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Photorefractive and photochromic properties of ruthenium-doped $Bi_{12}SiO_{20}$

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Abstract

Ruthenium can easily be incorporated into $Bi_{12}SiO_{20}$ (BSO) and an unusually high (1.3 cm^{-1}) photorefractive gain was measured in the diffusion regime with a krypton laser at 647 nm. One particular experiment demonstrated that electron and hole gratings could eventually be formed with different time constants, thus leading to a reduction of the gain. Several complementary spectroscopic techniques were used to characterise our crystals. Magnetic circular dichroism (MCD) demonstrated that Ru substitutes under several valences for Bi in the pseudo-octahedron formed by bismuth and oxygen atoms. This was confirmed by electron paramagnetic resonance detected either classically (EPR at 9 GHz) or optically (ODMR, 35 GHz). Photochromism was investigated via a series of absorption and MCD experiments on oxidized and reduced samples. Our results in the visible spectral range could be understood via a correlation with the behaviour of the Ru^{5+} and Ru^{3+} MCD features in the near-IR, under similar illuminations. The primary process with red light is the ionisation of electrons from the VB to the $Ru^{4+/3+}$ acceptor level and the subsequent capture of the left holes at the $Ru^{5+/4+}$ level. Under blue light, paramagnetic $Bi_{Si}{}^{4+}$ is formed via the ionisation of $Bi_{Si}{}^{3+}$. The charge transfer transitions of Ru^{5+} were assigned via additional experiments on Ru-doped lithium niobate and garnets. The build-up and decay of photochromism were investigated, three different behaviours being observed, depending upon the initial conditions. The three-valence-two-level model is not adequate to explain the bi-exponential temporal behaviour of photochromism. It is suggested that a third relatively shallow level, possibly associated to iron, plays an important role.

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1. Introduction

Photorefractive crystals are technologically important materials that can be used for holographic purposes, phase conjugation or optical switching. Among these, bismuth sillenites $Bi_{12}MO_{20}$ (BMO with M = Si, Ge, Ti) play an important role in the visible spectral range. After decades of intensive fundamental and applied research, real applications have recently started to arise. For example, a compact holographic interferometer [1] using a sillenite crystal has been assembled and applied in various metrological problems. The availability of laser diodes operating in the near infrared is presently stimulating the search for dopants or for optical or thermal treatments aimed at optimizing the photorefractive properties of BMO crystals in this spectral region [2].

Photorefractivity occurs in photoconductive crystals with a non-centrosymmetric structure, when two

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coherent beams are used to create an interference pattern. In illuminated areas, electrons (holes) are ionised from a defect (intrinsic or extrinsic) to the conduction or the valence band of the material. Once in this state, they can move (diffusion or drift regime) to dark areas and be efficiently trapped on the same or on a different defect. A space-charge field is thus created, this implying a modulation of the refractive index via the electrooptic (Pockels) effect. When trapping occurs on a level different from the original one, a modification of the absorption spectrum (photochromism) is frequently observed, especially at low temperature, due to the change in the concentration of intrinsic or extrinsic defects.

By means of a combination of optical and magneto-optical techniques, we have conducted a rather systematic spectroscopic study of undoped and doped BMO crystals [2–6]. A challenging goal was to understand at a microscopic level the nature of the defects (site symmetry, charge state) and the recharging processes implied in the photorefractive phenomenon. The present paper concerns a detailed optical and spectroscopic study of ruthenium-doped BSO. This research was in part motivated by the fact that ruthenium improves the photorefractive properties of $KNbO_3$ in the red [7] whereas another 4d element, Rh, plays the same role in the case of $LiNbO_3$ [8] and $BaTiO_3$ [9,10]. The photorefractive and photochromic properties of Ru-doped strontium baryum niobate were also investigated [11] and Ru was shown to increase the conductivity of barium titanate [12].

The photochromic effect in Ru-doped BSO was first demonstrated in our early accounts [13,14] and we reported on an unusually large photorefractive gain at 647 nm (Kr*) at a conference [15]. There was a short report on the transmission spectra at room temperature and the optical rotatory power of BSO doped with 4d and 5d transition elements [16]. More relevant to the present contribution are two recent studies of the optical and photorefractive properties of Ru-doped bismuth titanate BTO [17,18].

The spectroscopic techniques used in the present work were essentially optical absorption and magnetic circular dichroism (MCD), as well as their changes under (or after) 10 min of an illumination with interference filters at a set of wavelengths. MCD is the differential absorption presented by a cubic or a uniaxial sample for left and right circularly polarised components propagating along the direction of an applied magnetic field. Large signals are expected for paramagnetic defects at very low temperatures, due to differences in population among the various Zeeman sublevels in the ground state. Actually, sillenite crystals are gyrotropic, i.e., they show natural circular dichroism (CD) in the absence of a magnetic field. We note that CD does not provide knowledge concerning the magnetic properties of defects, informing about their structure. By contrast, MCD has long been established [19] to be invaluable to characterise both the optical and the magnetic properties of a large variety of materials or defects showing relatively broad bands, and therefore not amenable to Zeeman effect studies. Furthermore, provided that a microwave field is added (35 GHz here, Gunn diode), MCD allows the optical detection of magnetic resonance (ODMR) [20,21]. Here, EPR is monitored by the changes it induces in the MCD signal whenever the microwaves energy matches some Zeeman splitting in the ground state. In many instances, ODMR (combined with optical absorption) is an ideal tool to correlate the optical and the magnetic properties of the defects present in a given crystal. The main results of an EPR study at the X-band (9 GHz) will also be briefly commented.

The crystals investigated were grown in Sofia by the Czochralski method in the [0 0 1] direction from a melt containing 0.1% weight (2.9% mole) RuO_2 (Alfa, 99.95% purity). The actual concentration of Ru in the crystal was estimated to a few 10^{18} at cm^{-3}. Absorption spectra were taken at liquid nitrogen temperature (LNT) and at room temperature (RT), on a Cary 5E spectrometer. MCD/ODMR experiments were performed at 1.4–1.5 K on a custom-build instrument, usually under a magnetic field of 2.5 T provided by a superconducting split-coil magnet. More instrumental details can be found elsewhere [5,6,22].

The organisation of this paper is as follows. The results of our holographic measurements are presented and discussed in Section 2. After a brief overview of defects in undoped sillenites, the valence states of Ru and the occupied lattice sites are determined in Section 3. Section 4 concerns optical absorption studies and the kinetics of absorption changes under various illuminations, both at LNT and at RT. Our MCD data in the visible and near-UV spectral ranges are presented in Section 5, while the significance of all our spectroscopic results in terms of recharging processes is discussed in Section 6. Our main conclusions are finally summarised in Section 7.

2. Holographic measurements

A large sample of dimensions $10 \times 10 \times 6\ mm^3$ was especially cut and polished for these experiments. In view of its preciousness, we could not take the risk of breaking it in the course of a thermal annealing process. We can only state that it had been kept in the dark for a least one month before our first measurement. A grating was formed within the crystal at room temperature via the interference of two linearly polarised ([1 1 0], vertical axis) coherent beams at 647 nm (Kr* laser). The angle between the beams on the (0 0 1) face was optimised to $2\theta = 40°$. The photorefractive gain Γ was measured as