Structural origin of the optical anisotropy in Ce^{3+}-doped fluoride crystals

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Cerium-doped lithium calcium hexafluoroaluminate (Ce:$LiCaAlF_6$ or Ce:LiCAF) crystal is by far the most successful solid-state gain medium for amplifying and generating ultrashort ultraviolet (UV) pulses [1-2]. Ce:LiCAF has a strong absorption band around 266 nm (UV) which enables direct optical pumping by the fourth harmonics of an Nd:YAG laser. The optical emission is characterized by a broad bandwidth, a large Stokes shift, and a nanosecond lifetime owing to the electric dipole-allowed interconfigurational 5d→4f transition of Ce^{3+} ion [3-7]. Ce:LiCAF's laser conversion efficiency is also high because it suffers less from solarization and excited-state absorption (ESA) which are prevalent in many rare-earth-doped materials. However, the gain spectrum has been found to exhibit polarization dependence [7]. The highest gain is obtained when the probe is polarized parallel to the optical axis of the crystal. This has been attributed to the anisotropic nature of ESA which is associated with the layered structure of the crystal. To investigate the origin of Ce:LiCAF's optical anisotropy, we performed x-ray absorption spectroscopy on a 1.0 mol% Ce-doped $LiCaAlF_6$ crystal. Through our Ce L_3-edge XANES analyses, we confirmed that the Ce:LiCAF crystal is dominated by Ce^{3+} ions. The crystal was also found to exhibit an extra feature similar to the CeO_2 reference which is associated to the Ce^{4+} oxidation state. However, our Ce K-edge XANES analysis affirmed the presence of Ce^{3+} oxidation state alone, not the coexistence of both Ce^{3+} and Ce^{4+}. We will employ combined DFT and FDMNES simulations in order to understand the charge transfer mechanism between the Ce^{3+} ion and its neighboring atoms, its correlation to the additional features in the Ce L_3-edge and ultimately to the luminescence of the crystal. Similar analyses will also be performed for related materials such as Ce-doped $KMgF_3$ (Ce:$KMgF_3$ or Ce:KMF) crystal to provide comparison with a fluoro-perovskite crystal with lower quantum efficiency. Our results will provide full understanding of Ce ion's role on the electronic properties of laser crystals in general.

References

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