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5d–4f luminescence of Ce^{3+}, Gd^{3+} and Lu^{3+} in $LiCaAlF_6$

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ABSTRACT

The emission and excitation spectra as well as decay kinetics of luminescence due to 5d–4f transitions in Ce^{3+}, Gd^{3+} and Lu^{3+} ions doped into $LiCaAlF_6$ crystals have been analyzed with high spectral and time resolution using synchrotron radiation for excitation. The rich fine structure originating from electronic origins of transitions and their phonon replica has been well resolved and identified. Experimental data are compared with the spectra simulated in the framework of the semiphenomenological models of the crystal field and the crystal lattice dynamics.

1. Introduction

The vacuum ultraviolet (VUV) spectroscopy of interconfigurational $4f^n$–$4f^{n-1}5d$ (hereafter abbreviated to 4f–5d) transitions of trivalent lanthanide (Ln^{3+}) ions doped into wide band-gap crystals is a well-established field of research in solid-state physics. The recent progress in this field was driven not only by the demand in new fast scintillators and efficient quantum-cutting phosphors, but also by the appearance of powerful setups for luminescence spectroscopy in VUV working with synchrotron radiation as an excitation source [1]. The new experimental results obtained with high spectral and time resolution stimulated theoretical work on calculations of electron–phonon 4f–5d excitations, in particular, taking into account the real crystal lattice vibrational spectra [2]. The combination of the high-resolution spectra with their theoretical treatment results in deeper understanding of Ln^{3+} 5d–4f luminescence and 4f–5d excitations in various wide band-gap hosts.

Up to recently, 5d–4f luminescence in VUV has been detected only from three lanthanide ions: Nd^{3+}, Er^{3+} and Tm^{3+}. However, our recent studies [3–8] have shown that 5d–4f luminescence in deep VUV region (at about 10 eV) is observed also from Gd^{3+} and Lu^{3+} ions if these ions are incorporated into some fluoride host with sufficiently wide band-gap, such as $LiYF_4$, YF_3 and CaF_2. One could expect that these ions will also show VUV 5d–4f luminescence if they are doped into the $LiCaAlF_6$ (LiCAF) crystals, which have one of the largest values of band-gap energy (12.65 eV) [9] among fluoride compounds.

The LiCAF crystals doped with lanthanide ions are considered as promising media for potential applications in laser and scintillation techniques. In particular, tunable laser operation on 5d–4f transitions of Ce^{3+} has been obtained under optical pumping of Ce^{3+} doped LiCAF [10]. LiCAF crystals doped with Ce^{3+} or Eu^{2+} have been proposed as promising scintillators [11–13] as well as potential dosimetric materials [14], doped with Pr^{3+} as possible phosphors with cascade radiative transitions [15], doped with Nd^{3+} as optical material for 157 nm photolithography [16].

In the present work the first observation and detailed characterization of VUV luminescence due to 5d–4f transitions in Gd^{3+} and Lu^{3+} ions doped into LiCAF crystals are reported. In particular, high-resolution VUV luminescence and excitation spectra, allowing for an analysis of electron–phonon coupling, have been measured. A comparison of experimental spectra with results of simulations performed for LiCAF crystals doped with Ce^{3+} and Lu^{3+} ions is also presented. The spectra were simulated

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