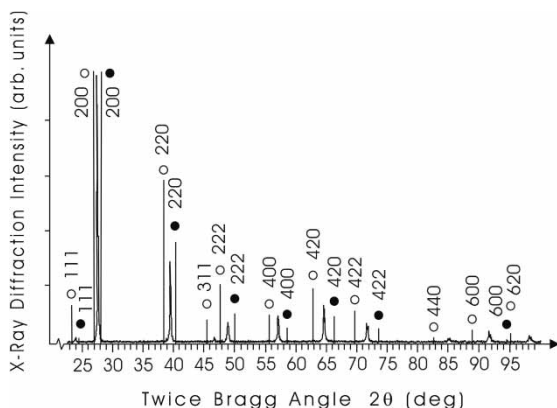


Figure 1. Powder X-ray diffractogram of a $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystal grown from a melt prepared with equal molar fractions of pure KCl and KBr salts and 0.1% in weight of EuCl_2 . The diffraction lines corresponding to KCl (○) and KBr (●) in the Powder Diffraction File of the International Centre for Diffraction Data are also shown.

This change was monitored by measuring the 2θ -position of the observed high-angle (600)-reflection for different values of x , and then calculating the corresponding a_0 values from these positions. Figure 2 shows the profile sequence of this reflection for $x = 1, 0.99, 0.95, 0.85, 0.75, 0.60, 0.50, 0.45, 0.30, 0.15, 0.10, 0.05$ and 0.01. The second column of table 1 shows the a_0 values obtained from these profiles. Figure 3 shows the graph then built by plotting a_0 against x . This graph shows for the first time that the Vegard's rule is strictly obeyed, in the whole range of x , by the crystalline $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ system, and therefore that, under the doping concentrations used, the mixed alkali-halide crystalline matrix of this system has the character of a typical disordered substitutional solid-solution. This result was confirmed by the results obtained from optical spectroscopy. Figure 4 shows the optical absorption spectrum of a typical freshly quenched $\text{KCl}_{0.5}\text{Br}_{0.5}:\text{Eu}^{2+}$ crystal after being irradiated with X-rays. In addition to the two absorption bands due to the impurity Eu^{2+} -ion, this spectrum consists of a single F-absorption band, indicating that the F-centres responsible for this band are immersed into a crystalline environment [20]. Figure 4 also shows that the observed F-absorption band lies between the spectral positions expected for the maximum of

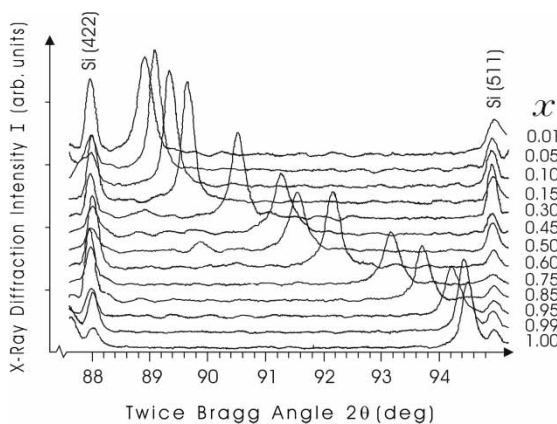


Figure 2. Graphical sequence of the observed X-ray powder (600)-reflections corresponding to $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystals for $x = 1, 0.99, 0.95, 0.85, 0.75, 0.60, 0.50, 0.45, 0.30, 0.15, 0.10, 0.05$ and 0.01. The (511) and (422)-reflections corresponding to silicon, used as internal standard, are also shown.

Table 1. F-Centre absorption band and unit-cell size data for $KCl_xBr_{(1-x)}:Eu^{2+}$ crystals.

Cl ⁻ -relative halide concentration x	Unit-cell size a_0 (± 0.002 Å)	F-band peak energy ε_m (± 0.005 eV)	F-band peak frequency ν_m (± 0.009) $\times 10^{14}$ s ⁻¹	F-band FWHM value w (± 0.006 eV)
0.00	6.600	1.976	4.769	0.360
0.05	6.585	1.989	4.800	0.374
0.15	6.551	1.998	4.823	0.397
0.30	6.505	2.034	4.909	0.387
0.45	6.462	2.068	4.917	0.406
0.50	6.447	2.074	5.007	0.414
0.60	6.414	2.100	5.067	0.411
0.75	6.361	2.125	5.145	0.411
0.85	6.332	2.162	5.190	0.406
0.95	6.306	2.181	5.263	0.391
1.00	6.293	2.212	5.338	0.380

this band in Eu^{2+} -doped KCl^{21} and Eu^{2+} -doped KBr^{22} crystals (these positions are indicated in the figure by vertical lines). Actually, the F-absorption band observed in figure 4 was found to shift between these two spectral positions, and also to change in shape, as x changes from 1 to 0. Figure 5 shows the profile sequence of this band for $x = 1, 0.95, 0.85, 0.75, 0.60, 0.50, 0.45, 0.30, 0.15, 0.05$ and 0.0 . The F-band-maximum energies ε_m and full-width-at-half-maximum values w corresponding to these profiles were measured in electron volts (listed in the third and fifth columns, respectively, of table 1) and then used to build the graphs shown in figures 6 and 7, respectively. Figure 6 shows that ε_m is not a linear function of x but deviates towards lower energy by an amount $\Delta\varepsilon_m$ (which reaches a maximum value at $x = 0.5$), in relation to an imaginary straight line (broken line in the figure) connecting the ε_m values corresponding to $x = 1$ and $x = 0$. This general behaviour was found to be similar to the studied behaviour [5] of the F-band-maximum energy in the case of pure $KCl_xBr_{(1-x)}$ crystals irradiated at room temperature by using 3 MeV electrons. However, in that case, a maximum value of about 0.03 eV was reported for $\Delta\varepsilon_m$, whereas in our case $\Delta\varepsilon_m$ was found to reach a maximum value of 0.021 ± 0.005 eV. The observed behaviour of ε_m , as a function of x , in Eu^{2+} -doped $KCl_xBr_{(1-x)}$ crystals was modelled well by a quadratic equation of the form

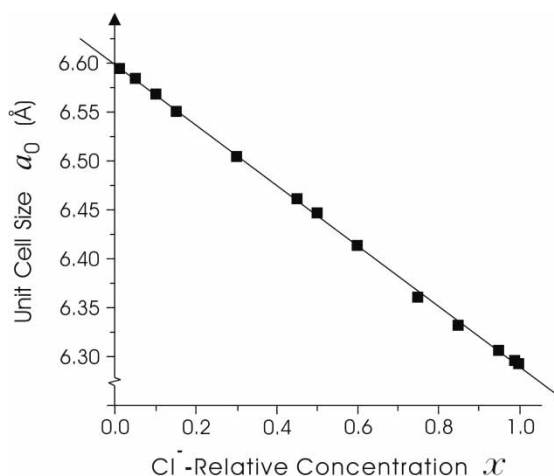


Figure 3. Plot of the unit-cell size a_0 against the concentration x for the crystalline $KCl_xBr_{(1-x)}:Eu^{2+}$ system. For the sake of comparison, a straight line (solid line) has been fitted to the plotted data.

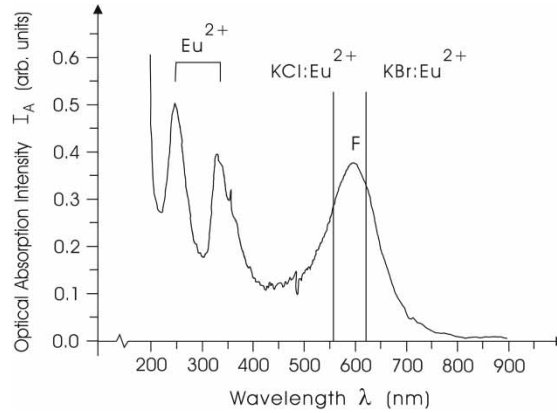


Figure 4. Optical absorption spectrum of an X-ray irradiated $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystal grown from a melt prepared with equal molar fractions of pure KCl and KBr salts and 0.1% in weight of EuCl_2 . The spectrum consists of a single F-band (F), in addition of other two bands due to the impurity Eu^{2+} -ion (Eu^{2+}). The spectral positions expected for the F-band peak in coloured $\text{KCl}:\text{Eu}^{2+}$ and $\text{KBr}:\text{Eu}^{2+}$ are indicated by means of vertical lines.

ε_m (eV) = $(0.06 \pm 0.01)x^2 + (0.16 \pm 0.01)x + (1.98 \pm 0.01)$ (full line in figure 6). It is worth mentioning that an equation of this form has been reported [6] to be satisfied by ε_m and x in the case of pure $\text{KCl}_x\text{Br}_{(1-x)}$ crystals irradiated with Cu-X-rays. In contrast figure 7 shows that w follows a hump-like curve, as the Br^- ions are substituted for the Cl^- ions,

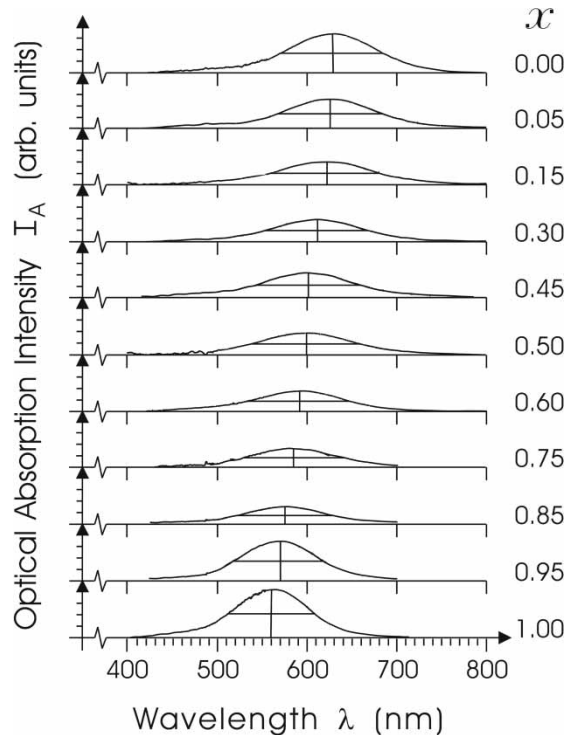


Figure 5. Graphical sequence of the observed F-absorption bands corresponding to coloured $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystals for $x = 1, 0.95, 0.85, 0.75, 0.60, 0.50, 0.45, 0.30, 0.15, 0.05$ and 0.0 . The peak positions and FWHM values of these bands are indicated by means of vertical and horizontal lines, respectively.

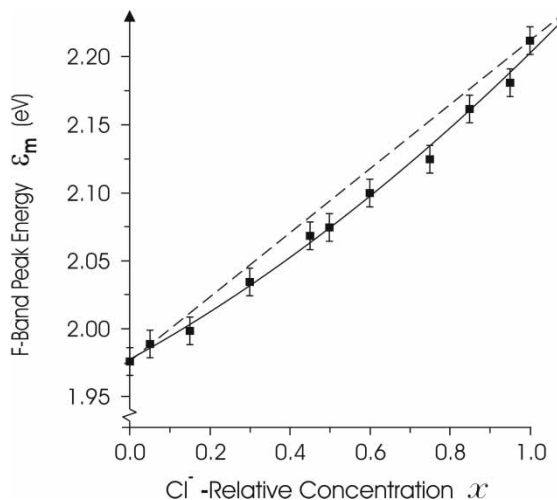


Figure 6. Plot of the F-band maximum energy ε_m against the concentration x for the crystalline $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ system. A quadratic curve of the form $\varepsilon_m = (0.06 \pm 0.01)x^2 + (0.16 \pm 0.01)x + (1.98 \pm 0.01)$ has been fitted (solid line) to the plotted data. For the sake of comparison, a straight line connecting the ε_m values corresponding to $x = 1$ and $x = 0$ is also shown (broken line).

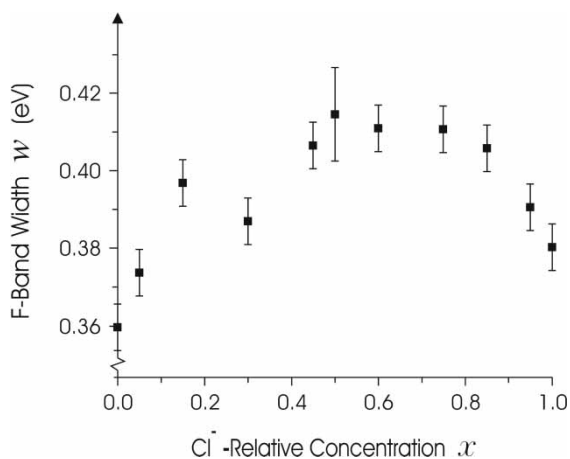


Figure 7. Plot of the F-band FWHM-value w against the concentration x for the crystalline $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ system.

starting at about 0.359 eV to reach a maximum value of about 0.414 ± 0.006 eV for $x = 0.5$ and then ending at about 0.374 eV. This behaviour does not differ experimentally from the reported behaviour for the F-band width in pure $\text{KCl}_x\text{Br}_{(1-x)}$ crystals [5].

4. Discussion

In order to compare easily the observed x -dependence of the spectral position of the F-absorption band in $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ crystals with the unit-cell size dependence of the spectral position of this band in different pure FCC alkali-halide crystals [8–11], the measured ε_m values listed in the third column of table 1 were translated to the corresponding frequencies ν_m (fourth column of the table) and then used, together with the a_0 measurements listed in

the second column of table 1, to build a graph by plotting $\log_{10} \nu_m$ against $\log_{10} a_0$. From this graph (shown in figure 8) it was found, by applying standard fitting procedures, that ν_m and a_0 satisfy the equation $\nu_m a_0^{2.24 \pm 0.09} = 26 \pm 2$. This equation is of the same general form as the one established [8–11] for pure FCC alkali-halide crystals, meaning that the size of the alkali and halide ions in Eu^{2+} -doped $\text{KCl}_x\text{Br}_{(1-x)}$ crystals drives mainly the F-band spectral position in these crystals. However, the exponent found, in the case of Eu^{2+} -doped $\text{KCl}_x\text{Br}_{(1-x)}$ crystals, is about 24% higher than the best-fitted exponent [7] in the case of FCC alkali-halide crystals, indicating that the F-band spectral position in the first case is more sensitive to changes in unit-cell size than in the second case. This enhancement in sensitivity may be ascribed, since the F-band spectral position in Eu^{2+} -doped $\text{KCl}_x\text{Br}_{(1-x)}$ crystals was found to behave with x in the same general way as it does [5, 6] in pure $\text{KCl}_x\text{Br}_{(1-x)}$ crystals, to the crystalline electric field distortion caused locally at the F-centre site by the mixed character of the F-centre halide surroundings. However, since the maximum value of $\Delta\varepsilon_m$ in Eu^{2+} -doped $\text{KCl}_x\text{Br}_{(1-x)}$ crystals was found to be about 30% smaller than the corresponding value [5] for pure $\text{KCl}_x\text{Br}_{(1-x)}$ crystals, this distortion affects to a lesser extent the F-band spectral position in the first case than in the second case. This effect of electric attenuation may be taken as an experimental evidence of the fact that, in freshly quenched Eu^{2+} -doped $\text{KCl}_x\text{Br}_{(1-x)}$ crystals irradiated with X-rays, the Eu^{2+} -cation vacancy dipoles existing in the vicinity of an F-centre site act like local electric screeners for the crystalline electric field distortion caused at this site by the mixed character of the F-centre halide surroundings. Local electric screening phenomena, due to the presence of extraordinary electric charge within crystals, are familiar protagonists in a number of colouring processes like the creation of F-centres either at the vicinity of a crystal dislocation (where the space charge around the dislocation causes a shift in the F-absorption band peak [23]) or at the interior of KCl crystals doped with Eu^{2+} -ions (in these crystals, the electric field associated to the resulting Eu^{2+} -cation vacancy dipoles perturbs the F-centre's radiative lifetime [24]), or, even with stronger effects, like the creation of F' -centres in ionic crystals doped, in general, with divalent cations (in this case, the repelling cation vacancy in the Eu^{2+} -cation vacancy dipole component of a Z-centre makes the F-centre component of this centre incapable of trapping a second electron to become an F' -centre [25]).

The result that, in freshly quenched Eu^{2+} -doped $\text{KCl}_x\text{Br}_{(1-x)}$ crystals, w depends on x in a way that is not experimentally distinct from the reported [5] x -dependence of the F-band width in pure $\text{KCl}_x\text{Br}_{(1-x)}$ crystals, may be taken as an experimental evidence of the fact

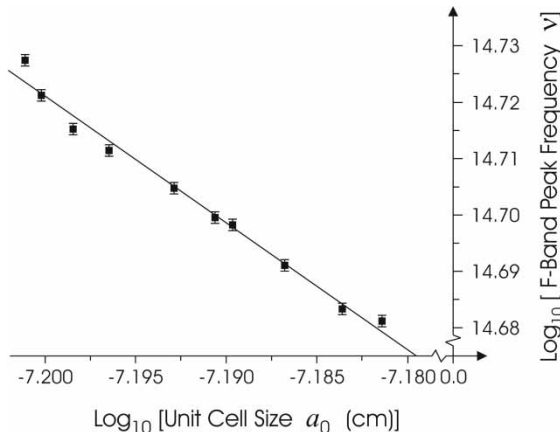


Figure 8. Plot of $\log_{10} \nu_m$ against $\log_{10} a_0$ for the crystalline $\text{KCl}_x\text{Br}_{(1-x)}:\text{Eu}^{2+}$ system. A straight line of the form $\log_{10} \nu_m = (-2.24) \log_{10} a_0 - (1.4 \pm 0.6)$ has been fitted to the plotted data (solid line).

that the presence of Eu^{2+} -cation vacancy dipoles in the Eu^{2+} -doped crystals does not affect sensitively, under the doping concentrations used, the F-centre–phonon coupling mechanism that led [26] to the statistical distribution of energies of the F-centre’s electron in alkali-halide crystals.

5. Conclusions

Freshly quenched Eu^{2+} -doped $KCl_xBr_{(1-x)}$ crystals grown by the Czochalski technique can be described, from the structural point of view, as being formed by a single mixed FCC-crystalline phase whose unit-cell size, as measured by X-ray diffraction, depends on x by strictly following the Vegard’s rule. The optical absorption spectrum of these crystals, once irradiated at room temperature with Cu-X-rays, consists of a unique F-absorption band, indicating that the F-centres that are responsible for this band are immersed within a crystalline environment. The spectral position of this band depends on the unit-cell size in a way similar to the unit-cell size dependence established for the F-absorption band spectral position in pure FCC alkali-halide crystals, by following the equation $\nu_m a_0^N = k$, where k and N are constants. This functional similarity means that the size of the alkali and halide ions forming the mixed alkali-halide crystalline matrix drives mainly the spectral position of the F-absorption band in Eu^{2+} -doped $KCl_xBr_{(1-x)}$ crystals. For these crystals, $k = 26 \pm 2$ and $N = 2.24 \pm 0.09$. As this last value is about 24% higher than the value of N in pure FCC-alkali-halide crystals, the F-absorption band spectral position in the studied crystalline system is inferred to be more sensitive to changes in unit-cell size than in pure FCC alkali-halide crystals. In contrast, the spectral position of the F-absorption band in Eu^{2+} -doped $KCl_xBr_{(1-x)}$ crystals behaves with x in the same general way as it does in pure $KCl_xBr_{(1-x)}$ crystals, by changing not linearly with x but deviating towards lower energy by following a quadratic equation which gives a maximum deviation at $x = 0.5$. This similarity in behaviour indicates that the deviation in spectral energy, from linearity, of the F-absorption band in Eu^{2+} -doped $KCl_xBr_{(1-x)}$ crystals is due to the crystalline electric field distortion caused locally at the F-centre site by the mixed character of the F-centre halide surroundings. For these crystals, the quadratic equation involving ε_m and x is ε_m (eV) = $(0.06 \pm 0.01)x^2 + (0.16 \pm 0.01)x + (1.98 \pm 0.01)$ and the maximum ε_m deviation from linearity is 0.021 ± 0.005 eV. This last value is about 30% lower than the maximum ε_m deviation in pure $KCl_xBr_{(1-x)}$ crystals, indicating that the crystalline electric field distortion caused locally at the F-centre site by the mixed character of the F-centre halide surroundings affects to a lesser extent the F-absorption band spectral position in Eu^{2+} -doped $KCl_xBr_{(1-x)}$ crystals than in pure $KCl_xBr_{(1-x)}$ crystals. This effect of electric attenuation is, as far as we know, the first experimental evidence of the Eu^{2+} -cation vacancy dipole’s influence on the F-absorption band spectral position in the $KCl_xBr_{(1-x)}\cdot Eu^{2+}$ system. Further investigations are needed to understand the action mechanism of this influence. However, such a mechanism could be explained by thinking of the Eu^{2+} -cation vacancy dipoles in the $KCl_xBr_{(1-x)}\cdot Eu^{2+}$ system as acting like local electric screeners for any distortion caused locally, by the lattice substitution of Cl^- -ions for Br^- -ions, on the crystalline electric field at the F-centre site.

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