Materials Science-Poland, 36(3), 2018, pp. 403-408
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/msp-2018-0069

Comparative analysis on microhardness and third order nonlinear optical traits of pure and Nd^{3+} doped zinc tris-thiourea sulphate (ZTS) crystal

MOHD ANIS[1,*], G.G. MULEY[1], MOHD SHKIR[2,3], S. ALFAIFY[2,3], H.A. GHRAMH[2,3]

[1]Department of Physics, Sant Gadge Baba Amravati University, Amravati-444602, Maharashtra, India

[2]Advanced Functional Materials & Optoelectronic Laboratory (AFMOL), Department of Physics, College of Science, King Khalid University, P.O. Box 9004, Abha-61413, Saudi Arabia

[3]Research Center for Advanced Materials Science (RCAMS), King Khalid University, P.O. Box 9004, Abha-61413, Saudi Arabia

Present investigation is aimed to explore the single crystal growth, microhardness and third order nonlinear optical (TONLO) properties of Nd^{3+} doped zinc tris-thiourea sulphate (ZTS) crystal. The commercial slow solvent evaporation technique has been chosen to grow a good quality ZTS (12 mm × 0.5 mm × 0.3 mm) and Nd^{3+} doped ZTS (11 mm × 0.6 mm × 0.4 mm) single crystals. Vickers microhardness test has been employed to analyze the influence of Nd^{3+} dopant on the hardness behavior of ZTS single crystal. The TONLO effects occurring in Nd^{3+} doped ZTS single crystal have been evaluated by means of Z-scan technique using a He–Ne laser operating at 632.8 nm. The close and open aperture Z-scan configuration have been used to determine the nature of TONLO refraction n_2 and absorption β, respectively. The magnitudes of vital TONLO parameters, such as refraction n_2, absorption coefficient β, figure of merit and susceptibility χ^3 of the Nd^{3+} doped ZTS single crystal, have been determined using Z-scan transmittance data. The n_2, β, and χ^3 of Nd^{3+} doped ZTS single crystal were found to be of the order of 10^{-10} cm^2/W, 10^{-6} cm/W and 10^{-5} esu, respectively.

Keywords: *photonic crystal; microscopic study; Z-scan study; nonlinear optical materials*

1. Introduction

The rigorous development in semiorganic nonlinear optical (NLO) thiourea metal complex (TMC) crystals has aroused the interest of research community as they offer excellent characteristics when compared with organic and inorganic counterparts. Currently, the NLO crystals are mainly processed for using in designing of distinct optoelectronic and photonic devices [1–3]. In the past few years a large range of TMC crystals have been reported and extensively studied by many researchers [4–8]. Amongst all reported TMC crystals, the zinc tris-thiourea sulphate (ZTS) crystal reveals higher second harmonic generation (SHG) efficiency and unique structural symmetry (orthorhombic crystal structure and $Pca2_1$ noncentrosymmetric space group). In addition, ZTS crystal exhibits outstanding physical, electrical, mechanical and thermal properties [9–11], which are vital parameters desired for processing and designing hi-tech optical devices. Recently, many research groups have aimed to grow excellent quality ZTS crystals and immense attention has been paid to enhance their performance. Several studies reported that doping of specific additive have significant impact on inherent properties of ZTS crystal [12, 13]. The doping effect of lithium, sodium, manganese, cadmium, nickel, magnesium, cesium, aluminum and antimony on different traits of ZTS crystal has been reported in literature [14–21]. Very recently, our research group has informed about the promising effect of Nd^{3+} on crystal growth, structural, optical and electrical properties of ZTS crystal [23]. However, up to now, the hardness and third order

*E-mail: loganees@gmail.com

nonlinear optical properties of Nd^{3+} doped ZTS crystal, which are vital for construction of photonic devices, have not been reported. The current extended studies of Nd^{3+} doped ZTS crystal involved crystal growth as well as microhardness and Z-scan studies.

2. Experimental

2.1. Starting materials

Double distilled water, zinc sulphate ($ZnSO_4$), thiourea ($CS(NH_2)_2$) and neodymium trioxide (Nd_2O_3) were used in the experiments.

2.2. Synthesis and crystal growth

The host material of ZTS crystal complex has been synthesized by dissolving AR grade zinc sulphate (1 mol) and thiourea (3 mol) in double distilled water. The solution was agitated continuously for four hours and ZTS crystal complex has been obtained according to the reaction: $3CS(NH_2)_2 + ZnSO_4 \rightarrow Zn[CS(NH_2)_2]_3SO_4$.

The purity of the ZTS crystal has been achieved by successive recrystallization process. In order to dope Nd^{3+} into ZTS crystal 2 mole of Nd_2O_3 was weighted using electronic balance and gradually added to the supersaturated solution of ZTS material. The Nd_2O_3 added ZTS solution was agitated to achieve homogeneous doping of Nd^{3+} throughout the solution. The Nd^{3+} doped ZTS (Nd-ZTS) solution was filtered in a beaker and kept for slow evaporation in a constant temperature bath at 36 °C (±0.01 °C). The ZTS crystal of dimensions 12 mm × 0.5 mm × 0.3 mm and Nd-ZTS crystal of dimensions 11 mm × 0.6 mm × 0.4 mm have been grown as depicted in Fig. 1a and Fig. 1b, respectively.

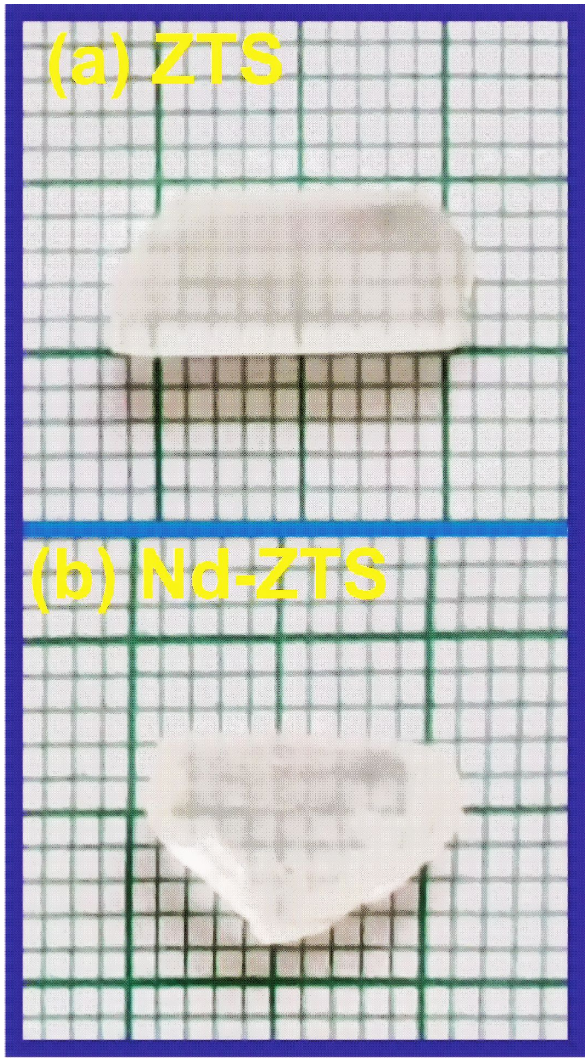

Fig. 1. Single crystals of (a) ZTS, (b) Nd-ZTS.

3. Results and discussion

The hardness is an essential physical parameter as far as polishing and processing of crystal is concerned. It definitely limits the wastage of crystal material and favors the commercial fabrication of various devices [24–26]. The intrinsic (heat of formation, interatomic bonding, internal lattice energy and Debye temperature) [27] and extrinsic (solvent inclusions, defects, impurity vacancy, dislocations and low angle grain boundaries) [28] factors are the decisive parameters influencing hardness of a material. The Vickers microhardness test has been employed to explore the effect of Nd^{3+} on the hardness of ZTS crystal using a Shimadzu HMV-2T microhardness analyzer. The hardness properties are connected with anisotropic nature along different crystal planes The effect of applied load on crystal surface may evolve in two ways (a) the hardness decreases with an increase in load, which is known as normal indentation size effect (NISE) phenomenon, and (b) the hardness increases

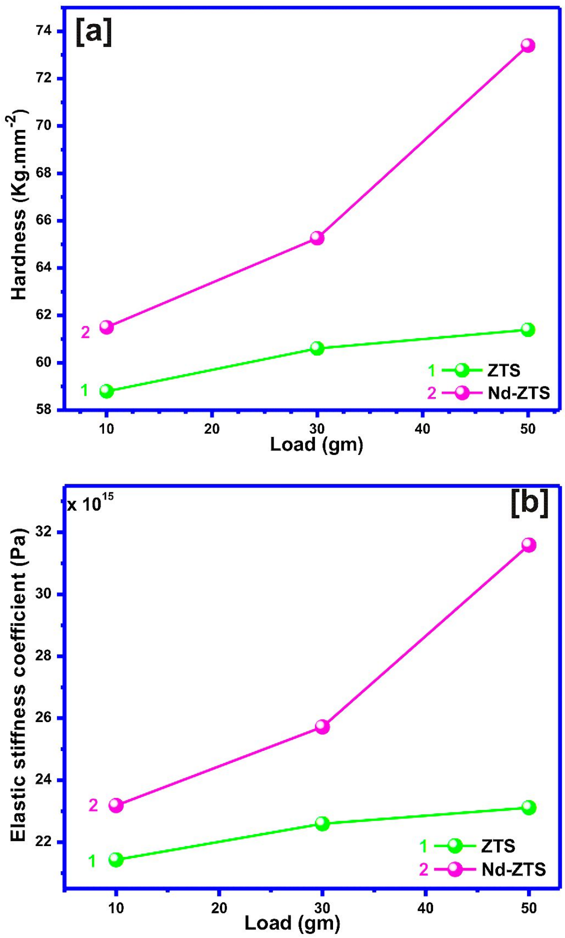

Fig. 2. (a) load dependent hardness, (b) load dependent elastic stiffness coefficient.

with an increase in load, which is known as reverse indentation size effect (RISE) phenomenon [29]. In present analysis, the surface of pure and Nd-ZTS crystal was exposed for a period of 10 seconds to increasing load (25 g, 50 g and 100 g) and the diagonal length of the indentation was measured to calculate the hardness (H_v) along the selected surface. The H_v of the grown crystals has been evaluated using the equation:

$$H_v = 1.8544 \times (P/d^2) \tag{1}$$

where P is the applied load in kg and d is the diagonal length of indentation in mm [30]. The variation of hardness with applied load is shown in Fig. 2a. It is observed that the hardness of the grown crystal increases with an increase in applied load due to the RISE phenomenon. The analysis reveals that the Nd-ZTS crystal exhibits higher hardness in comparison to ZTS crystal which indicates that doping of Nd^{3+} significantly enhanced the threshold of dislocation density of ZTS crystal and minimized the effect of lattice imperfections [31]. The increased hardness confirms the superiority of Nd-ZTS crystal over ZTS and evidences that the wastage of Nd-ZTS crystal will be minimum during polishing and processing of the material before subjecting it to practical device fabrication as observed in several doped crystals [32, 33]. In the material two consecutive atoms are hold by a mutual bond whose strength can be identified by evaluating the elastic stiffness coefficient ($C_{11} = H_v^{7/4}$) of the material [34]. The variation of elastic stiffness with reference to the applied load is shown in Fig. 2b. It reveals that this magnitude for pure and Nd-ZTS crystals increases with the load confirming that the dopant Nd imparts a positive effect on improving the hardness parameters of ZTS crystal.

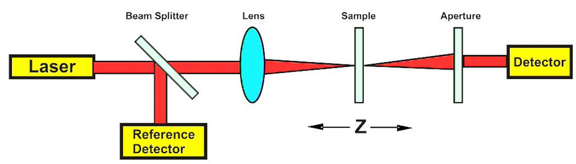

Fig. 3. Schematic diagram of Z-scan setup.

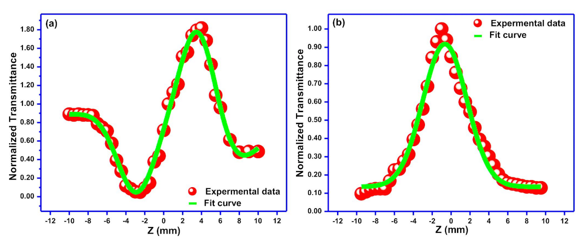

Fig. 4. Z-scan transmittance curve (a) close, (b) open.

The thorough understanding of third order nonlinear optical (TONLO) behavior of discrete materials (organic, inorganic, semiconductors and nanoparticles) is absolutely demanded for development and designing of advanced photonic devices [35]. In current era of technology, the Z-scan

Table 1. Optical resolution of Z-scan setup.

Parameters	Magnitude
Laser wavelength λ	632.8 nm
Laser power P	10 mW
Lens focal length f	20 cm
Optical path distance Z	113 cm
Beam waist radius ω_a	1 mm
Aperture radius r_a	1.5 mm
Incident intensity at the focus I_o	2.3375 kW/m^2

is found to be the most influential, sensitive and potential technique, developed by Bahae et al. [36], to explore the TONLO refraction n_2, susceptibility χ^3 and absorption coefficient β of material. The Z-scan experimental setup was designed using the optics with parameters as tabulated in Table 1 and its schematic diagram is shown in Fig. 3. In present Z-scan analysis, the polished crystal sample of 0.5 mm thickness was mounted on the sample holder positioned at the focus (Z = 0). The sample was later moved along the beam irradiation path (i.e. Z-direction) and the transmitted intensity from the crystal was recorded using the photodetector placed at far field. The transmitted optical signal from Nd-ZTS crystal sample recorded with close aperture of detector is shown in Fig. 4a. It reveals that the Nd-ZTS crystal offers the pre-focus valley to post-focus peak phase change in TONLO refraction n_2. It confirms the occurrence of positive refraction nonlinearity in Nd-ZTS crystal which is primarily attributed to material exhibiting self-focusing character [37, 38]. The TONLO refraction in material is governed by the phenomenon of localized absorption of incident optical beam of high frequency, giving rise to thermal lensing effect (spatial distribution of energy along the crystal surface) [39–41]. The positive refraction nonlinearity of high magnitude leads to Kerr lens mode-locking (KLM) whose ability is highly desirable for shorter pulse generation and laser stabilization systems [42, 43]. The dependence of peak to valley transmittance ΔT_{p-v} in terms of on axis phase shift $\Delta\Phi$ is expressed as [36]:

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}\,|\Delta\phi| \qquad (2)$$

where $S = [1-\exp(-2r_a^2/\omega_a^2)]$ is the aperture linear transmittance, r_a is the aperture radius and ω_a is the beam radius at the aperture. The value of n_2 has been calculated using the equation [36]:

$$n_2 = \frac{\Delta\phi}{KI_0L_{eff}} \qquad (3)$$

where $K = 2\pi/\lambda$ (λ is the laser wavelength), I_0 is the beam intensity at the focus, $L_{eff} = [1-\exp(-\alpha L)]/\alpha$, is the effective thickness of the sample depending on linear absorption coefficient α and L is the thickness of the sample. The magnitude of n_2 was found to be of order of 10^{-10} cm^2/W. The open aperture Z-scan analysis gives the precise idea of TONLO absorption tendency of the grown crystal. The recorded open aperture Z-scan curve of Nd-ZTS crystal is shown in Fig. 4b. The analysis of the plot reveals that when the sample reaches the focus point the propagation of light through the signal increases leading to high transmittance at the focus. This confirms the presence of saturable absorption (SA) effect in the grown crystal [44]. The increase in transmittance at the focus is facilitated by the dominance of ground state linear absorption over the excited state absorption [45, 46]. The TONLO absorption coefficient β of the grown crystal has been evaluated using the following equation [36]:

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{eff}} \qquad (4)$$

where ΔT is the one valley value at the open aperture Z-scan curve. The β of Nd-ZTS crystal was found to be of order 10^{-6} cm/W. The Nd-ZTS crystal with significant SA effect might serve as a potential candidate for designing Q-switching elements for lasers [47]. The χ^3 was calculated using the following equations [36]:

$$\mathrm{Re}\chi^{(3)}(esu) = 10^{-4}(\varepsilon_0C^2{n_0}^2n_2)/\pi(cm^2/W) \qquad (5)$$

$$\mathrm{Im}\chi^{(3)}(esu) = 10^{-2}(\varepsilon_0C^2{n_0}^2\lambda\beta)/4\pi^2(cm/W) \qquad (6)$$

$$\chi^{(3)} = \sqrt{(Re\chi^{(3)})^2 + (Im\chi^{(3)})^2} \qquad (7)$$

Table 2. Comparison of TONLO parameters.

Crystal	n_2 [cm^2/W]	β [cm/W]	χ^3 [esu]	Literature
ZTS	-5.36×10^{-12}	4.24×10^{-4}	3.5×10^{-4}	[9]
Nd-ZTS	8.27×10^{-10}	6.10×10^{-6}	3.87×10^{-5}	This work

where ϵ_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum. The polarizing ability of the material is the most decisive parameter which is proportional to the high magnitude of TONLO susceptibility χ^3 of the material [48]. The χ^3 of the grown crystal was found to be of the order of 10^{-5} esu. The high magnitude of susceptibility might have been attributed to the enhanced charge transfer and delocalization of π-electrons due to incident optical energy [48–50]. The materials exhibiting figure of merit (FOM) less than 1 have very high credibility for designing photonic devices [51, 52]. The FOM of Nd-ZTS crystal has been evaluated using the relation [53]:

$$FOM = \beta\lambda/n_2 \quad (8)$$

The FOM of Nd-ZTS crystal was found to be 0.46 which confirms its suitability to photonics device applications. The TONLO properties of the grown crystals were systematically compared and tabulated in Table 2.

4. Conclusions

Optimum size pure and Nd-ZTS single crystals have been grown by slow solvent evaporation technique at temperature of 36 °C. The microhardness study and Z-scan analysis of Nd-ZTS crystal have been successfully accomplished. The microhardness analysis revealed that the Nd-ZTS crystal has higher dislocation density threshold as compared to ZTS, resulting in high hardness of Nd-ZTS crystal. The enhanced elastic stiffness coefficient confirmed the strong interatomic bonding in Nd-ZTS crystal. The close and open aperture Z-scan analysis confirmed the potential TONLO behavior of Nd-ZTS crystal. The Nd-ZTS crystal was found to be an important material exhibiting self-focusing tendency, i.e. positive refraction nonlinearity due to thermal lensing effect. The magnitude of n_2 of Nd-ZTS crystal was found to be 8.27×10^{-10} cm^2/W. The dominance of linear absorption coefficient over the excited state absorption led to SA effect in Nd-ZTS crystal and the TONLO absorption coefficient β was found to be 6.10×10^{-6} cm/W. The susceptibility of Nd-ZTS crystal was found to be as high as 3.87×10^{-5} esu which resulted from the enhanced charge transfer facilitated by delocalization of π-electron. The magnitude of FOM of Nd-ZTS crystal was determined to be 0.46 which confirms the dominating effect of n_2 over β. The excellent third order nonlinear optical nature of Nd-ZTS crystal confirms its potential reliability for using in designing photonic devices.

Acknowledgements

The Author, Mohd Anis, is thankful to the UGC, New Delhi, India, for awarding the Maulana Azad National Fellowship, and H.A. Ghramh would like to express his gratitude to the RCAMS-King Khaled University, Saudi Arabia, for support.

References

[1] RAMTEKE S.P., ANIS M., BAIG M.I., PAHURKAR V.G., MULEY G.G., *Optik*, 137 (2017), 31.
[2] PAHURKAR V.G., ANIS M., BAIG M.I., RAMTEKE S.P., BABU B., MULEY G.G., *Optik*, 142 (2017), 421.
[3] ANIS M., BAIG M.I., MULEY G.G., HUSSAINI S.S., SHIRSAT M.D., *Optik*, 127 (2016), 12043.
[4] SANKAR R., RAGHAVAN C.M., JAYAVEL R., *Cryst. Growth Des.*, 7 (2007), 501.
[5] CHITHAMBARAM V., DAS S.J., KRISHNAN S., *J. Alloy. Compd.*, 509 (2011), 4543.
[6] SENTHIL MURUGAN G., BALAMURUGAN N., RAMASAMY P., *Mater. Lett.*, 62 (2008), 3087.
[7] ANIS M., HUSSAINI S.S., SHIRSAT M.D., *Optik*, 127 (2016), 9734.
[8] LYDIA CAROLINE M., VASUDEVAN S., *Mater. Chem. Phys.*, 113 (2009), 670.
[9] MURALEEDHARAN R., RAMAJOTHI J., BASHEER AHAMED M., *Indian J. Sci. Technol.*, 8 (2015), 165.
[10] SABARI GIRISUN T.C., DHANUSKODI S., *Cryst. Res. Technol.*, 44 (2009), 1297.

[11] VENKATARAMANAN V., SUBRAMANIAN C.K., BHAT H.L., *J. Appl. Phys.*, 77 (1995), 64049.

[12] SHEJWAL N.N., ANIS M., HUSSAINI S.S., SHIRSAT M.D., *Int. J. Mod. Phys. B*, 30 (2016), 1650159.

[13] SHEJWAL N.N., ANIS M., HUSSAINI S.S., SHIRSAT M.D., *Optik*, 127 (2016), 6525.

[14] KRISHNAN C., SELVARAJAN P., FREEDA T.H., *Mater. Manuf. Process.*, 23 (2008), 800.

[15] KRISHNAN C., SELVARAJAN P., PARI S., *Curr. Appl. Phys.*, 10 (2010), 664.

[16] BHAGAVANNARAYANA G., KUSHWAHA S.K., PARTHIBAN S., SUBBIAH MEENAKSHISUNDARAM, *J. Cryst. Growth*, 311 (2009), 960.

[17] GOPINATH S., PALANIVEL R., RAJASEKARAN R., *Int. J. Pure Appl. Sci. Technol.*, 1 (2010), 104.

[18] MULEY G.G., *J. Electron. Mater.*, 43 (2014), 439.

[19] RAJASEKAR M., MUTHU K., MEENATCHI V., MAHADEVAN C.K., MEENAKSHISUNDARAM SP., *Optik*, 125 (2014), 710.

[20] MUTHU K., BHAGAVANNARAYANA G., MEENAKSHISUNDARAM SP., *J. Alloy. Compd.*, 548 (2013), 201.

[21] MUTHU K., MEENAKSHISUNDARAM SP., *J. Phys. Chem. Solids*, 73 (2012), 1146.

[22] MEENA K., RAMASAMY G., RAJASEKAR M., MUTHU K., MEENAKSHISUNDARAM SP., *Optik*, 125 (2014), 4876.

[23] ANIS M., MULEY G.G., PAHURKAR V.G., BAIG M.I., DAGDALE S.R., *Mater. Res. Innov.*, 22 (2018), 99.

[24] ANIS M., MULEY G.G., BAIG M.I., HUSSAINI S.S., SHIRSAT M.D., *Mater. Res. Innov.*, 21 (2017), 439.

[25] SHKIR M., GANESH V., ALFAIFY S., YAHIYA I.S., ANIS M., *Chin. Phys. B*, 27 (2018), 54216.

[26] STEPHENS J., GEBRE T., BATRA A.K., AGGARWAL M.D., LAL R.B., *J. Mater. Sci. Lett.*, 22 (2003), 179.

[27] ROBERT R., RAJ C.J., KRISHNAN S., UTHRAKUMAR R., DINAKARAN S., DAS S.J., *Phys. B*, 405 (2010), 3248.

[28] ANIS M., MULEY G.G., *Phys. Scripta*, 91 (2016), 85801.

[29] SANGWAL K., *Cryst. Res. Technol.*, 44 (2009), 1019.

[30] SHAIKH R.N., ANIS M., SHIRSAT M.D., HUSSAINI S.S., *Optoelectron. Adv. Mat*, 10 (2016), 526.

[31] ANIS M., SHIRSAT M.D., HUSSAINI S.S., JOSHI B., MULEY G.G., *J. Mater. Sci. Technol.*, 32 (2016), 62.

[32] RASAL Y.B., ANIS M., SHIRSAT M.D., HUSSAINI S.S., *Mater. Res. Innov.*, 21 (2017), 45.

[33] RAMTEKE S.P., ANIS M., PANDIAN M.S., KALAINATHAN S., BAIG M.I., RAMASAMY P., MULEY G.G., *Opt. Laser Technol.*, 99 (2018), 197.

[34] PABITHA G., DHANASEKARAN R., *Mater. Sci. Eng. B-Adv.*, 177 (2012), 1149.

[35] ELAVARASU N., SATHYA P., PUGAZHENDHI S., VIJAYAN N., MAURYA K.K., GOPALAKRISHNAN R., *Opt. Laser Technol.*, 84 (2016), 107.

[36] BAHAE M.S., SAID A.A., TAI-HUE WEI, HAGAN D.J., VAN STRYLAND E.W., *IEEE J. Quant. Electron.*, 26 (1990), 760.

[37] BAIG M.I., ANIS M., MULEY G.G., *Opt. Mater.*, 72 (2017), 1.

[38] ARIVAZHAGAN T., SOLANKI S.S.B., RAJESH N.P., *Opt. Laser Technol.*, 88 (2017), 188.

[39] ANIS M., BAIG M.I., HUSSAINI S.S., SHIRSAT M.D., SHKIR M., GHRAMH H.A., *Chin. Phys. B*, 27 (2018), 47801.

[40] SHAIKH R.N., ANIS M., SHIRSAT M.D., HUSSAINI S.S., *Optik*, 154 (2018), 435.

[41] BAIG M.I., ANIS M., KALAINATHAN S., BABU B., MULEY G.G., *Mater. Technol.*, 32 (2017), 560.

[42] MAJOR A., AITCHISON J.S., SMITH P.W.E., DRUON F., GEORGES P., VIANA B., AKA G.P., *Appl. Phys. B*, 80 (2005), 199.

[43] ANIS M., SHKIR M., BAIG M.I., RAMTEKE S.P., MULEY G.G., ALFAIFY S., GHRAMH H.A., *J. Mol. Struct.*, 1170 (2018) 151.

[44] RAMTEKE S.P., BAIG M.I., SHKIR M., KALAINATHAN S., SHIRSAT M.D., MULEY G.G., ANIS M., *Opt. Laser Technol.*, 104 (2018), 83.

[45] KUMAR R.A., VIZHI R.E., VIJAYAN N., BHAGAVANNARAYANA G., BABU D.R., *J. Pure Appl. Indian Phys.*, 1 (2010), 61.

[46] SHAIKH R.N., ANIS M., SHIRSAT M.D., HUSSAINI S.S., *Mater. Technol.*, 31 (2016), 187.

[47] JIN W., NING G., HUI-TIAN W., XIAO-WU N., *Opt. Commun.*, 283 (2010), 3525.

[48] SRINIVASAN P., NOORALDEEN A.Y., KANAGASEKARAN T., DHINAA A.N., PALANISAMY P.K., GOPALAKRISHNAN R., *Laser Phys.*, 18 (2008), 790.

[49] AZHAR S.M., RABBANI G., SHIRSAT M.D., HUSSAINI S.S., BAIG M.I., GHRAMH H.A., ANIS M., *Optik*, 165 (2018), 259.

[50] AZHAR S.M., ANIS M., HUSSAINI S.S., KALAINATHAN S., SHIRSAT M.D., RABBANI G., *Mater. Sci.-Poland*, 34 (2016), 800.

[51] ANUSHA P.T., REETA P.S., GIRIBABU L., TEWARI S.P., RAO S.V., *Mater. Lett.*, 64 (2010), 1915.

[52] ANIS M., MULEY G.G., HAKEEM A., SHIRSAT M.D., HUSSAINI S.S., *Opt. Mater.*, 46 (2015), 517.

[53] ANIS M., SHIRSAT M.D., GAJANAN M., HUSSAINI S.S., *Phys. B*, 449 (2014), 61.

Received 2017-05-01
Accepted 2018-04-19