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2002 J. Phys.: Condens. Matter 14 7265

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Negatively charged Pb^- ion produced by electrolytical colouration of KCl crystals containing Li^+ , Na^+ and Rb^+ ions

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Received 26 April 2002

Published 17 July 2002

Online at stacks.iop.org/JPhysCM/14/7265

Abstract

Electrolytical colouration has been undertaken for not only a KCl crystal containing Pb^{2+} ions but also KCl crystals containing alkali impurity ions (Li^+ , Na^+ and Rb^+) besides Pb^{2+} ions. Absorption spectra of these electrolytically coloured crystals have been studied, together with the emission spectra. Similar spectra were observed among these crystals. Eight weak absorption bands are observed in the 290–700 nm region, while five intense bands are observed in the 200–290 nm region. It is suggested that these bands arise from Pb^- ions with tetragonal crystal field symmetry. The energy-level assignment for these absorption bands is made using the energy-level diagram of the isoelectronic Bi^0 atom with C_{4v} crystal field symmetry. It is suggested that an off-centre position effect of the Li^+ ion is observed in the KCl crystal codoped with Li^+ ions. Broad emission bands at 1530 and 1580 nm have been observed in electrolytically coloured KCl containing Pb^{2+} ions and KCl containing Li^+ and Pb^{2+} ions, respectively.

1. Introduction

Cation metal impurities (e.g. Cu^+ and Ag^+) present in alkali halide crystals are changed to anion metal impurities (e.g. Cu^- and Ag^- , respectively) by electrolytical or additive colouration [1–3]. The creation of such negatively charged metal ions has been confirmed by the optical measurements. Of various negatively charged metal ions and their dimers, the energy-level assignment of the absorption bands has been established for Cu^- , Ag^- , Au^- [1–7], Sn^- [8, 9], $(\text{Ag}^-)_2$ and $(\text{Au}^-)_2$ ions [10, 11].

When a KCl crystal containing Pb^{2+} ions (called a KCl: Pb^{2+} crystal) is electrolytically coloured, several absorption bands are observed in the visible and UV region besides absorption

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bands due to colour centres such as the F centre (i.e. a negative ion vacancy trapping an electron) [12, 13]. Unlike the cases of alkali halides containing Cu^+ , Ag^+ and Au^+ , it is unclear what kinds of Pb centre are created, although it is believed that the electrolytic colouration gives rise to capture of electrons, which were released from the cathode, by Pb^{2+} ions, i.e. it gives rise to creation of Pb^0 , Pb^- , $(\text{Pb}^-)_2$, Pb^{2-} and Pb^- aggregate centres. The reason is that the observed absorption spectra are complicated and the observed spectra are changed depending on (1) the impurity ions (e.g. OH^- , Ca^{2+}) present in the crystal and (2) colouration conditions (e.g. temperature and applied electric field). It has been confirmed by electron spin resonance (ESR) measurement that several Pb^- monomer centres with different site symmetries (called Pb^- (1), Pb^- (2), Pb^- (3) and Pb^- (4)) are also created in KCl:Pb^{2+} crystals by x-ray irradiation [9].

The present work was undertaken to try to clarify what kind of Pb centre is responsible for the absorption bands appearing in KCl:Pb^{2+} crystals after electrolytical colouration. If negatively charged Pb ions such as Pb^- and $(\text{Pb}^-)_2$ are responsible, it is expected that the absorption spectrum is changed when the KCl:Pb^{2+} crystal contains rare-earth, alkali-earth or alkali impurity ions. From such a change, we might obtain information about the origin of the centre created by the electrolytical colouration. Electrolytical colouration for alkali halide crystals containing alkali-earth ions has been studied [12–14], but no work has been undertaken for alkali halides containing alkali impurity ions. Here we study the absorption spectra of an electrolytically coloured KCl:Pb^{2+} crystal ('an electrolytically coloured KCl:Pb^{2+} crystal' means a KCl crystal after electrolytic colouration has been performed for a KCl:Pb^{2+} crystal) and compare them with those of electrolytically coloured KCl crystals containing Li^+ , Na^+ and Rb^+ besides Pb^{2+} (called electrolytically coloured $\text{KCl:Pb}^{2+} + \text{Li}^+$, $\text{KCl:Pb}^{2+} + \text{Na}^+$ and $\text{KCl:Pb}^{2+} + \text{Rb}^+$ crystals, respectively, or simply $\text{KCl:Pb} + \text{Li}$, $\text{KCl:Pb} + \text{Na}$ and $\text{KCl:Pb} + \text{Rb}$ crystals). When such alkali impurity ions are present, there is a possibility that some of these ions are located as neighbours of Pb^{2+} ions [15]. As a result it is expected that the absorption spectra of the electrolytically coloured crystals are different from those of crystals containing no alkali impurity ions and they give important information on the created Pb centres. In this short paper we also try to give an energy-level assignment for the absorption bands.

2. Experimental procedure

Pure KCl powder, KCl powder containing 0.018 mol% PbCl_2 powder and KCl powder containing 0.018 mol% PbCl_2 powder together with a small amount of NaCl, LiCl or RbCl powder were dried at 250 °C to eliminate the other impurities (especially OH^- ions), and then put in a fusion zone at 780 °C to make the polycrystalline materials. In this way, the re-crystallization and purification processes were undertaken to avoid invasion of OH^- ions. The polycrystalline materials were heated up to the melting point, and then single KCl crystals containing no impurity and single KCl:Pb^{2+} , $\text{KCl:Pb}^{2+} + \text{Li}^+$, $\text{KCl:Pb}^{2+} + \text{Na}^+$ and $\text{KCl:Pb}^{2+} + \text{Rb}^+$ crystals were grown by Kyropoulos and Bridgman methods in inert atmosphere.

The electrolytic colouration was performed in air at about 450 °C and at an electric field of 500 V cm^{-1} . All crystals were coloured under the same conditions at the Romanian National Institute of Materials Physics. The crystals before colouration were uncoloured and transparent in the UV, visible and near-infrared spectral regions. After colouration, they became pink. During the electrolytic colouration process, electrons are injected from the cathode into the warmed KCl crystal, which contains Pb^{2+} ions. The cathode is formed by a sharp iron needle, while the anode is formed by a flat platinum plate to apply the electric field to the crystal uniformly. The electrons are captured by negative ion vacancies to form the F centres. The F

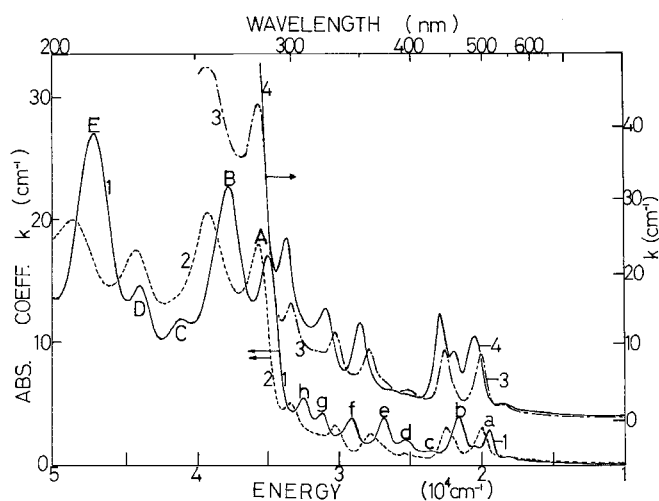


Figure 1. Absorption spectra, measured at 20 K, of an electrolytically coloured KCl:Pb²⁺ crystal (curve 1) and electrolytically coloured KCl:Pb²⁺ + Rb⁺, KCl:Pb²⁺ + Na⁺ and KCl:Pb²⁺ + Li⁺ crystals (curves 2, 3 and 4, respectively). The concentration of Pb²⁺ ions is 0.018 mol% in the melt for all crystals, while the concentrations of Li⁺, Na⁺ and Rb⁺ ions are 0.968, 0.935 and 0.93 mol%, respectively. *k*: absorption coefficient.

centres were removed by changing the polarity of the electrodes immediately after colouration. The F centre gives rise to an absorption band at 540 nm in KCl. The removal of the F centre was confirmed by the measurement of absorption spectra.

Optical absorption spectra were measured with a Cary 5E spectrophotometer at Kyoto Sangyo University. Crystals were excited with an Ar⁺ laser operated at 366 nm. The excitation spectra were obtained using a grating monochromator with a 500 W xenon lamp. The emission measurement was undertaken at University of Pierre and Marie Curie, Paris. Crystals were also excited with 266 nm Nd:YAG laser at Kyoto Sangyo University, where the emission spectra were measured with an Advantest Q8381A spectral analyser.

3. Experimental results

Curve 1 of figure 1 shows the absorption spectrum of an electrolytically coloured KCl crystal containing Pb²⁺ ions at 20 K. Before colouration, it was observed that KCl:Pb²⁺ crystals exhibit three absorption bands at 271, 211 and 199 nm in the UV region and no other absorption band in the UV, visible or near-infrared regions as shown in figure 2. The 271, 211 and 199 nm absorption bands are caused by Pb²⁺ ions, i.e. they are attributed to the electronic transition from the ¹S₀ ground state to the ³P₁, ³P₂ and ¹P₁ excited states of Pb²⁺ ions, respectively [16–18]. After colouration these Pb²⁺ bands disappear completely, while several absorption bands appear in the 200–600 nm region as shown in figure 1. Weak bands are observed in the 300–600 nm region, while intense bands are observed in the 200–290 nm region. These bands are named *a*, *b*, *c*, *d*, *e*, *f*, *g* and *h* in order of increasing energy for the weak absorption bands, while *A*, *B*, *C*, *D* and *E* for the intense absorption bands (see figure 1).

Curves 2, 3 and 4 of figure 1 show the absorption spectra, at 20 K, of electrolytically coloured KCl:Pb²⁺ + Rb⁺, KCl:Pb²⁺ + Na⁺, and KCl:Pb²⁺ + Li⁺ crystals (i.e. KCl:Pb + Rb, KCl:Pb + Na and KCl:Pb + Li, respectively). The absorption bands become narrow and the

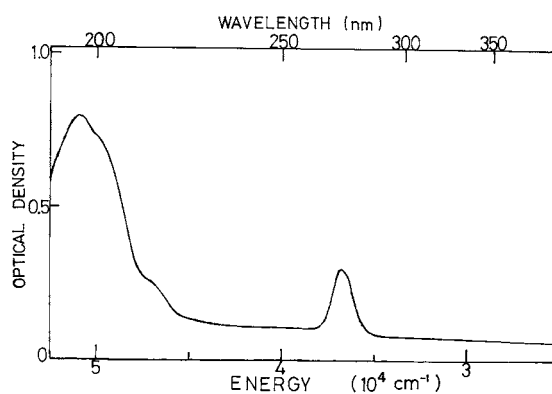


Figure 2. Absorption spectrum, at room temperature, of a KCl crystal containing Pb^{2+} ions prior to electrolytical colouration.

Table 1. Peak positions (in cm^{-1}) of absorption bands observed in electrolytically coloured KCl: Pb^{2+} , KCl: $\text{Pb}^{2+} + \text{Rb}^+$, KCl: $\text{Pb}^{2+} + \text{Na}^+$ and KCl: $\text{Pb}^{2+} + \text{Li}^+$ crystals (i.e. KCl:Pb, KCl:Pb + Rb, KCl:Pb + Na and KCl:Pb + Li, respectively) at 20 K. $E(\text{Li}) - E(\text{Pb})$ means the amount of shift of the band in KCl:Pb + Li from the corresponding band in KCl:Pb.

Band	KCl:Pb	KCl:Pb + Rb	KCl:Pb + Na	$E(\text{Na}) - E(\text{Pb})$	KCl:Pb + Li	$E(\text{Li}) - E(\text{Pb})$
<i>a</i>	19 376	20 049	20 049	633	20 503	1127
<i>b</i>	21 633	22 649	22 649	1016	22 982	1349
<i>c</i>	23 686					
<i>d</i>	25 348		25 452	104	26 055	707
<i>e</i>	26 702	27 834	27 834	1132	28 508	1806
<i>f</i>	29 070	30 199	30 199	1129	30 873	1803
<i>g</i>	31 113					
<i>h</i>	32 435	33 246	33 246	811	33 579	1144
<i>A</i>	32 995	35 612	35 612	2617		
<i>B</i>	37 764	39 106	39 106	1342		
<i>C</i>	41 034					
<i>D</i>	43 860	44 187				
<i>E</i>	47 125	48 468				

peaks become high with decreasing temperature. The half width W of the absorption band is varied with temperature T obeying the equation $W^2(T) = W^2(0) \coth(h\omega/4\pi kT)$, where ω is the vibration frequency and h is the Planck constant. For example, the frequency is $2.38 \times 10^{12} \text{ s}^{-1}$ and $2.83 \times 10^{12} \text{ s}^{-1}$ for the lowest-energy band (i.e. the *a* band) in KCl:Pb and KCl:Pb + Li, respectively. The spectra of KCl:Pb + Li, KCl:Pb + Na and KCl:Pb + Rb are quite similar to that of KCl:Pb (i.e. electrolytically coloured KCl: Pb^{2+}). Therefore we can give the same names *a*, *b*, *c*, *d*, *e*, *f*, *g* and *h*, which were used for KCl:Pb, to the bands observed in KCl:Pb + Li, KCl:Pb + Na and KCl:Pb + Rb. The peak positions of these bands are summarized in table 1. All the bands observed in KCl:Pb + Li, KCl:Pb + Na and KCl:Pb + Rb crystals are shifted to the high-energy side from the corresponding bands of KCl:Pb. The amount of the shift from KCl:Pb is larger in KCl:Pb + Li than in KCl:Pb + Na and KCl:Pb + Rb crystals (see table 1). All these bands shift to low energy with increasing temperature from 15 K to room temperature. This behaviour is observed in not only KCl:Pb but also each of KCl:Pb + Li, KCl:Pb + Na and KCl:Pb + Rb.

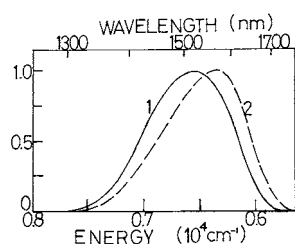


Figure 3. Emission spectra (normalized), at 5 K, of electrolytically coloured KCl:Pb²⁺ and KCl:Pb²⁺ + Li crystals. These crystals were excited with a 5 mW 366 nm Ar⁺ laser.

A broad emission band is observed in the infrared region by excitation into the absorption band in the KCl:Pb crystal. The emission peak is at about 1530 nm at 5 K as shown in figure 3. In KCl:Pb + Li the emission band shifts to low energy and the peak position is about 1580 nm. The excitation spectrum for this infrared emission was measured in the range of 320–600 nm. The spectrum was similar to the absorption spectrum. The same emission spectra were obtained by excitation with a 266 nm Nd:YAG laser. This indicates that the excitation into not only the *a*, *b*, *c*, *d*, *e* and *f* absorption bands but also the *B* band gives rise to the same infrared emission band.

4. Discussion

After colouration the absorption bands due to Pb²⁺ ions are observed to disappear; therefore, it is believed that the Pb²⁺ ions are converted to centres with different valencies. Possible centres are Pb⁺, Pb⁰, Pb⁻ and Pb²⁻. In KCl crystals containing Pb²⁺ ions, Pb²⁺ ions are in K⁺ lattice sites before colouration. During the electrolytic colouration, which was undertaken when crystals were heated at about 450 °C, Pb²⁺ ions capture electrons released from the needle-shape cathode and then Pb⁺ ions and Pb⁰ atoms are formed together with F centres. The Pb⁰ atoms subsequently trap another electron from the cathode, and then Pb⁻ ions are formed and moved to anion sites as in the cases of Cu⁻, Ag⁻ and Au⁻ [1–5].

If only Pb⁺ and Pb⁰ are created, they give rise to absorption bands at 253 nm (39 525 cm⁻¹) and 285 nm (35 087 cm⁻¹), respectively, and there is no absorption band at wavelength longer than 300 nm [16]. In the present work, we have not observed the absorption bands at 253 and 285 nm. This indicates that absorption bands *a*–*h* are not caused by Pb⁺ and Pb⁰. It might be considered that Pb⁰ colloid is formed by the colouration. The half width, however, is observed to obey the equation $W^2(T) = W^2(0) \coth(h\omega/4\pi kT)$. This equation is well known for the absorption bands due to the electronic transition in localized centres [19]. Therefore, it is suggested that the observed absorption bands are not caused by such a colloid centre.

When monovalent ions Li⁺, Na⁺ and Rb⁺, which are substituted for K⁺, are present in KCl crystals, it might be suggested that the alkali impurity ions change the valence during the colouration (i.e. by electron injection). However, such a case is impossible. The reason is that (1) their electron affinities are smaller than that of the Pb²⁺ ion and (2) as observed in the case of F_A centre, which is an F centre with an alkali impurity ion at the nearest neighbouring site, the alkali impurity ions do not trap electrons released from alkali atom vapour during the additive colouration or released from the cathode during electrolytic colouration [20].

Absorption bands which correspond to the bands observed in KCl:Pb are also observed in each of KCl:Pb + Li, KCl:Pb + Na and KCl:Pb + Rb. Their spectra are similar to each other. It is observed in KCl:Pb and KCl:Pb + Li that excitation into each of these bands gives rise to the same infrared emission band. Therefore it is suggested that all these bands are caused

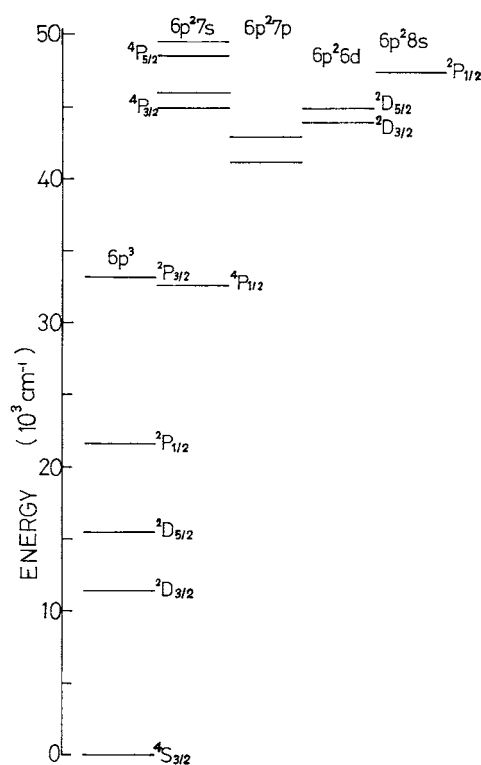


Figure 4. Energy-level diagram of $6p^3$, $6p^2 7s$, $6p^2 7p$, $6p^2 6d$ and $6p^2 8s$ electron configurations in the free Bi^0 atom.

by the same centre in each crystal. The responsible centre might be attributable to a centre containing a Pb^- or Pb^{2-} negative ion.

So far, absorption spectra have been reported for the electrolytically coloured $\text{KCl}:\text{Pb}^{2+}$ crystals where divalent ions such as Ca^{2+} are codoped [13, 14]. The absorption spectra are quite different from those observed in the present study. The Schoemaker group found that (1) the absorption bands observed in the Ca^{2+} -containing KCl crystals may be attributed to the Pb^- (Rh) centre (i.e. a Pb^- monomer with orthorhombic symmetry) [13] and (2) the orthorhombic symmetry is caused by a static Jahn–Teller distortion and anion vacancies [9, 13]. Therefore the absorption bands shown in figure 1 cannot be assigned to the bands due to the Pb^- (Rh) centre.

Pb^- ion has the same $6p^3$ outer-shell electron configuration as Bi^0 atom. Figure 4 shows the energy-level diagram of the free Bi^0 atom up to $50\,000\text{ cm}^{-1}$ [21]. The ground state is $4S_{3/2}$. The $6p^3$ configuration gives four excited states $2D_{3/2}$, $2D_{5/2}$, $2P_{1/2}$ and $2P_{3/2}$ in order of increasing energy [9, 21]. The excited electron configuration of Bi^0 is $6p^2 7s$, $6p^2 7p$, $6p^2 6d$ and $6p^2 8s$ in order of increasing energy as shown in figure 4. The electric dipole transition from the ground state $4S_{3/2}(6p^3)$ is allowed to the $4P_{1/2}$, $4P_{3/2}$ and $4P_{5/2}$ states of the $6p^2 7s$ configuration by selection rules. The transition to the $2P_{1/2}$ state of the $6p^2 8s$ configuration is spin–orbit allowed. The transition to the excited states $2D_{3/2}$, $2D_{5/2}$, $2P_{1/2}$ and $2P_{3/2}$ of the same $6p^3$ configuration is forbidden but it would be partially allowed by the spin–orbit interaction with the states of $6p^2 7s$ configuration. Therefore we expect an absorption spectrum which consists of three intense bands at higher energy and three very weak bands at lower energy.

If the Bi^0 atom is located at the octahedral lattice site in the KCl crystal, the ${}^2\text{D}_{5/2}(6\text{p}^3)$ state splits into two sub-levels but the other ${}^2\text{D}_{3/2}$, ${}^2\text{P}_{1/2}$ and ${}^2\text{P}_{3/2}$ states do not give a splitting. On the other hand, if the Bi^0 atom is located at the tetragonal position with C_{4v} symmetry, each of the ${}^2\text{D}_{3/2}$, ${}^2\text{P}_{3/2}$ and ${}^2\text{S}_{5/2}$ ground state splits into two sub-levels and the ${}^2\text{D}_{5/2}$ state splits into three sub-levels, but the ${}^2\text{P}_{1/2}$ state does not split.

From comparison of the KCl:Pb absorption spectrum with the energy-level diagram of isoelectronic Bi^0 with C_{4v} symmetry, it is proposed that the Pb^- ion has C_{4v} crystal symmetry in KCl, and the weak *a* and *b* bands are attributable to the two sub-levels of the ${}^2\text{D}_{3/2}$ state, the *c*, *d* and *e* bands to the three sub-levels of the ${}^2\text{D}_{5/2}$ state, the *f* band to the ${}^2\text{P}_{1/2}$ state and the *g* and *h* bands to the two sub-levels of the ${}^2\text{P}_{3/2}$ state, while the intense *A*, *B*, *C*, *D* and *E* bands are attributable to the upper ${}^4\text{P}_{1/2}$, ${}^4\text{P}_{3/2}$ and ${}^4\text{P}_{5/2}$ electric-dipole-allowed states of the $6\text{p}^27\text{s}$ configuration. It is difficult to identify the energy states of the *A*–*E* bands exactly because the crystal field splitting of the $6\text{p}^27\text{s}$ states is complicated. Similarly, we suggest that the absorption bands observed in KCl:Pb are caused by the Pb^- ion. The Pb^- ion is substituted for the Cl^- ion in the KCl crystal. The Pb^- ion at the Cl^- site gives rise to a deformation to the surrounding ions. Thus, we suggest that a crystal field with low symmetry such as C_{4v} symmetry is induced on the Pb^- ion.

Unlike the case of KCl crystals containing divalent impurity ions, a charge-compensating vacancy is not necessary in KCl crystals containing alkali impurity ions. The presence of alkali impurity ions gives rise to changes in the local site symmetry of Pb^- to tetragonal when they are located as neighbours of Pb^- , since Pb^- and alkali impurity ions are substituted for Cl^- and K^+ ions, respectively. Taking into account that the absorption spectrum of KCl:Pb is not so different from spectra of KCl:Pb + Rb and KCl:Pb + Na, it is suggested that Pb^- appearing in KCl:Pb already has a tetragonal site symmetry. Since only a blue shift from bands of KCl:Pb is observed for the absorption bands in KCl crystals containing alkali impurity ions, it is also suggested that the presence of alkali impurity ions enhances the strength of the tetragonal crystal field.

A negative metal ion with tetragonal site symmetry has been produced for Sn^- , which is isoelectronic with Pb^- , in KCl: Sn^{2+} crystals by x-ray irradiation [8, 9]. Unlike the case of Pb^- , Sn^- with orthorhombic symmetry has not been observed by x-ray irradiation. Electrolytical colouration was undertaken during heating of the crystal, while x-ray irradiation was performed without heating the crystal, therefore it is possible that Pb^- ions with various symmetries are produced by electrolytical colouration. Therefore creation of Pb^- with tetragonal symmetry by electrolytical colouration is not an unreasonable suggestion. No ESR study has been undertaken for this Pb^- centre. We hope our suggestion will be confirmed by ESR measurements made using our samples in future.

The absorption spectra are almost the same for KCl:Pb + Na and KCl:Pb + Rb but different for KCl:Pb + Li and KCl:Pb + Rb. As shown in table 1, the bands of KCl:Pb + Li, KCl:Pb + Na and KCl:Pb + Rb are shifted to higher energy from those of KCl:Pb. The shift is larger for KCl:Pb + Li than for KCl:Pb + Na and KCl:Pb + Rb, e.g. the *a* band of KCl:Pb + Li and KCl:Pb + Na is shifted by 1127 and 633 cm^{-1} from the *a* band of KCl:Pb, respectively. This is understood as follows.

The ionic radii of Li^+ , Na^+ and Rb^+ are 0.068, 0.097 and 0.147 nm, respectively, while the ionic radius of K^+ is 0.133 nm [22]. The Li^+ ion is considerably smaller than the other ions, indicating that Li^+ , which is substituted for K^+ in the KCl crystal, has an off-centred position, while Na^+ and Rb^+ have on-centred positions. Therefore the Pb^- accompanied by Li^+ at the nearest-neighbour site has a lower local site symmetry than the Pb^- accompanied by Na^+ or Rb^+ , giving rise to a larger shift of the energy levels in the former centre than in the latter centres. As a result, it is expected that a larger shift is observed for KCl:Pb + Li than for KCl:Pb + Na and KCl:Pb + Rb.

5. Summary

Weak absorption bands at low energy and intense absorption bands at high energy are observed in electrolytically coloured KCl:Pb^{2+} , $\text{KCl:Pb}^{2+} + \text{Rb}^+$, $\text{KCl:Pb}^{2+} + \text{Na}^+$ and $\text{KCl:Pb}^{2+} + \text{Li}^+$ crystals. Similar spectra are observed between these crystals. It is suggested that these bands are attributable to the Pb^- ion with tetragonal symmetry. To check this suggestion we shall measure the magnetic circular dichroism spectra at low temperatures in the near future.

Acknowledgments

We thank Professor S Nistor for discussion. One of the authors (TT) is indebted to the Japan Society for Promotion of Science for a partial support by the Grant-in-Aid for Scientific Research (C).

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