

$\text{Sn}_2\text{P}_2\text{S}_6$ Crystals for Fast Near-Infrared Photorefraction

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Optical and physical properties of $\text{Sn}_2\text{P}_2\text{S}_6$ ferroelectric crystals suitable for photorefractive applications in the red and near-infrared spectral range are reported. The main advantage of $\text{Sn}_2\text{P}_2\text{S}_6$ is its high beam-coupling gain combined with considerably faster response in the near infrared compared to conventional oxide-type photorefractive materials. We show that modifying the growth conditions and doping with Te can efficiently improve the photorefractive properties of $\text{Sn}_2\text{P}_2\text{S}_6$. Photorefractive two-beam coupling gain at 860 nm increases from about 2 cm^{-1} in conventional “yellow” $\text{Sn}_2\text{P}_2\text{S}_6$ to about 7 cm^{-1} in Te-doped samples and 14 cm^{-1} in modified “brown” samples. We examine the self-pumped optical phase conjugation properties of $\text{Sn}_2\text{P}_2\text{S}_6$ in a ring-cavity scheme. Phase-conjugate signals with amplitudes close to the theoretical limit and rise times of about 10 ms for 4 W/cm^2 pump intensity at 780 nm and 50 ms for 2.5 W/cm^2 pump intensity at 860 nm are obtained.

Keywords $\text{Sn}_2\text{P}_2\text{S}_6$; photorefractive effect; two-beam coupling; phase conjugation

Introduction

Materials with high photorefractive sensitivity in the near-infrared range of widely available laser diodes are attractive for several potential applications, such as real-time wave-front corrections and improvement of the spectral properties of light sources. Unfortunately the conventional photorefractive materials tend to be less sensitive in the near infrared. Nowadays the mostly used material for near-infrared photorefraction, Rh doped BaTiO_3 , exhibits high photorefractive nonlinearity but suffers from domain problems and has a rather slow response [1]. Semiconductors on the other hand are fast but exhibit small nonlinearities. This work investigates another near-infrared sensitive ferroelectric material, tin hypothiodiphosphate ($\text{Sn}_2\text{P}_2\text{S}_6$, SPS) that exhibits a relatively fast response combined

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with high nonlinearity, thus filling the gap between photorefractive semiconductors and oxide ferroelectrics [2].

$\text{Sn}_2\text{P}_2\text{S}_6$ crystals belong to monoclinic symmetry at ambient temperature and undergo a second order phase transition from ferroelectric to paraelectric phase at about 65°C [3]. Compared to oxide ferroelectrics, which are wide band-gap dielectrics, these crystals are characterized by a narrower band gap (2.3 eV) and a higher photorefractive sensitivity. $\text{Sn}_2\text{P}_2\text{S}_6$ crystals of high optical quality and dimensions up to $2\text{--}3\text{ cm}^3$ can be grown using the conventional vapor-transport technique [3] employing SnI_4 as a transporter agent. Conventional crystals are yellow in color and transparent for the wavelengths above $\lambda = 530\text{ nm}$. Until recently, all photorefractive studies on $\text{Sn}_2\text{P}_2\text{S}_6$ were performed with nominally pure yellow samples. However, the properties of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals critically depend on the crystal growth procedure. A first type of modification was obtained by using SnI_2 as a transporter agent and increasing the temperature gradient during growth, which leads to modified $\text{Sn}_2\text{P}_2\text{S}_6$ crystals of brown color, presumably with a variation of non-stoichiometric defects [4]. More recently, the addition of Te into the initial compound of stoichiometric polycrystalline $\text{Sn}_2\text{P}_2\text{S}_6$ has led to samples of light brown color with interesting properties [5]. The defect centers that are responsible for photorefraction in $\text{Sn}_2\text{P}_2\text{S}_6$ are not yet clearly identified, however, the characteristic properties are varying considerably in various crystal types, as will be also presented below.

Basic photorefractive properties of yellow $\text{Sn}_2\text{P}_2\text{S}_6$ are well described with a transport mechanism due to diffusion of carriers [2]. Two-beam interaction without applying external fields is thus possible. The measured two-beam coupling gain coefficients were up to 7.5 cm^{-1} at $\lambda = 633\text{ nm}$ [6]. In a certain type of yellow samples (called of the type I) the grating formation is accompanied by a strong electron-hole competition [2]. This leads to a transient behavior and decreases the gain value in the steady state. The photorefractive sensitivity of these samples can be also increased by a factor of 2–3 after pre-exposure to white light [2]. In contrast to nominally pure yellow $\text{Sn}_2\text{P}_2\text{S}_6$, brown samples do not show a pronounced electron-hole competition and are not sensitive to pre-illumination [4]. Gain coefficients as high as 38 cm^{-1} at $\lambda = 633\text{ nm}$ [4] and 18 cm^{-1} at 780 nm [7] were measured in brown $\text{Sn}_2\text{P}_2\text{S}_6$ samples. An important process in several of applications using diode or solid-state near-infrared lasers is phase conjugation of laser beams. Self-pumped phase conjugation was demonstrated in brown $\text{Sn}_2\text{P}_2\text{S}_6$ at 780 nm with a very fast response, which is below 50 ms at 1 W/cm^2 [7, 8].

In this paper we report on the photorefractive sensitivity of $\text{Sn}_2\text{P}_2\text{S}_6$ at a longer wavelength $\lambda = 860\text{ nm}$. We compare the characteristic properties of the above-mentioned types of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals, and their performance as phase conjugation mirrors in the near infrared at 780 nm and 860 nm .

Experiments and Discussion

At room temperature $\text{Sn}_2\text{P}_2\text{S}_6$ crystals have a ferroelectric monoclinic structure with point group m . We use a coordinate system with z -axis parallel to the crystallographic c -axis, y -axis normal to the mirror plane, and x -axis normal to z and y . The spontaneous polarization lies in the xz plane and is about 13° off the x -axis at room temperature. Several $\text{Sn}_2\text{P}_2\text{S}_6$ crystal samples (yellow, modified brown, and with various Te-doping levels) were cut along the xyz axes and their faces normal to the z -axis were polished. The major main axis of the optical indicatrix at room temperature and 780 nm is rotated in the xz plane by about 46° from the x -axis [9]. The transmission spectra measurements reveal an enhanced absorption “shoulder” in brown crystals (see Fig. 1), which leads to a significant rise of the absorption

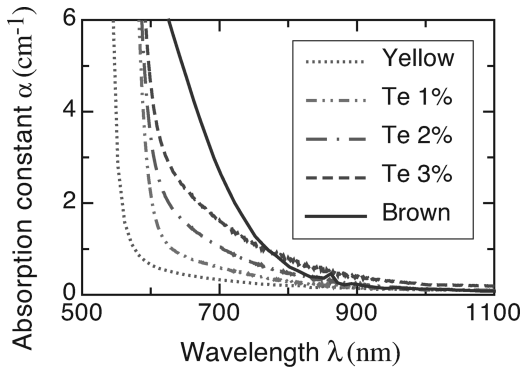


Figure 1. Absorption spectra of nominally pure yellow, brown and Te-doped $\text{Sn}_2\text{P}_2\text{S}_6$ crystals at room temperature for x -polarized light.

coefficient in the red. The absorption spectra of Te-doped crystals also show an additional absorption band that increases with Te-concentration. Note that the Te-concentration given here corresponds to the concentration in the initial compound and not in the final sample. The absorption values in the infrared remain low in all investigated samples.

Two-Beam Coupling

For the measurements of the two-beam coupling gain the usual experimental setup was used with the crystal x -axis oriented in the incident plane xz and perpendicular to the bisector of the two incident beams. Both waves were extraordinarily polarized in the plane of incidence. The intensity ratio of the weak signal wave to the pump wave was 1:1000. In this case the two-beam coupling gain coefficient Γ can be defined as the exponential amplification factor of the weak signal wave according to $\Gamma = 1/d \ln(I_{\text{signal with pump}}/I_{\text{signal without pump}})$. Figure 2 shows the measured two-beam coupling gain Γ dependence on the grating spacing $\Lambda = \lambda/2 \sin \theta$, where λ is the light wavelength in vacuum and 2θ the external angle between the intersecting beams. In this case a Ti:Sapphire laser operating at 860 nm was used. Large values of the two-beam coupling gain coefficients are observed in brown (up to 14 cm^{-1}) and Te-doped crystals (up to 8 cm^{-1}), while the gain in yellow samples remains below 3 cm^{-1} .

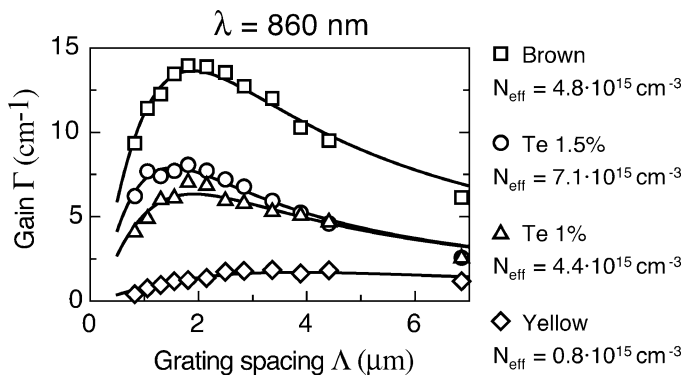


Figure 2. Grating spacing Λ dependence of the two-beam coupling gain coefficient Γ in brown, yellow, and Te-doped $\text{Sn}_2\text{P}_2\text{S}_6$ crystals. Solid lines are theoretical curves.

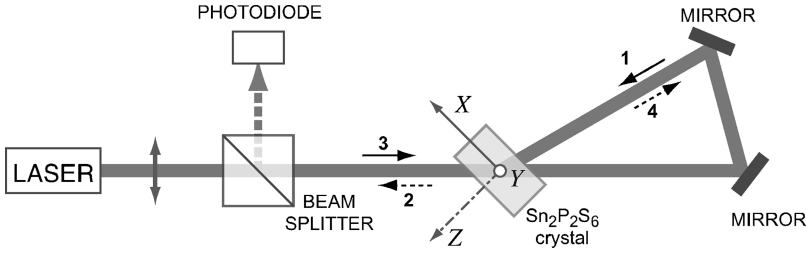


Figure 3. Experimental set-up for the ring-cavity self-pumped phase conjugation with $\text{Sn}_2\text{P}_2\text{S}_6$. Without the external loop the input beam 3 was fanned towards the $+x$ direction. All beams are polarized in the plane of the loop. The transmission grating is written by the beam 3 with its self-diffracted beam 4 and by the beams 1 and 2 counter-propagating in the loop.

For the diffusion case and assuming an isotropic photoexcitation cross-section one can express the stationary two-beam coupling gain coefficient within the weak probe beam approximation as a function of the grating spacing, see for example [10]. The theoretical curves that correspond to our measurement are given with solid lines in Fig. 2. From the fitting parameters we can estimate the effective electro-optic coefficient r^{eff} and the effective concentration of traps N^{eff} . We obtained r^{eff} of 48, 88, and 189 ($\pm 5\%$) pm/V in yellow, Te-doped, and brown sample respectively. The effective concentration of traps (see Fig. 3) is, as we expected, increasing from yellow to Te-doped samples, where it increases with the concentration of Te. The concentration of traps is also high in the brown sample. The higher gain obtained in brown $\text{Sn}_2\text{P}_2\text{S}_6$ is a result of a larger effective electro-optic coefficient, which is close to the directly measured electro-optic coefficient $r_{111}^T = (170 \pm 10)$ pm/V [11].

Self-Pumped Optical Phase Conjugation

Self-pumped phase conjugation schemes that can be realized in high-gain photorefractive crystals have several advantages compared to usual four-wave mixing schemes due to the simplicity of optical alignment, the absence of certain coherence length limitations, and relatively low generation threshold [12]. Our experimental setup for the ring-cavity self-pumped phase conjugation is depicted in Fig. 3. The results were obtained with the above-mentioned 860 nm laser and an external cavity diode laser operating at 780 nm (Rainbow Photonics AG). The light beams were polarized in the plane of the ring-cavity loop and almost parallel to the X -axis in the crystal. Such a configuration uses the largest electro-optic coefficient r_{111} . The external angle 2θ was adjusted to the angle corresponding to the maximum measured two-beam coupling gain Γ (see Fig. 2). The crystals were rotated by about 45° with respect to the incident beam for reducing the Fresnel losses. In this experiment yellow, brown and Te1%-doped crystals of respectively 9.7 mm, 2.4 mm and 6.0 mm thickness were used. The yellow and brown crystals were coated with around 100 nm thick Al_2O_3 layer to additionally reduce the reflection losses by about 60%. The phase-conjugate reflectivity R is defined as the ratio between the measured intensity of the phase-conjugated wave 2 and the input wave 3 (see Fig.3). In the beginning the phase-conjugated signal emerges from the noise gratings of the scattered input beam. After the external loop is restored, the desired transmission grating dominates and the phase-conjugated signal increases sharply and finally it saturates at its maximum value. The reflectivity rise time can be defined as a time in which the reflectivity rises from 10% to 90% of its saturation

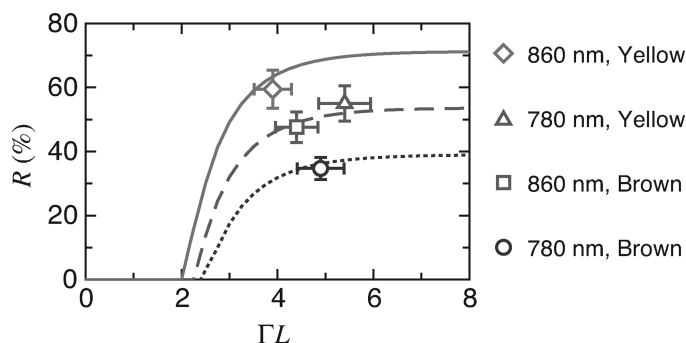


Figure 4. Theoretical dependencies of the saturated phase-conjugation reflectivity R on the coupling strength ΓL for loop transmissions $T = 0.45$ (dotted curve), $T = 0.62$ (dashed curve), and $T = 0.82$ (solid curve) and experimentally measured values for brown Sn₂P₂S₆ sample of 2.4 mm thickness and yellow Sn₂P₂S₆ sample of 9.7 mm thickness at 780 nm and 860 nm.

value [7]. In the yellow sample the rise time is in the order of 5 s at 780 nm and an input beam intensity of 4 W/cm², while the maximum phase-conjugate reflectivity is 55%. In the brown sample the response is much faster with a rise time of only about 10 ms. This is two orders of magnitude faster than typical times obtained with Rh doped BaTiO₃, which are in the order of 10 s at 1.06 μ m and 5 W/cm² [1]. The maximum phase conjugate reflectivity in brown Sn₂P₂S₆ at 780 nm is 35%. By decreasing the ring-cavity loop losses, it is still possible to improve the phase conjugation performance further. For example, the maximum phase conjugate reflectivity was already increased from about 25% [7] to about 35% in a brown sample and from about 40% to about 55% in a yellow sample by decreasing the reflection losses using a (partial) antireflection coating. The Te 1%-doped crystal was not coated and the reflectivity (up to \sim 30%) build-up was even slightly faster than in the brown sample.

The higher saturated reflectivity of the yellow sample is attributed to a higher loop transmission of the ring-cavity scheme owing to a lower absorption of this sample (Fig. 1). One can then expect even higher phase-conjugate reflectivities for longer light wavelengths λ provided that the performance is not yet limited by the coupling strength, which is expected to decrease with λ . At 860 nm the measured saturated reflectivity in the brown sample was around 48% and in the yellow Sn₂P₂S₆ sample around 60%, considerably higher than at 780 nm. A phase-conjugation rise time of 50 ms for 2.5 W/cm² pump intensity at 860 nm was obtained for the brown sample. To check whether the reflectivities in Sn₂P₂S₆ samples are also limited by the coupling strength ΓL , theoretical dependencies of the reflectivity as a function of the coupling strength were plotted in Fig. 4 considering loop transmission parameters that were obtained similarly as in Ref. [7]. Above the coupling-strength threshold the reflectivity increases with ΓL until it saturates at a value equal to the transmission of the ring-cavity loop. For the experimental points in Fig. 4 the saturation of the reflectivity is already reached, therefore the reflectivity is limited by the ring-cavity transmission and not by the coupling strength.

Conclusions

Photorefractive properties and self-pumped phase conjugation were studied in the near-infrared using conventional yellow Sn₂P₂S₆, modified brown Sn₂P₂S₆ with increased number

of intrinsic defects, and Te-doped samples. The photorefractive gain is greatly improved from about 2 cm^{-1} in yellow samples to 7 cm^{-1} in Te-doped and 14 cm^{-1} in brown samples at 860 nm. Self-pumped phase conjugation was demonstrated in the above crystal types with a maximum reflectivity limited by the reflection and absorption losses in the material and configuration, and not by the available gain. The phase-conjugate rise time at 780 nm and 20 mW was in the order of 5 s in yellow $\text{Sn}_2\text{P}_2\text{S}_6$. In brown and Te-doped sample the phase conjugation rises in only about 10 ms. $\text{Sn}_2\text{P}_2\text{S}_6$ can be therefore considered as a very promising material for faster photorefractive and phase-conjugation applications in the near infrared.

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