

The $5f^2 \rightarrow 5f^1 6d^1$ absorption spectrum of $\text{Cs}_2\text{GeF}_6:\text{U}^{4+}$ crystals: a quantum chemical and experimental study.

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Artykuł

Single crystals of U^{4+} -doped Cs_2GeF_6 with 1% U^{4+} concentration have been obtained by the modified Bridgman-Stockbarger method in spite of the large difference in ionic radii between Ge^{4+} and U^{4+} in octahedral coordination. Their UV absorption spectrum has been recorded at 7 K, between 190 and 350 nm; it consists of a first broad and intense band peaking at about $38\,000\text{ cm}^{-1}$ followed by a number of broad bands of lower intensity from $39\,000$ to $45\,000\text{ cm}^{-1}$. None of the bands observed shows appreciable fine vibronic structure, so that the energies of experimental electronic origins cannot be deduced and the assignment of the experimental spectrum using empirical methods based on crystal field theory cannot be attempted. Alternatively, the profile of the absorption spectrum has been obtained theoretically using the U–F bond lengths and totally symmetric vibrational frequencies of the ground $5f^2-1A_1g$ and $5f16d(t_2g)^1-iT_{1u}$ excited states, their energy differences, and their corresponding electric dipole transition moments calculated using the relativistic ab initio model potential embedded cluster method. The calculations suggest that the observed bands are associated with the lowest five $5f^2-1A_1g \rightarrow 5f16d(t_2g)^1-iT_{1u}$ ($i = 1-5$) dipole allowed electronic origins and their vibrational progressions. In particular, the first broad and intense band peaking at about $38\,000\text{ cm}^{-1}$ can be safely assigned to the 0-0 and 0-1 members of the a_{1g} progression of the $5f^2-1A_1g \rightarrow 5f16d(t_2g)^1-1T_{1u}$ electronic origin. The electronic structure of all the states with main configurational character $5f16d(t_2g)^1$ has been calculated as well. The results show that the lowest crystal level of this manifold is $5f16d(t_2g)^1-1Eu$ and lies about 6200 cm^{-1} above the $5f^2$ level closest in energy, which amounts to some 11 vibrational quanta. This large energy gap could result in low nonradiative decay and efficient UV emission, which suggest the interest of investigating further this new material as a potential UV solid state laser.

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