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Dynamic Shock Wave Induced Amorphous to Crystalline Switchable Phase Transition of

2 Lithium Sulfate

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Abstract

In recent years, there have been significant efforts put forth by the materials science researchers to search for new phase – change materials especially possessing the caliber of influencing switchable phase changes i.e., from crystal – crystal and crystal – amorphous. Phase–change materials of such kind have attracted a tremendous demand for the technologically important applications such as current resistive memories and thermal energy storage. In the present article, the switchable phase transitions of amorphous – glassy - crystalline – amorphous occurring in the samples of lithium sulfate have been systematically experimented and demonstrated at dynamic shock wave loaded conditions of various counts of shock pulses. The shocked samples have been evaluated by the powder X-ray diffraction (PXRD), Ultraviolet Visible spectroscopy (UV-Vis) and Raman spectroscopy. Shock wave induced orientational order-disorder of the SO₄ tetrahedron and the positional disorders of the lithium atoms have led to the observed switchable phase transitions with respect to the number of shock pulses.

Keywords: Li₂SO₄, shock waves, switchable phase transition, orientational order-disorder,

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Introduction

Switchable crystallographic phase transitions always have the special position of creative interest in solid state materials due to their controllable structural formation and functional diversity as compared to the forward and backward irreversible solid state phase transitions. This phenomenon can be applied in various applications as found in pressure transmitters, molecular switches, resistive memories, etc. Moreover, studies on the reversible phase transition of crystals would further push forward the current level of understanding of the molecules and their structures with respect to temperature and pressure. 1-4 It is well known that pressure serves as a thermodynamic variable which induces various solid state phase transition routes such as crystalcrystal, crystal-amorphous and amorphous-crystal that are very much possible to be obtained in the laboratory conditions.^{5,6} On the one hand, the majority of static high pressure experiments that have been carried out on materials have the potential to authenticate the occurrence of reversible crystallographic phase transition when pressure is released.⁷⁻¹⁰ In recent years, studies on the impact of shock waves imposed on solids have gained remarkable attention attracting a lot of materials scientists due to the variety of changes observed in properties of materials such as phase transitions and deformations. 11-14 On the other hand, reversible crystallographic phase transition occurring at dynamic shock wave loaded conditions is quite an unexpected behavior as compared to the results of static high pressure compression experiments so that in-depth research is further required in order to get a systematic understanding of the shock wave induced reversible crystallographic phase transitions. Moreover, even though several thousands of shock wave induced irreversible phase transitions have been observed and reported over the past 100 years of shock wave research in materials science 11-14, it could be noted that there are not many reports available for the dynamic shock wave induced crystallographically reversible phase transitions in solid state. Reversible magnetic phase transitions and crystallographic phase transition behaviors at dynamic shock wave loaded conditions have been observed in a few recent publications.

It has been demonstrated that cobalt oxide (Co₃O₄) nano- crystalline particles undergo reversible magnetic phase transition from super-paramagnetic to paramagnetic nature¹⁵ and Zinc

ferrite (ZnFe₂O₄) nano-crystalline particles undergo paramagnetic to super-paramagnetic behavior with respect to the number of shock pulses. ¹⁶ Furthermore, potassium sulfate (K₂SO₄) crystal exhibits the reversible crystallographic phase transition (from orthorhombic to hexagonal) with respect to the number of shock pulses.¹⁷ On this note, lithium sulfate has been scrutinized for the present investigation, considering the possible switching behavior between the crystallographic phases by the impact of shock waves since both the crystals belong to the family of divalent metal sulfate crystals (A₂BO₄). In general, sulfate materials are used as a classical example of materials so as to be investigated for the phase transition behaviour subjecting to experiments involving high-pressure and temperature. 18-20 Most of the sulfate materials obey the first order phase transition caused by orientation order-disorder effect occurring at high-pressure and high temperature regions. 18-20 Hence, the present investigation on shock wave induced phase changes of Li₂SO₄ has a strong research objective in academic level as well as industrial point of view. The title sample has five crystallographic structures such as α , β , γ , δ and ϵ wherein β - Li_2SO_4 belongs to the room temperature phase which is phase transformed to α - Li_2SO_4 at 845 K and it is used as a solid electrolyte because of its outstanding electrical conductivity i.e. particularly α -Li₂SO₄ and the remaining phases are represented as high-pressure phases. ²¹⁻²⁵ Even though several publications are available for Li₂SO₄ crystal on phase transitions occurring at high-pressure and high temperature conditions, to date, no one has reported the reversible amorphous –glassy - crystalline – amorphous phase transitions of Li₂SO₄ sample.

The present research article is aimed at demonstrating the reversible crystallographic phase transition with respect to the number of shock pulses as it has been already witnessed for potassium sulfate crystal. Since shock wave induced reversible phase transition is very fast and cost effective, such kind of experiments may bring about a systematic methodology with which it would be possible to induce the reversible phase transition in potential materials such that a lot of insights could be derived. On those lines, many of the requirements which are based on phase – change materials can be fulfilled for the scientific world as well as industrial applications.

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Experimental methodology

In this study, Lithium sulfate (Li_2SO_4) samples were obtained by employing the conventional slow evaporation method. Commercially available Li_2SO_4 (98.5%) was bought from Sigma Aldrich and was used without further purification for the growth process. The saturated solution of Li_2SO_4 was prepared by dissolving it in double distilled water. The solution was stirred continuously for 5 hours with the help of a magnetic stirrer in order to completely dissolve Li_2SO_4 which was filtered into a beaker. The solution was kept undisturbed for the crystallization. After 34 days, an optically transparent specimen with the dimension of $14\times6\times1$ mm³ was obtained as shown in Fig.1.

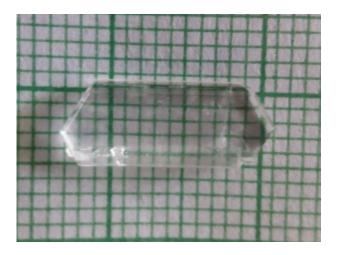


Fig.1 As grown Li₂SO₄ specimen by the slow evaporation method

In total, four identical samples (1mm thickness) have been cut and polished maintaining a high quality. Before beginning the shock wave loading experiment, it has been confirmed that all the four samples belong to the amorphous state. Among the four samples, one sample has been kept as the control while the other three samples have been utilized for the respective 1st, 2nd, and 3rd shocked conditions which means that for the first sample, one shock pulse has been applied while for the second sample, two shock pulses have been applied and for the 3rd sample, three shock pulses have been exposed. In the present investigation, a shock wave of Mach number 2.2 is utilized that has the transient pressure of 2.0 MPa and temperature 864 K. The shock waves have been generated by an in-house tabletop pressure driven shock tube (Reddy tube). The shock tube has three sections such as driver, driven and diaphragm sections which are made of

seamless steel. The driver and driven sections consist of long tubes of 48 cm and 180 cm, respectively and both have 1.5 cm of inner diameter with the wall thickness of 3mm and the atmospheric air is used as the input source for the required shock wave generation. The working methodology of the shock tube and the loading process have been detailed in our previous publications.^{14, 15}

The shock wave loaded samples have been further investigated using a powder XRD (Rigaku - SmartLab X-Ray Diffractometer, Japan in which Cu K α has been used as the X-ray source, λ =1.5407 Å) and UV-Vis spectroscopy (with a varian Cary 5E UV – Visible spectrometer between 200 and 800 nm). Raman spectrometry (LabRAM HR Evolution, France) has been employed to understand the phase details of the test materials over the wavenumber region of 100^{-1} to 1300 cm⁻¹ with the laser source of wavelength 532 nm.

Results and Discussion

Structural properties of Li₂SO₄ samples

The diffraction patterns of the control and the shock exposed Li_2SO_4 samples are presented in Fig.2 (a-d). The control sample looks well-shaped and transparent; however, the X-ray diffraction study reveals that the sample is in amorphous nature (Fig.2a). In general, particularly for Li_2SO_4 , it is a critical task for the crystal growers to grow a good quality single crystal with the monoclinic phase due to the discontinuous changes occurring for Li atoms in the tetrahedral site which may induce a large number of improper locations for Li atoms in the crystal lattice.

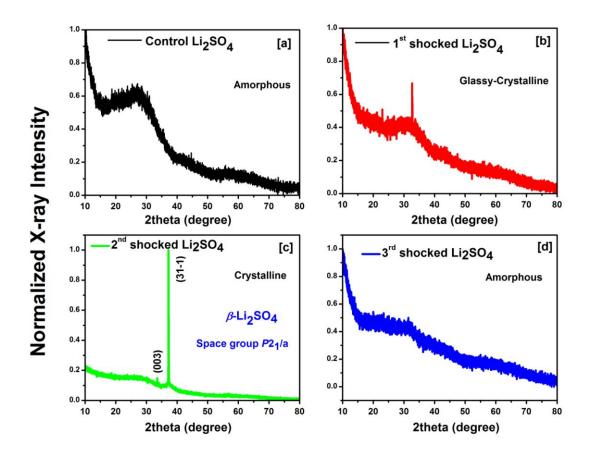


Fig.2 Powder XRD profiles of the control and shocked Li_2SO_4 (a) the control, (b) 1^{st} shocked (c) 2^{nd} shocked (c) 3^{rd} shocked samples

Moreover, the test sample has two lithium atoms such as Li (1) and Li (2) bonded with oxygen atoms. Among these two atoms, Li (1) atom is static while Li (2) is mobile and SO₄ tetrahedral is coordinated with Li atoms. Due to its mobile nature, Li (2) and SO₄ orientation may generate positional disorder along with orientational disorder and the corresponding schematic diagram is presented in Fig.3. As per the crystallographic structures of the test sample, Li⁺ ions have three different lattice sites such as ¼, ¼, ¼, ½, ½, ½ and ¾, ¾. Among the listed lattice sites, ¼, ¼, ¼ provides too small space whereas ½, ½, ½ and ¾, ¾, provide too large space. ^{26,27} However, Li⁺(1) ions are occupied in the tetrahedral site quiet easily compared to Li⁺ (2) site due to the different lattice site sizes. On the other hand, the test sample has two lithium atoms in the structure which are non-equivalent to the symmetric operation. Moreover, among the two lithium atoms, one (Li-1) is static and the second (Li-2) is mobile. ^{27,28}

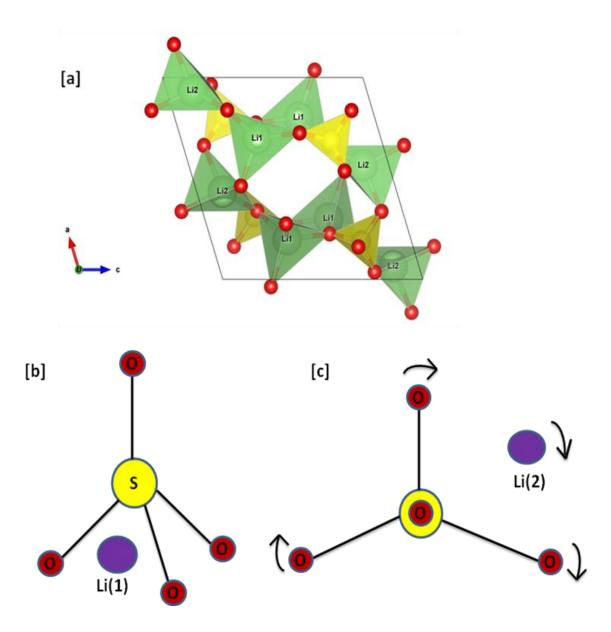


Fig.3 (a) Crystal packing of β -Li₂SO₄ (b) Li(1)-SO₄ (c) Li(2) –SO₄

Due to the mobile nature of Li (2) atom, the interaction between the Li (2) and oxygen atom is significantly reduced so that the lattice disorder enhances. Hence, it leads to the amorphization during the crystal growth.^{25, 26} At the first shocked condition, the corresponding XRD profile (Fig. 2b) shows a low intensity peak at 32.5° which does not match with either α or β or else with any other high-pressure phases so that it is considered as a glassy material.²⁹ Moreover, such kind of a crystal with this phase may be called as plastic crystal. The XRD profile of the test sample obtained upon the exposure of 2^{nd} shock wave is presented in Fig. 2c.

Tiny and intense crystalline peaks are observed at 33.4° and 37.2°. The observed crystalline peak positions match well with the simulated peak position of β - Li₂SO₄ as shown in Fig.4.

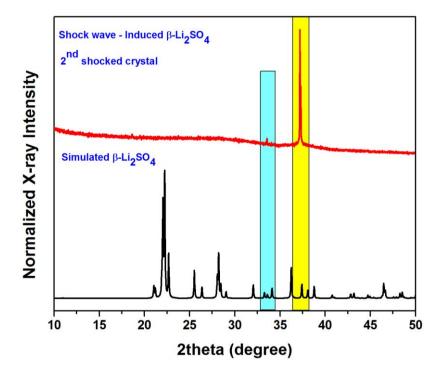


Fig.4 Powder-XRD patterns of simulated and shock induced β-Li₂SO₄

The applied 2^{nd} shock wave has induced a phase transition from amorphous to crystalline for the test sample via glassy phase at 1^{st} shocked condition. From the literature, it is noted that β to α - Li₂SO₄ phase transition is due to the enhancement of the orientational disorder of SO₄ tetrahedron. On the other hand, the results of several high-pressure and high temperature experiments have revealed that SO₄ tetrahedron plays a major role in the phase transitions of crystalline to amorphous and vice versa. In the case of the cationic LiO₄, the tetrahedra has 14 times higher compressibility than that of the anionic SO₄ tetrahedra. At shocked conditions, deformation of the LiO₄ tetrahedra might have taken place, whereas the SO₄ groups are expected to undergo tilting which plays a key role in the order-disorder process. At shocked conditions, the tilting angle of the SO₄ tetrahedron changes with respect to the number of shock waves such that the Li⁺ ions' atomic sites, especially Li(2) is changed due to the existence of positional disorder caused by the impact of shock waves. As per the reported phase transition

studies, it could be suggested that during the shock wave loaded condition, orientational order of the SO_4 tetrahedron with static and mobile lithium atoms might have appeared during the second shock wave loaded condition. The bond angles between lithium and oxygen atoms of O-Li(1)-O is 106.5- 115.2° and O-Li(2)-O is 88.6- 124.5° . Due to the presence of wider angle, Li(2) has undergone maximum deformation level. Moreover, the bond energies of Li-O and S-O are 333.5 (± 8.4) and 110 kJmol⁻¹, respectively which makes the SO₄ tetrahedra less stable compared to the LiO₄ tetrahedron. In addition to that, the applied shock waves may supply the sufficient latent heat to crystallize the glassy phase of Li₂SO₄ which can be called as shock wave induced dynamic re-crystallization. As seen in Fig.4, β - phase of the test sample's standard powder XRD pattern has several diffraction peaks appearing between 20 and 50 degree. But, the observed shocked crystal's XRD profile shows the strong diffraction peak (31-1) and a tiny diffraction peak (300) which confirms that the phase transition has occurred at the 2^{nd} shocked condition.

Furthermore, the 3rd shock wave loading process has been enabled for the test sample in such a way that XRD measurement could make a clear phase diagram of Li₂SO₄ specimen with respect to the number of shock pulse. It has been strongly expected that the XRD pattern would provide the high-pressure phase of the test sample (α-Li₂SO₄) as exhibited by potassium sulfate.¹⁷ On the other hand, it has been a surprise to observe the amorphous nature of Li₂SO₄ specimen at the 3rd shock wave loaded condition as reflected by the disappearance of diffraction peaks in the XRD pattern. The corresponding XRD profile is presented in Fig.2d. In this context, the orientational – disorder of the SO₄ tetrahedron plays a significant part to initiate and enable the crystalline - amorphous phase transition. Since the SO₄ tetrahedron is absolutely free for the rotation, it could enforce the orientational – disorder behavior at shock wave loaded conditions.¹⁷ At the 3rd shock wave loaded condition, the thermodynamic barrier of the system and the critical phase transition region could have experienced break-down because of the higher transient pressure and temperature so that the test sample might have undergone the process of complete atomic disorder. The lattice symmetry of Li₂SO₄ is completely broken at the 3rd shock wave paving the way for the crystalline – amorphous phase transition. On the other hand, Li(2) sites might have experienced the positional disorder occurring at this stage that could have stimulated the shock wave induced amorphization of Li₂SO₄. It is worthwhile to note that the control and

the 3rd shocked test samples have the amorphous nature which confirms that the test sample has undergone the reversible amorphization phase transition via glassy phase and crystalline phase by the influence of the shock waves. The shocked phase-profile of the test sample with respect to the number of shocks is presented in Fig.5a and the static pressure compression phase profile of the material is displayed in Fig.5b [20].

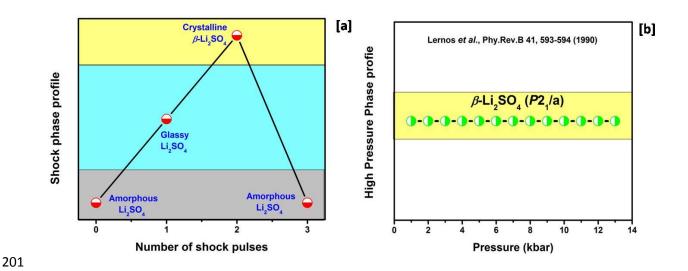


Fig.5 (a) Schematic shocked phase-profile of the control and shocked Li_2SO_4 samples (b) Static pressure compression phase profile of β - Li_2SO_4 [20]

UV-Visible spectroscopic studies

For optically transparent materials, UV – Vis spectroscopic analysis is one of the prime studies to understand the electronic structure and optical properties. In Fig 6, the observed optical transmittance spectra of the control and the shocked test samples are reported. The absence of characteristic absorption peak in Fig. 6 for the control sample is one of the evidences of its amorphous nature. At the 1st shocked condition, the test sample shows the absorption band edge at 243 nm and it exhibits 37% optical transmittance at 800 nm. At shocked condition, the appearance of absorption band edge for the 1st shocked sample is due to the phase transition from amorphous – glassy phase.

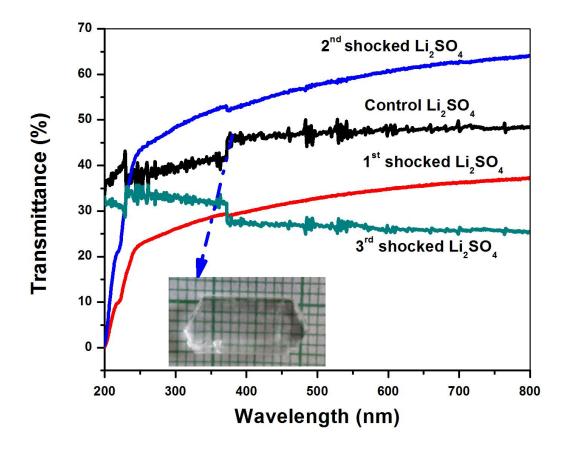


Fig.6 Optical transmittance spectra of the control and shock exposed Li₂SO₄

At the second shocked condition, the test sample's absorption band edge of the test sample has got shifted towards the lower wavelength and the optical transmittance has significantly increased from 37 % to 64 % at 800 nm. These two factors give rise to the considerable authentication for the phase transition occurring due to the shock wave induced orientational disorder-order process which might have led to the changes in optical transmittance for the test sample. It has been observed similar changes in the α -phase of potassium sulfate crystal which undergoes red shift resulting to lower optical transmittance than that of β -phase at shock wave loaded condition.¹⁷ Making a comparison, it can be represented that the glassy phase has a partial disorder phase as against the β -phase of Li₂SO₄. Hence, it has lower optical transmittance than that of β -phase of Li₂SO₄. Furthermore, after the 3rd shock, the crystal showcases the optical transmittance spectrum similar to the control sample with slight changes in

terms of optical transmittance percentage and shape of the pattern. Hence, it confirms categorically that the test sample has undergone the amorphous nature because of the disappearance of orientational order of β -phase of Li₂SO₄ by the impulsion of shock waves. It could be noted that the results of structural and optical transmittance are found to be well matched with respect to the number of shock pulse which clearly indicates the reproducibility of the unprecedented results at shocked conditions.

In Fig. 7, the optical band gap energies of the control and shock exposed samples are presented as calculated by classical Tauc plot.³⁵ As it is known from the XRD and optical transmittance measurements, the control Li₂SO₄ has the amorphous nature so that it is not possible to calculate the band gap energy for the control sample. Moreover, the values of absorption coefficient are not satisfied for Tauc plot so that it is not possible to find the band gap energy. Hence, it is confirmed that the control sample has high electrical resistant behavior. Moreover, the absence of lithium ions (Li₂) in the tetrahedral position is the major reason behind the high electrical resistance. The initial phase of the amorphous nature is represented as the RESET phase since it has a very high resistivity.

At the 1st and 2nd shocked conditions, the direct band gap energies are observed to be 5.70 and 5.98 eV, respectively. From the obtained values, it is clear that the crystalline samples have higher values of band gap energy than that of the glassy phase. Hence, the crystalline sample has lower electrical conductivity than the glassy phase. So far, numerous researchers have reported the electrical conductivity of the test sample based on their phases and found that α -Li₂SO₄ has higher electrical conductivity than that of the β -Li₂SO₄ due to the rotor type phase based on the peddle wheel and percolation mechanism. ^{27,28,36,37} From the available literature reports, there could be two prominent reasons behind the changes in electrical conductivity observed for the order and the disordered phases. Firstly, β -Li₂SO₄ is the ordered phase such that the rotational freedom of the SO₄ tetrahedron is quite lower than that of the disordered phase. Hence, the mobility of the lithium ions is low so that it has low electrical conductivity. Secondly in the case of β -Li₂SO₄ phase, interaction of the lithium and oxygen atoms is quite low because of the higher bond length. Hence, the crystalline phase has lower electrical conductivity than that of the glassy phase.

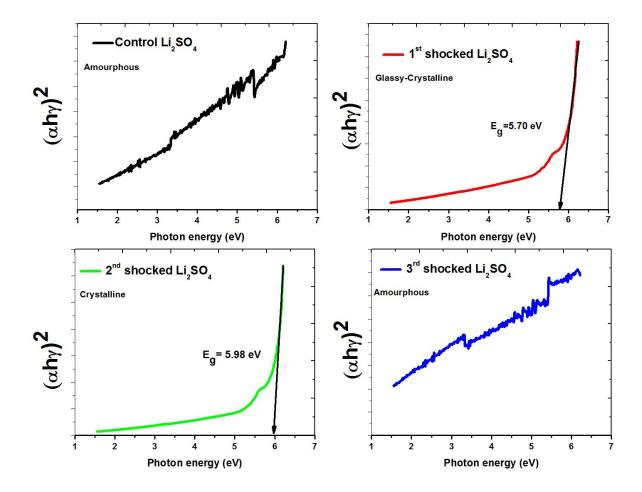


Fig.7 Band-gap energy of the control and shocked Li₂SO₄

The crystalline phase can be represented as the SET phase due to the conduction behavior. At the 3rd shock, the disappearance of the crystalline phase and the appearance of the amorphous nature occur and as per Tauc plot, it exhibits the similar results when compared to the control test sample. Hence, again it comes to the RESET phase. Such kind of SET and RESET reversible phase changing materials are highly used in sensors.^{38,39}

Raman Spectral Analysis

As seen in Fig.8, the normal Raman bands of Li_2SO_4 are observed at 484, 634, 1007 and 1103 cm⁻¹ in the control sample for the respective υ_2 , υ_4 , υ_1 and υ_3 SO₄ vibration bands. As per the previous reports of β -Li₂SO₄, ⁴⁰⁻⁴³ the SO₄ of υ_2 , and υ_4 double degenerate Raman bands and one lithium Raman lattice mode should have evolved at 385 or 362 cm⁻¹. ^{40,41}

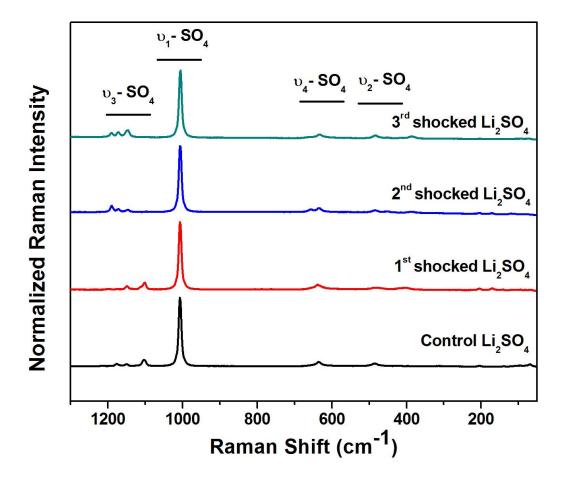


Fig.8 Raman spectra of the control and shocked Li₂SO₄

But, such kinds of characteristics Raman bands of β-Li₂SO₄ are completely not visible. It may be due to the formation of positional disorder of lithium atoms and rotational disorder of SO₄ tetrahedral. Hence, due to such kind of defects and disorders, the control sample might have the amorphous nature which is very well corroborated with the results of XRD and UV-Visible

studies. At shocked conditions, the normal SO_4 Raman bands are not significantly altered. But, in the case of characteristic Raman band positions, considerable changes have been observed. The Raman band of v_3 region has also undergone significant changes whereas the Raman bands of v_2 , and v_4 are highly coupled with lithium atoms. Hence, it is worthwhile to investigate more on these two Raman bands so that, for better visibility of such changes, the zoomed-in versions of the prominent region of Raman bands (v_2 , and v_4) of the control and shocked samples are provided in Fig.9.

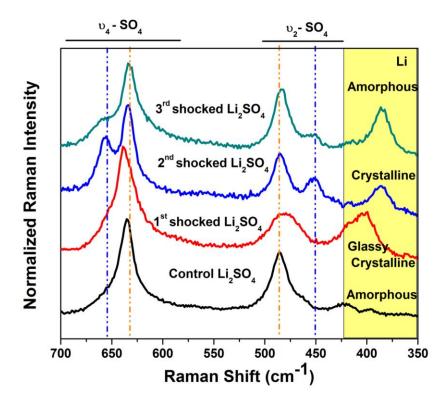


Fig.9 Zoomed-in versions of Raman spectra of the control and shocked Li₂SO₄ (350-700 cm⁻¹)

As seen in Fig.9, at the 1st shocked condition, the normal ν_4 and ν_2 bands are reproduced with a very little Raman shift whereas a new Raman band appears at 399 cm⁻¹. As per the previous reports, this particular Raman band belongs to lattice mode of lithium ion for the ambient crystalline phase which indicates the reduction of net degree of positional disorder of lithium atoms reflecting the formation of the glass-crystalline nature of Li₂SO₄. Moreover, the presence of single band at ν_4 and ν_2 regions support that the sample is not still crystalline.^{40,41}

Surprisingly, at the 2^{nd} shocked condition, the singlet SO_4 Raman bands of v_4 and v_2 are completely converted as doublet. Furthermore, the lithium Raman band is shifted from 399 to 385 cm⁻¹ and this position is found to be well matched with Bg polarization of lattice lithium mode. ^{40, 41} The Raman spectrum of the 2^{nd} shocked condition well corroborate with β -Li₂SO₄ which demonstrates the crystalline nature of the test sample because of the rapid reduction of positional disorder and rotational disorder of SO_4 . In addition to that, at the 3^{rd} shocked condition, the lithium Raman band position is not altered. But the doublet Raman bands at v_4 and v_2 regions become singlet that indicates the enhancement of rotational disorder of the SO_4 tetrahedral which leads to the amorphous nature of the test sample. Note that, in the case of dynamic shocked conditions and high-pressure compression conditions, SO_4 anionic units are found to have undergone significant rotational order-disorder effects and such results have been well documented. ⁴⁴⁻⁴⁷

Conclusion

The switchable phase transformation of Li₂SO₄ samples from amorphous-glassycrystalline-amorphous phase under the influence of dynamic shock wave is reported for the first time. The observed switchable nature is due to the orientational order-disorder processes occurring in Li₂SO₄ specimen. Under the influence of shock wave, the position of the mobile Li atom changes which is reflected in the post-shock measurements such as XRD, UV-Visible and Raman spectral studies. The interesting switchable phase transition behavior of Li₂SO₄ has been authentically demonstrated by crystallographic, optical and vibrational spectroscopic techniques. Among the listed shock wave induced phases of the test sample, glassy phase has higher electrical conductivity because of the presence of higher mobility of lithium ions based on peddle -wheel mechanism. It is firmly believed that the present approach could be the starting point which may trigger the pathway to find many more materials of possible reversibility occurring at shocked conditions i.e., from amorphous to crystalline nature and vice versa. From the observed results, it is very realistic that Li₂SO₄ sample has the suitability for the applications of phase – change memory, sensors, molecular switches, pressure transmitters and thermal energy storage devices. The investigations on the electrical conductivity and magnetic properties of the control and shocked Li₂SO₄ samples are under progress.

Compliance with ethical standards 322 323 None **Conflict of interest** 324 The authors declare that they have no conflict of interest. 325 326 Acknowledgement 327 The authors thank Department of Science and Technology (DST), India for funding through DST-FIST progarmme (SR/FST/College-2017/130 (c)) and Abraham Panampara Research 328 329 Fellowship. The project was supported by Researchers Supporting Project number (RSP-2021/231), King 330 331 Saud University, Riyadh, Saudi Arabia. 332 References 333 [1] Bhattacharyya, S.; Maity, M.; Chowdhury, A.; Saha, M.L.; Panja, S.K.; Stang, P.J.; and 334 Mukherjee, P.S. Coordination-Assisted Reversible Photoswitching of SpiropyranBased 335 336 Platinum Macrocycles. *Inorg. Chem.* **2020**, *59*, 2083–2091. [2] Yang, L.; Xiu-Ni, H.; Wei-Qiang, L.; Ji-Xing, G.; Zi, Y. A room temperature reversible 337 phase transition containing dielectric switch of a host-guest supramolecular metal-halide 338 compound. Dalton Trans., 2017,46, 12760-12765. 339 340 [3] Hu, J.; Ichiyanagi, K.; Takahashi, H.; Koguchi, H.; Akasaka, T.; Kawai, N.; Nozawa, S.; Sato, S.; Sasaki, Y.C.; Adachi, S.; and Nakamura, K.G. Reversible phase transition in 341 342 laser-shocked 3Y-TZP ceramics observed via nanosecond time-resolved x-ray diffraction. J. Appl. Phys. 2012, 111, 053526. 343

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