2010-11

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Current Applied Physics, Amsterdam : Elsevier, v. 10, n. 6, p. 1411-1415, Nov. 2010
http://www.producao.usp.br/handle/BDPI/50164

Current Applied Physics 10 (2010) 1411–1415

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

# Raman spectroscopy analysis of structural photoinduced changes in $GeS_2 + Ga_2O_3$ thin films

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## ARTICLE INFO

*Article history:*
Received 18 January 2010
Received in revised form
27 April 2010
Accepted 10 May 2010
Available online 20 May 2010

*Keywords:*
Photoexpansion
Photobleaching
Micro-Raman spectroscopy
Photostructural changes
Thin films

## ABSTRACT

Photoexpansion and photobleaching effects have been observed in amorphous $GeS_2 + Ga_2O_3$ (GGSO) thin films, when their surfaces were exposed to UV light. The photoinduced changes on the surface of the samples are indications that the structure has been changed as a result of photoexcitation. In this paper, micro-Raman, energy dispersive X-ray analysis (EDX) and backscattering electrons (BSE) microscopy were the techniques used to identify the origin of these effects. Raman spectra revealed that these phenomena are a consequence of the Ge–S bonds' breakdown and the formation of new Ge–O bonds, with an increase of the modes associated with Ge–O–Ge bonds and mixed oxysulphide tetrahedral units (S–Ge–O). The chemical composition measured by EDX and BSE microscopy images indicated that the irradiated area is oxygen rich. So, the present paper provides fundamental insights into the influence of the oxygen within the glass matrix on the considered photoinduced effects.

## 1. Introduction

Sulphide glasses have been shown to exhibit higher optical non-linearity due to the greater polarizability of sulphur and have attracted attention as candidate materials for many photonic devices [1,2]. However, the number of their practical applications has been found to be reduced due to their poor chemical durability attributed to weaker bond strengths. So, they tend to be chemically reactive with air and water [3]. It is interesting to explore mixtures of oxysulphide toward the development of new glasses that are more resistant to atmospheric attack and combine high optical non-linearity with moderate photosensibility [4]. As well as chalcogenide glasses, the oxysulphides undergo structural transformations upon exposure to laser light with near bandgap energy. Photoinduced structural changes in amorphous films have been broadly investigated for more than 30 years [5,6] and it is well known that these effects are associated with volumetric changes [7], so-called photoexpansion or photocontraction, and changes in the optical absorption edge [8], so-called photobleaching or photodarkening.

Previous structural study of photoinduced changes in $Ga_{10}Ge_{25}S_{65}$ (GGS) glasses [9] has shown that Ge–S bonds are broken and new strong Ge–O bonds are formed. These results revealed that the photoexpansion and photobleaching are associated with an increase of the oxygen amounts due to environment exposure, since this element was not present during glass formation. Although the exact role of oxygen in the photoinduced phenomena is not totally clear, the presence of this element in this kind of glasses became a relevant factor. So, the present paper provides fundamental insights into the influence of the oxygen (incorporated into the glass matrix) on the photoinduced effects in $90\ GeS_2 + 10\ Ga_2O_3$ (in mol%) system. This composition was selected because of its stability and, in terms of atomic percentage ($Ge_{28}Ga_6S_{56}O_9$), this glass system can be compared to the previously studied GGS glasses.

The mechanistic origin behind photoexpansion and photobleaching is not fully understood, but these photoinduced effects can be interpreted as a consequence of optically induced changes in local bonding configurations [10]. If a large number of bonds is altered, then we can expect measurable changes in the vibration properties of the irradiated samples. Micro-Raman spectroscopy and other techniques, like EDX and BSE microscopy, were used to evaluate the photostructural changes in GGSO films. The understanding of the relationship between the film structure and its response under laser irradiation leads to a better knowledge of the oxysulphide photosensibility.

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doi:10.1016/j.cap.2010.05.005

## 2. Materials and methods

Oxysulphide glass ingots ($90\ GeS_2 + 10\ Ga_2O_3$) were prepared by the method of melt quenching using an appropriate mixing of GeS, $Ga_2O_3$ and S (all crystalline powders with 99.9999% of purity) that was sealed in a quartz ampoule evacuated up to $10^{-3}$ Pa and melted at 900 °C for 6 h. A rocking furnace was used to rock the ampoule during the melting to increase the homogeneity of the mixture. Once homogenized, the melt-containing ampoule was water-quenched to room temperature.

Films with different thicknesses (0.36–7.00 μm) and compositions were deposited onto borosilicate substrates (known as B270 substrate) by electron beam evaporation from the crushed ingots using an electron beam voltage of 7 kV and an evaporation rate of $1\ \text{Å}\ s^{-1}$ in a vacuum of $10^{-6}$ Torr.

The Raman scattering spectra were recorded with a confocal micro-Raman instrument from Renishaw (resolution of $4\ cm^{-1}$) in normal backscattering configuration at room temperature. The excitation wavelength (633 nm, 1.96 eV) has energy shorter than the energy bandgap of the samples (2.4–3.2 eV) to minimize absorption and to avoid photoinduced effects during the measurement. Micro-Raman scattering spectroscopy was used to determine the structural modifications in thin film samples after exposure to UV laser light from a $Kr^+$ ion laser (350 nm, 3.5 eV) for 8 h. The micro-Raman measurements were made on both polarization cases: HH (the incident and scattered electric vectors are parallel) and HV (the incident and scattered electric vectors are perpendicular). The incoming polarized laser light was focused at the lateral profile of the film in order to consider only the expanded region.

The chemical compositions of the films, before and after exposure to UV light, were analyzed using a scanning electron microscope to which an EDX is coupled (Philips XL 30 FEG). A thin layer of gold (10 nm) was deposited onto the film samples by sputtering to avoid the charging effects of the electron beam that is accelerated to 20 kV. Compositional contrast of the exposed and non-exposed areas was determined by BSE images.

To evaluate the photoinduced structural changes, three samples of the deposited films were selected: Film A (0.36 μm thickness), Film B (1.80 μm thickness) and Film C (7.00 μm thickness).

## 3. Results and discussion

Photoinduced effects such as photoexpansion and photobleaching were observed in GGSO films. The phenomenon known as photobleaching is related to an increase of the optical bandgap, while photoexpansion is characterized by an increase of the film thickness. A surface expansion of the thin films and a shift to shorter wavelengths of the optical absorption edge were observed as a result of UV laser irradiation (wavelength of 350 nm) and they are dependent on the laser power density, exposure time and film composition.

The photoinduced changes on the surface of the samples are, mainly, the first indications that the structure of the material has been changed as a result of photoexcitation. To evaluate the importance of oxygen in the investigated films, the structural changes induced by laser exposure have been studied using micro-Raman spectroscopy, which is a valuable tool for revealing the photostructural changes on the film's surface after its exposure to UV light. Taking into account the typical spatial resolution of our experimental setup (spot area ~2 $\mu m^2$) and the fact that the incident laser light was focused at the lateral profile of the film, only the Raman spectra of the thicker film (Film C) were considered in detail in the present analysis. Primarily, in order to compare the scattering configurations, the HH and HV spectra for a non-irradiated 7.00 μm thickness film are presented in Fig. 1.

For comparison purpose, all Raman spectra were normalized to the most intense band because of the different signal intensities. The broad bands reflect considerable structural disorder and due to differences between the spectra, one can conclude that these bands are polarizable. The dependence of molecular vibrations on light polarization can suggest the classification of such material as anisotropic. According to Lyubin [11], studies with $Ge_{20}As_{20}S_{60}$ glasses exposed to polarized light demonstrated that not only the orbital defects or free electrons can be oriented and reoriented, but also the covalent network of the glass becomes anisotropic due to orientation and reorientation of the main covalent bonds.

In order to observe photostructural changes, the micro-Raman spectra of the same sample were measured, before and after irradiation to UV light with power density of $24.3\ mW/mm^2$ (value that optimizes the photoexpansion effect) for 8 h. The results are shown in Fig. 2. Only the HV spectra were considered, because in this configuration the differences between the irradiated and non-irradiated spectrum are more considerable.

Each spectrum was deconvoluted by several Gaussian curves. A least-squares fitting method was used for the deconvolution and the variables used for calculation were location and relative area of the bands. The variation of the Raman bands is clearly illustrated from the deconvoluted spectra (Fig. 3 and Table 1).

Moreover, structural studies of pure $GeS_2$, $GeO_2$ and $Ga_2S_3$ by Raman spectroscopy have been reported in the literature. Structure of Ge–S glasses is well known [12,13] and in the case of $GeS_2$ and $GeO_2$, each one is built up from tetrahedral units of $GeS_{4/2}$ and $GeO_{4/2}$, respectively [14,15]. In addition, $Ga_2S_3$ forms $GaS_4$ tetrahedral units and participates in the formation of edge-shared cross-linked structure, since the S/Ga is 1.5 instead of 2, which is necessary to form $GaS_4$ tetrahedral. These tetrahedral units are also observed when $Ga_2S_3$ is incorporated into $GeS_2$-based glasses, as reported by Loireau-Lozac'h et al. [16]. The addition of gallium in the structure may maintain the global structure, but distorting it through edge or corner-sharing $GeS_4$ tetrahedral linkages substituted for $GaS_4$ units. When Ga is incorporated into Ge-based glass, we can expect that the capacity of the material to incorporate oxygen into the glassy matrix increases. Regarding Raman measurements, the frequencies of fundamental vibration modes of Ga units are very close to those $GeS_{4/2}$ tetrahedra because of similarities in the electronic configuration and atomic mass of the

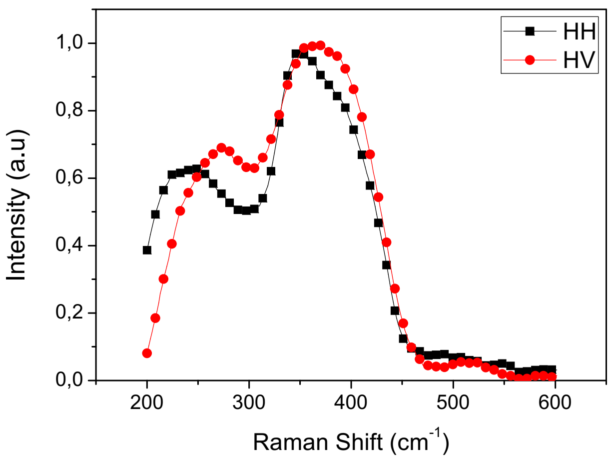

**Fig. 1.** Normalized micro-Raman spectra of a non-irradiated GGSO film with 7.00 μm thickness (Film C) on both HH and HV scattering configurations. The differences between the spectra reveal that the bands are polarizable.

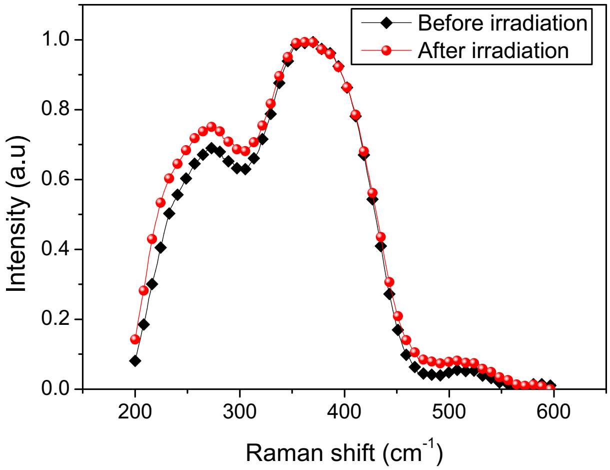

**Fig. 2.** Normalized HV micro-Raman spectra of the Film C (GGSO film with 7.00 μm thickness) before and after exposure to UV light with power density of 24.3 mW/mm$^2$ for 8 h (condition that optimizes the photoexpansion effect).

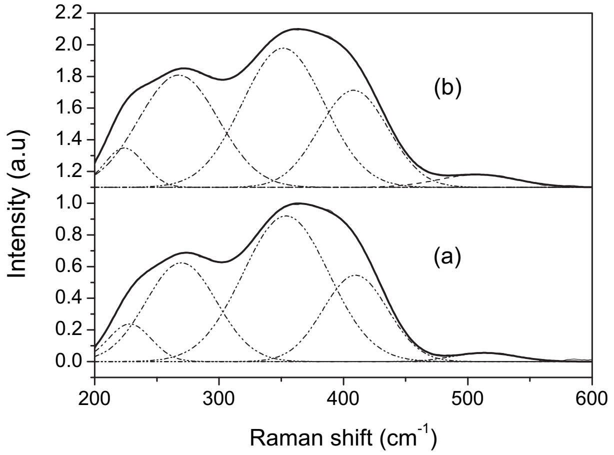

**Fig. 3.** Deconvoluted micro-Raman spectra of the Film C (a) non-irradiated and (b) irradiated to UV light with power density of 24.3 mW/mm$^2$ for 8 h. Correlation coefficients between the observed and the fitted spectra after deconvolution were larger than 0.98 in both cases.

two glass-forming cations [17–20]. For the composition under investigation, the vibrational spectra are more likely to be dominated by responses of Ge-based units because of the small content of Ga.

As a result of the deconvolution process, the spectrum for the non-irradiated film (Fig. 3a) could be deconvoluted using five main vibrations, which are described below.

In accordance with the literature for $GeS_2$ glasses, a main band around 342 cm$^{-1}$ has been associated with $A_1$ symmetric stretching vibrations of S atoms in $GeS_4$ units [21]. For the composition under investigation, Table 1 shows that this bridging sulphur peak is shifted to higher wavenumbers (354 cm$^{-1}$). The increase in the frequencies can be explained by the increase of the stretching force constant for the Ge–S–Ge unit involving Ge atoms bonded to O atoms.

The 410 cm$^{-1}$ peak (Table 1) has been interpreted in two ways. In accordance with recent studies on systems such as $GeS_2$–$GeO_2$ (GSO) [22,23], because of the presence of oxygen atoms in the glass network, this band may be attributed to symmetric stretching of Ge–O–Ge bridging bonds. But Maurel et al. suggested that a band between 360 and 400 cm$^{-1}$ can be attributed to the new vibrational mixed oxysulphide species ($GeS_{3/2}O_{1/2}$, $GeS_{2/2}O_{2/2}$ and $GeS_{1/2}O_{3/2}$), with both Ge–S–Ge and Ge–O–Ge bridging bonds [24].

To complement the structural analysis, the origins of the vibration at 513 cm$^{-1}$ are speculative, because this peak can be assigned to bending modes of Ge–O–Ge linkages [25] or can be attributed to the breathing motion of oxygen atoms in three-membered $GeO_4$ rings [24].

The interpretation is less clear when one concerns the vibration around 230 and 270 cm$^{-1}$. In accordance to recent compositional studies on GSO system, the last band may be attributed to bending modes of S–Ge–O linkages [22]. Similar bands have been reported by several authors as the ethane-like $S_3Ge(Ga)$–$(Ga)GeS_3$ units, seen as a structural alternative to compensate the sulphur deficiency [17–19]. In our case, we cannot exclude the possibility that such phenomenon occurs during film deposition.

After exposure to UV light, structural changes can be inferred from an analysis of Figs. 2 and 3b. From data of Table 1, the relative area decrease of the main band may be related to the simultaneous increase of the band around 410 cm$^{-1}$, indicating that the laser exposure decreases the number of Ge–S bonds in $GeS_{4/2}$ units leading to an increase of the symmetric stretching mode of Ge–O–Ge bridging bonds (according to Refs. [22,23]) or an increase of the number of mixed oxysulphide tetrahedral units with both Ge–S–Ge and Ge–O–Ge bridging bonds (according to Ref. [24]). The formation of mixed oxysulphide tetrahedral units favors the S–Ge–O modes, leading to a relative area increase of the band around 270 cm$^{-1}$. On the other hand, an increase in the intensity of the modes associated with the Ge–O–Ge bonds after UV exposure can explain the relative area increase of the band at 513 cm$^{-1}$. All these photostructural changes can be inferred and better visualized in Fig. 4. In this figure, $\Delta A$ corresponds to the increase (positive change) or the decrease (negative change) of the relative area of each band associated with a vibrational mode after UV exposure. To be more clear, this parameter can be written as $\Delta A = A_E - A_{NE}$, where $A_E$ is the relative area after irradiation and $A_{NE}$ is the relative

**Table 1**
Values of Raman shift and relative area of each Gaussian curve obtained from micro-Raman spectra deconvolution (Fig. 3).

| Raman shift (cm$^{-1}$) | Non-exposed relative area (%) | Exposed relative area (%) | Assignments |
|---|---|---|---|
| 230 | 5.92 | 5.29 | - It is still speculative |
| 270 | 25.70 | 30.23 | - Bending modes of S–Ge–O linkages [22]<br>- Ethane-like $S_3Ge(Ga)$–$(Ga)GeS_3$ units [17–19] |
| 354 | 45.96 | 38.47 | - $A_1$ symmetric stretching vibrations of S atoms in $GeS_4$ units [21] |
| 410 | 20.43 | 22.64 | - Symmetric stretching of Ge–O–Ge bridging bonds [22,23]<br>- New vibrational mixed oxysulphide species ($GeS_{3/2}O_{1/2}$, $GeS_{2/2}O_{2/2}$ and $GeS_{1/2}O_{3/2}$) [24] |
| 513 | 2.00 | 3.36 | - Bending modes of Ge–O–Ge linkages [25]<br>- Breathing motion of oxygen atoms in three-membered $GeO_4$ rings [24] |

The assignment of each vibrational mode is also presented.

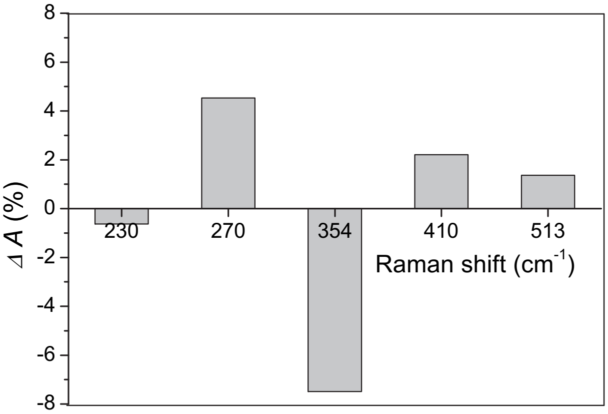

**Fig. 4.** Schematic representation of the increase (positive change) or the decrease (negative change) of the relative area ($\Delta A$) after exposure to UV laser light for each considered vibrational mode. $\Delta A = A_E - A_{NE}$, where $A_E$ is the relative area after irradiation and $A_{NE}$ is the relative area before the exposure to UV.

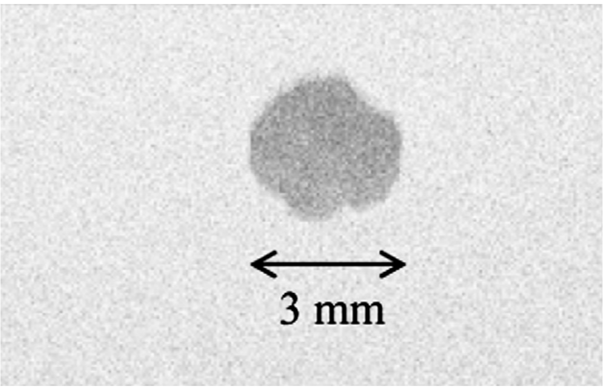

**Fig. 5.** BSE microscopy image of the irradiated surface area of Film B. The brighter region represents the non-exposed area, while the darker region is the photoexpanded and photobleached region that is oxygen rich.

area before the exposure to UV. An appreciable increase of the relative area of the vibrational modes associated with oxygen (270, 410 and 513 $cm^{-1}$) suggests that this element has a great participation on photoexpansion, since Ge–S bonds are broken to form Ge–O bonds after irradiation.

In order to observe changes in the amount of oxygen at the photoexpanded region, quantitative analyses by EDX (Table 2) of different films (0.36 μm – Film A, 2.40 μm – Film B), before and after illumination, were realized. The films were exposed to UV light with power density of 24.3 $mW/mm^2$ for 2 h. The results for Film C were not presented, since no compositional differences could be observed when this sample was exposed to the same conditions of irradiation.

The data of Table 2 show a great increase of the oxygen content as a result of exposure to UV light with above bandgap energy. This increase could be confirmed by analyzing the irradiated area of Film B by backscattering electrons (BSE) images, presented in Fig. 5. A BSE image is built in contrast caused by the difference among the atomic number ($Z$) of the elements in the material. When a beam passes through a region of larger $Z$, the intensity of the signal due to backscattering increases and, consequently the image brightness also increases. So, in Fig. 5, one can distinguish two regions: the brighter area (non-exposed) and the darker area, corresponding to the oxygen-rich region (photoexpanded and photobleached).

The experimental evidences of an increase of oxygen in the exposed area confirm that this element is correlated with the photoexpansion effect on such materials. Micro-Raman spectra revealed that the photoexpansion is a result of photostructural changes, in which Ge–S bonds are broken and Ge–O bonds are formed. In comparison to the results obtained in $Ga_{10}Ge_{25}S_{65}$ amorphous films [9], the fractional expansion ($\Delta d/d$, where $\Delta d$ is the thickness variation after expansion and $d$ is the film thickness) measured ($\Delta d/d$~30% for a 4 μm thickness film) is greater than that observed in GGSO films ($\Delta d/d$~4% for a film with the same thickness). Since in GGSO the oxygen is already incorporated into the structure, the chances of occurence of the structural changes that lead to photoexpansion are smaller. Thus, GGSO films exhibit less photosensibility to UV light with energy equal to 3.52 eV than GGS films.

**Table 2**
The chemical compositions (in atomic %) by EDX analysis of GGSO films with different thicknesses (0.36 μm – Film A, 2.40 μm – Film B) before and after exposure to UV light with 24.3 $mW/mm^2$ for 2 h.

| Element | Film A (non-irradiated) | Film A (irradiated) | Film B (non-irradiated) | Film B (irradiated) |
|---|---|---|---|---|
| O (+/– 10%) | 24 | 53 | 14 | 42 |
| S (+/– 5%) | 32 | 15 | 32 | 18 |
| Ga (+/– 5%) | 1 | 1 | 1 | – |
| Ge (+/– 5%) | 43 | 32 | 53 | 40 |

Several models have been proposed to explain the considered photoinduced effects. The mechanistic origin behind these effects is not fully understood, but has been interpreted as a consequence of optically induced changes in local bonding configurations. In the model proposed by Elliot [26], the oxygen enters into the film network forming strong covalent bonds with germanium and chalcogen atoms. In its normal twofold coordination, a neutral chalcogen atom has two electrons out of its four p electrons on the bonding orbital, two empty quantum states on the nonbonding orbital and two states filled by electrons on the nonbonding orbital, called the lone-pair (LP) orbital. In general, photoinduced phenomena occur through a series of photo–electro–structural processes [27]. It is recognized that these effects originated from the light-induced formation of electron–hole pairs that allow the bond rearrangement upon recombination. Photon absorption excites localized electrons from LP state (located at the top of valence band) leading to the formation of self-trapped excitons, also called valence alternation pairs (VAPs). These charged defects allow structural changes as they decay [28]. So, these amorphous networks display noteworthy structural openness and freedom that should play an important role in their photosensibility. As well as chalcogenide, oxysulphide glasses exhibit a structural flexibility composed of Ge and Ga ions weakly bonded [29]. There also exists consensus that in the presence of oxygen, illumination with near bandgap energy induces photo-oxidation of the Ge–S film surface, which affects various physical properties of the thin film. Thus, the absorption of light with above bandgap energy results in the breakdown of Ge–S bonds and creation of new Ge–O bonds in the irradiated area. These structural changes can be considered to be responsible for the photoinduced effects observed on GGSO films.

## 4. Conclusions

The present paper shows the structural investigation of the photoinduced effects on the surface of GGSO thin films using micro-Raman spectroscopy. The obtained spectra suggest that, after illumination, the breakdown of Ge–S bonds is accompanied by an increase of the modes associated with Ge–O–Ge bonds and mixed oxysulphide tetrahedral units (S–Ge–O). In addition, EDX and BSE microscopy images indicated that the irradiated area is oxygen rich. We suggest that this element, which is already incorporated into the glass matrix, has an important participation in the photoinduced phenomena. On the basis of these experimental results, photoexpansion and photobleaching are probably associated with the increase of Ge–O bonds, i.e., it is a result of photo-oxidation. Although the role of oxygen is not clear, the understanding of the relation between the structural changes of the film surface and its response under irradiation with above bandgap energy leads to a better knowledge of the oxysulphide photosensibility.

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