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Characterization of doped $Bi_4Ge_3O_{12}$ single crystals by light-induced absorption, electrical and photoelectrical measurements

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Measurement of light-induced absorption changes, dark- and photoconductivity have been performed on $Bi_4Ge_3O_{12}$ crystals doped with Fe, Rh and Fe+Rh. All samples exhibited a strong photochromic effect at room temperature, which was fully reversible after thermal annealing. It was found that Rh-doped $Bi_4Ge_3O_{12}$ crystals possess a lower dark conductivity ($\sigma_d = 5.2x10^{-14}$ $(\Omega.cm)^{-1}$) at room temperature in comparison with other investigated samples. New centers in the $Bi_4Ge_3O_{12}$ inter-band structure, with thermal activation energies between 0.25 and 0.37 eV, have been created by doping with Fe and Rh. Fe–doped and Fe+Rh co-doped samples showed a non-linear photoconductivity dependence on light intensity, under illumination with a 514-nm laser.

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1. Introduction

Bismuth germanate $Bi_4Ge_3O_{12}$ (BGO) is one of the few crystals which shows a photorefractive effect in the deep ultraviolet (UV) range at room temperature [1]. Despite of the storage ability, not so much attention has been paid to these materials, since there is not a high enough density of charge carriers to modulate the refractive index in the visible spectral range.

Doping with appropriate elements is a convenient method to improve the photosensitivity in the visible spectral range, and to increase the density of suitable traps. BGO crystals possess a large energy gap (4.1eV), which appears to be a suitable matrix for extrinsic impurities such as transition metals or rare-earth elements. Furthermore, BGO crystals are easy to grow to a relatively large size with good optical quality [2,3]. These features of BGO crystals make them attractive to be new candidates for producing a photorefractive effect in the visible spectral range. For example, using a doping approach, an improvement in the photosensitivity has been observed in Cr-doped BGO [4], in Fe-doped and Mn-doped BGO crystals in the blue-green spectral region [5], and in Co- and V-doped BGO crystals [6,7]. The possibility to extend the photorefractive sensitivity into the red spectral range has also been demonstrated in Ru-doped BGO [8,9].

Recently, much interest has been directed to optimizing photorefractive crystals for holographic data storage and processing of information, by adding various suitable dopants [10]. It is well known that Fe is the most suitable and effective dopant in $LiNbO_3$ crystals so far. It improves both the photosensitivity and the diffraction efficiency [11]. Rhodium is another promising element which, doped in a $BaTiO_3$ crystal, has attracted considerable attention due to its high sensitivity and photorefractive efficiency [12]. Usually, the presence of doping ions in the crystal structure leads to the generation of a charge transfer process responsible for the photochromic and photorefractive phenomena, which can be incorporated to achieve more efficient and stable hologram recording. Recently, two-center recording in Fe and Mn doubly doped $LiNbO_3$ has been realized, to achieve persistent (non-volatile) holographic data storage [13].

In this paper, we study the influence of Fe-, Rh- and Fe+Rh co-doping on the optical, electrical and photoelectrical properties of BGO, crystals for future holographic applications.

2. Experiments

Fe, Rh and Fe+Rh co-doped BGO crystals were grown by the Czochralski technique, with automatic diameter-weight control. Stoichiometric Bi_2O_3:GeO_2 powders were mixed in the molar proportion 2:3. Dopants were introduced into the melt solution during the crystal growth, in the form of Fe_2O_3 and RhO_2 oxides. The doping concentrations in the grown crystals, determined by inductively coupled plasma atomic absorption spectrometry, are given in Table 1.

Optical transmittance spectra were measured in the wavelength range 250-800 nm, using the Cary 5E model spectrophotometer on double polished plates of thickness around 1 mm. The optical measurements were performed after thermal annealing of the samples and after 1 hour exposure with ultraviolet light. The UV source was an arc lamp and the whole spectrum of the lamp was used in order to have the maximum UV output. In the bleaching process, thermal annealing for 1 hour at 200°C in an oxygen atmosphere was used.

For the dark- and photo-conductivity characteristics, silver surface electrodes with capacitor cell geometry were made on the crystal plates. The conductivity measurements were carried out using a Keithley 6487 Pico-Ammeter /Voltage Supply. For temperature dependence measurements, we used a custom made holder with cartridge heaters. The crystal temperature was measured by a Pt thermocouple, mounted just above the sample, and was controlled with an error of ± 1K.

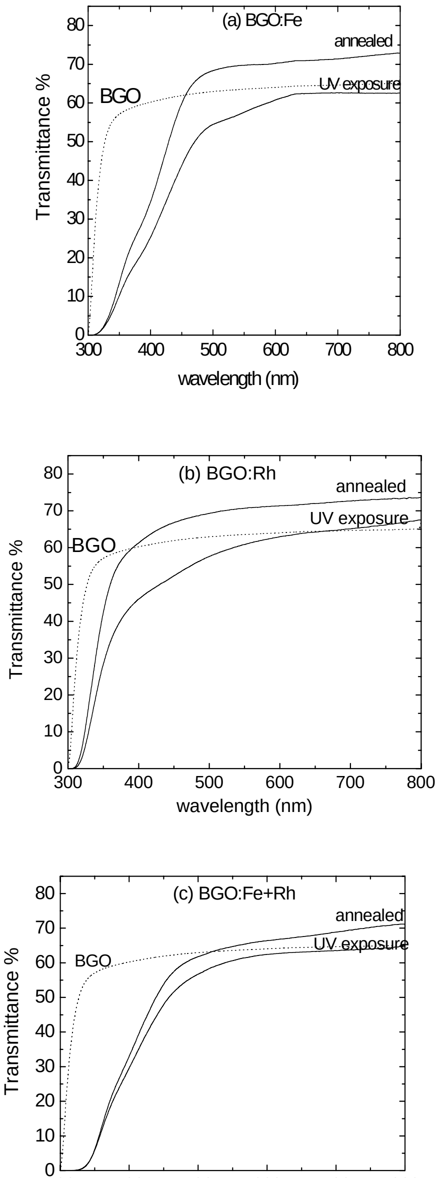

Fig. 1. Optical transmittance spectra after thermal annealing and UV exposure: (a) Fe-doped; (b) Rh-doped; (c) Fe+Rh co-doped BGO. The dotted line is spectrum of an undoped BGO crystal.

An argon laser source operating at 514 nm was used for photoconductivity measurements. During the study of the photocurrent dependence on the light intensity, we waited several minutes after any change of intensity before the measurement to be taken, in order the sample to reach an equilibrium state.

2.1. Results and discussion

The optical transmittance spectra of Fe-, Rh and Fe+Rh co-doped BGO, measured after UV exposure and after thermal annealing, are shown in Figs. 1 (a), (b) and (c), respectively. The transmittance of non-doped BGO is also presented for comparison. As shown, iron addition shifted the optical transmittance to the visible spectral range. However, the studied Rh concentration did not significantly change the absorption edge in comparison to non-doped BGO. As seen from Fig. 1(c) in the case of Fe+Rh, the Fe contribution showed a dominant influence in the co-doping effect, and the absorption edge was shifted into the visible spectral range, as was the case in Fig. 1(a). The photochromic magnitude, defined as the difference of the crystal absorption after UV exposure and after thermal annealing, was stronger in the case of single doping. It is assumed that the photochromic effect is due to the valence change of dopant, caused by the photoinduced charge transfer from the UV-sensitive absorption centers to the visible-light sensitive centers, via the conduction (or valence) band in such oxide materials [14]. We suppose that Fe and Rh ions increase the effective trap center concentration in a BGO structure, and as a consequence the absorption throughout the investigated spectral range increases.

Current-voltage characteristics for all investigated samples in dark conditions at room temperature are shown in Fig. 2.

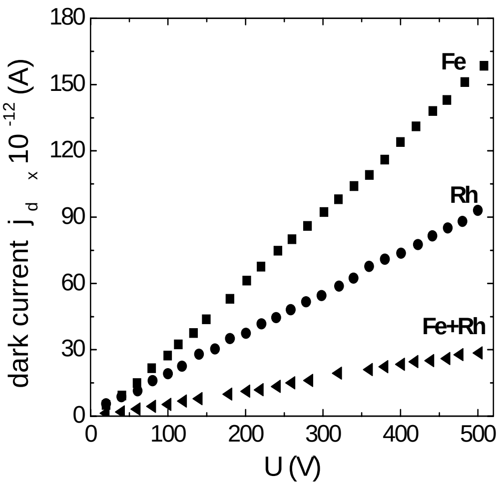

Fig. 2. I-V characteristics under dark condition at room temperature.

The values of dark conductivity σ_d at room temperature are summarized in Table 1. Rh-doped BGO possessed the lowest dark conductivity of the investigated samples, and the values are of the same order of magnitude as those reported previously for un-doped BGO, $\sigma_d = 5.2\times10^{-14}$ $(\Omega.\text{cm})^{-1}$ [1]. A low dark conductivity is very important for future holographic recording applications.

The dark conductivity temperature dependence is shown in Fig. 3. As can be observed, the conductivity increased with increasing temperature. The activation energies values were derived from plot, which follows the Arrhenius law:

$$\sigma = \sigma_0 \exp(-E_a / k_B T) \qquad (1)$$

where σ_0 is a pre-exponential factor, E_a is the activation energy for conduction, T is the absolute temperature and k_B is Boltzmann's constant. The calculated activation energies are summarized in Table 1. Fe and Rh- created new centers in the BGO inter-band structure, with thermal activation energies between 0.25 and 0.37 eV. The calculated activation energy for an undoped BGO crystal, as reported by Montemezzani et al. [1] is $E_a = 0.9$ eV.

Table1. Doping concentration, dark conductivity σ_d and activation energy (E_a) values of Fe-, Rh - doped and Fe+Rh co-doped BGO crystals.

dopant	concentr. (cm^{-3})	σ_{dark} $(\Omega.\text{cm})^{-1}$	E_a (eV)
Fe	3×10^{18}	5.8×10^{-13}	0.32±0.03
Rh	3×10^{18}	7.8×10^{-14}	0.25±0.04
Fe+Rh	Fe- 2×10^{18} Rh-4×10^{18}	2.8×10^{-12}	0.37±0.04

The photocurrent density j_i was measured in an external electric field E_0, for different light intensities at 514 nm wavelength. The photocurrent j_i was detected by measuring the dark current j_d and the current under illumination. Subtracting j_d from j_i yields the photocurrent, j_{ph} ($j_{ph} = j_i - j_d$). From the photocurrent density, j_{ph}, we calculate the photoconductivity $\sigma_{ph} = j_{ph} / E_0$. Figure 4 shows the photoconductivity σ_{ph} dependence on light intensity using at 514 nm. As can be seen the illumination caused a large increase in the conductivity. It is supposed that a reduction in the number of recombination centers, and as a result an increased photo-carrier lifetime, led to the photoconductivity increase. A saturation effect was observed in the case of Rh-doping. However, in the case of Fe-doped and Fe+Rh-doped BGO, the photoconductivity increased non-linearly with the light intensity. Similar behaviour has been reported for Cr-doped BGO [4], where the photoconductivity is not saturated even at high light intensities at 442 nm. The light-induced absorption changes and non-linear dependence of photoconductivity on the light intensities indicate that both deep and shallow photoactive levels contributed to the charge transport process.

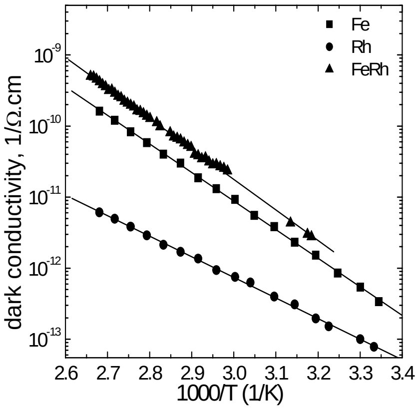

Fig. 3. Arrhenius plot of the dark conductivity σ_d. The symbols are the measured data, the dotted line is a linear fit yielding the activation energy E_a

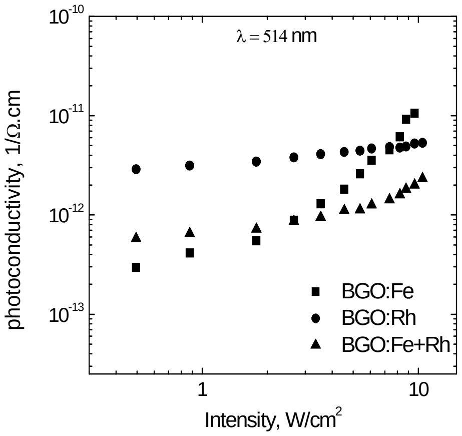

Fig. 4. Photoconductivity dependence on the light intensity f or BGO:Fe, BGO:Rh and BGO:Fe+Rh doped crystals at 514 nm.

3. Conclusions

BGO single crystals doped with Fe, Rh and their combination Fe+Rh were successfully grown using the Czochralski technique. Preliminary treatments of annealing or UV exposure were used to modify the defect structure in the crystal lattice and the corresponding absorption bands. The dark conductivity followed the Arrhenius law. Rh-doping effect in BGO crystals led to a lower dark conductivity and saturation under illumination at 514 nm.

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