

Optical spectroscopy and crystal-field analysis of U^{3+} : Ba_2YCl_7 .

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Streszczenie

High resolution absorption spectra of a U^{3+} (0.3%) : Ba_2YCl_7 single crystal were recorded in the 4000–50 000 cm^{-1} range at 7 K. The observed crystal-field levels were assigned and fit to the parameters of the simplified angular overlap model (AOM) as well as a semi-empirical Hamiltonian representing the combined atomic and one-electron crystal-field interactions. The starting values of the AOM parameters were obtained from *ab initio* calculations. The analysis of the spectra allowed the assignment of 65 crystal-field levels with a relatively small rms deviation of 25 cm^{-1} and has shown that the AOM approach can predict quite well the B^k_q crystal-field parameters. The value determined for the crystal-field strength parameter, N_q corresponds well with those determined for U^{3+} in other chloride single crystals. In recent years we have reported the results of crystal-field analyses for U^{3+} doped RbY_2Cl_7 ,¹ K_2UX_5 (X = Cl, Br or I),² Cs_2NaYCl_6 ³ and Cs_2LiYCl_6 ³ single crystals as well as for some polycrystalline samples.^{4–6} Since, in all these chloride crystals, the U^{3+} ions readily undergo hydrolysis and oxidation in the presence of traces of water, we have searched for moisture resistant crystals. To date only fluoride hosts provide such properties. However, due to experimental difficulties, no high quality U^{3+} doped single crystals of a fluoride compound could be grown. Simoni *et al.* have converted U^{4+} ions doped in $LiYF_4$ single crystals into U^{3+} ions by γ -irradiation.⁷ This method, however, inevitably leads to a number of site defects. Another important disadvantage is that only a very small UF_4 concentration could be reduced to the U^{3+} state. Since Wickleder *et al.*⁸ synthesized, in a systematic search for new host lattices, a series of relatively air-stable Ba_2MCl_7 type of compounds (where M = Gd–Yb, Y) and determined their crystal structure, we turned our attention towards the relatively moisture-stable Ba_2YCl_7 crystal. Ba_2YCl_7 crystallizes in the monoclinic space group $P2_1/c$ (No. 14).⁸ The Y^{3+} ions are seven-coordinated and the characteristic feature of

the crystal structure is the $[YCl_7]$ polyhedra, build in the form of a trigonal prism and capped on one rectangular face. Due to a slight distortion of the polyhedra, the Y^{3+} site symmetry is C_1 . The $[YCl_7]$ units are isolated with an extremely long $Y^{3+}-Y^{3+}$ distance of approximately 6.5 Å. The Y–Cl distances, approximately 2.7 Å, are typical for yttrium complex chlorides. In this paper the absorption and emission spectra for U^{3+} : Ba_2YCl_7 are presented and discussed. A crystal-field analysis, based on both the angular overlap model (AOM) and the conventional parametric Hamiltonian, is presented.

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