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LUMINESCENCE AND EXCITATION SPECTRA
OF U^{3+} DOPED RbY_2Cl_7 SINGLE CRYSTALSM. KARBOWIAK^a, K. MURDOCH^b, J. DROŹDŹYŃSKI^a, N. EDELSTEIN^b
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Uranium(3+) doped single crystals of RbY_2Cl_7 with a uranium concentration of 0.05% and 0.2% were grown by the Bridgman–Stockbarger method using RbU_2Cl_7 as the doping substance. Polished plates of ca. 5 mm in diameter were used for measurements of luminescence and excitation spectra. Since the U^{3+} ions occupy two somewhat different site symmetries, a splitting of all observed $f-f$ bands was observed. The analysis of the spectra enabled definitively an assignment of 22 crystal field bands for both site symmetries as well as the total crystal field splitting of the ground level, equal to 473 cm^{-1} and 567 cm^{-1} for the first and second site symmetry, respectively.

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1. Introduction

The preparation along with some structural, magnetic IR and Raman characterization of $RbDy_2Cl_7$ is given in Ref. [1]. X-ray structural investigations [1–4] show that the compound crystallizes in the orthorhombic system, space group $Pnma$ (D_{2h}) and is isotypic with RbY_2Cl_7 and RbU_2Cl_7 . The central metal ions occupy two distinct positions of the same $m(C_s)$ symmetry. In an idealized manner one may assume for the metal ion the C_{2v} point symmetry of a monocapped trigonal prism. A comparison of the two polyhedrons shows that the difference consists in somewhat different metal–chloride distances [2].

In this paper we present an analysis of low temperature luminescence and site-selective excitation spectra of 0.05% and 0.2% U^{3+} doped RbY_2Cl_7 single crystals. So far similar investigations have been performed for the $U^{3+}:\text{LaCl}_3$ [5], $U^{3+}:\text{LaBr}_3$ [6] and $U^{3+}:\text{LiYF}_4$ [7] single crystals, where U^{3+} ions occupy only one site.

2. Experimental

Single crystals of RbY_2Cl_7 doped with U^{3+} ions to 0.05% and 0.2% were grown by the Bridgman–Stockbarger method using RbU_2Cl_7 as the doping substance. Polished plates of *ca.* 5 mm in diameter, with two different concentrations 0.2% and 5%, were used for measurements of the luminescence and excitation spectra at 4.2 and 15 K using Oxford Instruments optical cryostats.

RbU_2Cl_7 was prepared according to the method reported in Ref. [1]. Laser-selective excitation and fluorescence spectra were recorded using a Spectra Physics model PDL-3 dye laser pumped by the third-harmonic output of a Spectra Physics model GCR-3 Nd:YAG laser. The dyes LDS 751, LDS 698, DCM, Rhodamine 610 were used as appropriate to excite the U^{3+} ions. Fluorescence was analyzed using a Spex model 1403 double-grating monochromator and detected by a thermo-electrically cooled Hamamatsu R943-02 photo-multiplier tube. The signal was amplified by a Stanford Research model SR250 gated integrator and boxcar averager.

3. Results and discussion

Since the U^{3+} ions replace the Y^{3+} ions in the host crystal they occupy the two optically somewhat different sites of the C_{2v} point symmetry, too. As a consequence each of the sharp crystal field bands of $5f^3 \rightarrow 5f^3$ origin consists of two components, which results from the somewhat different crystal field strength of the intrinsic sites.

Laser-selective excitation spectra were recorded in order to identify the transitions associated with the two sites occupied by the U^{3+} ions, henceforth labeled as U(1) and U(2). All transitions observed in the spectra are electric dipole transitions which are allowed in the crystal-field symmetry C_{2v} . Vibronic side bands were not observed. In the C_{2v} symmetry, the ground multiplet $^4I_{9/2}$ is splitted by the crystal-field in 5 components for each site U(1) and U(2). The analysis of the emission spectra allows us to determine the ground multiplet sublevels for the two sites.

The five crystal-field components of the $^4I_{9/2}$ ground level of both U(1) and U(2) intrinsic sites have been definitively determined from emission and excitation spectra. Emission transitions to the five crystal-field components have been observed:

(a) from the lowest component of the $^4F_{9/2}$ level by selective excitation of the $f-f$ absorption lines of the U(1) and U(2) ions at 15145 cm^{-1} and 15088 cm^{-1} , respectively. The emission spectra of the two sites were measured in the $13600\text{--}14400 \text{ cm}^{-1}$ range;

(b) from the lowest component of the $^4G_{7/2}$ level by selective excitation of the same absorption lines (emission spectrum measured in the $12300\text{--}13000 \text{ cm}^{-1}$ range);

(c) from the lowest crystal-field component of the $^4F_{3/2}$ level by selective excitation of the $f-f$ absorption lines of the two sites at 14433 cm^{-1} and 14399 cm^{-1} , respectively;

(d) from the lowest crystal-field component of the $^4I_{11/2}$ level by excitation of the absorption line at 17289 cm^{-1} .

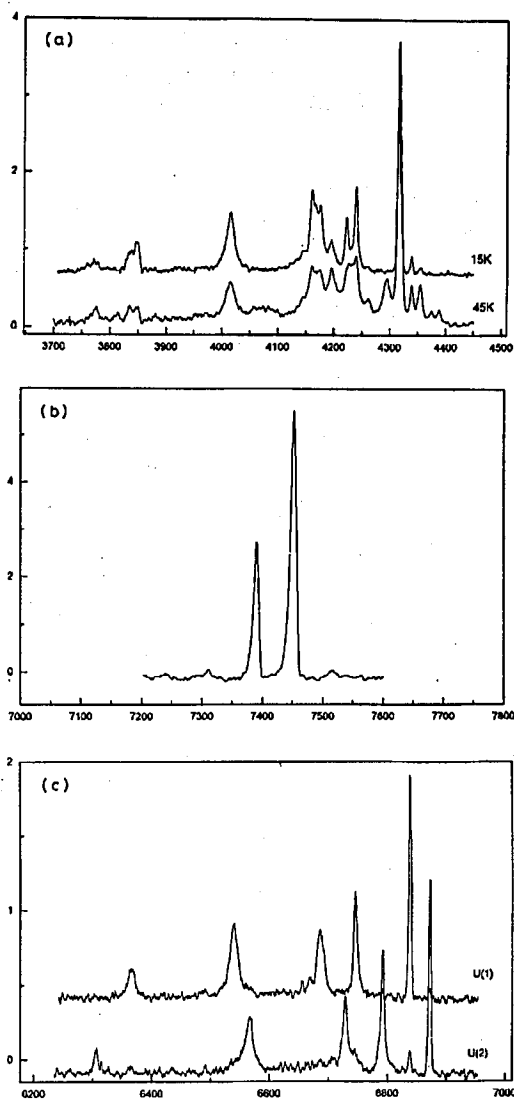


Fig. 1. Emission spectra of U^{3+} : RbY_2Cl_7 crystals (0.2%) at 15 K, in different spectral regions (as indicated).

Some additional lines which appear in the emission spectrum at 45 K were assigned to transitions from the second and third crystal field component of the $^4I_{11/2}$ multiplet to the lowest three and two levels of the ground manifold, respectively. From the analysis of the emission spectra selectively excited in each site U(1) and U(2) the total crystal-field splitting of the ground level is deduced equal to 473 cm^{-1} for U(1) and 567 cm^{-1} for U(2).

All the crystal-field energy levels of the $^4G_{7/2}$, $^4F_{9/2}$ and $^2H_{9/2}$ multiplets

TABLE I
Emission transition energies of the 0.2% and 0.05% $U^{3+}:\text{RbY}_2\text{Cl}_7$ crystals. The labeling follows the nomenclature of Cook [8] and Crosswhite et al. [9].

| U(1) [cm ⁻¹] | U(2) [cm ⁻¹] | Assignment | |
|-----------------------------|-----------------------------|-----------------------|--|
| 4317 | 4314 | $Y_1 \rightarrow Z_1$ | |
| 4222 | 4239 | $Y_1 \rightarrow Z_2$ | |
| 4160 | 4175 | $Y_1 \rightarrow Z_3$ | |
| 4019 | 4011 | $Y_1 \rightarrow Z_4$ | |
| 3846 | 3770 | $Y_1 \rightarrow Z_5$ | |
| 4355 | 4338 | $Y_2 \rightarrow Z_1$ | ${}^4I_{11/2} \rightarrow {}^4I_{9/2}$ |
| 4261 | 4257 | $Y_2 \rightarrow Z_2$ | |
| 4200 | 4194 | $Y_2 \rightarrow Z_3$ | |
| 4386 | 4373 | $Y_3 \rightarrow Z_1$ | |
| 4294 | 4292 | $Y_3 \rightarrow Z_2$ | |
| 6839 | 6872 | $X_1 \rightarrow Z_1$ | |
| 6745 | 6791 | $X_1 \rightarrow Z_2$ | |
| 6684 | 6728 | $X_1 \rightarrow Z_3$ | ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ |
| 6539 | 6567 | $X_1 \rightarrow Z_4$ | |
| 6365 | 6306 | $X_1 \rightarrow Z_5$ | |
| 7453 | 7390 | $G_1 \rightarrow X_1$ | ${}^4F_{9/2} \rightarrow {}^4F_{3/2}$ |
| 12981 | 12981 | $E_1 \rightarrow Z_1$ | |
| 12887 | 12900 | $E_1 \rightarrow Z_2$ | |
| 12826 | 12837 | $E_1 \rightarrow Z_3$ | ${}^4G_{7/2} \rightarrow {}^4I_{9/2}$ |
| 12681 | 12674 | $E_1 \rightarrow Z_4$ | |
| 12508 | 12414 | $E_1 \rightarrow Z_5$ | |
| 14290 | 14261 | $G_1 \rightarrow Z_1$ | |
| 14196 | 14180 | $G_1 \rightarrow Z_2$ | |
| 14135 | 14117 | $G_1 \rightarrow Z_3$ | ${}^4F_{9/2} \rightarrow {}^4I_{9/2}$ |
| 13990 | 13954 | $G_1 \rightarrow Z_4$ | |
| 13817 | 13694 | $G_1 \rightarrow Z_5$ | |

were assigned definitively from site-selective excitation spectra. The lowest energy fluorescing level for the ${}^4G_{7/2} \rightarrow {}^4I_{9/2}$ transition has been found to be at the same energy at 12981 cm⁻¹ for both sites U(1) and U(2). The excitation spectrum in the 14200–14800 cm⁻¹ range of the ${}^4F_{9/2} \rightarrow {}^4I_{9/2}$ transition has been obtained by monitoring the luminescence lines at 12887 cm⁻¹ and 12900 cm⁻¹

TABLE II
Transition energies in the excitation spectra of the 0.2% and 0.05% $U^{3+} : RbY_2Cl_7$ crystals. The labeling follows the nomenclature of Cook [8] and Crosswhite et al. [9].

| U(1) [cm ⁻¹] | U(2) [cm ⁻¹] | Assignment |
|-----------------------------|-----------------------------|------------|
| 14290 | 14261 | G_1 |
| 14356 | 14327 | G_2 |
| 14433 | 14399 | G_3 |
| 14577 | 14592 | G_4 |
| 14693 | 14731 | G_5 |
| 15140 | 15084 | H_1 |
| 15184 | 15120 | H_2 |
| 15209 | 15182 | H_3 |
| 15229 | 15194 | H_4 |
| 15274 | 15252 | H_5 |
| 15363 | 15325 | H_6 |
| 15415 | 15389 | I_1 |
| 15524 | 15479 | I_2 |
| 15577 | 15554 | I_3 |
| 15630 | 15665 | I_4 |
| 15705 | 15718 | I_5 |
| 15861 | 15889 | I_7 |
| 15993 | 16028 | I_8 |

$${}^4I_{9/2} \rightarrow {}^4F_{9/2}$$

$${}^4I_{9/2} \rightarrow {}^2H_{11/2}$$

$${}^4I_{9/2} \rightarrow ({}^2H_{11/2} + {}^4D_{1/2} + {}^2K_{13/2})$$

for the U(1) and U(2) sites, respectively. Similarly, the excitation spectrum in the 15000–16100 cm⁻¹ has been recorded by monitoring the intensities of the emission lines at 14290 and 14261 cm⁻¹. The emission and excitation spectra are shown in Figs. 1–2 while in Tables I and II the transition energies are summarized. The nominal *SLJ* labels as well as an arbitrary alphabetic labeling of the multiplets given by Cook [8] and Crosswhite et al. [9] were used.

An additional minor U^{3+} site, labeled as U(3), was also observed in the laser excitation spectra. It exhibited a similar structure to the two principal sites but with its line groups 100 to 300 cm⁻¹ higher in energy. Their origin is unknown.

The investigations showed that the crystal-field splittings between the pairs of levels are always larger than the apparent splittings of the pairs themselves, i.e. that one of the components belongs to the U(1) and the other one to the U(2) site. The analysis of the spectra enabled the definitive assignment of 22 crystal field bands to the U(1) as well as to the U(2) site symmetry which is a good starting point for a complex spectrum analysis [10].

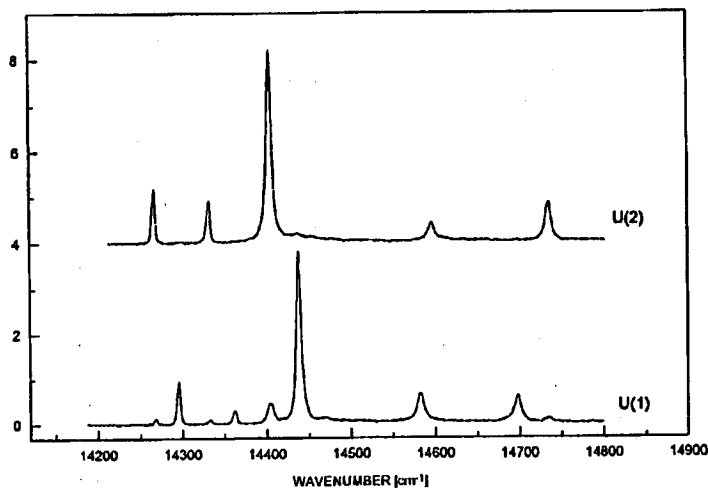


Fig. 2. Excitation spectra of $U^{3+}:\text{RbY}_2\text{Cl}_7$ crystals (0.2%) at 15 K.

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