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LETTER TO THE EDITOR

Luminescence from KCl co-doped with Eu^{2+} and Eu^{3+} ions

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Abstract. Distinct holes are found in the blue emission from KCl co-doped with divalent and trivalent europium ions. This extraordinary emission feature is associated with the process of reabsorption from Eu^{2+} to Eu^{3+} ions in KCL.

Alkali halide phosphors activated with the divalent europium ion emit bright blue luminescence and have been recognized as suitable candidates for the active media of broadly tunable solid-state lasers and dosimetric applications. A large number of studies have examined the spectroscopic properties of Eu^{2+}-doped alkali halides (many references appear in Rubio (1991)). In the solid state, europium ions can occur in either the divalent or the trivalent state. Unlike Eu^{2+}, the trivalent europium ion produces a number of sharp lines in the $f \rightarrow f$ transitions, depending on its symmetry. Of the trivalent lanthanide ions, the europium ion offers versatility in its luminescence properties, coupled with an understanding of its structural configuration and the effects of the environment on it. LaF_3, $LaCl_3$, and CaF_2 crystals doped with trivalent europium ions have been studied extensively to characterize their luminescence features (Carnal *et al* 1989). To date, however, the luminescence properties of $KX{:}Eu^{3+}$ phosphors have not been reported. This might be due to the difficulty in substituting the Eu^{3+} ion into the KX lattice. In this study, we attempted to prepare KCl co-doped with divalent and trivalent Eu ions, and to characterize its luminescence properties. In view of their versatile spectroscopic properties, co-doping with Eu^{2+} and Eu^{3+} in the solid state might be useful for constructing optical devices for technological applications.

Three samples were prepared in this study: 400 ppm $EuCl_3$ (hereafter called sample A), 1 mol% $EuCl_3$ (sample B), and 10 mol% $EuCl_3$ (sample C) in KCl. For sample A, a mixture of KCl (99.99%+, Aldrich) and anhydrous $EuCl_2$ (99.99%, Strem) or $EuCl_3$ (99.9%+, Aldrich) was ground thoroughly and mixed well. The mixture was transferred to a quartz ampoule, which was sealed under high vacuum after flushing the sample with Ar gas (99.999%) a few times. Crystals were grown under vacuum using the vertical Bridgeman method. If the amount of $EuCl_3$ is very high, an explosion can result from the decomposition of $EuCl_3$ during crystal growth. For samples B and C, heat treatment was first applied below the melting point to avoid such an explosion. The mixtures were pressed into a pellet and baked for a day at 500 °C in air. The baked sample was thoroughly ground and baked again in the same manner. This process was repeated 3–4 times. Unexpectedly, samples B and C were opaque crystals. Details of the optical arrangements have been given in previous publications (Kim *et al* 1998, Kang *et al* 1999).

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The emission spectra from samples A, B, and C were measured in the UV–visible region at $T = 78.8$ K under 325 nm He–Cd excitation. Sample A produced only a bright emission band peaking at 420 nm, which was attributed to the characteristic emission of Eu^{2+} ions in the host crystal. Previously, we investigated the optical properties of KCl:Eu^{2+} (Kang *et al* 1999). The characteristic features of the blue emission from KCl:Eu^{2+} are the unusual polarization, multiple components, the strong Stokes shift, and the widened bandwidth. Figure 1 shows the emission spectrum from sample B, measured at 78.8 K. The 325 nm excitation produced a very strong, wide band, peaking at 422 nm, and a series of very sharp lines in the visible region. These sharp lines were more intense for sample C. The series of sharp lines in the visible region apparently results from the $f \rightarrow f$ transitions of the trivalent europium ion in the KCl host. This suggests that both the divalent and trivalent states can coexist in KCl after heat treatment in air.

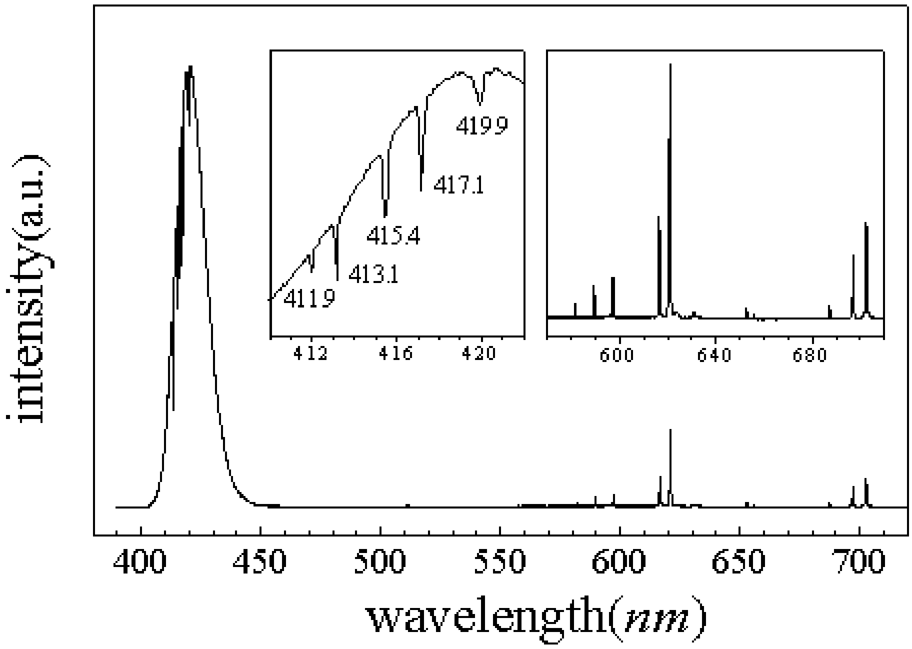

Figure 1. The emission spectrum from KCl co-doped with Eu^{2+} and Eu^{3+} ions ($\lambda_{exc} = 325$ nm and $T = 78.8$ K).

In sample B, the structure of the 422 nm band is somewhat different from that of the 420 nm band produced by Eu^{2+} in KCl. A series of holes in the emission profile were present at 411.9, 413.1, 415.4, 417.1, and 419.9 nm. These holes also appeared for sample C. As illustrated on the expanded scale, the holes are very distinct. They could be due to reabsorption phenomena associated with Eu^{2+} and Eu^{3+} ions in KCl. To examine whether the holes are associated with the aggregation of Eu^{2+} ions, an additional KCl sample containing 10 mol% $EuCl_2$ was also prepared using the heat treatment process (sample D). However, this sample did not produce holes in the 422 nm emission.

The excitation spectra of the 422 and 619 nm emissions were also measured at $T = 78.8$ K. The excitation spectrum of the 422 nm emission is almost identical to a previously reported spectrum. As shown in figure 2, this emission is associated with the divalent state only. The 619 nm emission excitation spectrum has two distinct features: a broad band peaking

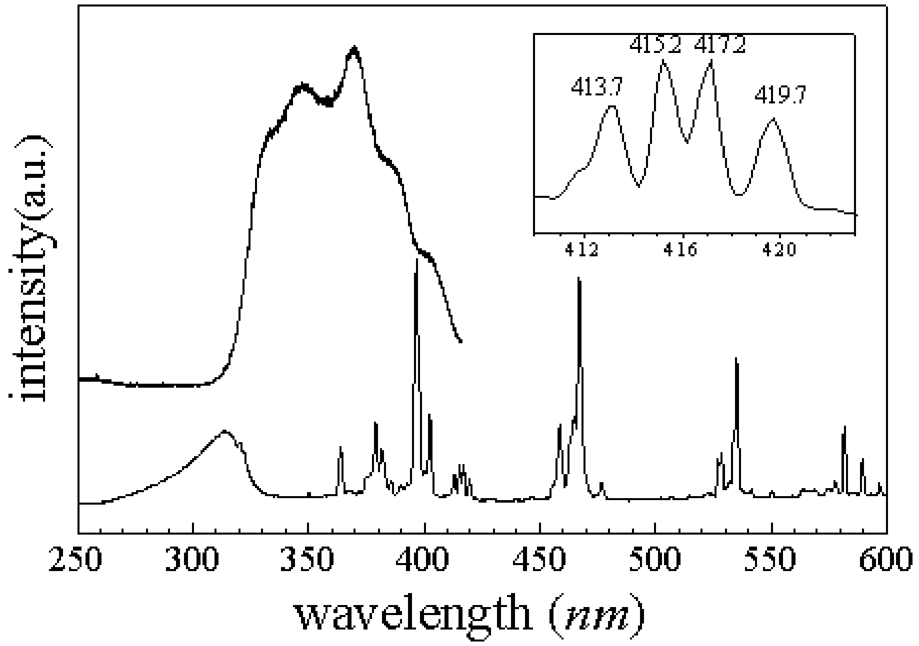

Figure 2. Excitation spectra of the 422 nm (upper) and 619 nm (lower) emissions from KCl co-doped with Eu^{2+} and Eu^{3+} ions (T = 78.8 K).

at 315 nm and a group of sharp lines between 360 and 600 nm. Obviously, the sharp lines correspond to transitions from the $^7F_0$ ground state to excited states that have arisen from the $3f^6$ ground configuration of the trivalent europium ion. Previously, the broad band was found in a $[Eu(DPA)_3]^-$ (DPA = dipicolinate) complex (Kim *et al* 1998). It could be due to energy transfer from the counter-anion to the Eu^{3+} ion. The characteristic feature of the excitation spectrum is the four well-defined lines between 410 and 425 nm.

These lines correspond to the $^7F_0 \rightarrow {}^5D_3$ transitions of Eu^{3+}. As illustrated on the expanded scale, the peaks of these four lines correspond exactly to the locations of the holes. Surprisingly, the holes in the blue emission resulted from the electronic transitions of trivalent europium ions. It would be worthwhile examining whether the sharp lines of Eu^{3+} can be produced by reabsorption of the blue emission from Eu^{2+}. We chose an exciting light that cannot be absorbed by Eu^{3+} ions. The 340 nm excitation reproduced the same luminescence spectrum as that shown in figure 1.

The sharp lines observed at wavelengths between 580 and 720 nm can be attributed to the $^5D_{0,1} \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4$) transitions. The extent to which the $(2J + 1)$ degeneracy is removed depends upon the site symmetry of the Eu(III) ion. Furthermore, the number of bands observed in the $^5D_0 \rightarrow {}^7F_J$ ($J = 2, 3, 4$) transitions is determined by the electric dipole selection rule for a given point group (Bünzil and Choppin 1989). Under octahedral symmetry, $^5D_0 \rightarrow {}^7F_{0,2,3,4}$ transitions are in principle forbidden by an electric dipole moment. The groups of sharp lines indicate that the Eu^{3+} ion in KCl has a reduced site symmetry rather than octahedral symmetry. In principle, an electric dipole moment forbids the weak line peaking at 581.6 nm, attributed to the $^5D_0 \rightarrow {}^7F_0$ transition. However, this transition can gain intensity through J-mixing in low symmetries such as C_s, C_n and C_{nv}. The most striking emission feature is found in the $^5D_0 \rightarrow {}^7F_2$ transition. The strongest lines, peaking at 616.6 and 621.0 nm, attributed to the $^5D_0 \rightarrow {}^7F_2$ transition, exhibit hypersensitivity. If the trivalent europium ion lies on an inversion centre, the hypersensitivity is absent. Furthermore, the hypersensitivity can be present when the chemical bonding between the Eu^{3+} ion and its environment is strong. This led us to assume that the characteristic f → f emission from KCl might arise from localized EuOCl acting as an activator. The very weak lines observed in the 650–660 nm region can be attributed to the $^5D_0 \rightarrow {}^7F_3$ transition, which is forbidden by an electric dipole moment. However, this transition reveals the removal of the $(2J+1)$ degeneracy to a certain extent, although the intensity is weak. Additionally, the two lines observed peaking at 652.7 and 655.8 nm rule out point groups including a C_3 symmetry element, which would be expected to produce five lines. As for the site symmetry of Eu^{3+}, a C_{4v} point group is more plausible than a C_4 group for two reasons: more lines in the $^5D_0 \rightarrow {}^7F_3$ transition would be expected from C_4 and the symmetry of EuOCl itself belongs to C_{4v}. The $^5D_0 \rightarrow {}^7F_4$ transition is sensitive to the ligand environment. For sample C, the intensity of this transition increased moderately. The characteristic feature of this transition is the three well-separated luminescence lines, peaking at 687.5, 696.9, and 702.6 nm, rather than the enhanced intensity. The C_{4V} crystal-field potential produces at most the four lines allowed by the electric dipole moment.

In conclusion, the extraordinary emission feature is produced via the process of reabsorption from Eu^{2+} to Eu^{3+} ions in KCl. This optical process is shown schematically in figure 3.

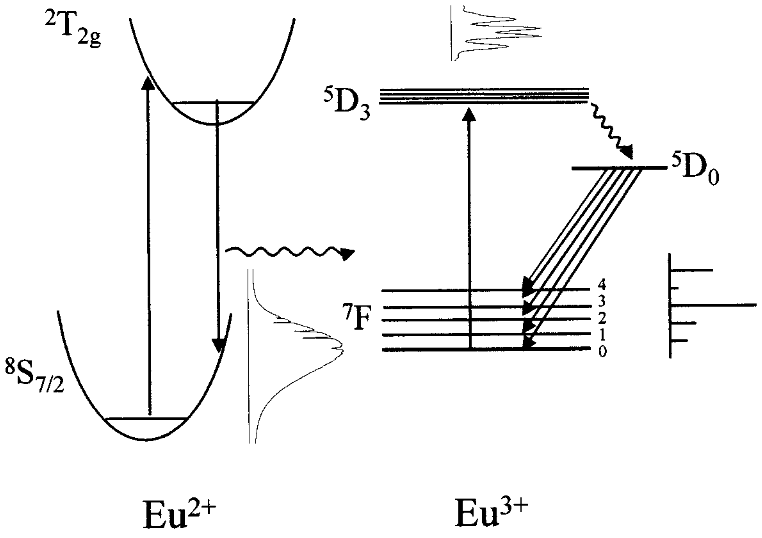

Figure 3. A schematic diagram of the emission from KCl resulting from a process of reabsorption from Eu^{2+} to Eu^{3+} ions.

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References

Bünzil J-C G and Choppin G R 1989 *Lanthanide Probes in Life, Chemical and Earth Science* (Amsterdam: Elsevier) pp 415–20

Carnal W T, Goodman G L, Rajnak K and Rana R S 1989 *J. Chem. Phys.* **90** 3443
Kang J-G, Sohn Y, Nah M-K, Kim Y-D and Ogryzlo E A 1999 *J. Phys.: Condens. Matter* submitted
Kim J-G, Yoon S-K, Sohn Y and Kang J-G 1998 *J. Alloys Compounds* **274** 1
Rubio J O 1991 *J. Phys. Chem. Solids* **52** 101