

phase due to the hydrophilic-OH group of hydroxyproline in the chelate. Their interactions are so weak that the DNS-amino acids are less retained in the Cu(II)-Hyd elution than in the Cu(II)-Pro elution as seen in Table 2 and 3.

The optical selectivity obtained in the use of Cu(II)-Hyd elution system for DNS-Ser and DNS-Thr was better than in the use of Cu(II)-Pro elution system. It seems that the resolutions of the optical isomers result in the hydrogen bonding of the hydroxy group of the chelate ligand when they make an attack for the ligand exchange reaction.

It can be concluded that a SN-2 reaction involving the *cis/trans* product for the ligand exchange reaction predominates the separation of the optical isomers of amino acids. The reaction schemes in the Cu(II)-Pro chiral mobile phase are seen in Figure 6. D-DNS amino acids except DNS-serine are able to have the *cis* and *trans* products, but the *cis* product of L-DNS amino acids are not available because of steric effect for the ligand exchange reaction.

Acknowledgment. This work was supported by a grant from the Korea Science and Engineering Foundation.

References

1. V.A. Davankov and S.V. Rogozhin, *J. Chromatogr.*, **60**, 280 (1971).
2. V.A. Davankov, S.V. Rogozhin, A.V. Semechkin, and T.P. Sachkova, *J. Chromatogr.*, **82**, 359 (1973).
3. G. Dotsevi, Y. Sogah and D.J. Cram, *J. Am. Chem. Soc.*, **97**, 1259 (1975).
4. W.H. Pirkle and D.W. House, *J. Org. Chem.*, **44**, 1975 (1979).
5. S. Hara and A. Dobashi, *J. Chromatogr.*, **186**, 543 (1979).
6. J.N. Lepage, W. Lindner, G. Davies, D.E. Seitz, and B.L. Karger, *Anal. Chem.*, **51**, 433 (1979).
7. N. Qi and H. Kithara, *J. Chromatogr.*, **285**, 198 (1984).
8. E. Grushka, R. Leshem, and C. Gilon, *J. Chromatogr.*, **255**, 41 (1983).
9. W. Lindner, J.N. Lepage, G. Davies, D.E. Seitz, and B.S. Karger, *J. Chromatogr.*, **185**, 323 (1979).
10. P.E. Hare and E. Gil-AY, *Science*, **204**, 1226 (1979).
11. S. Lam, F. Chow and A. Karmen, *J. Chromatogr.*, **199**, 295 (1980).
12. C. Gilon, R. Leshem, Y. Tapuhi, and E. Grushka, *J. Am. Chem. Soc.*, **103**, 7612 (1979).
13. T. Tapuhi, N. Miller, and B.L. Karger, *J. Chromatogr.*, **205**, 325 (1981).
14. E. Gil-AY, A. Tishbee, and P.E. Hare, *J. Am. Chem. Soc.*, **102**, 5115 (1980).
15. C. Gilon, R. Leshem, and E. Grushka, *Anal. Chem.*, **52**, 1206 (1980).
16. I.D. Hay, T.M. Annesley, N. S. Jiang, and C.A. Gorman, *J. Chromatogr.*, **203**, 365 (1981).
17. C. Gilon, R. Leshem, and E. Grushka, *J. Chromatogr.*, **203**, 365 (1981).
18. A.A. Kurganov and V.A. Davankov, *J. Chromatogr.*, **218**, 559 (1981).
19. S. Lam and A. Karmen, *J. Chromatogr.*, **289**, 339 (1984).
20. J.F. Lawrence and R.W. Frei, "Chemical derivatization in liquid chromatography" Elsevier Scientific Pub, Co. New York., 1976.
21. V.A. Davankov and P.R. Mitchell, *J.C.S. Dalton*, 1012 (1972).
22. O. Yamauchi, T. Sakurai, and A. Nakahara, *Bull. Chem. Soc. Jpn.*, **50**, 1776 (1977).

Emission for Pb²⁺ Centers in RbCl Single Crystal Excited within the A-Absorption Band

Jun-Gill Kang

Department of Chemistry, College of Sciences, Chungnam National University, Chungnam 300-31

Received July 31, 1985

The emission spectra of RbCl: Rb²⁺ excited in the A-absorption band at various temperatures are reported and the excitation spectra are also investigated. The relaxed excited states able to explain the two A-emission bands are proposed.

Introduction

In many ways, the study of luminescence of divalent cation ions (Sn²⁺, Ge²⁺, Pb²⁺) doped in alkali halide single crystals has only just begun. Most of the work^{1,2} to date has been formulated in terms of the Jahn-Teller effect, spin-orbit interaction and an effect of the charge compensating cation vacancy (CCV, v_c). Since, for Sn²⁺ ions, the Jahn-Teller effect is dominant, the emission from Sn²⁺ was interpreted in terms of a model which includes the Jahn-Teller effect, the spin-orbit interaction in the second order and an additional effect due to the CCV. In the previous works,^{3,4} the comprehensive

energy-level scheme for Pb²⁺ color centers in KX (X = Cl, Br, I) was presented. The spin-orbit interaction of Pb²⁺ ion in the crystal field is exceptionally strong, compared, for example, with the Sn²⁺ ion. The spin-orbit interaction causes a mixing of ³T_{1u} and ¹T_{1u} states and results in ³T_{1u}^{*} and ¹T_{1u}^{*} described as

$$|^3T_{1u}^*\rangle = -\nu|^1T_{1u}\rangle + \mu|^3T_{1u}\rangle$$

$$|^1T_{1u}^*\rangle = \mu|^1T_{1u}\rangle + \nu|^3T_{1u}\rangle$$

where μ and ν ($\mu^2 + \nu^2 = 1$) are mixing coefficients. The Jahn-Teller effect coupling to the E_g (Q₂, Q₃) vibrational modes splits the ³T_{1u}^{*} state into a twofold degenerate state with E-symmetry

at lower energy and a singlet state with A-symmetry at higher energy. The lower-energy doublet may be further split depending on the relative orientation of the vacancy and the Jahn-Teller axes. These two levels and the metastable ³A_{1u} level are involved in A-band emission processes.

Excitations of KCl:Pb²⁺,⁴ and RbCl:Pb²⁺,⁵ within the A-absorption band (¹A_{1g} → ³T_{1u}) were observed to produce a strong emission band and an additional band. In the case of KCl:Pb²⁺, the additional band appeared at lower energy and showed an uncharacteristic temperature-dependence, while for RbCl:Pb²⁺ it appeared at higher energy. The additional band for both KCl:Pb²⁺ and RbCl:Pb²⁺ has not been identified. The present work was undertaken to investigate the A-band emission from RbCl:Pb²⁺ as a function of both temperature and exciting energy and to permit a more definitive relaxed excited state in terms of the adiabatic potential energy surface (APES).

Experimental

RbCl:Pb²⁺ single crystal was grown in a nitrogen atmosphere and was kindly provided by Professor P.W.M. Jacobs (University of Western Ontario). Thin sample, cleaved from the ingot, was annealed at 550°C for one hour and then rapidly quenched to room temperature immediately before commencing measurements. The emission and the excitation measurements were performed in an Oxford Instruments Co. CF-100 continuous flow cryostat combined with a high-pressure 1000-W Xe arc lamp, a Jobin-Yvon and a

Bausch and Lomb monochromators. A CoSo₄ solution filter and a UG-11 filter were used to further improve the monochromaticity of the exciting radiation. A Hamamatsu photomultiplier (R-928) transformed the light signal into an electric signal which was amplified by a preamplifier and recorded on an X-Y Recorder.

Results and Discussion

The intensity spectra of the A-band emission from RbCl:Pb²⁺ excited at 270 nm (4.59 eV) were measured at various temperatures. As shown in Figure 1, the A-band excitation at T = 14.8 K produces a strong emission band centered at 354 nm and a weak band at 322 nm. As temperature increases, the intensity of the high energy band decreases and vanishes above T = 65.0 K. It is strikingly different from the temperature behavior of KCl:Pb²⁺, whose additional A-band emission has a maximum intensity at T = 150 K and does not appear at very low and room temperatures.⁴ In the contrast with the high energy band, the 354 nm emission band is nearly constant over a wide temperature range. Excitation spectra of these two emission bands were measured at T = 13.4 K and the emission from RbCl:Pb²⁺ was also investigated as a function of the exciting energy at the same temperature. As shown in Figure 2, the excitation within the

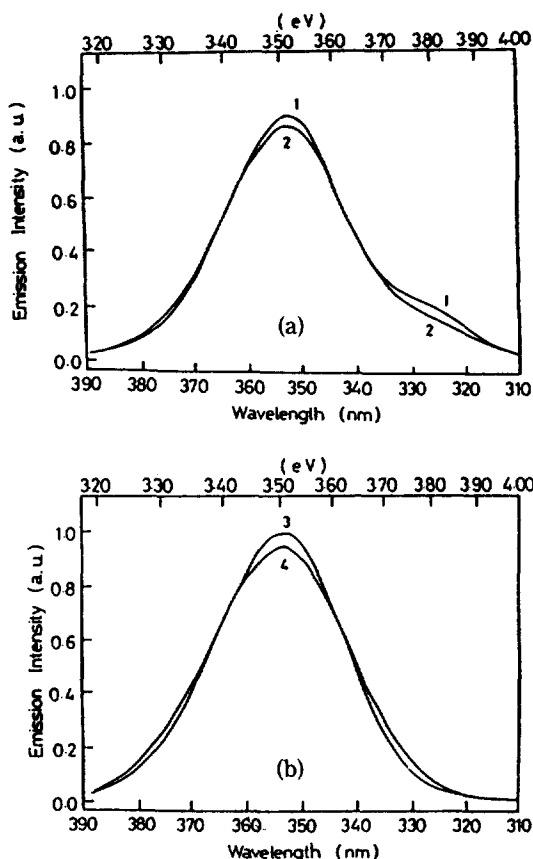


Figure 1. Emission spectra of RbCl:Pb²⁺ excited in the A-band (270 nm) at various temperatures: (a) 1; 14.8 K, 2; 36.0 K, (b) 3; 65.0 K, 4; 100.0 K.

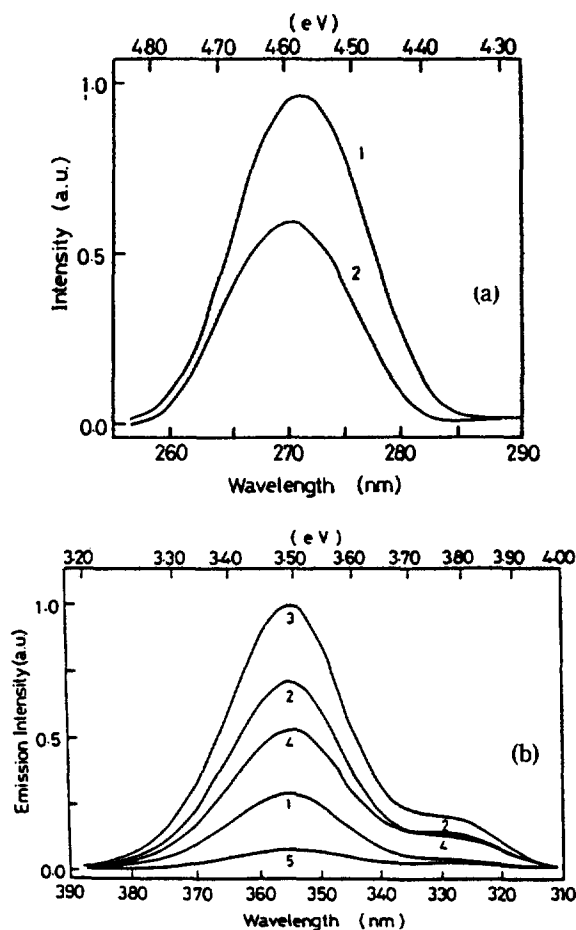


Figure 2. (a) Excitation spectra for 1; 355 nm and 2; 322 nm, (b) intensity spectra of RbCl:Pb²⁺ emission for various excitation wavelengths: 1; 280 nm, 2; 276 nm, 3; 272 nm, 4; 265 nm and 5; 260 nm.

A-absorption band produces both of the two emission bands. If the additional band arises from an aggregation of Pb^{2+} ion, it shows a complex dependence of the exciting energy as $\text{KI}:\text{Pb}^{2+}$ does.⁴ All of the above features can permit one to assign the two emission bands of $\text{RbCl}:\text{Pb}^{2+}$ as the principal emission which arises from isolated $\text{Pb}^{2+} - \nu_c^-$ dipoles.

According to the A-absorption spectra of $\text{RbCl}:\text{Pb}^{2+}$,⁶ the spin-orbit interaction has a value of 0.975 eV. Assuming

that the Jahn-Teller energy, $E_{JT} = \frac{1}{2}$ Stoke's shift, it can be estimated from the experimental results of the A-band emission from $\text{RbCl}:\text{Pb}^{2+}$: $E_{JT} = 0.42$ eV for 322 nm emission and 0.55 eV for the 354 nm emission. It is reasonable to choose ${}^3T_{1u}^*$ state due to the mixing of ${}^3T_{1u}$ and ${}^1T_{1u}$, and ${}^3A_{1u}$ for the relaxes excited states. The next step is to consider the effect of the Jahn-Teller effect on the ${}^3T_{1u}^*$ state. In this case, the coupling to the tetragonal $E_g(Q_2, Q_3)$ modes is much stronger than it is to the trigonal $T_{2g}(Q_4, Q_5, Q_6)$ modes. Taking into account the linear Jahn-Teller effect in terms of the E_g modes, Ranfagni and his group⁷ showed that two kinds of minima, tetragonal (T^*) and rhombic (X, nearly tetragonal), can coexist on the ${}^3T_{1u}^*$ APES, depending on values of the lattice energy and the spin-orbit coupling constant. Figure 3 shows the cross section of the APES along one of the two tetragonal vibration modes. It suggests a possible clue for the assignment of the two A-band emissions from $\text{RbCl}:\text{Pb}^{2+}$. On the basis of this

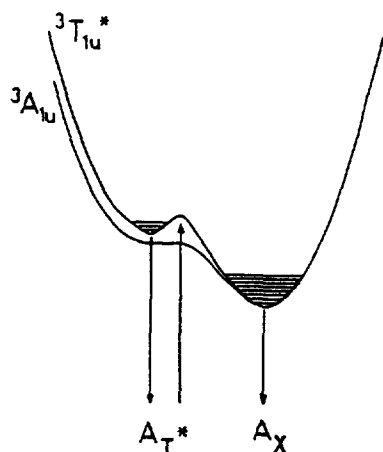


Figure 3. Schematic diagram of ${}^3T_{1u}^*$ and ${}^3A_{1u}$ APES's section along the coordinate Q_2 (or Q_3). The A-band excitation produces both A_{T^*} and A_X emissions which account for the high and low energy bands, respectively.

scheme, the low energy emission could be attributed to transitions from the X minima to the ground state and the high energy emission to transitions from the T^* minima: the former is referred to as A_X and the latter referred to as A_{T^*} .

At very low temperature, both of the two minima could be populated by the A-band excitation. The A_{T^*} emission is observed with very weak intensity, compared with the intensity of the A_X emission, due to the shallow depth of T^* minima. As temperature increases, nonradiative transitions from the T^* parabola to the X increase and result the decrease of intensity of the A_{T^*} emission band. A characteristic feature of the schematic diagram is that the ${}^3A_{1u}$ level is underlying the X minima as a trap level, while for the T^* minima it exists only as a saddle point. Accordingly, it can be seen that the A_{T^*} emission has only a fast component of decay time (ca. 10 ns), while the A_X emission has both fast and slow (ca. millisecond) components due to nonradiative processes between the X level and the trap level. This is very consistent with the experimental results of the decay time of the A-band emission from $\text{RbCl}:\text{Pb}^{2+}$, reported by Schmitt *et al.*⁵

If we further investigate the polarization of the emission from $\text{RbCl}:\text{Pb}^{2+}$ as a function of both azimuthal angle and temperature, a more satisfactory picture of the A-band emission mechanism and a symmetry of the luminescent center can be determined.

Acknowledgments. The author gratefully acknowledges the Korean Science and Engineering Foundation for financial support and is also very grateful to Professor D. J. Simkin for many helpful discussion, and to Professor P. W. M. Jacobs for providing the crystal used in this work.

References

1. F.S. Ham, *Phys. Rev.*, **138**, A1727 (1965)
2. Y. Kamishima, P.W.M. Jacobs, D.J. Simkin, J.-P. Martin and K. Oyama-Gannon, *Phys. Rev.*, **B22**, 3010 (1980).
3. J.G. Kang, T.F. Belliveau and D.J. Simkin, *Chem. Phys. Lett.*, **101**, 381 (1983).
4. J.G. Kang, F. Cusso, T.F. Belliveau and D.J. Simkin, *J. Phys. C*, 1985 (in press).
5. K. Schmitt, V.S. Sivasankar and P.W.M. Jacobs, *J. Lumin.*, **27**, 313 (1982).
6. K. Schmitt, *Phys. Stat. Sol.*, (b)**113**, 559 (1982).
7. A. Ranfagni, *Phys. Rev. Lett.* **28**, 743 (1972); D. Mugnai, A. Ranfagni and G. Vilianni, *Phys. Rev.*, **B25**, 4284 (1982).