Luminescence studies of Ce:YAG using vacuum ultraviolet synchrotron radiation

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Abstract

Photoluminescence spectrum of Ce:YAG single crystal was studied employing vacuum ultraviolet (VUV) synchrotron radiation. Intrinsic absorption edge at about 52,000 cm⁻¹ was observed in the absorption spectrum. From the VUV excitation spectrum, the energy of the highest d-component of 53,191 cm⁻¹ (188 nm) for the Ce³⁺ ions in YAG was obtained at 300 K. The disappearance of the third 5d level at 37,735 cm⁻¹ (265 nm) in absorption and excitation spectra in our samples may be due to the impurity Fe³⁺ ions absorption.

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1. Introduction

Cerium activated yttrium aluminum garnet crystal (Ce:Y₃Al₅O₁₂), which show extremely high mechanical and chemical stability, high light yield and short luminescence decay times, have proved to be an excellent scintillator. The peak emission due to the allowed 5d–4f transition of Ce³⁺ ions peaking at 500–550 nm fits well to the sensitivity spectrum of Si photodiodes [1–7]. The optical properties of trivalent cerium ions doped into YAG have been extensively studied and the general features of its spectra are now well understood [8–10]. The majority of the transition that have been studied occur between Stark manifolds belonging to the 4f and 5d electronic configuration and fall in the infrared and visible portions of the spectrum. In most cases, the strong ultraviolet absorption of the host lattice materials has limited the ultraviolet (UV) spectral study of the rare earth ions. Since the radial wave function for the excited 5d electron of Ce³⁺ ions extends spatially well beyond the closed 5s²5p⁶ shells, 5d states are strongly

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perturbed by the ligand field of the host. In YAG, Ce$$^{3+}$$ substitutes for Y$$^{3+}$$ at sites of D$_2$ symmetry. Therefore, all degeneracy except Kramer’s degeneracy is removed and the excited 5d states are split into five levels. The unusual magnitude of this crystal field splitting places the lowest 5d state only 22,000 cm$^{-1}$ above the ground state.

It was shown previously that only four of the five 5d levels are observed before the onset of YAG intrinsic absorption which occurs at $\sim$52,000 cm$^{-1}$ [11]. The four features were reported in the excitation spectrum at about 45,000, 37,000, 29,400 and 22,000 cm$^{-1}$, respectively [12]. The splitting of the 5d states due to the crystalline field is so wide that no description has ever been given to date on the position of the highest energy d-component in the excitation spectrum for this luminescence.

The use of synchrotron radiation from an electron storage ring might allow one to surmount many of the traditional experimental difficulties facing the spectroscopist working in this region. Synchrotron radiation could be an effective UV source in finding the high excitation state of rare earths ions in a variety of host materials. In the present work, we investigate the highest 5d state of Ce$$^{3+}$$ ions in YAG using vacuum ultraviolet synchrotron radiation.

2. Experiments

Ce:YAG single crystals were grown by Czochralski technique in an inert atmosphere (high-purity Ar gas). The highly pure oxide powders Y$_2$O$_3$ (>99.999%), CeO$_2$ (>99.99%) and Al$_2$O$_3$ (>99.95%) were used as starting materials. Samples were sliced into disks with diameter of several millimeters and 1.5 mm thickness for optical measurements. Details of the growth apparatus and procedures have been given previously [13]. For comparison, undoped YAG crystals were also grown by CZ method under the same conditions. The raw materials were the same as those used in the Ce:YAG. The vacuum ultraviolet (VUV) photoluminescence spectra were recorded at the VUV Spectroscopy Station in National Synchrotron Radiation Laboratory, Hefei, China. The resolution of the primary monochromator (1 m Seya) and the secondary monochromator is 0.3 and 3 nm, respectively. The measuring temperature of the sample was varied from 12 to 300 K. The excitation spectra were corrected using sodium salicylate. The absorption spectra were recorded by means of a V-570 UV/VIS/NIR spectrophotometer. The light sources were a deuterium lamp (190–350 nm) and a halogen lamp (340–1200 nm), and the spectral resolution was 1 nm.

3. Results and discussion

Fig. 1 presents the absorption spectrum of Ce:YAG crystals and undoped YAG crystals at 300 K. The increase of absorption toward shorter wavelengths is caused by intrinsic absorption and the fundamental absorption edge of YAG at about 52,000 cm$^{-1}$ (192 nm) was observed. The band gap of our YAG sample agrees well with those reported by Slack et al. [14]. The onset of strong absorption at absorption edge obscures the higher energy absorption of Ce$$^{3+}$$ ions. It is a well established fact that four bands at about 45,045 cm$^{-1}$ (222 nm), 37,735 cm$^{-1}$ (265 nm), 29,411 cm$^{-1}$ (307 nm), and 22,000 cm$^{-1}$ (314 nm) were observed.

![Fig. 1. Absorption spectrum of Ce:YAG and pure YAG.](image)
(340 nm) and 21,834 \text{ cm}^{-1} (458 nm) could be observed in the absorption spectrum of Ce:YAG [11]. However, the peak at 265 nm does not occur in our sample. In fact, the phenomenon has been observed by other authors [15,16]. It can be seen that one peak appears at 255 nm in pure YAG but is absent in Ce:YAG. Previous [17–19] studies have shown that Fe$^{3+}$ ions exists in Ce:YAG crystals and it exhibit an oxygen–iron charge transfer band at about 255 nm. The 255 nm band in pure YAG is associated with Fe$^{3+}$ ions. It is most probable that there was significant energy transfer from the Ce$^{3+}$ ions to Fe$^{3+}$ ions. The disappearance of the 265 nm band may be interpreted as the Fe$^{3+}$ impurity ions absorption. However, there are some different opinions on the origin of the 265 nm band [20,21] and further investigation will be required for a better understanding of this problem.

The luminescence spectrum of a Ce:YAG crystal at 300 K is shown in Fig. 2. Ce$^{3+}$ ion has a 4f$^1$ configuration, the ground state consists of a doublet ($^2F_{5/2}$ and $^2F_{7/2}$). The lower excited states are the crystal-field components of the 5d configuration. The UV luminescence of Ce$^{3+}$ ions doped into YAG crystals is due to interconfiguration transitions from the lowest level of the 5d configuration to different levels near the ground state of the 4f$^1$ configuration. This is an allowed electric dipole transition [12]. The emission exhibit a broad band peaks at 528 nm. Since the ground state of the Ce$^{3+}$ ion is a doublet ($^2F_{5/2}$ and $^2F_{7/2}$) with a separation of about 2000 cm$^{-1}$, each emission band is expected to show two peaks. Although the nonsymmetrical shape of the peak exhibits some feature of two peaks, the doublet character is less distinct at high temperature. Fig. 2 also shows the temperature dependence of the 528 nm peak. Two peaks locate at about 523 and 575 nm are more easily resolved at lower temperature up to 20 K, respectively, as that shown in Fig. 2. These two peaks are corresponding to the transitions to the ground manifolds $^2F_{5/2}$ and $^2F_{7/2}$, respectively. It is should be noted that the luminescence peak shift to shorter wavelength with decreasing temperature. In configuration coordinate model, the potential curves of the ground and excited states can be expressed in quadratic functions of the normal coordinates of lattice vibrations. With decreasing temperature, the excited 5d level moves downwards in the excited potential curve. As a result, the peak position should shift to the shorter wavelength side.

Fig. 3 shows the excitation spectrum of Ce:YAG crystals monitored in the region of the observed emission bands at 300 K measured by synchrotron radiation apparatus. In addition to the three well-known low energy peaks, one prominent peak at 53,191 cm$^{-1}$ (188 nm) below YAG intrinsic absorption edge was observed, which is ascribed to the highest 5d state. Our experimental results are quite different with that reported by Tomiki et al., who obtained the energy of highest 5d state by curve fitting [16]. It should be noted that only four of the five d-components were observed in the excitation spectrum. The 265 nm band is also absent in the excitation spectrum of Ce:YAG. Our excitation spectra are similar to that observed by Jacobs et al. [15] and Wong et al. [22]. It was suggested by Wong et al. that the absorption from 200 to 300 nm is due to lattice defects or impurities. Since the impurity Fe$^{3+}$ ions absorption band at 255 nm appears in the absorption spectrum of pure YAG but is absent in Ce:YAG, the disappearance of the 265 nm band in excitation peaks may be due to the impurity Fe$^{3+}$ ions absorption as well. According to the excitation spectrum, the locations of the 5d levels of Ce$^{3+}$ ions in YAG at 300 K are shown in Fig. 4. The energy difference between the $^2F_{5/2}$ and $^2F_{7/2}$ levels is known to be about 2000 cm$^{-1}$. This difference almost does not depend on the host lattice because the 4f shell is shielded by the outer 5s$^2$5p$^0$ shells.
In conclusion, employing vacuum ultraviolet synchrotron radiation, we observed highest energy 5d state of $53,191 \text{ cm}^{-1}$ (188 nm) for the Ce$^{3+}$ ions in YAG at 300 K. According to the VUV excitation spectrum, the locations and energy-level diagram of the splitting 5d levels of Ce$^{3+}$ ions were obtained. The absence of the fourth 5d level at $37,735 \text{ cm}^{-1}$ (265 nm) in absorption and excitation spectrum in our samples is most probable due to the impurity Fe$^{3+}$ ions absorption.

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