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The complexity of the CaF_2:Yb system: evidence that CaF_2:Yb2+ is not an impurity trapped exciton system CAMERON MACKEEN, FRANK BRIDGES, University of California, Santa Cruz, MICHAEL KOZINA, APURVA MEHTA, Stanford Synchrotron Radiation Lightsource, M. F. REID, J.-P. R. WELLS, Dodd-Walls Centre for Photonic and Quantum Technologies, University of Canterbury, ZOILA BARANDIARN, Universidad Autnoma de Madrid — Fluorite crystal structures doped with rare-earth elements exhibit an anomalous redshifted luminescence upon UV excitation, generally attributed to the relaxation of impurity trapped excitons (ITE). We find that the intensity of this luminescence decreases as the total concentration of Yb 2+ increases in unexposed samples, which is in conflict with the currently accepted ITE model. Further, using x-ray absorption spectroscopy and UV-vis studies of CaF_2:Yb, we find a large (but reversible) Yb valence reduction upon x-ray exposure at 200 K - from mostly 3+ to 2+. This valence reduction is stable for long time periods at low T ¡ 50 K, but reverts to the initial state upon warming to 300 K. After reverting to the initial valence state of 3+ the anomalous luminescence does not reappear; only after annealing at 900 K do we again observe the anomalous emission below 150 K. To explore the mechanism at work, we employ extended x-ray fine-structure absorption spectroscopy (EXAFS) to probe local structure and its role in the anomalous luminescence. The x-ray and emission studies show that CaF_2:Yb is not described by the ITE model; the data appear more consistent with an intervalence charge transfer (IVCT) model. It is likely that many similar ITE systems have also been misidentified.

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