Optical and holographic properties of $Bi_4Ge_3O_{12}$ crystals doped with ruthenium

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$Bi_4Ge_3O_{12}$ single crystals doped with different concentration of Ru were grown by the Czochralski technique. Optical absorption bands were induced by illumination with ultraviolet light at room temperature. The absorption coefficient values increased with increasing ruthenium concentration. The induced photochromic effect was completely reversible: all samples recovered their transparency after thermal treatment. Preliminary holographic recording experiments showed a fast response time and a relatively slow erase time during the reading process.

1. Introduction

$Bi_4Ge_3O_{12}$ (BGO) crystals have found many applications such as scintillator detectors [1], components of opto-electronic devices [2], and media for planar optical waveguides [3]. Undoped BGO is one of the few crystals showing photorefractivity in the UV spectrum [4]. However, it is impossible to modulate the refractive index in the visible range, since there is not a sufficient density of suitable traps for photoinduced charge carriers. In order to improve the photosensitivity, appropriate dopants can be added. Recently, a photorefractive effect in the visible range has been observed in Cr-, Co-, Fe-, and Mn-doped BGO [5, 6]. Since they are responsible for the photorefractivity, the relationship between the defects and the optical properties is an important research field in the search for better photorefractive crystals.

In this paper, we report the presence of a strong photochromic effect and holographic recording in Ru-doped BGO crystals, for the first time to our knowledge.

2. Experimental details

BGO crystals with different Ru concentrations were obtained by the Czochralski technique, with automatic diameter-weight control. The Ru concentrations were determined by inductively coupled plasma atomic absorption spectrometry, and are presented in Table I.

In order to confirm the existence of photochromism, the as-grown BGO samples were illuminated with UV light from a 300-W Xe lamp. After each illumination, the crystals were bleached completely by heating in an oven at 500 °C for 3 h. The transmission spectra of double-polished crystal-plate samples (as-grown, UV-exposed, and heat-treated) were recorded using an Agilent UV-VIS 8453 spectrophotometer.

Holographic recording was performed with a two-wave mixing set-up using 514 nm light from an Ar^+ laser. Read-out was performed using a 2-mW He-Ne laser probe beam, incident upon the crystals at the Bragg angle. A shutter was used to block one of the writing beams during the reading mode. Before experiments, samples were illuminated with UV light for 1 h.

3. Results and discussion

3.1. Photochromism

The photochromism is caused by a photoinduced charge transfer of electrons (holes) from one localized impurity or defect site in the crystal to another, via the conduction (valence) band. This phenomenon is characterized by two extreme states of the material: a bleached (thermodynamically stable) state and a colored (metastable) one. The photochromic effect increased with increasing Ru content, as shown in Fig. 1. After UV illumination, the absorption coefficient α is changed, due to charge-carrier redistribution between different traps.

In addition, the induced photochromism was fully reversible. Crystals recovered their transparency upon heating. The dark decay of the UV light-induced

TABLE I Description of samples used in the experiments

Notation	BGO : Ru(1)	BGO : Ru(2)	BGO : Ru(3)
Concentration, (at cm^{-3})	1.1×10^{18}	1.2×10^{18}	5.7×10^{18}

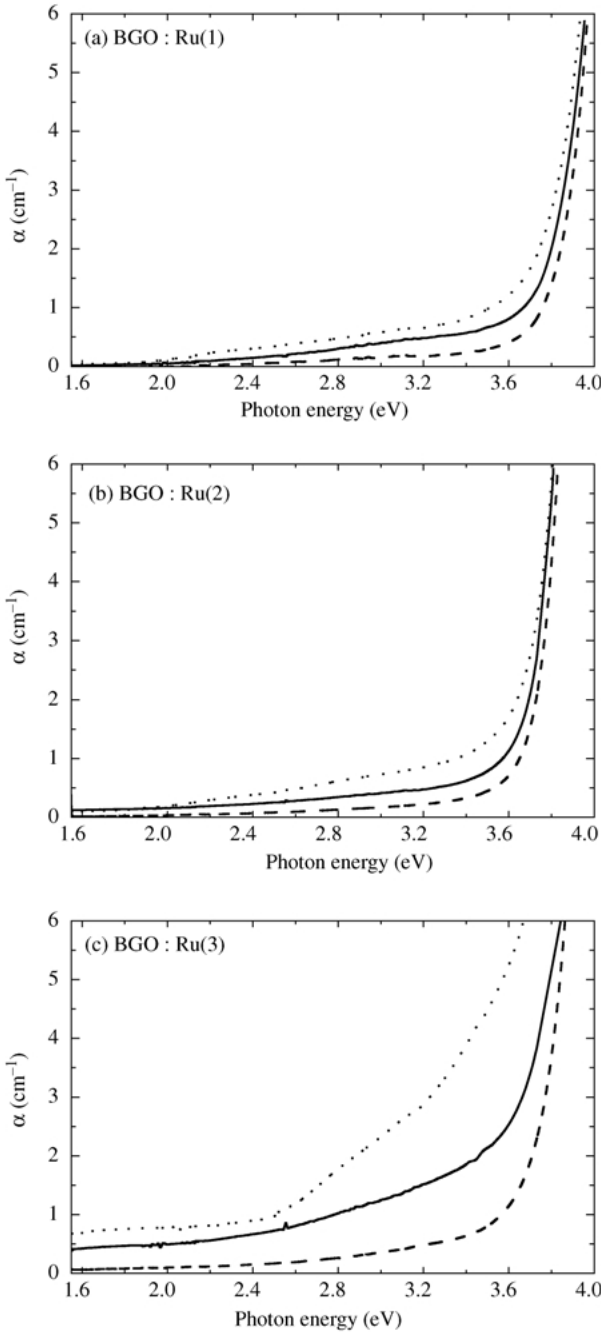

Figure 1 Optical absorption spectra of the as-grown state (solid line) after UV exposure (dotted line) and after heat treatment (dashed line) of (a) BGO : Ru(1), (b) BGO : Ru(2), (c) BGO : Ru(3).

coloration was very slow. It took several days at room temperature before changes became noticeable.

3.2. Holographic recording

A typical temporal behavior of the diffracted beam during holographic recording and readout of Ru(3)-doped BGO is shown in Fig. 2. Due to the enhanced absorption and the photochromic effect, we suppose that simultaneously with a phase grating (due to the refractive-index modulation) an amplitude grating (due

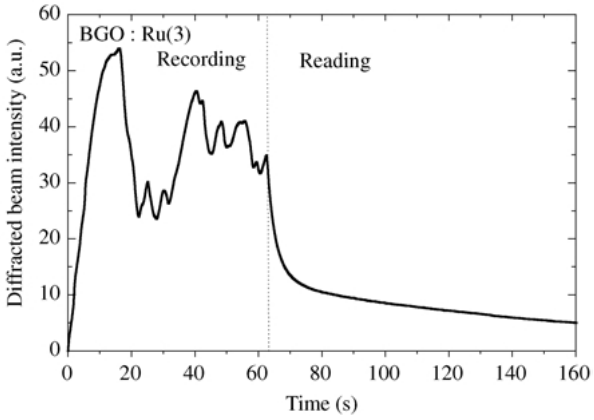

Figure 2 Temporal evolution of the writing and reading processes during holographic recording in BGO doped with the highest Ru concentration. The space grating Λ was 0.8 μm. The crystal was illuminated with UV light for 1 h before recording.

to the absorption coefficient modulation) is formed during hologram writing. Probably, the absorption grating arises because of the presence of shallow traps, which are filled with photo-excited carriers. As shown in Fig. 2, the diffracted signal first increased rapidly. After a few seconds, some fluctuations appeared, presumably due to the competition between the phase and amplitude gratings. During the reading process, the erase time is relatively slower than the time necessary to reach the saturation state during the recording process.

During these preliminary holographic tests, no external electric field was applied to the crystal, so it was not possible to obtain a high diffraction efficiency. Additional experiments are being performed to gain more information about the assumed charge-transport model and to examine the holographic behavior in more detail.

4. Conclusions

Ru was found to be a suitable dopant in BGO, and to make it photorefractive in the visible spectral range. Furthermore, Ru addition enhanced the photochromic behavior and the phenomenon became stronger with increasing Ru concentration.

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