$5f^N$-$5f^{N-1}6d^1$ transitions of U^{3+} and U^{4+} ions in high-symmetry sites.

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Streszczenie

$5f^N$ → $5f^{N\text{-}1}6d^1$ absorption spectra of U^{4+}- and U^{3+}-doped Cs_2NaYCl_6, Cs_2LiYCl_6, Cs_2NaYBr_6, $CsCdBr_3$, and $Cs_3Lu_2Cl_9$ single crystals were recorded at 4.2 K in the 14 000−50 000 cm^{-1} spectral range. The $5f^2$ → $5f^16d^1$ absorption bands of U^{4+} ions were observed in the 30 000−37 000 cm^{-1} energy range, and have been assigned as transitions from the $^3H_4$ ground multiplet of the $5f^2$ configuration to crystal-field levels of the $5f^16d(t_{2g})^1$ manifold. The energies of the lowest levels of the $5f^16d(t_{2g})^1$ configuration have been for the first time determined for U^{4+} ions doped in a chloride or bromide host crystal. They are equal to 26 360 and 28 590 cm^{-1} for U^{4+}:$CsCdBr_3$ and U^{4+}:Cs_2NaYBr_6 respectively and range from 30 360 to 31 010 cm^{-1} for U^{4+} doped in the chloride hosts. Highly structured vibronic bands of $5f^3$ → $5f^26d(t_{2g})^1$ absorption transitions of the U^{3+} ions appeared at an energy as low as 14 158 cm^{-1}, and have been assigned to transitions from the $^4I_{9/2}$ ground multiplet of the $5f^3$ configuration to crystal-field levels arising from the configurations $5f^2(^3H_4)6d(t_{2g})^1(\Gamma_{8g})$ (barycenter at ∼16 000 cm^{-1}) and $5f^2(^3H_4)6d(t_{2g})^1(\Gamma_{7g})$ (barycenter at ∼19 000 cm^{-1}). Besides, some low intensity bands observed at ∼18 600 and above 21 000 cm^{-1} have been assigned as transitions to the $5f^2(^3F_2)6d(t_{2g})^1(\Gamma_{8g})$ and $5f^2(^3F_2)6d(t_{2g})^1(\Gamma_{7g})$ levels, respectively. Transitions to the $5f^26d(e_g)^1$ levels of U^{3+} ions have been observed as broad and unstructured bands at wavenumbers higher than 38 000 cm^{-1}. The crystal field splitting ($10Dq$) of the $5f^26d^1$ configuration for U^{3+} doped in Cs_2NaYCl_6 single crystals amounts to ∼23 000 cm^{-1}, and the separation between Γ_{8g} and Γ_{7g} components of the t_{2g} state, resulting from spin−orbit interaction for the 6d electron, can be evaluated as 3350 cm^{-1}. The splitting of the $5f^2(^{2S+1}L_J)6d(\gamma)^1(\Gamma_{ig})$ ($\gamma = t_{2g}$ or e_g; $i = 7$ or 8) configurations, resulting from the coupling of the $5f^2$ core electrons with the 6d electron is somewhat smaller and amounts to ∼3000 cm^{-1}. The main feature of the crystal level structure observed in the $5f^3$−$5f^26d^1$ absorption spectra of U^{3+} ions reflects the dominating influence of the crystal field splitting and spin−orbit coupling of the 6d electron.

Słowa kluczowe

Absorption spectroscopy, Crystal structure, Crystals, Energy, Ions

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