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ANALYSIS OF EMISSION AND VIBRONIC TRANSITIONS IN URANIUM(3+) DOPED $\text{Cs}_2\text{LiYCl}_6$ SINGLE CRYSTALS

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Uranium(3+) doped single crystals of $\text{Cs}_2\text{LiYCl}_6$ with a 0.3 and 2.0% U^{3+} concentration have been obtained by the Bridgman–Stockbarger method. Luminescence spectra of the crystals were recorded at 27 and 15 K, respectively. The emission bands observed in the visible and near infrared regions have been assigned to transitions from the $^4I_{11/2}$, $^4F_{3/2}$, and $^4G_{7/2}$ levels to the $^4I_{9/2}$ ground level.

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1. Introduction

In this paper we present an analysis of luminescence spectra of uranium(3+) doped $\text{Cs}_2\text{LiYCl}_6$ single crystals at 15 and 45 K. A preliminary study of similar, $\text{Cs}_2\text{NaYCl}_6:\text{U}^{3+}$ single crystals, has been presented earlier [1]. Since in the investigated elpasolite crystals the central metal ion possesses the O_h site symmetry vibronic transitions are an order of magnitude stronger than the electric dipole ones and are very suitable for spectroscopic investigations.

2. Experimental

Uranium(3+) doped single crystals of $\text{Cs}_2\text{LiYCl}_6$ with a 0.1% uranium concentration were grown by the Bridgman–Stockbarger method using $\text{Cs}_2\text{LiUCl}_6$ as the doping substance. Polished plates of ca. 6 mm in diameter and 1 to 5 mm thick were used for measurements of the luminescence spectra.

For the preparation of $\text{Cs}_2\text{LiUCl}_6$ a well-grinded stoichiometric mixture of CsCl , NaCl and $\text{NH}_4\text{UCl}_4 \cdot 4\text{H}_2\text{O}$ [2] was first heated in a quartz tube at a non-static vacuum of ca. 10^{-6} hPa. In order to convert $\text{NH}_4\text{UCl}_4 \cdot 4\text{H}_2\text{O}$ into UCl_3 , the temperature of the furnace was slowly increased from 20 to 350°C. Next the tube was sealed off and the mixture heated for 24 h at 300°C. Subsequently the temperature was slowly decreased and the mixture heated at 400°C for 7 days. An ink blue fine crystalline powder was obtained. The compound was stored under nitrogen in

sealed tubes. $\text{Cs}_2\text{LiYCl}_6$ was obtained by evaporating stoichiometric amounts of Cs_2CO_3 , LiCl and Y_2O_3 from a 10 M HCl solution.

The emission spectra were recorded at 15 K and 45 K on a Jobin-Yvon HR 1000 monochromator using an Oxford cryogenic cryostat. As detectors the Hamamatsu R928 photomultiplier and a PbS diode were used. The emission spectrum was obtained by selective excitation of particular $f-f$ lines with a YAG laser pumped dye laser.

3. Results and discussion

In Figs. 1, 2 the emission spectra of the $\text{Cs}_2\text{LiYCl}_6 : \text{U}^{3+}$ single crystals in the visible and infrared range are presented. The bands observed in the 12000–13000 cm^{-1} range were assigned to transitions from the $^4G_{7/2}$ level to the three crystal-field components of the $^4I_{9/2}$ ground level. In this range one does not observe zero-phonon transitions but only the vibronic structures connected with these transitions. The positions of the zero-phonon transitions were determined basing on the Stokes and anti-Stokes transition symmetry as well as on an analysis of the observed repetitive vibronic structures.

Fig. 1. Fluorescence spectra showing the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transitions at 15 K in the $\text{U}^{3+}:\text{Cs}_2\text{LiYCl}_6$ crystals.

A similar rich and well-resolved vibronic structure was observed in the 6000–7000 cm^{-1} range from which emission to the three crystal-field components of the ground manifold $a\Gamma_8$, Γ_6 and $b\Gamma_8$ takes place from the lowest crystal-field component of the $^4F_{3/2}$ level. In this range one may observe also two zero-phonon lines most probably connected with magnetic-dipole transitions at 6995 cm^{-1}

TABLE
 ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ and ${}^4G_{7/2} \rightarrow {}^4I_{9/2}$ luminescence spectra of the $U^{3+}:\text{Cs}_2\text{LiYCl}_6$ crystals
 at 15 K.

${}^4G_{7/2} \rightarrow {}^4I_{9/2}$ transition			${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition		
Line ^a	Wave number [cm ⁻¹]	Assignment of lower level ^b	Line	Wave number [cm ⁻¹]	Assignment of lower level ^c
(1)	12967	$a\Gamma_8$	1	6995	$a\Gamma_8$
2	12918	$a\Gamma_8 + S_9(50)$	2	6955	$a\Gamma_8 + S_5(40)$
3	12902	$a\Gamma_8 + S_{10}(65)$	3	6945	$a\Gamma_8 + S_9(50)$
4	12884	$a\Gamma_8 + S_{10}(83)$	4	6933	$a\Gamma_8 + S_{10}(62)$
(5)	12874	Γ_6	5	6914	$a\Gamma_8 + S_{10}(81)$
6	12872	$a\Gamma_8 + S_7(95)$	6	6902	Γ_6
			7	6898	$a\Gamma_8 + S_7(97)$
			8	6887	$a\Gamma_8 + S_7(108)$
7	12828	$\Gamma_6 + S_9(46)$	9	6855	$\Gamma_6 + S_9(47)$
			10	6834	$\Gamma_6 + S_{10}(68)$
			11	6817	$\Gamma_6 + S_{10}(88)$
8	12777	$\Gamma_6 + S_7(97)$			
9	12735	$a\Gamma_8 + S_6, S_2ZB(232)$	12	6764	$a\Gamma_8 + S_6, S_2ZB(231)$
10	12726	$a\Gamma_8 + S_6(241)$	13	6752	$a\Gamma_8 + S_6(243)$
11	12649	$\Gamma_6 + S_6, S_2ZB(225)$	14	6701	$\Gamma_6 + S_6, S_2ZB(201)$
12	12632	$\Gamma_6 + S_6(242)$	15	6668	$\Gamma_6 + S_6(234)$
(13)	12371	$b\Gamma_8$	16	6400	$b\Gamma_8$
14	12321	$b\Gamma_8 + S_9(50)$	17	6350	$b\Gamma_8 + S_9(50)$
15	12305	$b\Gamma_8 + S_{10}(66)$	18	6337	$b\Gamma_8 + S_{10}(63)$
16	12289	$b\Gamma_8 + S_{10}(82)$	19	6319	$b\Gamma_8 + S_{10}(81)$
17	12274	$b\Gamma_8 + S_7(97)$	20	6302	$b\Gamma_8 + S_7(98)$
18	12242	$b\Gamma_8 + S_7(129)$	21	6291	$b\Gamma_8 + S_7(109)$
19	12150	$b\Gamma_8 + S_6, S_2ZB(221)$	22	6169	$b\Gamma_8 + S_6, S_2ZB(231)$
20	12128	$b\Gamma_8 + S_6(243)$	23	6157	$b\Gamma_8 + S_6(243)$

^a Lines in brackets are zero-phonon lines, not observed in the spectra.

^b The upper level is ${}^4G_{7/2}(\Gamma_7)$.

^c The upper level is ${}^4F_{3/2}(\Gamma_8)$.

($\Gamma_8 \rightarrow a\Gamma_8$) and 6400 cm⁻¹ ($\Gamma_8 \rightarrow b\Gamma_8$). The third one is most probably covered by the strong vibronic side bands.

In the 4000–4400 cm⁻¹ spectral range one observes together with some low intensity vibronic transitions, two distinct zero-phonon lines connected with the forbidden electric-dipole transitions from the lowest crystal-field level of the ${}^4I_{11/2}$ manifold to the excited crystal-field components of the ground level.

The performed analysis enabled the determination of the energies of the excited components of the ground level equal to 93 (Γ_6) and 595 ($b\Gamma_8$) cm⁻¹ as well as the assignment of the observed vibronic modes which are summarized in Table. In the assignment of the vibronic bands we followed the earlier reported analysis of Nd³⁺ [3] and U³⁺ [4] ions in Cs₂NaYCl₆ single crystals.

Fig. 2. Fluorescence spectra showing the ${}^4G_{7/2} \rightarrow {}^4I_{9/2}$ transitions at 15 K in the $\text{U}^{3+}:\text{Cs}_2\text{LiYCl}_6$ crystals.

References

- [1] P.J. Dereń, W. Stręk, J. Drożdżyński, *J. Appl. Spectrosc.* **62**, 58 (1995).
- [2] J. Drożdżyński, *J. Less-Common Met.* **138**, 271 (1988).
- [3] P.A. Tanner, J. Quagliano, F.S. Richardson, *J. Chem. Soc. Faraday Trans.* **87**, 1707 (1991).
- [4] P.A. Tanner, *J. Mol. Struct.* **355**, 299 (1995).