Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Luminescence 119–120 (2006) 28–32
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Two-photon excitation to $4f^6 5d$ configuration of Gd^{3+} in $LiGdF_4$ crystal by KrF excimer laser

D. Lo[a], V.N. Makhov[b,*], N.M. Khaidukov[c], J.C. Krupa[d]

[a]*Physics Department, Chinese University of Hong Kong, Hong Kong SAR, China*
[b]*Lebedev Physical Institute, 119991 Moscow, Russia*
[c]*Kurnakov Institute of General and Inorganic Chemistry, 119991 Moscow, Russia*
[d]*Institut de Physique Nucléaire, 91406 Orsay Cedex, France*

Available online 30 January 2006

Abstract

The two-photon excitation to high-lying levels of Gd^{3+} via the intermediate ^6D_J levels in $LiGdF_4$ and GdF_3 crystals has been studied under pumping by 248 nm radiation from a KrF excimer laser. Luminescence in the UV (204 nm), orange (570–640 nm) and IR (720–810 nm) regions, which is due to ^6G_J–$^8S_{7/2}$, ^6G_J–^6P_J and ^6G_J–^6I_J transitions in Gd^{3+}, respectively, has been observed from the $LiGdF_4$ crystal at room temperature. No radiative transitions from the $4f^7\ ^6G_J$ levels of Gd^{3+} have been detected from the GdF_3 crystal. It was assumed that at low temperatures the two- photon excitation of the $LiGdF_4$ crystal with a KrF laser could result in the observation of short-wavelength upconverted VUV luminescence at ~127 nm due to $4f^6 5d$–$4f^7\ ^8S_{7/2}$ transitions in Gd^{3+} .

PACS: 78.55.Hx; 71.55.Ht; 42.72.Bj

Keywords: 5d–4f and 4f–4f luminescence; Trivalent gadolinium ion; Fluoride crystals; Upconverted UV/VUV luminescence; $LiGdF_4$; GdF_3

1. Introduction

Wide band-gap crystals doped with rare earth (RE) ions, which exhibit radiative interconfigurational $4f^{n-1}5d$–$4f^n$ transitions, are well-known solid-state VUV emitters and are considered as promising candidates for laser action in the VUV range [1]. However, up to now, only 172 nm laser emission from Nd^{3+}-doped LaF_3 crystals has been reported for this region [2,3]. The upconversion (two-photon) pumping seems to be more favourable because it is expected that in such pumping schemes the effect of excited state absorption [4] is less important than in the case of one-photon optical pumping. VUV/deep UV upconversion emission sources are also of practical interest, in particular, for sub-micron photolithography.

*Corresponding author. Fax: +7 095 9382251.
E-mail address: makhov@sci.lebedev.ru (V.N. Makhov).

0022-2313/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2005.12.007

In this context, VUV/UV $4f^2 5d$–$4f^3$ luminescence of Nd^{3+} under two-photon excitation at 355 nm with a pulsed-frequency-tripled Nd:YAG laser for $LiYF_4$, $LiLuF_4$, BaY_2F_8 and $Na_{0.4}Y_{0.6}F_{2.2}$ doped with Nd^{3+} [5–7] and under two-photon excitation at 351 nm with a XeF excimer laser for Nd^{3+}-doped $LiYF_4$ [8] has been detected.

Recently, rather short-wavelength VUV luminescence at 125–127 nm, which is due to $4f^6 5d$–$4f^7$ interconfigurational transitions in the Gd^{3+} ion, has been discovered in the $LiGdF_4$ and GdF_3 crystals under one-photon excitation [9]. In the present paper the two-photon excitation to high-lying levels of Gd^{3+} in $LiGdF_4$ and GdF_3 crystals has been studied under pumping by 248 nm radiation from a KrF excimer laser.

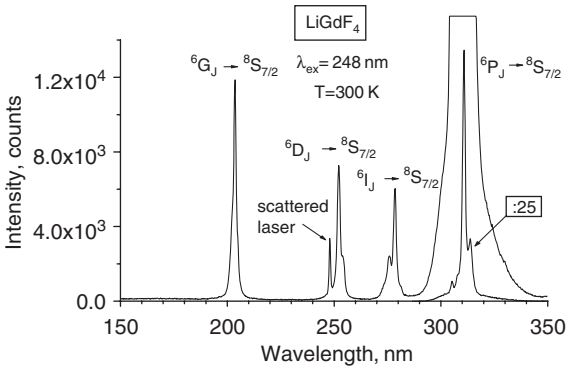

Fig. 1. UV emission spectrum of the $LiGdF_4$ crystal excited by 248 nm radiation from a KrF excimer laser at 300 K. The assignments of emission lines to corresponding $4f^7$–$4f^7$ transitions in the Gd^{3+} ion are shown.

2. Experiment

A KrF excimer laser AQX-150 (MPB Technologies Inc.) operating at 248 nm was used for the two-photon excitation experiments. Luminescence emitted from the samples was analyzed by a 0.4 m Czerny–Turner vacuum monochromator (SpectraPro VM-504, Acton Research Corporation) equipped with a gated diode array detector (IVUV-700, Princeton Instruments). The instrumental resolution of the spectrometer was 0.2 nm. The energy in the 25 ns pulse of the KrF laser was 150–170 mJ.

Single crystals of $LiGdF_4$ and GdF_3 were grown by the Czochralski method as described in Ref. [10]. For the experiments polished cubic samples with a characteristic length of 5 mm were used. All the experiments were performed at room temperature.

3. Results and discussion

Under excitation of the $LiGdF_4$ crystal by 248 nm radiation from a KrF laser, the UV luminescence is observed (Fig. 1), including the upconverted emission at 204 nm which is due to electronic transitions from the $4f^7$ ^6G_J levels to the $4f^7$ $^8S_{7/2}$ ground state in the Gd^{3+} ion [11]. The presence of the 204 nm emission in the spectrum undoubtedly evidences that two-photon excitation to high-lying Gd^{3+} levels takes place in the $LiGdF_4$ crystal under KrF laser pumping. Radiative transitions from low-lying levels within $Gd^{3+}4f^7$ configuration, namely from ^6D_J, ^6I_J and ^6P_J to the ground state, are also observed in the spectrum. As expected, the most intense emission is observed at 311 nm from the lowest excited Gd^{3+} ^6P_J levels separated from the ground state by the gap $\sim 32,000\,cm^{-1}$. The energy gaps between ^6D_J and ^6I_J multiplets and between ^6I_J and ^6P_J multiplets are around $2800\,cm^{-1}$, whereas the cut-off phonon energy for the $LiGdF_4$ crystal is $\sim 560\,cm^{-1}$ [12], i.e. these gaps can be bridged by 5-phonon relaxation process resulting in high enough rate of non-radiative relaxation from the respective levels. The rate of $^6I_{7/2} \rightarrow {}^6P_J$ non-radiative relaxation has been estimated to exceed the probability of radiative decay of the $^6I_{7/2}$ level to the ground state [13], which results in additional population of the lowest excited ^6P_J levels.

In the long-wavelength range, orange (570–640 nm) and IR (720–810 nm) luminescence is also observed under KrF laser excitation (Fig. 2), which is due to ^6G_J–^6P_J and ^6G_J–^6I_J transitions in Gd^{3+}, respectively [11]. These visible and IR emissions as well as the UV (204 nm) luminescence can be observed, in principle, under excitation both to the high-lying $4f^7$ levels (higher than $^6G_{7/2}$) and to the Gd^{3+} $4f^6 5d$ levels.