Shock Wave Induced Switchable Phase Transition (Molecular Distortion Type) of Ammonium Sulfate Crystal

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Abstract

In the present context, ammonium sulfate (NH$_4$)$_2$SO$_4$ crystal phase stability has been examined at shocked conditions and observed that the title crystal undergoes the reversible crystallographic phase transitions with respect to the number of shock pulses and the observed phase transition sequence is Pnam-Pnam-distorted Pnam- Pnam-Pnam for 0,1,2,3, and 4 shocks, respectively and the observed phase transition sequence is evaluated by X-ray diffraction (XRD), Raman spectroscopy and optical spectroscopy (UV-DRS). Based on the observed analytical experimental results, it is authenticated the occurrence of the reversible phase transition which is caused by the molecular distortions accompanied by the rotational disorder of ammonium and sulfate groups of ions because of the impact of shock waves. This report is the first of its kind regarding the switchable phase transition inclusive of static temperature experiments observed for title crystal.

Introduction

Over the years, the outcome of the results of shock wave experiments conducted on materials authentically mirror that there have been numerous breakthroughs witnessed which bypass remarkably instructive and profound ideas that steer researchers with an unambiguous force enabling various pathways of impending progress in the field of frontier science. The existing rapid enrichment of the experimental research on materials could bring out their functional properties at ambient conditions as well as under external stimuli conditions such as temperature and pressure which have been well documented in recent times such that several spectacular results have been revealed, especially in crystallographic structural phase transitions. However, still there are lots of fundamental aspects to be unearthed as to how specific changes are enforced in materials with respect to their crystallographic structural features at high-pressure and high-temperature conditions [1–5]. Moreover, some of the materials show stable crystallographic configuration even at a considerably high pressure of GPa range [6, 7] whereas a few materials undergo reversible [8–11] and irreversible [12, 13] phase transitions during pressure compression and decompression. Hence, it has become increasingly ubiquitous prospect for researchers to understand better the basic concepts of structural phase transition of materials under external stimuli conditions [14, 15]. In the perspective of crystallographic structural phase transitions, reversible and irreversible phase transitions are the focal point such that the concepts behind the phenomena occurring in materials at high-pressure and high-temperature ought to be explored. Surprisingly, the concept of the reversible phase transitions with respect to pressure and temperature is by and large remaining in the dark that is to be brought to light since identified highly efficient switchable materials are very less than that of irreversible materials [8–11]. Scarcity of switchable phase transition materials have kept numerous industrial emergency applications on wait such as molecular switches, resistive memories, phase filters, transmitters, etc.[16–19]. Hence, researchers are offered a promising pipeline with which working on and trying with a variety of roots to find efficient switchable materials that can control their functions with respect to external stimuli is very much possible.
In addition to the static high-pressure and high-temperature experiments, dynamic shock waves also have a significant contribution in structural phase transitions on solids and several results on irreversible phase transitions in a variety of materials have been reported [20–24]. As a part of shock wave research in material science, tuning the crystallographic states of materials inclusive of both bulk and nano sized crystals at dynamic shock wave loaded conditions have gained remarkable momentum such that reversible crystallographic states [25] and magnetic states have been reported recently [26–28] which envision new endeavors of continually fueling the process to enrich the shock wave physics in materials science division. Sivakumar et al have demonstrated the first shock wave induced switchable crystallographic states (orthorhombic - hexagonal) of potassium sulfate crystal with respect to 0, 1 and 2 shock pulses, respectively [25]. Followed by this article, quite a few types of switchable magnetic states have been demonstrated for the technologically important nano-crystalline materials such as Co$_3$O$_4$, α-MnO$_2$, and ZnFe$_2$O$_4$ [26–28].

It could be noted that sulfate anionic materials such as potassium sulfate [29, 30], sodium sulfate [32, 32], lithium sulfate [33, 34], and ammonium sulfate [35, 36] are highly sensitive to temperature and pressure such that they undergo phase transitions based on the order-disorder of $SO_4$ ions at high-temperature and these kinds of reports have been very well documented. Dynamic shock waves trigger the switchable crystallographic phase transition of potassium sulfate which is followed by lithium sulfate and sodium sulfate single crystals whose phase stability also been examined at shocked conditions thereby the crystallographic reversible phase transitions with respect to the number shock pulses have been enabled and the observed results have been communicated elsewhere. On those lines, it is expected that the ammonium sulfate crystal might also follow the shock wave induced switchable phase transition trend with respect to the number of shock pulses and hence, we have conducted the shock wave recovery experiment on ammonium sulfate crystal at shocked conditions. So far, several researchers have demonstrated variety of phase transition routes with respect to static temperature [37–41]. Ammonium sulfate is crystallized in the space group Pnam at ambient temperature and the values of lattice configuration are $a = 7.782$ Å, $b = 10.639$ Å and $c = 5.993$ Å. The title crystal is para-electric in nature at room temperature and it undergoes ferroelectric transition at 223 K along with changes in its crystal symmetry crystallizing in the space group of Pna2$_1$ and the values of lattice configuration are $a = 7.837$ Å, $b = 10.61$ Å and $c = 5.967$ Å [42–45]. While comparing the work on low temperature phase transitions, high temperature experimental analysis on the test crystal is quite low. Gaffar et al have demonstrated the analysis of phase stability with respect to temperature and found the breaking of crystal symmetry at 423 K but it is not a pure structural phase transition [37]. Ahmed et al have performed a similar experiment with respect to temperature and found anomalous changes in the dielectric constant at 423 K, but while considering the crystallographic phase transition, this paper also found the breaking of crystal symmetry [38]. Syamaprasad et al have conducted temperature dependent phase stability up to 151.5°C and found significant changes in the dielectric constant due to the occurrence of the order-disorder type phase transition [39]. Recently, Chandra Kumar et al have calculated the electrical conductivity of ammonium sulfate crystal with respect to temperature up to 480 K and found significant changes between 400K and 500K due to local disorder of ammonium ions and sulfate ions which are significantly
increased because of the protonic defects in the host lattice [40]. El-Korashy et al have observed the hypothetical phase transition of the orthorhombic (Pnam) to the hexagonal (P63/mmc) of ammonium sulfate crystal at 508 K that is very close to the melting point of the title crystal [41]. Considering the overall phase transitions reports of the title crystal at high-temperature, it is clear that the test crystal may experience the order-disorder type phase transitions at high temperature and similar kind of order-disorder type phase transition results might also appear at shocked conditions.

In the present context, switchable phase transitions (not purely structural) of ammonium sulfate crystals at shocked conditions with respect to the number of shock pulses have been experimented and the results have been evaluated by diffraction and spectroscopic techniques.

**Experimental Section**

Pure ammonium sulfate compound (99% purity) was purchased from the Sigma-Aldrich and the slow evaporation technique was utilized to grow required good quality as well as optically transparent crystals for the shock wave recovery experiments. A volume of 50ml of deionized water was taken in a beaker and the title compound was added slowly till the saturation was obtained. Thereafter, the solution was stirred for three hours constantly using a magnetic stirrer to obtain homogeneous solution. Then solution was filtered and kept separately in a dust free environment without any external disturbance and allowed for the crystallization at room temperature. After 20 days, optically transparent crystals have been harvested and utilized for the shock experiments. Working of the shock tube [46] and the procedure of shock wave loading on the crystals has been discussed in our previous articles [47] and clear details are provided in the supplementary section. For the present experiment, we have taken totally five optically transparent with equal dimension (10×10×1 mm^3) of single crystals oriented along the plane (011). Among the five test crystals, one crystal has been kept as the control crystal and the remaining four crystals have been used for shock wave impact studies. In the present experiment, we have used shock waves of Mach number 2.2 and the title crystals have been treated by shock waves of the order of 1, 2, 3, and 4 counts, respectively. One shock pulse has the transient pressure and temperature of 2.0 MPa and 864 K, respectively. After the completion of the shock wave loading procedure, the crystals have been sent for the analytical studies such as XRD, Raman and UV-DRS spectral analyses.

**Results And Discussion**

**X-ray diffraction results**

Powder X-ray diffractometry has been performed to investigate the structural features of the title crystal at shocked conditions. The title material is one of the most studied ferroelectric crystals at low temperature region due to its significant change in hydrogen atom positions and reorientation of the ammonium ions. As the title crystal’s unit cell contains twelve radicals, they are found to be of three different types of which NH₄ ions NH₄ (I) and NH₄ (II) belong to the two of the types and the rest is SO₄ ions. NH₄ (II) is highly distorted than that of NH₄ (I) because of the variation in the bond angle and bond
distances between N-H atoms [37–41]. On the other hand, the SO$_4$ tetrahedral is almost perfectly ordered tetrahedral as the bond lengths and bond angles are similar inside the tetrahedral [48]. According to the literature reports, the title crystal has the Pnam crystal symmetry at ambient temperature and the corresponding CIF (amcsd 0012986) generated power XRD patterns are presented in Fig. 1a. In addition to that, the bond lengths and bond angles of the tetrahedral sulfate ions and ammonium ions are presented in Fig. 1b, c and d. At room temperature, NH$_4$ (II) ions of the para-electric phase of ammonium sulfate crystal are surrounded by the six SO$_4$ tetrahedral units such that this type of molecular arrangement is highly favorable configuration for rotational order – disorder types of phase transitions and molecular distortions types of phase transitions at high-temperature, high-pressure and dynamic shocked conditions [25, 29–36]. On the other hand, NH$_4$(I) ions have five SO$_4$ tetrahedral units surrounding it and the shortest O-H bond length is 1.97Å so that it gives rise to a slightly weaker binding between ammonium ions and sulfate ions [48]. Hence, it is pretty clear that the title crystal’s molecular arrangements are highly favorable for the shock wave induced phase transition study in which the probable significant changes can be suspected as it happens for potassium sulfate crystal with respect to the number of shock pulses exposed [25]. The XRD patterns of the control and shocked crystals are presented in Fig. 2 wherein the test crystal has three diffraction peaks of (011), (022) and (033) which are well corroborated with the previous reports [48]. The XRD pattern of the control sample show cases the higher order diffraction planes such as (022) and (033) clearly demonstrate the higher crystalline nature of the control sample.

At the first shocked condition, the XRD pattern of the control crystal is re-produced and no significant diffraction peak shift or peak disappearance is observed. Hence, it is clear that the Pnam crystal symmetry is retained at first shocked conditions. But while considering the diffraction peak intensity and full width half maximum of the diffraction peaks, a few minor changes are noticed. The diffraction peak intensity of (011) is slightly reduced whereas it remains to be the same for (022) and (033) planes at the first shocked conditions. It reveals that the surface and nearly surface atomic planes are slightly affected by the impulsion of the shock waves which might have enforced deformations on the top surface of the crystal and hence the (011) of the crystal shows a slight reduction of diffraction intensity. On the other hand, there is a possibility of the beginning of the SO$_4$ tetrahedral rotational disorder and re-orientation of NH$_4$ tetrahedral unit [25]. Similar results have been noticed for the temperature depended ammonium sulfate crystal [37–41]. Furthermore, at the 2nd shocked condition, there are significant changes clearly visible and the corresponding XRD pattern is presented in Fig. 2. As seen in Fig. 2, the observed diffraction peak intensity is significantly reduced while compared to the 1st shocked crystal’s diffraction peak intensity.

At the 2nd shocked condition, not only the intensity of the first order diffraction peak (011) is reduced but also the intensity of the second order diffraction peak (022) is significantly reduced and a few minor diffraction peaks are observed at 20.76° and 39.27°. Among the three diffraction patterns, third order diffraction plane (033) is completely vanished at the 2nd shocked condition. Furthermore, significant changes have been observed in the XRD pattern at the 2nd shocked conditions whereas no
crystallographic phase transition is observed as that of K$_2$SO$_4$ crystal [25] and the observed phase is considered to be the distorted-Pnam crystal symmetry based on the results of previous high temperature experiments of the title crystal [37, 38]. Hence, at this context, a couple of concepts such as order-disorder of the sulfate ions, positional displacement of hydrogen atoms as well as their network and most importantly re-orientation of ammonium ions have to be considered to explain the observed XRD results at the 2nd shocked condition. According to the previous high temperature experiments, the title crystal ought to have experienced the distorted-Pnam crystal symmetry without undergoing any crystallographic phase change which is referred as the second order phase transition (molecular distortion type) [37, 38]. At this stage, significant re-orientation of the ammonium ions is observed wherein especially NH$_4$ (II) has higher contribution than that of NH$_4$ (I) due to its higher disorder tetrahedral and rotational disorder of SO$_4$ tetrahedral which have significantly altered the atomic position of the host crystal symmetry resulting into the disordered phase. Moreover, in the case of K$_2$SO$_4$ crystal at shocked conditions, order-disordered SO$_4$ tetrahedral units are observed and as a result highly ordered orthorhombic structure is transformed into highly disordered hexagonal crystal structure [25]. Similar kind of rotational disorder of SO$_4$ units and re-orientation of NH$_4$ ions might have occurred that could have induced the distortion – Pnam crystal symmetry at the 2nd shocked conditions. In addition to that, during the formation of distortion – Pnam crystal symmetry of the title crystal, sudden expansion along a,b, and c lattice vectors ions might have occurred and the corresponding information can be extracted from the zoomed version of the XRD patterns of the control and shocked crystals for which the selected diffraction regions are presented in Fig. 3. As seen in Fig. 3, the most intense diffraction peak of (022) is shifted towards lower angle at the 1st and 2nd shocked conditions which clearly indicates that the expansion of the unit cell and positional disorder of the atomic sites [47]. Accordingly, the distortion-Pnam phase transition is triggered by distortion arising in the structure of the SO$_4$ ion which means that the orthorhombic phase has two stable states of SO$_4$ ions that can jump easily from one stable state to another by temperature and pressure [49]. Furthermore, the number of shock pulses has been increased to 3 and 4 so as to make the possible phase diagram with respect to the number of shock pulses and for a better understanding of the crystal structure of the title crystal at shocked conditions such that the obtained XRD patterns are presented in Fig. 2 while the zoomed version is portrayed in Fig. 3.

As seen in Fig. 2 and Fig. 3, the XRD patterns of the 3rd and 4th shocked crystals are closely similar to the XRD patterns of the control and the 1st shocked crystals which reveals that the reversible phase transition from distorted – Pnam to order-Pnam crystal symmetry is achieved at the 3rd shocked condition due to the rotational order of SO$_4$ ions and the same crystal symmetry is retained at the 4th shocked condition. As reflected in Fig. 3, the (022) plane has twin and sharp diffraction peak at the 3rd shocked condition whereas the twin peak is partially reduced at the 4th shocked condition which indicates the enhancement of the degree of crystalline nature of the test sample based on the dynamic re-crystallization [47, 50, 51]. Similar kind of results have been observed in ammonium dihydrogen phosphate crystals at shocked conditions [47] and the corresponding phase diagram of the title crystal with respect to the number of shock pulses is presented in Fig. 4.
Raman Spectroscopic Results

Followed by the X-ray diffraction results, Raman spectroscopic results are required to make a conclusion on the crystallographic phase stability of the title crystal with respect to the number of shock pulses and the observed Raman spectra of the control and shocked crystals are presented in Fig. 5 wherein the characteristic Raman bands of the SO$\text{}_4$ ions such as $\nu_4$, $\nu_2$, and $\nu_1$ are located at 444 cm$^{-1}$, 611 cm$^{-1}$, and 970 cm$^{-1}$, respectively. Raman band positions at 1064 cm$^{-1}$ and 1099 cm$^{-1}$ belong to $\nu_3$ mode of Raman band which are well corroborated with the previous articles [52]. In addition to that, N-H vibration of Raman bands are located at 1407 cm$^{-1}$, 1407 cm$^{-1}$ and 3162 cm$^{-1}$.

While looking through the macroscopic view of the Raman band positions as well as shape of the bands of the control and shocked crystal, almost all the Raman spectra look similar. To extract the possible supporting evidences for the XRD from the Raman results, the zoomed version of a few interesting results of the SO$\text{}_4$ ions and NH$\text{}_4$ ions provided in Fig. 6 - 8. As seen in Fig. 6, the $\nu_2$ - SO$\text{}_4$ Raman band has quite higher intensity than that of $\nu_4$-SO$\text{}_4$, moreover it has a very fine shoulder peak at the higher frequency region. The $\nu_4$-SO$\text{}_4$ Raman band positions are 611, 624, 622, 622, and 621 cm$^{-1}$ with respect to the number of shock pulses of 0, 1, 2, 3 and 4. At the first shocked condition, the $\nu_4$-SO$\text{}_4$ Raman band intensity is significantly increased and also shifted towards the higher frequency region which reveals that the enhancement of degree of crystalline nature at shocked conditions and it is well corroborated with the XRD results in particular to the most intense XRD peak (022). At the 2nd shocked conditions, it is clearly seen the splitting of $\nu_4$-SO$\text{}_4$ Raman band and the intensity is also reduced which may be due to the occurrence of the rotational disorder of the SO$\text{}_4$ ions at shocked conditions [29, 30]. Such rotational disorder of the SO$\text{}_4$ ions may break the crystal symmetry of the Pnam and induce the distorted Pnam crystal symmetry at the 2nd shocked condition. At the 3rd and 4th shocked conditions, the shapes of Raman bands become sharper and remain in the same positions due to the occurrence of the rotational order of the SO$\text{}_4$ ions. Based on the Raman spectroscopic results, the shock wave induced phase transitions triggering force lies in the SO$\text{}_4$ ions.

In Fig. 7, the $\nu_3$-SO$\text{}_4$ Raman bands of the control and shocked (NH$\text{}_4$)$_2$·SO$\text{}_4$ crystals are presented wherein considerable changes could be found at shocked conditions. In the case of the control sample, $\nu_3$-SO$\text{}_4$ Raman band has doublet bands (1064 and 1099 cm$^{-1}$). At the first shocked condition, the doublet Raman band is converted to singlet band (1104 cm$^{-1}$) and remains to be singlet Raman band at 2nd, 3rd and 4th shocked conditions while the Raman band position also remains to be quite similar. But, at the 2nd shocked condition, there is a shoulder band that is located at the lower frequency region which might be due to the occurrence of the distortion and disorder of the SO$\text{}_4$ ions. It could be noted that such kind of shoulder Raman band doesn’t appear in any other shocked conditions.

In Fig. 8, Raman spectral regions of both the ammonium ions NH$\text{}_4$ (I) and NH$\text{}_4$ (II) corresponding to the control and shocked crystals are presented wherein considerable changes are observed at shocked
conditions. As seen in Fig. 8, the NH$_4$ (II) ion has a high intense broad Raman band whereas NH$_4$ (I) has a couple of low intense Raman bands. At the first shocked condition, the intensity of NH$_4$ (II) Raman band is reduced whereas the intensity of NH$_4$ (I). At 2nd, 3rd, and 4th shocked conditions, the Raman spectra of both the NH$_4$ (I) and NH$_4$ (II) ions are quite similar. Hence, based on the anion and cation Raman spectral features of the test crystal at shocked conditions, the induced disorder of the SO$_4$ tetrahedral ions leads to the major contribution of the observed distorted Pnam crystal symmetry at shocked conditions.

**Ultra-violet Diffused Reflectance Spectroscopic Analysis**

Furthermore, the ultra-violet diffused reflectance spectroscopic (UV-DRS- Shimadzu- UV-3600 plus) analysis has been performed to understand the optical properties of the title crystal at shocked conditions and the acquired profiles of optical transmittance of the control and shocked crystals are presented in Fig. 9a. The obtained optical transmittance spectrum of the control sample is well-matched with the previous reports [53, 54]. At shocked conditions, there are considerable changes observed and especially at the 2nd shocked condition where significant reduction of optical transmittance is observed due to the formation of the distorted –Pnam crystal symmetry. The distorted –Pnam crystal surface is significantly affected by the photon depended transport properties and hence the net optical transmittance is remarkably reduced at the 2nd shocked conditions. Furthermore, the increases in optical transmittance at 3rd and 4th shocked conditions are due to the formation of the order Pnam crystal symmetry which enhances the degree of crystalline nature. For a better understanding of the reversibility of the title crystal with respect to number of shock pulses, the optical transmittance values with respect to the number of shock pulses and it is depicted in Fig. 9b. The profiles of optical transmittance pertaining to several materials have been investigated, so far at shocked conditions [55–58] and found that the optical transmittance is usually reduced by the defective crystal structures [56–58]. Most importantly, the optical transmittance profiles of K$_2$SO$_4$ crystal also exhibit the similar trend with respect to the number of shock pulses [25].

**Conclusion**

In summarizing the present experimental results, the reversible phase transitions (molecular distortion type) of the ammonium sulfate crystal with respect to the number of shock pulses have been analyzed and the observed phase transition sequence is Pnam-Pnam-distorted Pnam- Pnam-Pnam for the 0,1,2,3, and 4 shocks, respectively. The above-mentioned phase transition results have been justified by X-ray diffraction, vibration and optical spectroscopic techniques. Based on the observed Raman spectroscopic results, it is clear that the SO$_4$ tetrahedral ions have the major contribution as against the ammonium ions for the observed interesting results of the test crystal at shocked conditions. Optical transmittance profiles of the test crystals also provide the possible supporting evidences as per the X-ray diffraction and Raman spectroscopic results. It could be noted that, as of now, this is the first report on such reversible phase transition for the ammonium sulfate crystal. Due to the switchable behaviour of the test material,
we strongly suggest it for the applications of thermo sensitive devices and molecular switching. Moreover, the para-electric nature and dielectric behavior of the test crystal may provide interesting results at shocked conditions such that these properties are going to be investigated experimentally in the near future.

**Declarations**

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**Competing financial interests**

The authors declare no competing financial interests.

**Availability of Data**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Figures
XRD pattern generated using CIF and molecule sub units of the title crystal (a) XRD pattern (b) SO$_4$ unit (c) NH$_4$ (I) unit (d) NH$_4$(II) unit

Figure 2

XRD patterns of the control and shocked (NH$_4$)$_2$SO$_4$ crystals
Figure 3

Zoomed version of the XRD patterns of the control and shocked \((\text{NH}_4)_2\cdot\text{SO}_4\) crystals

\((\text{NH}_4)_2\cdot\text{SO}_4\)
Figure 4

Phase diagram of (NH$_4$)$_2$SO$_4$ crystals with respect to the number of shock pulses

Figure 5

Raman spectra of the control and shocked (NH$_4$)$_2$.SO$_4$ crystals
Figure 6

$\nu_4$ and $\nu_2$-SO$_4$ Raman bands of the control and shocked (NH$_4$)$_2$SO$_4$ crystals

Figure 7

$\nu_3$-SO$_4$ Raman bands of the control and shocked (NH$_4$)$_2$SO$_4$ crystals
Figure 8

$\text{NH}_4$ (I) and $\text{NH}_4$ (II) Raman bands of the control and shocked $(\text{NH}_4)_2\text{SO}_4$ crystals

Figure 9

(a) Optical transmittance profiles of the control and shocked $(\text{NH}_4)_2\text{SO}_4$ crystals (b) optical transmittance percentage with respect to the number of shock pulses
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