

Europium ions in electrolytic colored $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$ crystals

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Abstract

The crystals of KCl doped with Pb^{2+} and Eu^{2+} ions were electrolytically colored at low temperature such as 300 °C and high electric field of 4000 V/cm. The absorption, magnetic circular dichroism and photoemission spectra were studied for the crystals before and after the coloration, and compared with those of colored KCl crystals doped with Pb^{2+} and Ca^{2+} , Sr^{2+} ions. It is concluded that Eu^{2+} ions do not change the valency by the coloration. Broad infrared emission bands are observed at 1200, 1450 and 1985 nm in the electrolytically colored crystal.

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1. Introduction

In the electrolytic coloration of alkali halide crystals doped with heavy metal ions, electrons are injected from the cathode and F centers are created together with the electron-trapped centers, resulting in the change of optical properties of the crystals [1-7]. Several new absorption bands which are due to Pb-associated center [1] appear in electrolytic colored Pb^{2+} -doped NaCl, KCl and KBr crystals by the conversion from Pb^{2+} ions.

Ta centers are produced in KCl:Pb^{2+} (concentration is about 10^{17} ions/cm³) crystals which are colored at high temperature of 450-500 °C and low electric field of about 400 V/cm [5]. Td centers are produced in $\text{KCl:Pb}^{2+}+\text{Me}^{2+}$ ($\text{Me}^{2+} = \text{Ca}^{2+}$, Sr^{2+} , Ba^{2+} , the concentrations of Pb^{2+} and Me^{2+} are about 10^{17} ions/cm³) crystals which are colored at low temperature of about 300-350 °C and high electric field of about 4000 V/cm [7]. Tx centers are produced in $\text{KCl:Pb}^{2+}+\text{Me}^{2+}$ (concentrations of Pb^{2+} are about 10^{17} ions/cm³, while the concentration of Me^{2+} is one order higher than that

of Pb²⁺) crystals which are colored at low temperature and high electric field [6].

Appearance of the Ta, Td and Tx centers is accompanied by decrease of the absorption intensity of the A band due to the transition from the ¹S₀ to the ³P₁ state of Pb²⁺ and by decrease of the Pb²⁺ emission intensity. Therefore it is confirmed that these bands are created by the conformation converted from Pb²⁺ ions. The Ta centers have been suggested to be due to Pb-associated center, while the Td and Tx centers to Pb⁻ accompanied by Me²⁺ at nearest neighbors.

The change of the valency of Pb²⁺ ions were also observed in CaF₂: Pb²⁺ crystals under X-ray irradiation at the temperatures over 300 K, where the Pb²⁺ ions are transformed into Pb⁺, Pb⁻-Pb²⁺ and/or Pb⁰ centers [8].

The divalent ions (Ca²⁺, Sr²⁺, Ba²⁺, Eu²⁺), which are co-doped into the Pb²⁺-doped crystals, give rise to increase the ionic conductivity by presence of charge-compensating vacancies. The electric conductivity of KCl:Ca²⁺ crystals becomes 2 times higher than those of KCl and KCl:Pb²⁺ crystals [9, 10].

It is unknown whether Ca²⁺, Sr²⁺ and Ba²⁺ ions are changed the valency (e.g. Ca⁺, Sr⁺ and Ba⁺, respectively) after the electrolytic coloration or not. The Ca²⁺, Sr²⁺ and Ba²⁺ ions doped in KCl crystals do not have absorption and emission bands in the ultraviolet-infrared region. Therefore we cannot check the valency change by the absorption and emission spectra. However, Eu²⁺ has the absorption and emission bands at ultraviolet-visible region, which make possible to clarify, by spectroscopic measurement, whether divalent Eu²⁺ ions change the valency or not.

The present study was undertaken to clarify whether Eu²⁺ ions change the valency in the electrolytic coloration of Pb²⁺-doped alkali halide crystals or not. We investigate the optical properties of Eu²⁺ in the electrolytic colored KCl: Pb²⁺+Eu²⁺ crystals and compare them with the properties of Ca²⁺, Sr²⁺ codoped KCl:Pb²⁺ crystals.

2. Experimental Procedure

The KCl:Pb²⁺+Eu²⁺ and KCl:Pb²⁺+Ca²⁺ single crystals were grown by Czochralski method in dry nitrogen atmosphere. The concentration of Pb²⁺ ions is around 10¹⁷ ions/cm³ in the crystals, determined using the absorption intensity of the A band of Pb²⁺ ions at 272 nm. The concentration of Eu²⁺ ions in KCl crystals is the same order of Pb²⁺ (10¹⁷ ions/cm³) which was determined using the Smakula formula $Nf=7.3 \times 10^{15} a W$, where N is the concentration of Eu²⁺ ions, f the oscillator strength, a and W are the absorption coefficient and half width of the 332 nm band due to Eu²⁺, respectively. The oscillator strength of 2×10^{-2} was used, which was determined by Rubio et al [11]. The concentration of Ca²⁺ ions was chemically determined to be about 10¹⁷ ions/cm³.

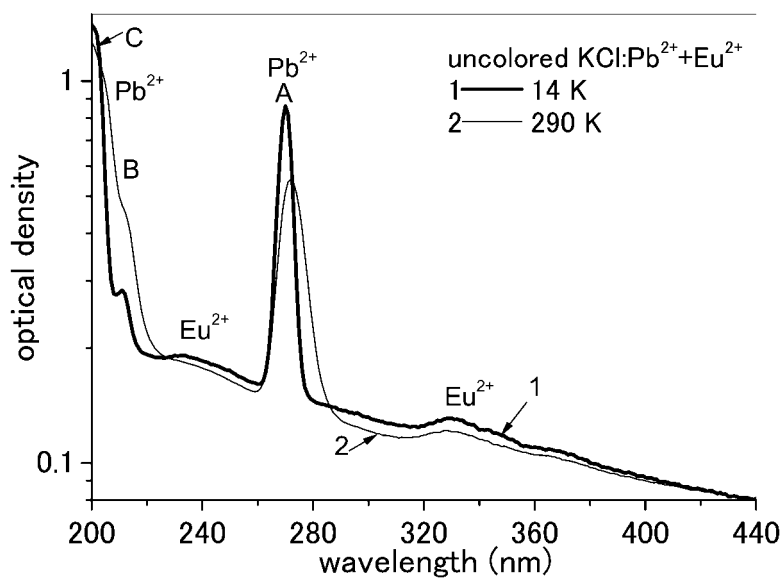


Fig. 1 Absorption spectra of KCl:Pb²⁺+Eu²⁺ crystal at 290 and 14 K.

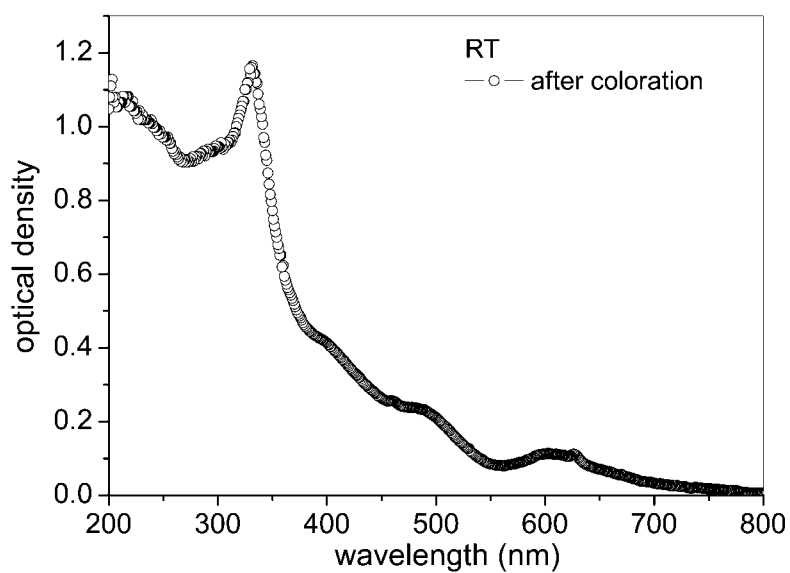


Fig. 2 Absorption spectra, at room temperature, of KCl:Pb²⁺+Eu²⁺ crystals after the electrolytic coloration.

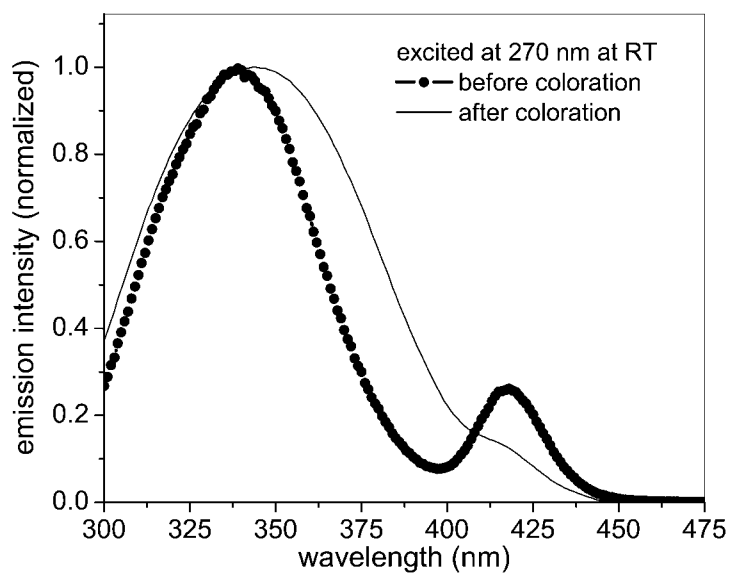


Fig. 3 Emission spectra of $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$ crystal before and after the electrolytic coloration. The crystal was excited at 270 nm at room temperature.

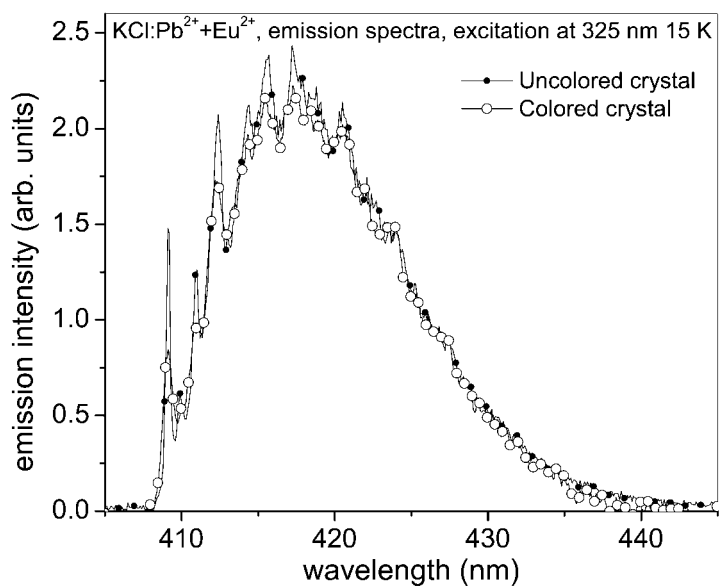


Fig. 4 Emission spectra of electrolytic colored and uncolored $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$ crystals, excited at 325 nm and measured at 15 K.

The electrolytic coloration were performed on the crystals placed between two electrodes, the sharp cathode of wolfram and the flat anode of platinum which were placed into the electric furnace. The temperatures were set between 300-350 °C and the electric field at 4000 V/cm and 0.5-1 mA.

Measurements of photoluminescence were made with a Spex Fluorolog-3 spectrofluorometer. The spectral resolution was set at 0.5 nm. Measurement of infrared emission was made with two liquid-nitrogen cooled InGaAs photodiodes which have sensitivity at different spectral ranges ; one is a Jobin-Yvon DSS-IGA020L with sensitivity at 800-1550 nm, the other is a Jobin-Yvon DSSX-IGA010L with sensitivity at 900-2400 nm. A Jasco J-40 A polarimeter was used for the magnetic circular dichroism (MCD) measurements in 200-750 nm range. Absorption spectra were measured with a Carry 5E spectrophotometer.

3. Experimental Results

Figure 1 shows absorption spectra, at room temperature (290 K) and 14 K, of KCl:Pb²⁺+Eu²⁺ crystal before the electrolytic coloration. Absorption bands due to Pb²⁺ are observed at 272, 211 and 197 nm at 290 K. From comparison with the absorption bands of KCl:Pb²⁺ crystal without Eu²⁺ ions, they are attributed to the A, B and C bands, which are due to the electronic transition from the ¹S₀ ground state to the ³P₁, ³P₂ and ¹P₁ state in Pb²⁺, respectively [12-15]. The 211 nm band is certainly observed to enhance with increasing temperature as expected for the B band due to the vibration-assisted transition. In addition to the Pb²⁺ bands, weak bands are observed at 320-400 and 225-255 nm. These bands are due to Eu²⁺ ions. Figure 2 shows absorption spectra, at room temperature, of KCl:Pb²⁺+Eu²⁺ crystal after the electrolytic coloration. After the coloration the Pb²⁺ bands become weak, while several new bands appear in the visible spectral region, for example at about 605, 485, 396, 332 and 215 nm. It is noted that the 332 nm band is the most intense in these bands.

Figure 3 shows the emission spectra, at room temperature, of KCl:Pb²⁺+Eu²⁺ crystal before and after the electrolytic coloration. The crystal was excited with 270 nm whose wavelength corresponds to the absorption band of Pb²⁺. Not only the Pb²⁺ emission band at about 340 nm but also Eu²⁺ emission band at 317 nm is observed in both crystals.

Figure 4 shows the emission spectra of electrolytic colored and uncolored KCl:Pb²⁺+Eu²⁺ crystals at 15 K. The uncolored crystal means crystal before electrolytic coloration. The emission spectrum was obtained by excitation at 332 nm whose wavelength corresponds to the absorption band of Eu²⁺. Identical spectra were obtained in the colored and uncolored crystals. Vibronic sharp lines

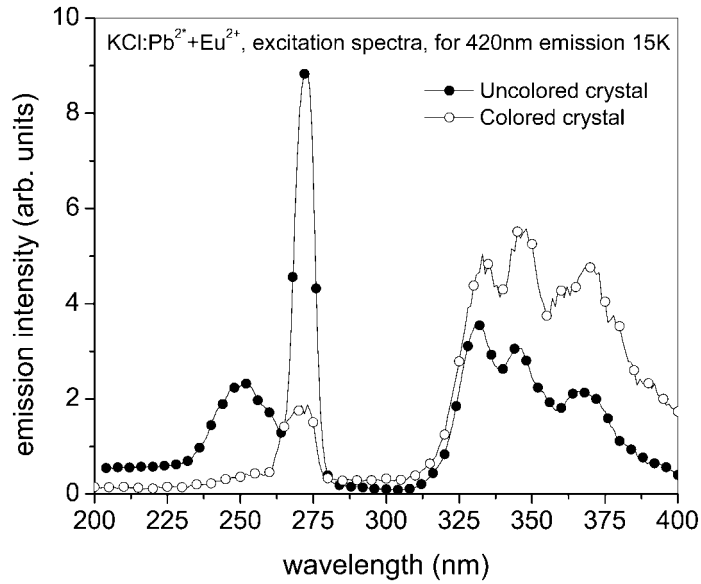


Fig. 5 Excitation spectra of electrolytic colored and uncolored $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$ crystals, for 420 nm emission at 15 K.

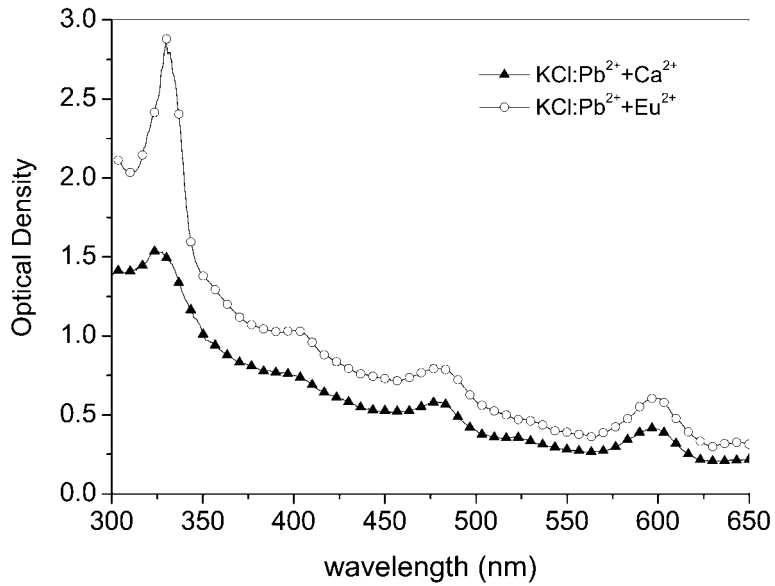


Fig. 6 Absorption spectra of electrolytic colored $\text{KCl:Pb}^{2+}+\text{Ca}^{2+}$ and $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$ crystals at 15 K. The concentrations of Ca^{2+} and Eu^{2+} ions are the same as that of Pb^{2+} ions (about 10^{17} ions/cm³).

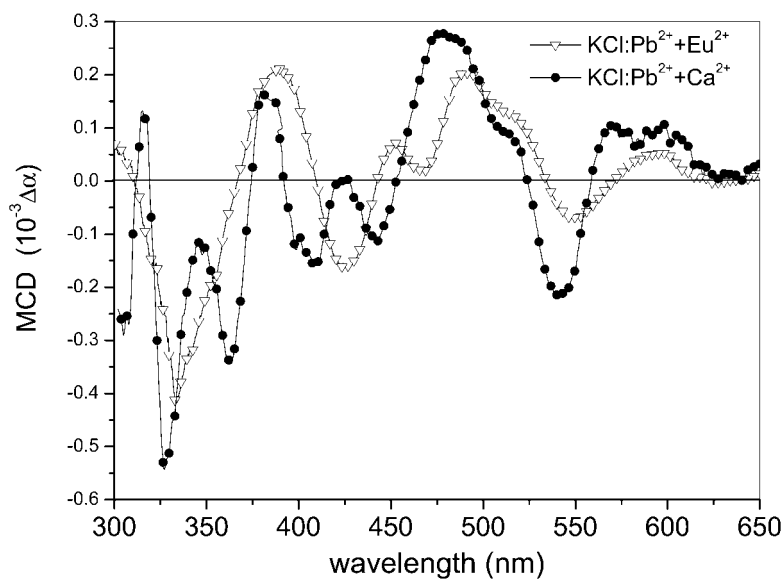


Fig. 7 Magnetic circular dichroism (MCD) spectra of electrolytic colored $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$ and $\text{KCl:Pb}^{2+}+\text{Ca}^{2+}$ crystals at 15 K. The applied magnetic field is 10 kG. Both crystals have the same thickness of 1 mm.

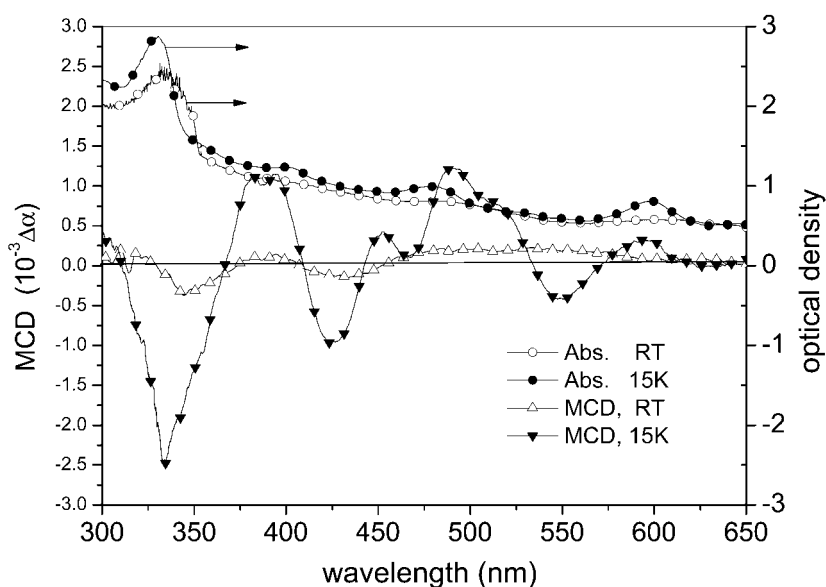


Fig. 8 Absorption and MCD spectra of electrolytic colored $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$ crystal at room temperature compared with the spectra at 15 K. The applied magnetic field is 10 kG. Both crystals have the same thickness of 1 mm.

of Eu²⁺-V_C dipoles are observed at 15 K, while no sharp line is observed at room temperature. It can be seen a series of at least six vibronic lines peaked at 409.2, 410.9, 412.2, 414.2, 415.4, 420.5 nm which are superposed on the broad emission from 417 nm of Eu²⁺ ions. These lines are quite similar with those observed by Perez-Salas et al [16], indicating the presence of the Eu²⁺-V_C dipoles. From this result, it is suggested that Eu²⁺ ions are never destroyed by the electrolytic coloration.

Kovalev found ten vibronic sharp lines in the emission bands associated with the 4f⁷-4f⁶5d transition of Eu²⁺-ions [17]. Lopez et al have studied in the emission spectra of uncolored KCl:Eu²⁺ crystals, and observed the same emission band peaked at 419 nm in freshly quenched crystals and an additional band at 427 nm in the crystals annealed at 100°C [18]. They attributed the 419 nm emission band to the free Eu²⁺-V_C dipoles and the 427 nm emission band to the Suzuki phase of aggregation of Eu²⁺-V_C dipoles. We observed only the 419 nm emission band (Fig. 4), indicating that no aggregation of Eu²⁺-V_C dipoles is present in both colored and uncolored crystals.

Figure 5 shows the excitation spectra of the same crystals used in Fig. 4. There are three groups of excitation bands ; the first band appears at 325-400 nm, the second at 230-260 nm, and the third at 260-275 nm. From the comparison with absorption bands due to Eu²⁺ and Pb²⁺ ions in KCl, the first and second bands are attributed to Eu²⁺ [19,20], while the third band to the A absorption band by the transition from the ¹S₀ ground state to the ³P₁ state of Pb²⁺. The A band intensity decreases after the coloration as seen in Fig. 5, indicating that Pb²⁺ ions are destroyed by the coloration. It is noted that intensity ratio of the 230-260 nm Eu²⁺ excitation band to the 325-400 nm Eu²⁺ excitation band becomes much lower before the coloration than after the coloration, suggesting that all the excitation energy in the former Eu²⁺ band does are used for non-radiative relaxation to excite the latter band.

Figure 6 shows the absorption spectra of electrolytic colored KCl:Pb²⁺+Eu²⁺ and KCl:Pb²⁺+Ca²⁺ crystals. The two crystals have same absorption band at 600, 488, 395 and 325 nm. In KCl:Pb²⁺+Eu²⁺ intense absorption band is observed at 332 nm. The 332 nm band is attributed to Eu²⁺. The 600, 488, 395 and 325 nm bands are attributed the color centers which are produced by the electrolytic reduction of Pb²⁺ ions.

Figures 7 and 8 show the absorption and MCD spectra of the electrolytic colored KCl:Pb²⁺+Eu²⁺ and KCl:Pb²⁺+Ca²⁺ crystals. Except the MCD signal of the 332 nm Eu²⁺ absorption band, the MCD spectra have the same structure as in the case of electrolytic colored KCl:Pb²⁺+Ca²⁺ crystals. The large differences between the room temperature and 15 K of the MCD spectra suggest the existence of at least one paramagnetic influenced by the presence of co-doped divalent ions. The MCD spectra are quite similar with those obtained for T_d centers [7].

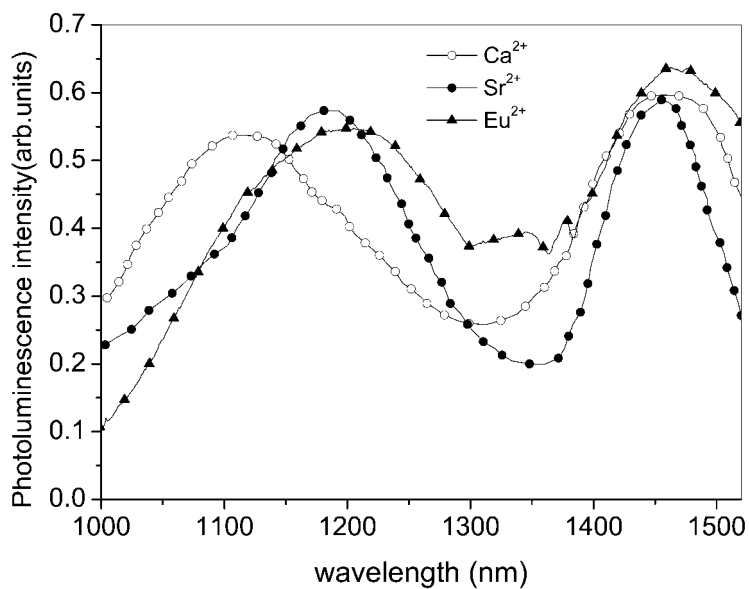


Fig. 9 Infrared emission spectra of electrolytic colored $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$, $\text{KCl:Pb}^{2+}+\text{Sr}^{2+}$, $\text{KCl:Pb}^{2+}+\text{Ca}^{2+}$ crystals, measured at room temperature. All crystals have the same concentrations of Pb^{2+} , Eu^{2+} , Ca^{2+} and Sr^{2+} ions. The spectra were measured with a 800-1550 nm sensitive photodiode.

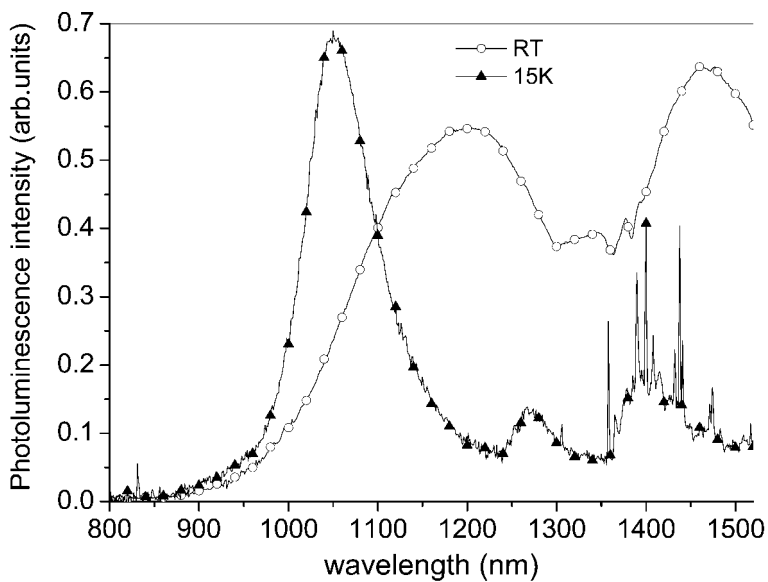


Fig. 10 Infrared emission spectra of electrolytic colored $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$ at room temperature and 15 K. The spectra were measured with a 800-1550 nm sensitive photodiode.

The absorption and emission spectra, which were caused by conversion from Pb^{2+} ions in electrolytically colored $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$ crystals, present similar spectra obtained electrolytically colored $\text{KCl:Pb}^{2+}+\text{Ca}^{2+}$, $\text{KCl:Pb}^{2+}+\text{Sr}^{2+}$ and $\text{KCl:Pb}^{2+}+\text{Ba}^{2+}$ crystals except small shift among these crystals, for example see Fig. 9 for the infrared emission spectra. This shift is caused by the difference of ionic radius R_i ; $R_i = 1.14, 1.49, 1.32$ and 1.31 \AA for Ca^{2+} , Ba^{2+} , Sr^{2+} and Eu^{2+} , respectively. The crystal field around Pb^{2+} ion depends on the ionic radius of co-doped divalent ion, resulting in change of the energy levels, i.e. shift of the emission band to the low energy with increasing the ionic radius.

When temperature is decreased from room temperature to 15 K, the 1200 nm emission band decreases, while emission band at 1050 nm increases as shown in Fig. 10. The 1050 nm emission band is attributed to the M center (i.e. F_2 center) because its optical characteristics are quite similar to the M-emission band observed in pure KCl crystals [21,22]. At 15 K, vibronic structure is observed in the 1400 nm emission band, and emission band is observed at 1270 nm.

When the infrared emission spectra were measured with a 900-2400 nm sensitive photodiode, intense band with a peak at 1985 nm was observed in electrolytic colored $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$ crystal as shown in Fig. 11 in addition to the 1200 and 1450 nm emission bands. It was found that the 1985 nm emission is excited with light of different wavelength from the case of the 1200 and 1450 nm emission, e.g. the high-energy emission bands are not observed by excitation at 600 nm (Fig. 10).

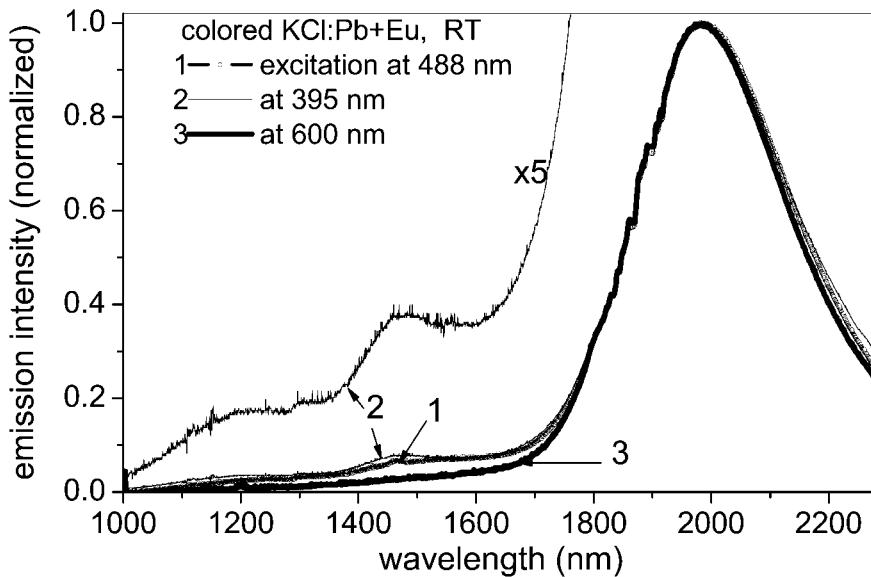


Fig. 11 Infrared emission spectra of electrolytic colored $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$ crystal excited at 488, 385 and 600 nm at room temperature. The spectra were measured with a 900-2400 nm sensitive photodiode.

4. Discussion

From the emission and excitation spectra of electrolytic colored $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$ in the ultraviolet range, it is suggested that Eu^{2+} forms $\text{Eu}^{2+}\text{-V}_c$ dipoles. Eu^{2+} ions gives rise to a splitting of $4f^65d$ excited state of Eu^{2+} ions in two components by changing the crystalline field around the $\text{Eu}^{2+}\text{-V}_c$ aggregates. One is the doubly-degenerated e_g state and the other is the triply-degenerated t_{2g} state. The former state is responsible for the double band around 240 nm while the later state is responsible for the triple band around 332 nm.

The absorption and emission spectra suggest that the Eu^{2+} ions do not change the valency by the electrolytic coloration. This is quite similar to the cases of Ca^{2+} , Sr^{2+} and Ba^{2+} ions. This is confirmed by the MCD spectra of electrolytic colored $\text{KCl:Pb}^{2+}+\text{Eu}^{2+}$ crystals, because the MCD spectrum of colored crystal is quite similar to that obtained in uncolored KCl:Eu^{2+} crystals by Ferre et al [23]. Change of valency has been observed for Cu^+ , Ag^+ , Tl^+ , Au^+ and Pb^{2+} [24-27]. The electronegativity for Ca, Sr, Ba, Eu, Cu, Ag, Tl, Au and Pb atoms are 1.00, 0.95, 0.89, 1.2, 1.9, 1.93, 1.62, 2.54 and 2.33, respectively. This indicates that atoms with low electronegativity of below 1.2 do not change the valency during electrolytic coloration. Therefore it is suggested that electronegativity is responsible for the change of valency.

Presence of Eu^{2+} ions is important to create color centers. Eu^{2+} ions in KCl:Pb^{2+} crystals decrease the coloration temperature to 300 °C and increase ionic conductivity. The presence of charge-compensating vacancies due to the doped Eu^{2+} ions enhances the migration of F centers, and then allows the formation of Td centers by the conversion from Pb^{2+} in the coloration, while the doped Eu^{2+} ions never change the valency by the electron injection from the cathode during the coloration.

Electrons are also injected in additive coloration as the case of electrolytic coloration. Nakata et al observed the decay of $\text{Eu}^{2+}\text{-V}_c$ by electron spin resonance after the additive coloration of KCl:Eu^{2+} crystal [20]. In KCl:Eu^{2+} crystal without co-doped divalent ions such as Pb^{2+} and Ca^{2+} , the injected electrons change conformation of Eu^{2+} by the additive coloration. No change, however, was observed by the electrolytic coloration of KCl:Eu^{2+} crystal clearly. It is suggested that the moving and trapping processes of the electrons are different between the additive and electrolytic colorations although electrons are injected in both the two colorations.

The 1200 and 1450 nm emission bands have different excitation bands from the 1985 nm emission band as seen from Fig. 11. This suggests that the 1200 and 1450 nm emissions are caused by the same defect center called Td-A, but the 1985 nm emission is caused by different defect center called Td-B which is responsible for the 1200 and 1450 nm emissions. From this result, one can conclude that the Td center consists of two centers and the Td-A center is responsible for the 396 and 488 nm absorption

bands (shown in Fig. 6), while the Td-B center is responsible for the 600 nm absorption band.

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