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Studies of light-induced charge transfer in $Sn_2P_2S_6$ by combined EPR/optical absorption spectroscopy

A. Ruediger [a,*], O. Schirmer [a], S. Odoulov [b], A. Shumelyuk [b], A. Grabar [c]

[a] *Department of Physics, University of Osnabrueck, 49069 Osnabrueck, Germany*
[b] *Institute of Physics, Ukrainian National Academy of Sciences, 252 650 Kiev, Ukraine*
[c] *Institute of Solid State Physics and Chemistry, Uzhgorod State University, 294 000 Uzhgorod, Ukraine*

Abstract

The light-induced charge transfer in ferroelectric tin hypothiodiphosphate $Sn_2P_2S_6$ is investigated by means of optical absorption and EPR spectroscopy and their combination. Light-induced metastability at 298 K, known to affect the holographic sensitivity, is observed via optical absorption. EPR measurements support the recent identification of holes as the dominating charge carriers. For excitation energies exceeding the band gap of 2.5 eV at 10 K, EPR reveals that the following processes are likely to occur: a hole is captured at one of two different Sn^{2+} sites, creating Sn^{3+}. At an energy of 1.5 eV the hole is first transferred to the other Sn^{2+} and for excitation of 2.0 eV to a further center. Since these defects are intrinsic and therefore not limited in quantity, the light-induced sensitisation is a very effective way to improve the holographic performance. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: $Sn_2P_2S_6$; Photorefractive effect; EPR; Optical spectroscopy; Charge transfer

1. Introduction

The increasing use of infrared semiconducting lasers in various fields of application requires corresponding devices, e.g., wave front conjugation and (de-)multiplexing. Available materials such as $BaTiO_3$:Rh have rather slow response times of about 1 s for usual intensities of 50 W/m^2 at 1060 nm. It was noticed in 1996 that $Sn_2P_2S_6$ overcomes this drawback when pre-illuminated with 'incoherent white light'. This pre-illumination enables response times of 10 ms and increases the photorefractive gain at 1060 nm and $I = 30$ W/m^2 by a factor of 6 ($\Gamma = 6$ cm^{-1}) [1]. At 298 K, this sensitisation lasts for several days. Illumination with white light does not only affect the holographic gain but can also be observed in thermally stimulated luminescence [2], EPR and electric conductivity as well. The aim of the subsequent pages is to show a way how to investigate the charge transfer paths and to establish a microscopic model for $Sn_2P_2S_6$.

2. Method

In order to measure EPR and optical absorption simultaneously, a commercial EPR spectrometer is combined with a fast optical absorption spectrometer by light guides, deflecting the pump light as well as probe light, through the EPR cavity. For additional information refer to [3].

* Corresponding author. Tel.: +49-541-969-2635; fax: +49-541-969-3512.
E-mail address: ruediger@uos.de (A. Ruediger).

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3. Samples

At 298 K $Sn_2P_2S_6$ is a monoclinic ferroelectric with space group Pc. A phase transition into the paraelectric phase is known to occur at 337 K. For pressure exceeding 0.2 GPa an incommensurate phase of type II occurs [4]. The band gap at 298 K is at 2.3 eV (530 nm) and at 2.5 eV at 10 K. All samples under discussion were grown by Grabar in the Institute of Solid State Physics and Chemistry of Uzhgorod State University by chemical vapour transport. Iodine was used as transport gas. The samples are of good optical quality. If not explicitly mentioned, the specimen were kept in the dark for several days before being investigated. The sample K3, with which the presented experiments have been performed, is nominally pure and has excellent holographic performance.

4. Results

4.1. Light-induced absorption at 298 K

See Fig. 1.

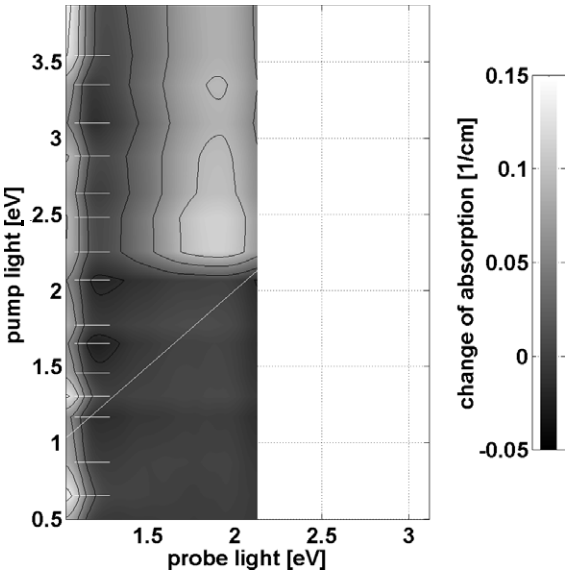

Fig. 1. Light-induced change of absorption of nominally pure $Sn_2P_2S_6$ at 298 K. For band to band excitation we observe a pronounced and wide absorption in the probe light energy range from 1.2 to 2.0 eV which remains for several days.

4.2. Light-induced absorption at 10 K

See Fig. 2.

4.3. Photo-EPR

See Fig. 3.

4.4. EPR

Fig. 4 shows a high resolution EPR spectrum of center 1 revealing detailed superhyperfine structure.

5. Discussion

The large signal sizes lead to the assumption that centers 1, 2 and 3 are intrinsic defects. The *g*-tensor and the anisotropy of the EPR of center 1 are in favour of a hole captured at one of two

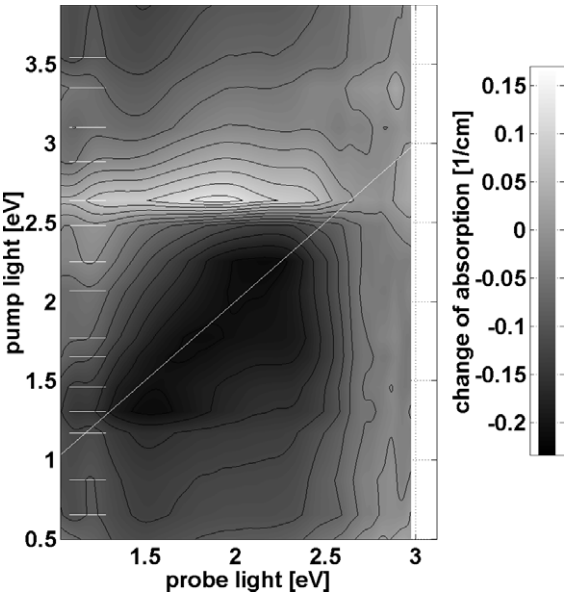

Fig. 2. Light-induced absorption of nominally pure $Sn_2P_2S_6$ at 10 K. The light-induced transparencies at probe energies 1.4 and 2.0 eV are caused by charge transfer processes. For band to band excitation a wide absorption in the range 1–2.5 eV occurs which disappears within a few minutes. The sample was previously exposed to white light at room temperature.

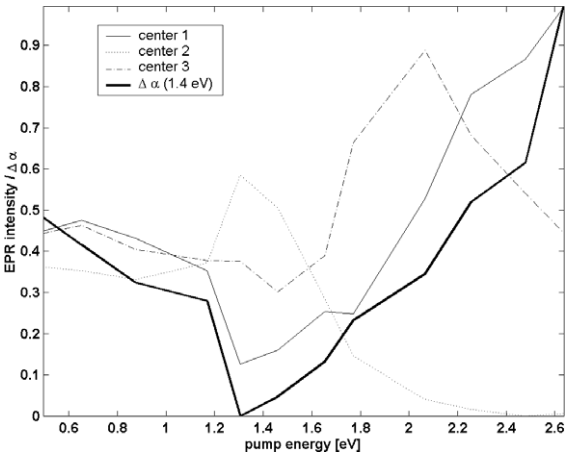

Fig. 3. Changes of EPR signals and optical absorption at $E_{probe} = 1.4$ eV induced by illumination with pump light energies given as abscissa. $\Delta\alpha$ and center 1 are evidently correlated, center 2 is anticorrelated to center 1 at $E_{pump} = 1.4$ eV and center 3 behaves different from centers 1 and 2 for $E_{pump} = 2.0$ eV. Without previous interband excitation there is no signal at all.

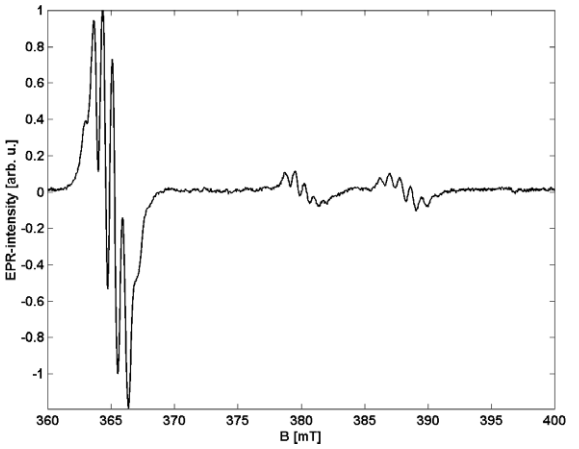

Fig. 4. EPR of center 1 under permanent illumination with 470 nm (2.6 eV). The signal is symmetric with respect to the left six lines. Due to overlap with other signals the left part is not shown.

different Sn^{2+} sites creating a 5 s^1 state (Sn^{3+}). Evaluation of Fig. 4 gives a best fit, if five slightly inequivalent P ions and two different Sn ions are assumed. The fact that the outer group of lines in Fig. 4 is slightly wider can be explained by the different dipole moments of the magnetic Sn isotopes. The smallness of these hyperfine splittings indicates that superhyperfine coupling is identified, i.e. interaction with nuclei some distance away from the Sn^{3+} ion. The very strong central hyperfine interaction of the Sn^{3+} cannot be observed with 9.5 GHz microwaves. The photo-EPR shows the capture of holes on the first Sn^{2+}, creating Sn^{3+}. Under excitation with 1.4 eV (885 nm) these holes are completely transferred to the other Sn^{2+} site. At 600 nm (2.0 eV) the holes disappear and create another hole-center which we attribute to S^-. The optical absorption measurements reveal the release of numerous carriers under interband excitation and the trapping at several different levels in the band gap, one of them leading to Sn^{3+} with an absorption at 1.4 eV.

6. Outlook

In order to establish the local defect structure of centers 1 and 2, EPR will be performed at higher microwave frequencies. It is expected that the analysis of further light-induced EPR signals and their dependence on pump energies, not mentioned here, will lead to a complete insight into the responsible processes.

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