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FIRST OBSERVATION OF VISIBLE LUMINESCENCE FROM TRIVALENT GADOLINIUM

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The $^6G_J \rightarrow {}^6P_J$ emission for Gd^{3+} in $LiYF_4$ around 600 nm is reported. As far as we are aware, this is the first observation of visible luminescence from trivalent gadolinium.

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1. Introduction

The development of new phosphors for vacuum ultraviolet (VUV) excitation is an important new challenge in the field of luminescent materials research. VUV phosphors can be applied in mercury free fluorescent tubes and in plasma display panels, in combination with a noble gas discharge. The xenon dimer discharge, which gives the highest efficiency of all noble gases, is still less efficient than the conventional mercury discharge. Therefore a phosphor with a quantum efficiency higher than 100% is needed, in other words: more than one visible photon should be obtained per absorbed VUV photon. One of the challenges in this research area is to find such a VUV phosphor, a so-called quantum cutter. For rare earth ions the phenomenon of quantum cutting is known [1], but based on the current knowledge no efficient quantum cutter in the visible is possible. However, the energy levels of rare earth ions in the VUV region (above 50 000 cm^{-1}) have hardly been investigated. The high energy of the VUV photons from a xenon dimer discharge (172 nm, 58 100 cm^{-1}) makes it possible (in theory) to obtain quantum cutting in the visible.

The research on quantum cutters will focus on the luminescence of rare earth ions under VUV excitation. First, the energy levels in the VUV will be resolved for a number of rare earth ions. The first ions to be investigated will be those ions which are able to give an efficient emission in the visible, either directly or after energy transfer, viz. Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Ho^{3+} and Er^{3+}. To resolve the energy levels in the VUV the lanthanides will be incorporated in fluoride lattices (e.g. $LiYF_4$ and LaF_3). In these host lattices the excited states ($4f^{n-1}5d$ and charge transfer) which can interfere with the energy levels of the

$4f^n$ configuration are at the highest possible energies. Next, it will be investigated if an efficient quantum cutter is possible for one of the rare earth ions studied. To this extent the emission spectra under VUV excitation will be analyzed. With the aid of Judd–Ofelt theory it can be determined if an efficient quantum cutter in the visible is feasible.

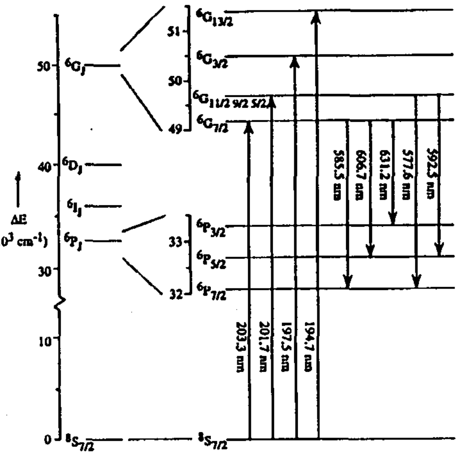

Fig. 1. Energy level scheme in the range 0–50 000 cm^{-1} for Gd^{3+} in fluoride lattices. Note the breaks in the energy scale. The arrows correspond to lines in the excitation spectrum in Fig. 2 and the emission spectrum in Fig. 3.

In this paper the first results on Gd^{3+} in $LiYF_4$ are presented. The schematic energy level diagram of Gd^{3+} ($4f^7$) as far as it is known is given in Fig. 1 (left side) [2]. The Gd^{3+} emission due to the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition is well known and is situated around 312 nm. Up until now, only emission to the $^8S_{7/2}$ ground state has been reported for Gd^{3+}, including the $^6G_J \rightarrow {}^8S_{7/2}$ emission around 200 nm, which has been found in several host lattices [3]. These emissions are all in the ultraviolet region. However, on the basis of the energy level scheme of Gd^{3+} one can expect a visible emission in the orange/red due to the $^6G_J \rightarrow {}^6P_J$ transition, followed by emission of a second photon from the ^6P_J level. It will be shown that this visible emission can indeed be observed.

2. Experimental

The polycrystalline sample of $LiYF_4$:Gd^{3+} 10 mol% was prepared by firing a mixture of LiF, YF_3 and GdF_3 at 550°C in a nitrogen atmosphere. GdF_3 was prepared by precipitation of Gd^{3+} in an acidic solution by NH_4F. Neutron activation analysis showed that the Gd_2O_3 used contained 1 ppm of Eu^{3+}. The other starting materials contained no significant amounts of rare earth ions as impurities. The polycrystalline sample of $LiYF_4$:Eu^{3+} 1 mol% was prepared in the same way.

The excitation and emission spectra were recorded at room temperature with a Spex 1680 spectrofluorometer, equipped with 0.22 m double monochromators.

The excitation source for the $LiYF_4:Gd^{3+}$ measurements was a D_2-lamp (Hamamatsu L1835, 150 W), for the $LiYF_4:Eu^{3+}$ a Xe-lamp (Ushio UXL, 450 W) was used. The signal was detected with a cooled Hamamatsu R928 photomultiplier tube.

3. Results and discussion

Figure 2 shows the excitation spectrum in the $^8S_{7/2} \rightarrow {}^6G_J$ region of the Gd^{3+} emission at 311.0 nm for Gd^{3+} in $LiYF_4$ at 300 K. The assignment of the lines is made based on the positions of the different energy levels found for $LaF_3:Gd^{3+}$ [2]. The resolution of the used apparatus was too low to observe all transitions to different Stark levels of one term separately. We were not able to assign the peaks at 190.6, 189.2 and 187.2 nm because the term symbol of the final state is not known yet. In Fig. 1 (right side) the energy level scheme for Gd^{3+} in $LiYF_4$ derived from the present and previous observations is depicted [4]. Upon excitation in the ^6G_J levels, $^6G_J \rightarrow {}^6P_J$ emission lines were observed in the visible, viz. around 600 nm. This can be seen in Fig. 3, in which the emission spectrum at 300 K is given (upper trace). The emissions at 577.6, 585.5, 592.5, 606.7 and 631.2 nm are assigned to $^6G_J \rightarrow {}^6P_J$ transitions of Gd^{3+}, and are also indicated in Fig. 1. The 585.5, 606.7 and 631.2 nm peaks are transitions from $^6G_{7/2}$ to the different ^6P_J terms. The 577.6 and 592.5 nm emissions originate from higher ^6G_J terms, which are thermally populated at room temperature. The emission wavelengths agree very well with the calculated energy differences between the measured ^6G_J energy values (Fig. 2) and the ^6P_J energy levels for $LiYF_4:Gd^{3+}$ from [4]. As far as we are aware, the $^6G_J \rightarrow {}^6P_J$ emission is the first observed visible luminescence from Gd^{3+}.

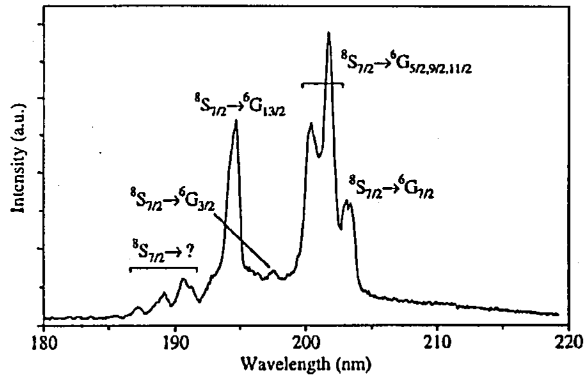

Fig. 2. $^8S_{7/2} \rightarrow {}^6G_J$ excitation spectrum of $LiYF_4:Gd^{3+}$ 10% monitoring $^6P_{7/2} \rightarrow {}^8S_{7/2}$ emission (311.0 nm) at 300 K.

The emission lines at 590.4 and 613.8 nm are assigned to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transition, respectively, of Eu^{3+} impurities originating from the starting compound Gd_2O_3. This becomes evident by comparing the emission spectrum of $LiYF_4:Gd^{3+}$ with the emission spectrum of $LiYF_4:Eu^{3+}$ in the same region

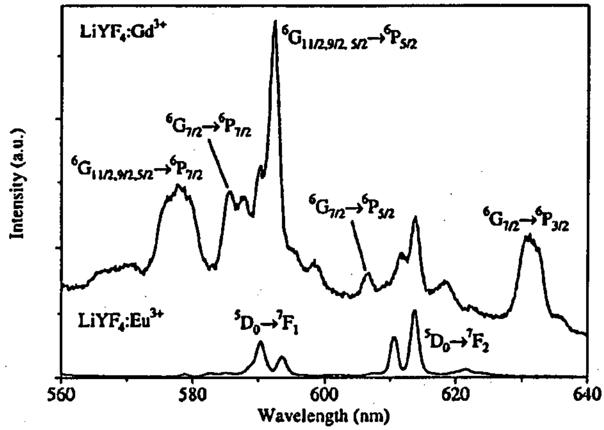

Fig. 3. Upper trace: $^6G_J \rightarrow {}^6P_J$ emission spectrum of LiYF$_4$:Gd^{3+} 10% upon $^8S_{7/2} \rightarrow {}^6G_J$ excitation (201.7 nm) at 300 K. Lower trace: $^5D_0 \rightarrow {}^7F_J$ emission spectrum of LiYF$_4$:Eu^{3+} 1% upon excitation at 222.7 nm at 300 K.

(Fig. 3, lower trace). Although the Eu^{3+} concentration is very low, the strong $^5D_0 \rightarrow {}^7F_{1,2}$ emissions are present because of the efficient energy transfer from the $^6P_{7/2}$ level of Gd^{3+} to the ^5H_J levels of Eu^{3+}. It should be mentioned that the $^6G_{11/2,\,9/2,\,5/2} \rightarrow {}^6P_{3/2}$ transitions of Gd^{3+} are expected to be present at *ca.* 614 nm, but cannot be observed in the emission spectrum of LiYF$_4$:Gd^{3+} because of the Eu^{3+} emission in the same region.

Just as for LiYF$_4$:Gd^{3+}, an excitation spectrum in the area around 200 nm was recorded for LiYF$_4$:Eu^{3+}. The highest energetic level detected was at 222.7 nm. This was used as excitation wavelength for the emission spectrum of LiYF$_4$:Eu^{3+} in Fig. 3, lower trace. The fact that the emissions at 592.5, 577.6, 585.5 and 631.2 nm in Fig. 3 upper trace (LiYF$_4$:Gd^{3+}) are not present in the lower trace (LiYF$_4$:Eu^{3+}) is a proof that these lines cannot be due to energy transfer to Eu^{3+} followed by emission. Other rare earth ions which could be present as impurities and give emission in the region around 600 nm are Tb^{3+}, Sm^{3+}, Dy^{3+} and Ho^{3+}, but there is no agreement between Fig. 3 upper trace and the emission spectra of these ions in LiYF$_4$. Besides, if Tb^{3+} were present in the LiYF$_4$:Gd^{3+} sample the lowest parity allowed $4f^75d^1$ band should be present in the excitation spectrum at 215 nm, which is not the case.

Upon excitation in the ^6G_J levels, also the $^6G_J \rightarrow {}^6I_J$ emission is observed in the near infrared, viz. around 750 nm. This observation supports the assignment of the emissions around 600 nm to Gd^{3+}.

Upon $^8S_{7/2} \rightarrow {}^6G_J$ excitation quantum cutting occurs because the $^6G_J \rightarrow {}^6P_J$ emission is followed by the $^6P_J \rightarrow {}^8S_{7/2}$ emission of Gd^{3+} around 311 nm, which is in the UV. A quantum cutter in the visible can be constructed by using the energy transfer from the ^6P_J levels of Gd^{3+} to Eu^{3+} or Tb^{3+}. These ions subsequently give an efficient emission in the red or in the green, respectively. However, it should be noted that the $^6G_J \rightarrow {}^6P_J$ emission of Gd^{3+} has a low efficiency. This can be derived from the fact that upon excitation in the ^6G_J levels the $^6G_J \rightarrow {}^6P_J$ emission is very weak in comparison with the $^6P_J \rightarrow {}^8S_{7/2}$ emission.

In the near future the measurements will be extended into the VUV region down to *ca.* 150 nm, for Gd^{3+} as well as for a number of other trivalent rare earth ions. The high energetic $4f$ levels will also be calculated, so that assignments to term symbols can be made. The possibilities for visible emission from these high energetic levels resulting in efficient quantum cutting in the visble will be investigated.

Acknowledgments

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