Impact Of Shock Waves on Structural and Optical Properties of $Li_2so_4.H_2o$ Doped L-Alanine Single Crystals for High Pressure and Temperature Applications

[1] M. Silviya, [2] L. Sweatha, [3] M. Anithalakshmi, [1*]R. Robert

PG & Research Department of Physics, Govt. Arts College For Men,
Krishnagiri- 635 001, Tamil Nadu, India

*Corresponding author E-mail : roberthosur@yahoo.co.in

Abstract: The current study discusses the impact of shock wave of Mach number 1.7 on structural, molecular and optical properties of $Li_2SO_4.H_2O$ doped L-Alanine single crystals. PXRD, Raman spectral results confirm that the test crystal does not undergo any crystallographic phase transitions and conformational transitions against the shock wave. Optical micrographs and UV-Visible analysis communicate the subtle morphological changes and optical properties which is not significantly changed by shock wave. The results of crystallographic studies provide the strong proof that the crystal has molecular stability and a stable crystallographic structure against the impact of applied shock waves and suitable for a wide range of uses in aerospace applications.

Keywords: Shock wave, $Li_2SO_4.H_2O$ Doped L-Alanine, Microelectronic device, Stable Plane

1. Introduction

Research starts innovation with greater potential, which builds the foundation for fabricating extraordinarily complex materials for various implementations. The radiation method, static pressure compression method, shock recovery experiments, and other techniques are used to find excellent materials with imposed properties for aerospace applications. Exploring materials' demeanour in utmost context leads the way to the advancement of unique rigid structural materials are favourable practices for utilization of inconsistent domains. Applications in aerospace and engineering necessitate characterising bulk materials or nanomaterial under extreme heat, pressure, vibration, and humidity [1-3]. The evolution of experimental approaches and procedures of atomistic simulation have invigorated concern in the process and kinetics of high-rate in extensible deformation and fracture of crystalline solid [4-15]. Investigations on the clout of the shock wave are the flickering area in Material Science. Shock waves are generated due to the abrupt discharge of energy in a few microseconds, and if they hit crystalline material, they may alter the material's crystallinity and followed by physicochemical properties [16, 17]. Plentiful reports are accessible on the significance of shockwave on crystalline materials in terms of theoretical and experimental research functioning worldwide [18-20]. Numerous practical implementations of nonlinear optical materials exist in the fields of optical information, optical communication, and optical storage [21]. The available assorted literature on shockwave-induced NLO crystals are witnessed that the NLO crystals exhibit desirable properties like structural stability, band gap tuning, enhanced NLO efficiency and thermal diffusivity at the shocking condition which could find applications in aerospace, microelectronic, Military, and high power laser systems [22-26].

L-Alanine is the basic element for amino acid compounds that exhibits substantial nonlinear behaviour, a typical phonon coupling and also manifesting vibrational solitons [27]. Numerous reports are available on L-Alanine-based crystals in respect of physical phenomena determination concerning NLO applications. There have been studies done on L-Alanine that involved doping or the addition of various organic and inorganic substances [28-36]. Dopants play a key role in the crystal altering the electric dipole-photon effect during energy-matter interaction and also enhancing crystalline perfection [37-40].The aforementioned fact made it easier to select $Li_2SO_4.H_2O$, an inorganic substance, as a dopant, which promoted the growth rate of the L-

Alanine crystals. This present investigation extensively proclaims the spectroscopic outcomes of $Li_2SO_4.H_2O$ doped L-Alanine single crystals under shocked conditions.

2. Experimental Section

2.1 $Li_2SO_4.H_2O$ doped L-Alanine single crystal growth

The slow evaporation method was adapted to grow $Li_2SO_4.H_2O$ doped L-Alanine single crystals. 1M of L-Alanine and 0.1M of $Li_2SO_4.H_2O$ were added in required quantity of deionized water used as the solvent. A magnetic stirred is used to make the homogeneous saturated solution. After filtering, the solution was left at room temperature to allow the solvent to evaporate. To obtain the high-quality single crystals, a recrystallization process was adopted, and the yield was achieved in three weeks. Grown crystals were polished with an emery sheet and obtained as 7 x 5 x 1 mm^3 dimensional crystal which is depicted in Fig.1.

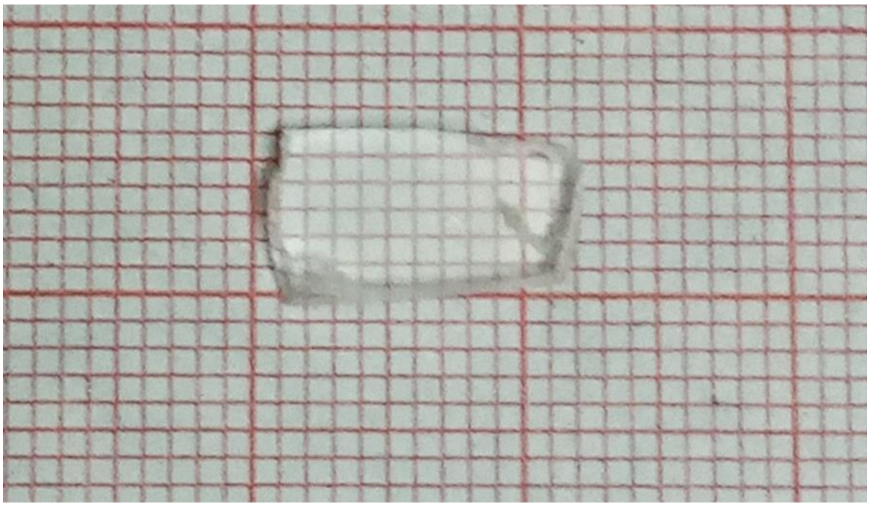


Fig 1: Photograph of the $Li_2So_4.H_2O$ doped L-Alanine Single Crystals

2.2 Shock wave Loading Procedure

A table-top Reddy shock tube was used to generate the shock wave [41]. The tabletop pressure-driven shock tube consists of three sections driver, diaphragm and driven section. The diaphragm segment connects the driver and driven segments. An air compressor supplies the driver section input pressure, and when the pressure reaches critical pressure, the diaphragm ruptures, creating shock waves in the driven section. The probing crystal is fixed in a sample holder which is situated 1cm from the open end of the shock tube. Shock wave of Mach number 1.7 with 0,1,2,3,4 shock pulses have been exposed on the crystal. The transient temperature and pressure of the shock wave is calculated as 1.048 MPa and 644 K. Optical microscope and other spectroscopic approaches such as XRD, Raman and UV-Visible were carried out for control and shockwave-loaded crystals. Spectroscopic outcomes for both the crystals were compared and elucidations are addressed in respective sections.

3. Results and Discussion

3.1 EDAX Analysis

Before perform the shock wave recovery experiment on the title sample, it is quite mandatory to confirm the presence of dopant in the grown crystal and hence EDAX analysis had been carried and obtained the spectra is presented in Fig.2. As seen in Fig.2, it represents that the elements such as carbon, oxygen, and nitrogen are present in the sample. In addition to that the hydrogen and lithium could not be identified and also the presence of sulphur indicated as yellow colour confirms the incorporation of dopant $Li_2So_4.H_2O$ with L-Alanine single crystals.

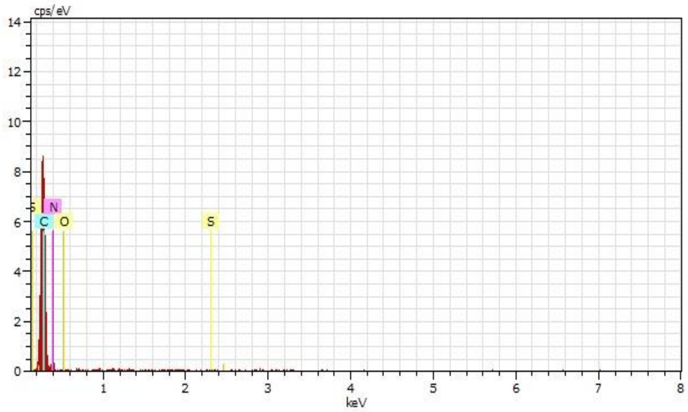


Fig 2: EDAX of $Li_2So_4.H_2O$ doped L-Alanine Single Crystals

3.2 Surface Morphology studies

An optical microscope (Weswox) was used to probe the variations caused by shock wave exposure. It is an effective and easy tool to identify the micro and macro-level surface defects in the bulk crystal [42]. Surface flatness, defect concentration and morphology variations could be recognised through an optical microscope [43]. It is obvious known from the Fig.3 (a&b), there is no visible defects could found in shocked crystal by the exposure of shock wave.

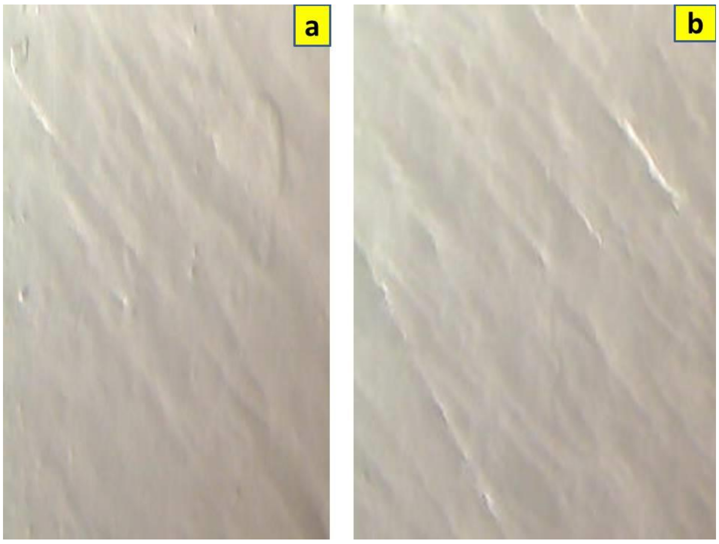


Fig 3: Optical Micrographs of control and Shocked $Li_2So_4.H_2O$ doped L-Alanine single crystals

3.3 Powder XRD Analysis

X-ray diffractometer (Rigaku Mini Flux) was used to record the diffraction pattern of control and shock wave loaded $Li_2SO_4.H_2O$ doped L-Alanine single crystals. Fig.4 illustrates that the PXRD pattern of the control crystal shows that the sharp diffraction peak along (120) confirms the orthorhombic crystal structure which is in good agreement with existing reported data [44]. It is to mentioned here that there is a slight change in the peak position confirms the dopant incorporation with L-Alanine single crystal which does not alters the crystal structure. Remarkably, the PXRD pattern of the shocked crystal show enhanced crystallinity and slight changes in the peak position along a degree of crystallinity being increased along the (120) plane is represented in Fig.5. The (120) plane and the twin peak is converted as a single diffraction peak and resulting in the net degree of crystallinity is increased compared than that of the control crystal and similar results have been found in the pyramidal face ADP crystal [45].The degree of crystallinity is linked as a consequence of active recrystallisation at the time of shockwave propagation. On account of this process, the internal grain boundary density is reduced and thus, the grain size is increased [46]. Noted that, there is no phase changes found at shocked conditions. It concludes that growing the crystal along the (120) plane is the stable plane, and it does not distort under shocking conditions. Structural parameters are estimated from the Scherrer equation [47] and tabulated in Table 1.

The evaluated structural parameters confirm the structural behaviour of both control and shocked crystal. Shock-loaded crystal has an enhanced grain size than the control crystal and exhibits enhanced peak intensity and good crystallinity at the prominent plane. Prime structural parameters like micro-strain and dislocation density are remarkably diminished. Precursor of examining crystal is an organic material on which existence of hydrogen bonds played a crucial act in active re-crystallisation at the time of shockwave propagation, low energy of hydrogen bonds are freely disposed of by shock wave [45]. Structurally stable crystals are highly demanded in industrial applications and device fabrication such as moving and vibrating devices and especially for space vehicles [48]. Thus, it can be inferred from the PXRD analysis that the shock-loaded $Li_2SO_4.H_2O$ doped L-Alanine Single crystals oriented along the (120) plane are suitable for the aforementioned implementations.

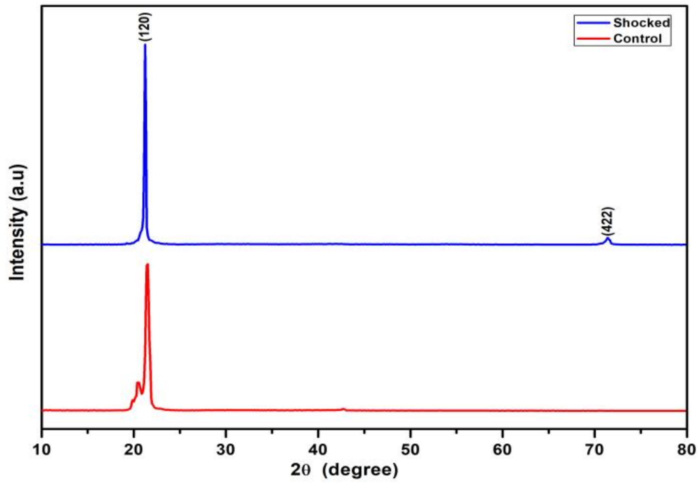


Fig 4: PXRD pattern of control and Shocked $Li_2So_4.H_2O$ doped L-Alanine single crystals

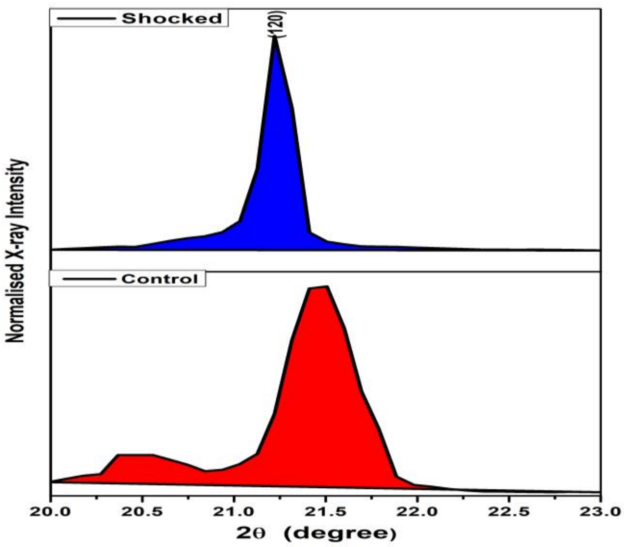


Fig 5: Normalised PXRD pattern of$Li_2So_4.H_2O$ doped L-Alanine Single Crystal

Table 1: Estimated Structural Parameters of control and Shocked $Li_2So_4.H_2O$ Doped L-Alanine single crystals

S.No	Structural Parameter	Control	Shocked
1	2θ position	21.5	21.3
2	Full Width Half Maximum (FWHM)	0.0497	0.0412
3	d-space	4.12	4.18
4	Micro strain (ε)	0.0122	0.0101
5	Dislocation density (δ) x 10^{16}lines/m^2	12.398	8.549

3.4 Raman Analysis

Raman analysis is an effective method to attest molecular fingerprints of the structural units [49]. Raman spectra of control and shocked crystals of $Li_2So_4.H_2O$ L-Alanine single crystals exhibit the same pattern depicted in Fig.6.There may be no variations found in the higher frequency region. Band positions are observed in the range between 3000-2800 cm^{-1} is assigned to asymmetric stretching of $NH_3^+$and stretching of CH bands. Symmetric deformation and asymmetric stretching of CO^-modes are observed at 1594cm^{-1}. It is inferred from the Raman spectrum that there is an appreciable expansion of peak intensity recognized in the region above 1000cm^{-1}. Enhancement of this peak intensity announces the action of crystal lattice which leads to partial movement with the corresponding polarisation. Raman band found at 918 cm^{-1} assigned to C-C-N-C stretching and also peaks appear at 770, 650 and 533$cm^{-1}$are assigned to CO_2^- deformations, scissoring and rocking respectively. Raman band found at 918cm^{-1} assigned to C-C-N-C stretching and also peaks appear at 770, 650 and 533cm^{-1} are assigned to CO_2^- deformations, scissoring and rocking respectively. Fig**.**7 illustrates that the observed attractive behaviour which is recorded in Raman spectrum. There is increased peak intensity observed at 850$cm^{-1}$for shock loaded crystal which shows that the enhancement of the crystallinity at shocked conditions. This enhanced crystallinity could be explained and reflected in XRD pattern of shocked crystal.

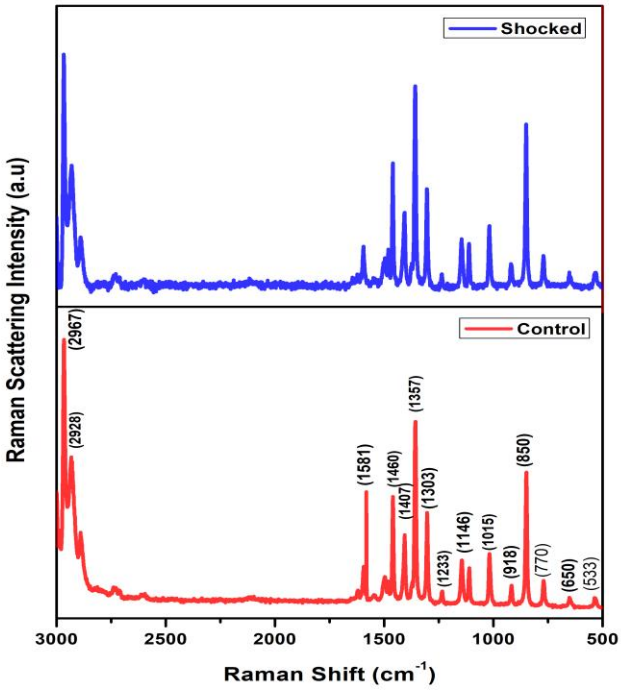


Fig 6: Raman Spectra of Control and Shocked $Li_2So_4.H_2O$ doped L-Alanine single crystals

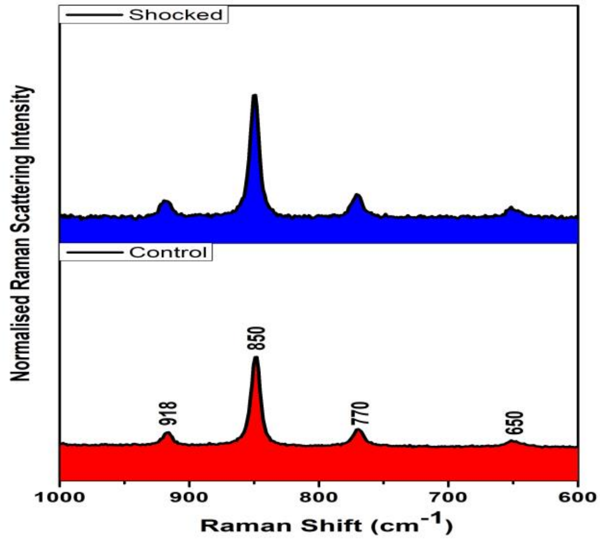
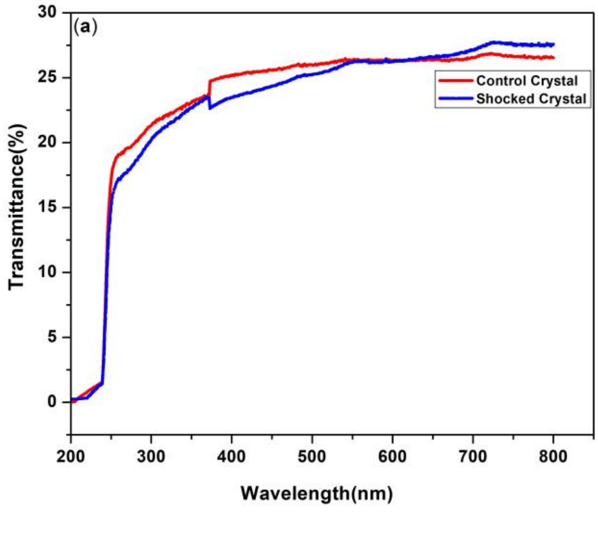


Fig 7: Normalised Raman Spectra of Control and Shocked $Li_2So_4.H_2O$ doped L-Alanine Single Crystals

3.5 UV-Visible Spectroscopy

UV-Visible spectroscopy is an effective tool to detect the materials applicable for optoelectronics applications it is assisted to observe optical parameters like transmittance, absorption of the non-linear optical materials [50]**.** Crystalline properties like defects either orderliness or disorderliness are vital parameters which influence the optical properties of the grown crystal.

The transmittance and absorption spectra of control and shocked crystals with wavelengths ranging from 256 to 800 nm are shown in Fig.8 (a&b). The absence of strong conjugated bonds in amino acids may assist in a wider transparency range in visible and UV regions [51]. It is reveals from that increased transmission percentage in 700-800 nm for shocked crystal is attributed with the shock wave exposure. Absorption rate is increased or decreased as the result of few crystalline factors are playing a major role such as oxygen vacancies, crystal defects, complexity of the material and relaxation of electron in the atomic sites and structural order and disorders etc [52-53].



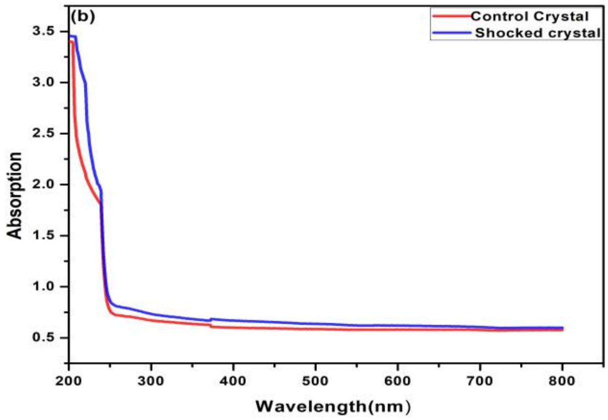


Fig.8 (a) & (b): Transmission & Absorption spectra of Control and Shocked $Li_2So_4.H_2O$ doped L-Alanine single Crystals

3.5.1 Optical Band Gap

Optical band gap values are estimated using the mathematical formulationrelation [50]. Fig.11 represents that the optical band gap values of control and shocked crystals are in the transition range (r=2) which gives indirect bandgap values. Crystalline defects and structural order/disorder are the prime factors., both these factors have direct correspondence with optical band energy [43]. Reports are obtainable to attest that these prime factors are at the back of reducing the optical band gap energy [54-55]. It is evident from Fig.9 (a & b) that the Eg value of shocked crystal (5.12eV) is slightly larger than control crystal (5.07eV) which conveys thatthe dielectric attitude of the crystal and also suitable for optical applications.

Hence it is concluded from UV-Visible analysis that the shock wave inciting surface defects influence the optical properties such as slightly increased transmission in 700-800nm and high absorption rate.

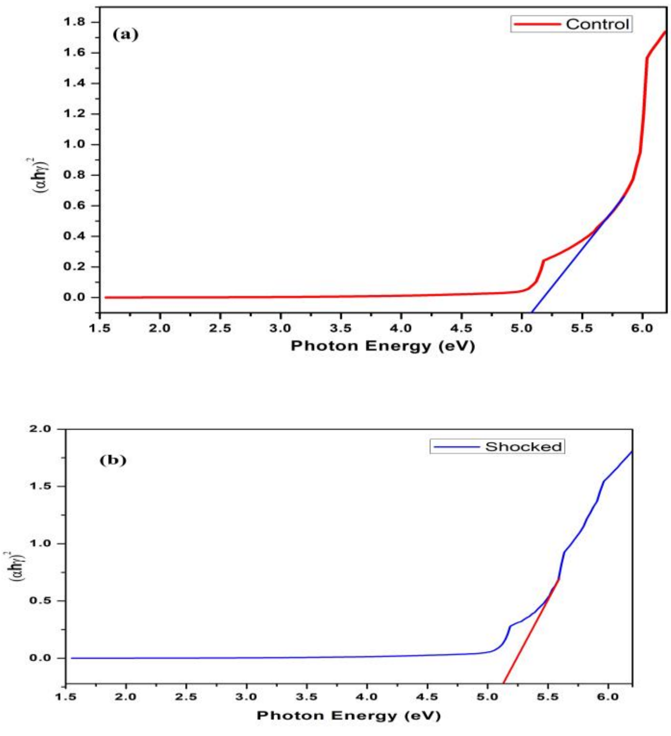


Fig. 9(a) & (b): Band gap energies of Control and Shocked $Li_2So_4.H_2O$ doped L-Alanine single Crystals

4. Conclusion

The ascendancy of shock waves on NLO crystal is a crucial exploration to confirm the adaptability of the material found in abundant applications. The captioned crystal has organic precursor material with an inorganic dopant. PXRD patterns and structural parameters demonstrate that the crystal structure remains stable with enhanced crystallinity. Shockwave loading, make a way to crystal growth researcher in recognising the stable plane with the required orientation. Raman spectra address the molecular fingerprint profiles and increased peak intensity address that the degree of crystalline nature at shock loaded condition. UV-Visible analysis shows that the shocked crystal's optical transmission has been slightly increased in 700-800nm. The extensive analyses of the entitled crystal lead to the conclusion that the structural and molecular stability at dynamic shocked condition address that the material is adaptable for aerospace, microelectronics and optoelectronic applications.

Conflict of Interest

The authors declared that they have no know competing for financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] R.M. Hazen, J.W.E. Mariathasan, Science **216**(4549)**,** 991(1982).
[2] A. Yu Fedorov, D.A. Rychkov, E.A. Losev, B.A. Zakharov, J. Stare, E.V.Boldyreva, CrystEngComm **19**(16), 2243(2017).
[3] R.M. Hazan, L.W. Finger, **52**(1),75(1981).
[4] G. I. Kanel, AIP Conf. Proc.,**1426**, 939 (2012).
[5] S. I. Ashitkov, M. B. Agranat, G. I. Kanel, P. S. Komarov, and V. E.Fortov, JETP Lett. **92** (8), 516 (2010).
[6] V. H. Whitley, S. D. McGrane, D. E. Eakins, C. A. Bolme, D. S. Moore, and J. F. Joiurnal of Applied Physics,**109**, 013505(2011).
[7] R. F. Smith, J. H. Eggert, R. E. Rudd, D. C. Swift, C. A. Bolme, and G. W. Collins, Journal of Applied Physics **110**,123515 (2011).
[8] E. B. Zaretsky and G. I. Kanel, Journal of Applied Physics, **112**(7), 073502 (2011).
[9] K. Baumung, H. Bluhm, G. I. Kanel, G. M€uller, S. V. Razorenov, J.Singer, and A. V. Utkin, Int. J. Impact Eng. **25**(7), 631 (2001).
[10] E. B. Zaretsky and G. I. Kanel, Journal of Applied Physics **112(7)**, 073504 (2012).
[11] E. B. Zaretsky and G. I. Kanel, Journal of Applied Physics . **114**(8), 083511 (2013).
[12] S. I. Ashitkov, P. S. Komarov, M. B. Agranat, G. I. Kanel, and V. E. Fortov, JETP Letters **98**(7), 384(2013).
[13] J. C. Crowhurst, B. W. Reed, M. R. Armstrong, H. B. Radousky, J. A. Carter, D. C. Swift, J. M. Zaug, R. W. Minich, N. E. Teslich, and M.Kumar, Journal of Applied Physics **115**(11), 113506 (2014).
[14] V. S. Krasnikov, A. Yu. Kuksin, A. E. Mayer, and A. V. Yanilkin, Physics of the Solid State **52**(7), 386 (2010).
[15] N. R. Barton, J. V. Bernier, R. Becker, A. Arsenlis, R. Cavallo, J. Marian, M. Rhee, H.- S. Park, B. A. Remington, and R. T. Olson, Journal of Applied Physics.**109**(7), 073501 (2011).
[16] E.N Borodin, S.A. Atroshenko, and A.E. Mayer**,** Technical Physics.**59**(8), 1163(2014).
[17] G.V. Garkushina, G.I.Kanel, and S.VRazorenov**,** Physics of the Solid State. **54**(5), 1079 (2012).
[18] Kadau K, Germann T C, Lomdahl P S and Holian B L, Science **296**(5573), 1681(2002).
[19] Kanel G I, Razorenov SV and Garkushin, Journal of Applied Physics, **119**(18), 185903(2016).
[20] Lin E, Shi H and Niu L, Modelling and Simulation in Material Science and Engineering, **22**(3) 035012 (2014)
[21] C. Justin Raj, S. Jerome Das, Journal of Crystal Growth **304**(1), 191(2007).
[22] A. Sivakumar. S. Reena Devi, J .Thirupathy R. Mohan Kumar and S.A. Martin Britto Dhas Journal of Electronic Materials, **48**(11),7216(2019).
[23] SivakumarAswathappa, ArumugamSaranraj, Sahaya Jude DhasSathiyadhas, Kondaviti Showrilu and Martin BrittoDhasSathiya Dhas Amalapushpam, Z. Kristallogr.,**236**(1– 2),1(2021).

[24] A. Sivakumar, S. Sahaya Jude DhasS.Balachandar and S.A Martin BrittoDhas ,Journal of Electronic Materials, The Minerals, Metals & Materials Society,**48**(12),7868 (2019).

[25] A. Sivakumar S. Sahaya Jude Dhas S. A. Martin Britto Dhas , Journal of Materials Science: Materials in Electronics, **31**, 13704 (2020).

[26] L. Anandaraja, L. Jothi c, Journal of molecular structure ,**1233**,130068(2021).

[27] D.Shanthi,P,Selvarajan, R. Jothi Mani Optik, **125**, 2531(2014) .

[28] A.S.J. Lucia Rose, P. Selvarajan, S. Perumal, Physica B, **406,** 412(2011).

[29] R.P. Jothi Mani, Selvarajan, Indian Journal of Applied Research, **3(**11**)**, 446(2013).

[30] G. Mani, S.Usha, Optic, **125**(18), 5069(2014).

[31] D. Jaikumar, S. Kalainathan, G. Bhagavannarayana , Physica B, **405**(10**)**, 2394(2010).

[32] S.J. Lucia Rose, P. Selvarajan, S. Perumal, Materials Chemistry and Physics **130**(3), 950(2011).

[33] R. Jothi Mani, P.Selvarajan, H. Alex Devadoss, D. Shanthi. Optik, **126**(2), 213(2014),

[34] K.C. Bright, T.H. Freeda, , Physica B, **405**(18), 3857(2010).

[35] S.K.Kushwaha, S.P.Rathee, K.K.Maury, G.Bhagavannarayana, Journal of Crystal Growth, **328**(1), 81 (2011).

[36] M. Vimalan, T.RajeshKumar, S.Tamilselvan, P.Sagayaraj, C.K.Mahadevan , Physica B, **405**(18), 3907(2010).

[37] G.J. Ashwell, G. Jefferies, D.G. Hamilton, D.E. Lynch, M.P.S. Roberts, G.S. Bahra, C.R. Brown, Letters to Nature **375**(6530), 385(1995).

[38] M.O. Ramirez, D. Jaque, L.E. Bausa, J. Garcia Sole, A.A. Kaminskii, Physical Review Letters, **95**(26), 267401(2005).

[39] D. Lim, M.C. Downer, J.G. Ekerdt, N. Arzate, B.S. Mendoza, V.I. Gavrilenko, R.Q. Wu, Physical Review Letters, **84**(15), 3406(2000).

[40] G.Bhagavannarayana, S.K. Kushwaha, Journal of Applied Crystallography, **43**(1), 154(2010).

[41] A. Sivakumar, S. Suresh S, Balachandar J. Thirupathy J. KalyanaSundar, S.A. Martin BrittoDhas Optics and Laser Technology,**111**, 284(2019).

[42] Aswathappa Sivakumar, Madeswaren Sarumathi, Sahaya Jude Dhas, SathiyaDhas Amalapuspham Martin Britto Dhas, Journal Of Materials Research, **35**(428),1(2020).

[43] SivakumarAswathappa, SaranrajArumugam, SathiyadhasSahaya Jude Dhas, Jose Michael And Sathiyadhas A. Martin BrittoDhas, Optical Engineering, **58**(7), 077104 (2019).

[44] B. Suresh Kumar, M. R. Sudarsana Kumar, and K. RajendraBabu , The Journal of Crystal Research and Technology,**43**(7), 745(2008).

[45] Sivakumar Aswathappa, Sahaya Jude DhasSathiyadhas, BalachandarSettu and Martin Britto Dhas Sathiyadhas Amalapusham, Z. Kristallogr, **234**(9), 557(2019).

[47] P. K. Shetty, P. P. Vinaya, R. Nakshatri, A. N. Prabhu, Optik , **156**, 224(2018).

[48] A. Sivakumar, S. Sahaya Jude Dhas, S.A. Martin BrittoDhas, Solid State Sciences, **110**, 106452(2020).

[49] Degen, I. A. Newman, G. A., Spectrochemica Acta, **49**(5-6), 859(1993).

[50] A Sivakumar, A Saranraj, S Sahaya Jude Dhas and S A Martin BrittoDhas, Materials Research Express, **6**, 046205(2019).

[51] C. Razzetti, M. Ardoino, L. Zanotti, M. Zha, C. Paorici, The Journal of Crystal Research and Technology,**37**(5),456(2002).

[52] Gaffar M A and Abu El-Fadl A, Crystal Research & Technology,**34**(7), 915(1999).

[53] Elena V and Boldyreva, Journal of Molecular Structure, **700**(1-3), 151(2004).

[54] A. Sivakumar, C. Victor, M MuralidhrNayak and S A Martin BrittoDhas, Material Research Express, **6**(4), 045031(2019).

[55] Binay Kumar, Harsh Yadav, NidhiSinha, NidhiTyagi, Crystal Growth & Design, **15**(10), 4908 (2015).