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The rare earth and transition metal codoped gallium garnet: experimental and the density functional theory study

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1 . Summary

Yb³⁺, Er³⁺, Bi³⁺ co-doped Gd₃Ga₅O₁₂ has been prepared by sol-gel method, which is activated by the visible light at 522.5nm and exhibits strong emission at 1533nm. By using EXAFS technique, our experiment provides strong evidence of atomic sites of Bi, Yb, and Er in Gd₃Ga₅O₁₂ crystal for constructing the structure model of GGG: Yb³⁺, Bi³⁺, Er³⁺ with first principles calculation. Moreover, the EXAFS of GGG: Yb³⁺, Bi³⁺, Er³⁺ at different prepared temperatures enable us to gain the variation of atomic sites as the change of prepared temperatures, and then to discuss the crystal of GGG: Yb³⁺, Bi³⁺, Er³⁺ at different prepared temperatures.

2 . Purpose of experiment and background

Inorganic luminescent materials have been rapidly developed in the past decade because they have aroused great interest in their versatility in devices, such as fiber-optic amplifiers, waveguide lasers, and displays [1-3], but also in photovoltaic and biomedical applications [4,5]. The rare-earth doped near-infrared luminescent materials have been developed for the well applications in solid state lasers [6-7] due to their unique optical property resulted from their electronic configuration [8]. The Er-doped light-emitting materials with great promise in telecom technology [9-10] have gradually attracted attention, because Er³⁺ has a ⁴I_{13/2} → ⁴I_{15/2} transition around 1540 nm which is corresponding to the third standard wavelength of communication window, largely stimulated by 980nm or 880nm laser [11,12]. Up to now, only a few visible excited NIR

(1550nm) materials have been reported in very recent years, with the strong intensity. However, the low solubility of erbium ions is always a problem, which would directly influence the emission intensity and lifetime. That limits its application in the field of miniature integrated optics.

Luckily, Er and other cations co-doped in host materials could improve the solubility and then enhance emission intensity and lifetime. The host material is another way to improve the solubility. The synthetic

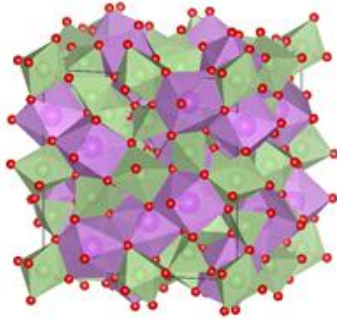


Fig. 1. The crystal structure of GGG. The small red ball is O atom, middle reseda ball is Ga atom and big purple ball is Gd atom.

inorganic compounds with a garnet structure have many interesting properties. However, there are few researches on gadolinium gallium garnet [$Gd_3Ga_5O_{12}$ (GGG)] glass, which has better solubility and lower phonon energy than other oxide glass. The crystal structure of $Gd_3Ga_5O_{12}$ is shown in Fig. 1. It is an important lasing host material for various dopants, especially, for several kinds of rare-earth ions. The change of crystal structure would induce its structure defects (the vacancies and change of round environment of dopant), and then influence its optical behavior, such as the wavelength blueshift or redshift, and the variation of emission intensity.

Also, the impacts of intensity and lifetime of emission wavelength caused by the defects due to dopant, are immensely important. Therefore, it is very important to study the location of different concentration dopants and their neighbors which are prepared in various temperatures for luminescence materials. In our research, as a perfect technique for our polybasic system, the novel setup of XAFS would determine the exact locations of dopant in GGG and its neighbors, then analyzing the performance of luminescence.

3. Experimental

The Bi, Yb, and Er atom positions of $Gd_{3-x-y-z}Ga_5O_{12}: xYb^{3+}, yBi^{3+}, zEr^{3+}$ ($x=0.042, y=0.042, z=0.042$) were determined at room temperature by X-ray absorption fine structure (XAFS), which is performed on a beamline BL11 with fluorescence mode XAFS (SAGA Light Source, Japan). The samples for XAFS were obtained by putting the powder into wafer with tablet press for diameter of 1cm at room temperature. Data analyses were carried out using Athena soft with theoretical treatment provided by the FEFF8 code.

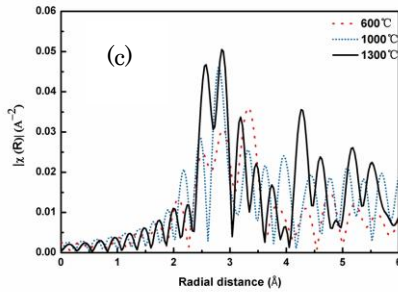
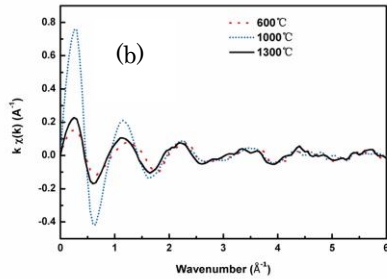
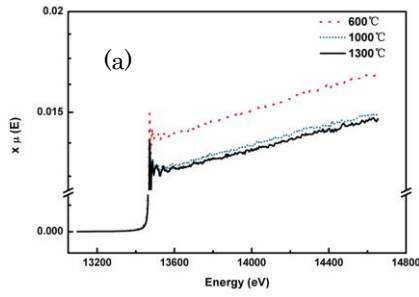


Fig. 2. EXAFS measurement for Bi in GGG: Yb^{3+} , Bi^{3+} , Er^{3+} at different prepared temperature. (a) EXAFS functions $x\mu(E)$ for Bi in GGG: Yb^{3+} , Bi^{3+} , Er^{3+} . (b) EXAFS functions $k\chi(k)$ for Bi in GGG: Yb^{3+} , Bi^{3+} , Er^{3+} . (c) Magnitudes of Fourier transforms of $k\chi(k)$ for Bi in GGG: Yb^{3+} , Bi^{3+} , Er^{3+} . The k region to be transformed is 0-6 \AA^{-1} .

4. Results and Discussions

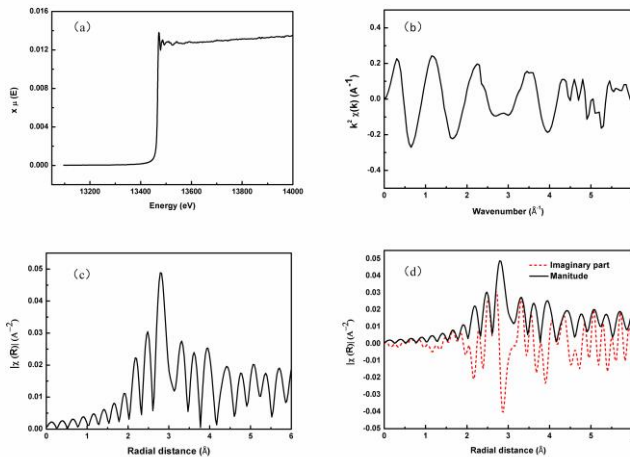


Fig. 3. XAFS measurement for Bi in GGG: Yb^{3+} , Bi^{3+} , Er^{3+} . (a) EXAFS functions $x\mu(E)$ for Bi in GGG: Yb^{3+} , Bi^{3+} , Er^{3+} . (b) EXAFS functions $k^2\chi(k)$ for Bi in GGG: Yb^{3+} , Bi^{3+} , Er^{3+} . (c) Magnitudes of Fourier transforms of $k\chi(k)$ for Bi in GGG: Yb^{3+} , Bi^{3+} , Er^{3+} . The k region to be transformed is 0-6 \AA^{-1} . (d) APCFT of Bi in GGG: Yb^{3+} , Bi^{3+} , Er^{3+} measured at room temperature. Black line, magnitude; red line, imaginary part.

The EXAFS functions $x\mu(E)$ and $k^2\chi(k)$ for Bi in GGG: Yb^{3+} , Bi^{3+} , Er^{3+} are shown in Fig. 3 (a) and Fig. 3 (b), respectively. A fast Fourier transform of r space is described in Fig. 3 (c). According to the crystallographic data [13], GGG has four O neighbors to each Gd at 2.36 \AA and four other ones to Gd at 2.47 \AA to form the dodecahedral coordination around Gd, which occupies the (c) site. The neighboring coordination around Ga consists of six O neighbors at 2.01 \AA to form the octahedral coordination about the (a) site on which fraction of Ga atoms located is 0.4, and four O neighbors at 1.85 \AA to form the tetrahedral coordination about

the (d) site on which the fraction of Ga is 0.6. Bi atoms in Bi₂WO are also around oxygen neighbors at 2.54 Å [14]. So, in Fig.3 (c), it can be distinguished that the strongest peak at about 2.76 Å, is corresponding to Bi-O atomic pairs. This peak has about 0.22 Å shift to the high r region in comparison with the neighboring Bi-O of previous studies [15] due to the phase-shift function.

In order to detect a possible atom from the imperfect cubic structure, we applied $k\chi(k)$ for Bi in GGG: Yb³⁺, Bi³⁺, Er³⁺, as shown in Fig. 3(d). The main peak of Bi in the magnitude of Fourier transform is at about 2.76 Å. This distance is close to the distance of neighboring coordination about Bi (2.54 Å). This is confirmed by the fact that imaginary part is also peaked at 2.53 Å. The small distance mismatch of the peaks between the magnitude and imaginary part mainly comes from the multi-distance subshell in neighboring coordination. There is one smaller peak in the imaginary part at about 2.47 Å as shown in Fig. 3(d). This distance for Bi (2.47 Å) is the same as the one of the Gd-O (2.47 Å) pair in which Gd is located at the (c) site. Therefore, Bi is located at the (c) site. According to the radii substitution principle, the difference of radii of Gd and Bi is larger than the difference of radii of Gd and Er (Yb), so Er (Yb) is more easily substitution for Gd than Bi dose. Therefore, for Yb³⁺, Bi³⁺, Er³⁺ co-doped GGG, because Gd is replaced by Bi, Gd is also replaced by Er and Yb. This EXAFS measurement has confirmed the hypothesis, with which we built the structure model of GGG: Yb³⁺, Bi³⁺, Er³⁺ for first principles calculation.

5. Future issues

The refined crystal structure will be obtained by using IFEFFIT software to analyze the EXAFS data, and then could determine the coordination number (N), interatomic distance (R), the difference of Debye-Waller factors.

6. References

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7. Publications, patents (Note: Typical deliverables related to this proposal.)

The experimental data obtained in this work will be submitted to an international scientific journal.

8. Keywords (Note: 2-3 words about samples and experimental methods.)

Gd₃Ga₅O₁₂, EXAFS, atomic sites, refined crystal structure

9. About the publication of research results

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