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Abstract

To date, even though a large number of shock wave induced irreversible crystal-crystal phase transitions have been reported for the past few decays, switchable phase transitions of solid state materials by dynamic shock waves remain to be quite un-known and also attainment of switchable phase transitions is somewhat a difficult task as compared to the irreversible phase transitions. Hence, experiments on switchable phase transition arising out of materials and the related publications are always considered to be valuable asserts for the materials researchers so as to master over the enhanced understanding of the behavior of materials and their probable applications. Moreover, materials of switchable phase have enormous number of spectacular industrial applications. In the present framework, we have presented and demonstrated the switchable phase transition of magnesium sulfate heptahydrate ($MgSO_4.7H_2O$) at shocked conditions and the switching behavior has been screened by diffraction, vibrational spectroscopic

and optical spectroscopic techniques so as arrive at X-ray diffraction (XRD), Raman scattering and UV-Visible spectral analyses, respectively. All the observed results clearly reveal that the switchable phase transition is achieved at dynamic shock wave loaded conditions. The interesting aspects of the present experimental results with respect to the number of shock pulses are discussed in the upcoming sections.

Key-words: Magnesium sulfate heptahydrate, Shock waves, Switchable phase transition, Re-crystallization

Introduction

Studies on the impact of shock waves on materials found in the Nature have started to receive a great deal of attention such that their influence on the properties of materials has attained a standpoint of pinnacle which has triggered a series of innovations that have driven efficiency and sustainability of materials to the levels of previously unattainable and this new sphere of activity offers multiple opportunities for the researchers to rise to the occasion. Structured reflection on those lines could provide remarkable scope of finding materials of prominence such that switchable phase transition could be very well established for a few materials by the impact of shock waves. Furthermore, switchable crystallographic phase transition is one of the special topics for materials scientists who work in the crystallographic phase transitions of solids because such materials are highly used in pressure transmitters, molecular switches, current flash memories and phase shifters etc. [1-3] To achieve such special phase transitions, knowledge of the crystal structures at high-pressure, high-temperature and low-temperature environments is highly required. Over the last couple of decades, several thousands of publications have been achieved in the field of static high pressure compression and de-compression enforced on materials such that an array of data have been accomplished through experiments which have paved the way for the switchable phase transitions emerging out of materials as that of solid state phase transitions which include crystal – crystal and crystal – amorphous phase transitions.[4-6] It could be noted that, in the case of static high-pressure experiments, many of the materials exhibit such reversibility which has been very well established in both inorganic and organic crystals.[4-6] Here we present a few examples of static high-pressure and high-temperature experiments wherein the obtained results of phase transitions

in materials could provide convincing substantiation on the above-mentioned statements. Yun-Zhi Tang et al have demonstrated the switchable phase transitions of 18-Crown-6 Clathrate that have been accomplished during the heating and cooling conditions.[7] Reversible double phase transitions have been observed in Hybrid Iodoplumbate ($C_4H_{12}NPbI_3$) during the process of heating as well as cooling.[8] Kai Wang et al have performed the static pressure compression and de-compression experiment on sulfamide and found the reversible phase transitions.[9] Thomas D. Bennett et al have demonstrated the crystal – amorphous reversible phase transitions in zeolitic imidazolate framework at pressure compression and de-compression stages.[10] Bo Zou and his team has performed the static high-pressure experiment and reported the reversible crystallographic phase transition for Ammonium Formate[11], Lithium Amide[12], Acetamide[13] and magnesium silicide (Mg_2Si).[14]

Followed by the static high-pressure and high-temperature observations analyzed, dynamic shock waves induced phase transition experiments conducted on solids also could provide significant information to the researches to understand the behaviors of molecules and atoms and their response at dynamic high transient pressure and temperature conditions which is identified to be one among the rising research topics in current years.[15-18] It is well known that, during the shock wave loaded conditions, a test sample possibly experiences crystallographic phase transitions of solid to solid[19,20] and crystal to amorphous phase[21], lattice deformations and defects[22,23] and stable crystallographic phase.[24] Among the listed three possible occurrences, stable crystallographic phase at dynamic shock wave loaded conditions is quite a rare case to occur since majority of materials experience lots of deformations without undergoing the phase transitions. Furthermore, it is quite interesting to achieve reversible crystallographic phase transitions of solids at shocked conditions as that of static high-pressure experiments. But tremendous amount of effort and energy have been continually paid to achieve such reversible phase transitions in materials at shock wave loaded conditions for the above-mentioned applications since shock wave induced phase transitions are highly rapid than that of the pressure and temperature induced phase transitions. Our research group has reported the switchable crystallographic phase transitions of potassium sulfate crystal at shock wave loaded conditions.[25] Furthermore, switchable magnetic phase transitions have been observed in $ZnFe_2O_4$[26]and Co_3O_4 NPs.[27]

In the present context, we have chosen magnesium sulfate heptahydrate ($MgSO_4.7H_2O$) single crystal to examine the crystallographic phase stability at shocked conditions. $MgSO_4.7H_2O$ is one of the familiar polymorphic hydrate salts which is available in the planetary materials.[28,29] With respect to pressure and temperature, it undergoes series of polymorphic phase transitions based on the prevailing processes of de-hydration and re-hydration.[30-32] On the one hand, so far, several material scientists and geological scientists have examined the crystallographic phase stability of the title single crystal with respect to pressure, temperature and humidity and have come up with several sequences of phase transitions which are highly associated with the temperature and pressure of the respective experimentation.[30-32] Moreover, such kinds of high-pressure and high-temperature conditions are highly required to get into the deep understanding of the formation of the present solid state – earth and other planets (Mars and Jupiter) as well as interior icy satellites. On the other hand, through such kind of high-temperature and high-pressure experiments only, we could be able to quantify the water resources of the planets.[28,29] In recent years, a lot of experiments have been performed on the minerals of Martian planet surface especially magnesium hydrates.[33,34] Several materials science research groups in the global arena have been continually working on this theme and providing their significant contributions so as to understand better on the phase stability of the title crystal. So far, the known phases of magnesium hydrates are $MgSO_4.11H_2O$, $7H_2O$ ($P2_12_12_1$), $6H_2O$ (C_2/C), $5H_2O$ (P-1), $4H_2O$, $3H_2O$, $2H_2O$, $1H_2O$, and anhydrate $MgSO_4$. But, among the listed phases, $MgSO_4.7H_2O$ is a thermodynamically stable phase at ambient conditions so that it is one of the promising candidates for heat storage applications due to its high energy density.[35-37] In some cases, the non-integer water content phase has been observed as that of mixed phase of magnesium hydrate ($MgSO_4.6/7\ H_2O$) due to the nature of the experiential conditions.[35-36] In 1948, Bridgman has performed high-pressure experiments (piston compression method) on the title crystal and observed a few sluggish phase transitions at 1.0 – 1.5 GPa and 2.5 GPa.[38] Followed by Bridgmen, Livshits et al have carried out high pressure experiments on crystalline hydrates of magnesium sulfate and found series of phase transitions such as I-II at 0.45 GPa, II-III at 1.2 GPa, III-IV at 1.6 GPa, IV-V at 2.5 GPa.[39] Gromnitskaya et al have performed high-pressure neutron powder diffraction study of crystalline $MgSO_4.7H_2O$ and found series of phase transitions at 1.4, 1.6, and 2.5 GP.[40] Very recently, Linfei Yang et al have carried out the

combined high-pressure and high-temperature experiments on the title crystal and found three steps of phase transitions with respect to temperature and also observed that the de-hydration rate is increased while increasing the pressure range.[41]

In the present framework, we have systematically examined the crystallographic phase stability of the title crystal at shocked conditions such that it has been screened by XRD, Raman and UV-DRS techniques. The present shock wave recovery experiments could provide the alternative way to be implemented so as to understand the behaviors of hydrate salts at icy moons and other planets so that it is very much possible to unearth the unknown facts as well as new structural formulations.

Experimental section

Commercially available, $MgSO_4.7H_2O$ was purchased from Sigma Aldrich Company and the material was dissolved in double distilled water. The saturated solution of $MgSO_4.7H_2O$ was prepared at room temperature and stirred continuously for 5 hrs with the help of a magnetic stirrer in order to obtain a homogenous solution. Furthermore, the saturated solution was allowed to begin the crystallization process by slow evaporation method and bulk size crystals (10×10×2 mm^3) were harvested after 25 days so as to be used for the present experiment and the photograph of the as grown crystal is presented in Fig.1 as an inset. The shock wave induced phase stability analysis has been performed using an in-house tabletop semi automatic Reddy Tube for which the details of working methodology have been discussed in our previous papers.[19,27,42]. In the present experiment, we have collected three samples of equal dimension (5×5×1 mm^3) and have ensured to be defect free crystals so as to be fit for the investigation. Among the three samples, one sample has been kept as the control sample and the remaining two samples have been used for shock wave impact experimentation. In the present experiment, we have used a semiautomatic Reddy Tube for the generation of shock waves of Mach number 2.2 possessing transient pressure 2.0 MPa. The crystal is placed in the sample holder such that one shock pulse is exposed on the crystal and two shock pulses are loaded on the other crystal. The time duration between the shock pulses are kept as 5 seconds. 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

XRD results

Herein, powder X-ray diffractometer has been used for notifying the shock wave induced structural changes of the title crystal and the observed XRD pattern is presented in Fig.1. As per the basic standard, it is quite mandatory to confirm the formation of the crystallographic phase of the test crystal since it is highly sensitive to temperature and pressure. There are enormous possibilities to observe the de-hydration process even at 25-30° C. If such changes occur, the final product structure must be of the lower hydrate phase or mixed phase structure. Hence, the conformation of the grown crystal structure is highly crucial before discussing the shock wave induced changes occurring on the test crystal.

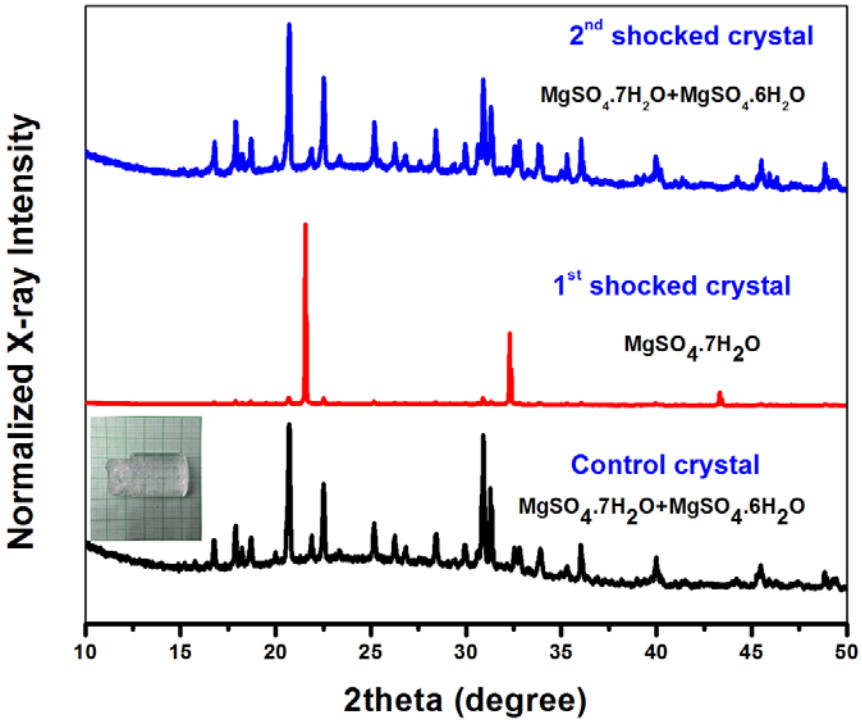

Fig.1 The XRD patterns of the control and shocked crystals and the photograph of the crystal as an inset

The grown crystal's XRD pattern is compared with simulated $MgSO_4.7H_2O$ and $MgSO_4.6H_2O$ and the corresponding XRD patterns are presented in Fig.2a. As seen in Fig.2a, the

prominent diffraction peak position of $MgSO_4.7H_2O$ phase is at 21.02 degree and for $MgSO_4.6H_2O$ phase is at 20.01 degree. But in the case of the control crystal (as grown crystal), the prominent X-ray diffraction peak position is at 20.6 degree and the corresponding XRD pattern is presented in Fig.2a. Hence, the control test crystal does not belong to a single phase of $MgSO_4.7H_2O$ ($P2_12_12_1$) as well as for $MgSO_4.6H_2O$ (C_2/C) so that it is considered as a mixed phase existing for both the cases. Fig.2a gives the clear justification for the consideration that has been also witnessed by several researchers i.e. existence of such kinds of mixed phases in magnesium salts hydrates.[35,36] There could be two prime reasons for the existence of the mixed phase for the grown crystal; the first point is, during the de-hydration process occurring at lower temperature region (25-30°C), the grains can obviously dehydrate into mixed phases because the dehydration process is incomplete due to in-sufficient temperature. To achieve complete de-hydration, it should reach the temperature transition line. As a result, the existing grains do not have the integer values for the hydrates.[35.36]

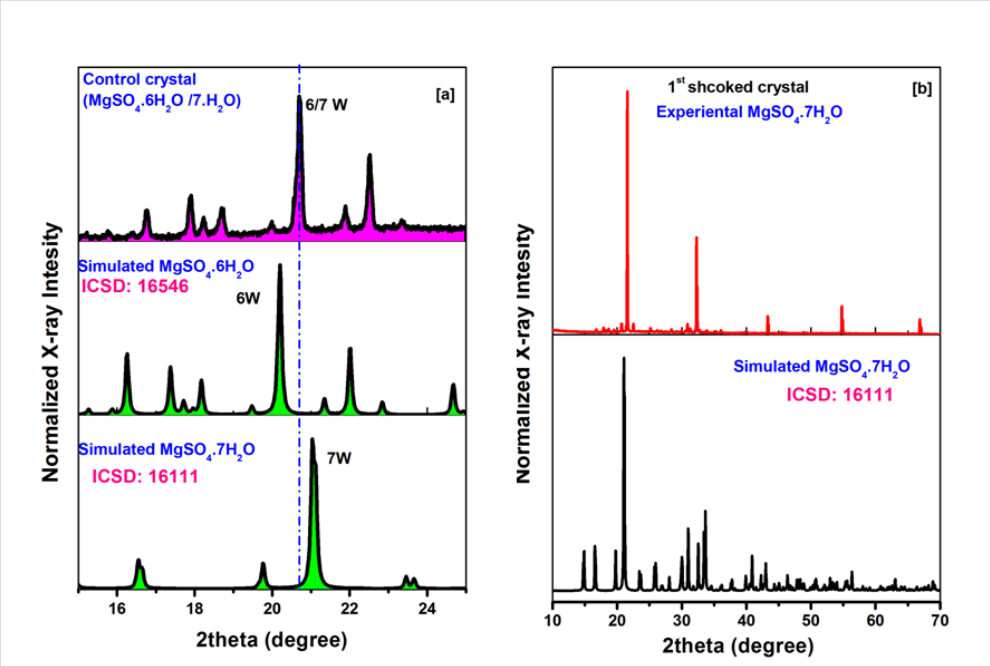

Fig.2 (a) Comparison of the XRD patterns of $MgSO_4.7H_2O$, $MgSO_4.6H_2O$ and the control crystal (b) The XRD patterns of simulated and shock wave induced $MgSO_4.7H_2O$

Second point is that some of the lattice waters are changed to pore water states in the same crystal. But, different phases are present due to the in-complete dehydration. Moreover, all the water molecules might not have involved to influence these changes in the crystal.[35,36] which induces the formation of mixed phases and the observed changes of water states of this crystal will be discussed with reference to the Raman spectroscopic results. As seen in Fig.1, the significant changes have been observed in the XRD pattern with respect to the number of shock pulses. The XRD pattern of the first shocked crystal is completely different from the control sample wherein the most prominent XRD peak is shifted towards the higher diffraction angle which reflects the formation of $MgSO_4.7H_2O$. As seen in Fig.2a, the prominent diffraction peak of $MgSO_4.6H_2O$ appears at lower diffraction angle as compared to $MgSO_4.7H_2O$. But, in the case of 1st shocked condition of the crystal, the prominent XRD peak experiences the higher angle shift and it appears at 21.5 degree. The diffraction value is little larger as compared to the XRD pattern of simulated $MgSO_4.7H_2O$. There is no signature for the occurrence of de-hydration process influenced by shock waves even though it has enough transient pressure and temperature. If such de-hydration process has happened, the diffraction peaks would have moved towards the lower diffraction angle and induced the formation of $MgSO_4.6H_2O$. But, such kind of reflection is not observed in the XRD pattern of the crystal at 1st shocked condition. Hence, it is very clear that the mixed phase of the test sample is phase transformed to single phase crystal at 1st shocked condition due to the re-organization of hydrogen bonds as well as dynamic re-crystallization. Due to the shock transient pressure and temperature, sufficient latent heat is supplied to the crystal and the extra pore water molecules might be pushed to the lattice water state so that the resultant formation becomes the single phase $Mg.SO_4.7H_2O$. The water molecules are connected with Mg octahedral and SO_4 tetrahedral such that the existing bond pattern is presented in Fig.3. In general, SO_4 tetrahedral is highly sensitive for pressure and temperature and it undergoes significant rotational order-disorder processes at high-pressure and high-temperature conditions.[25] Due to the lattice water states changes, the rotational order-disorder of SO_4 tetrahedral is also possible to take place at shocked conditions.[25] Due to the existence of the mixed phase during the crystal growth, we can assume in such a way that the disorder SO_4 tetrahedral may be present in the control crystal and specially ordered SO_4 tetrahedral appears at 1st shocked condition due to the dynamic re-crystallization which results

into single phase $Mg.SO_4.7H_2O$ with the $P2_12_12_1$ space group. At 2nd shocked condition, the original mixed phase is observed as it is noticed in the control crystal and Fig.1 clearly shows the reversibility of the phases with respect to the number of shock pulses. Hence, at this stage, it is clear that the switchable phase transition is achieved with respect to the number of shock pulses similar to that of K_2SO_4 crystal[25] and the schematic diagram of the claimed phase transition is presented in Fig.4.

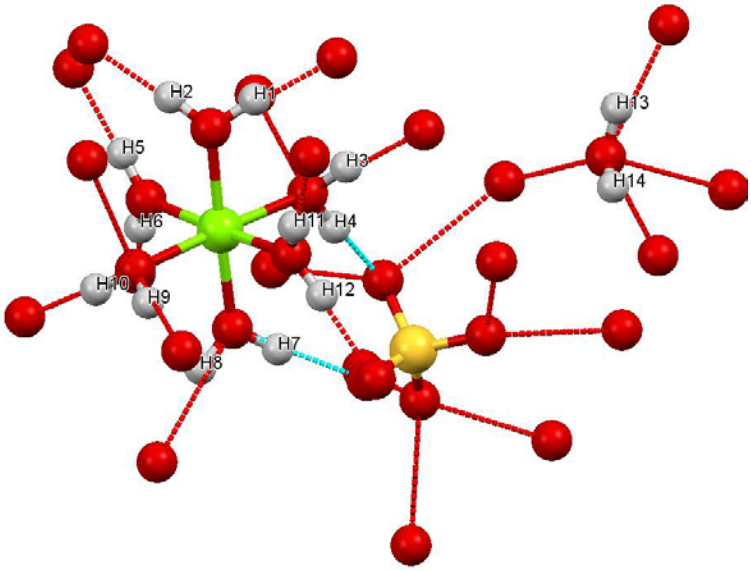

Fig.3 Single molecular bonding pattern of $MgSO_4.7H_2O$

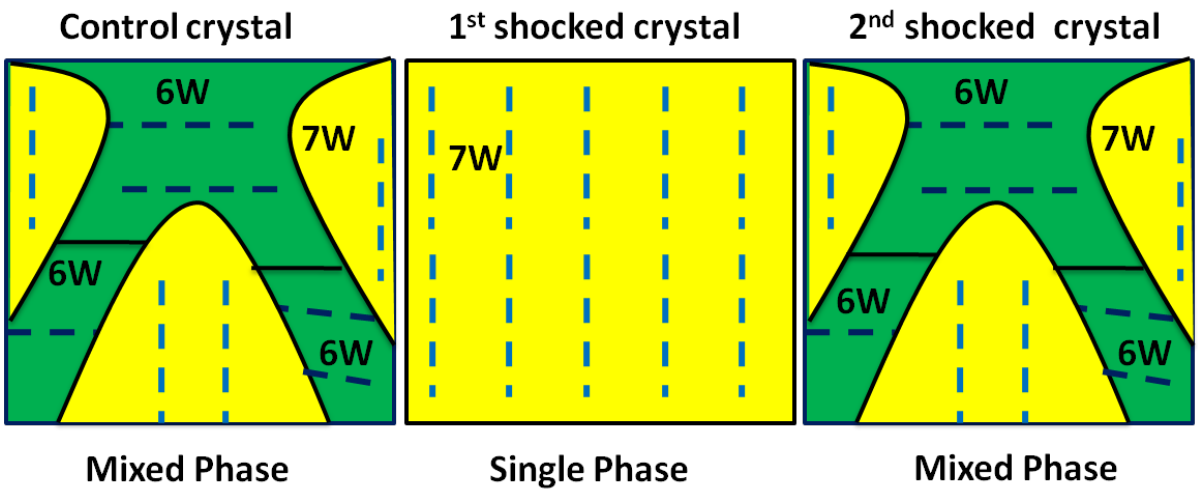

Fig.4 Schematic diagram of shock wave induced reversible phase of $MgSO_4.7H_2O$

During the 2nd shocked condition, some of the lattice water molecules are transferred into pore water states and as a result the mixed phase is observed. In particular, the seventh water molecule (H13 and H14 atom in Fig.3) has the maximum possibility to have induced the mixed phase of $MgSO_4.7H_2O$. During the shock wave loaded conditions, the actual $MgSO_4.7H_2O$ crystal structure is unable to withstand its own state due to low energy hydrogen bonding network and try to begin the de-hydration process. Since the existence of the shock wave within the sample is very short period, the water molecules cannot be able to be removed from the substance but the seventh water molecule is displaced from its original position where the hydrogen bond cannot be able to form. Hence the distortion of the crystal structure is highly possible at shocked condition without the removal of the actual water quantity of the test sample. In addition to that, the test crystal is a solid substance so that the internal vapor transport is highly constrained.[35] However, the water molecules create a different configuration which leads to deliquescence and formation of the mixed phase of the crystal. As per the previous reports, hydrated sulfates undergo dehydration reactions under high temperature and pressure conditions and result into the formation of lower hydrate structures.[35,36,40,41] But in the present case, we have not observed such dehydration process in $MgSO_4.7H_2O$.

Raman Spectroscopic Study

Raman spectroscopic study is one of the powerful techniques to authenticate the molecular fingerprints and solid –state phase transitions of the materials. In the present research work, Raman spectral analysis has been performed so as to justify the XRD results and to understand better the mechanism of the reversible phase transitions of the title crystal such that the observed Raman spectra of the control and shocked crystals are presented in Fig.5.

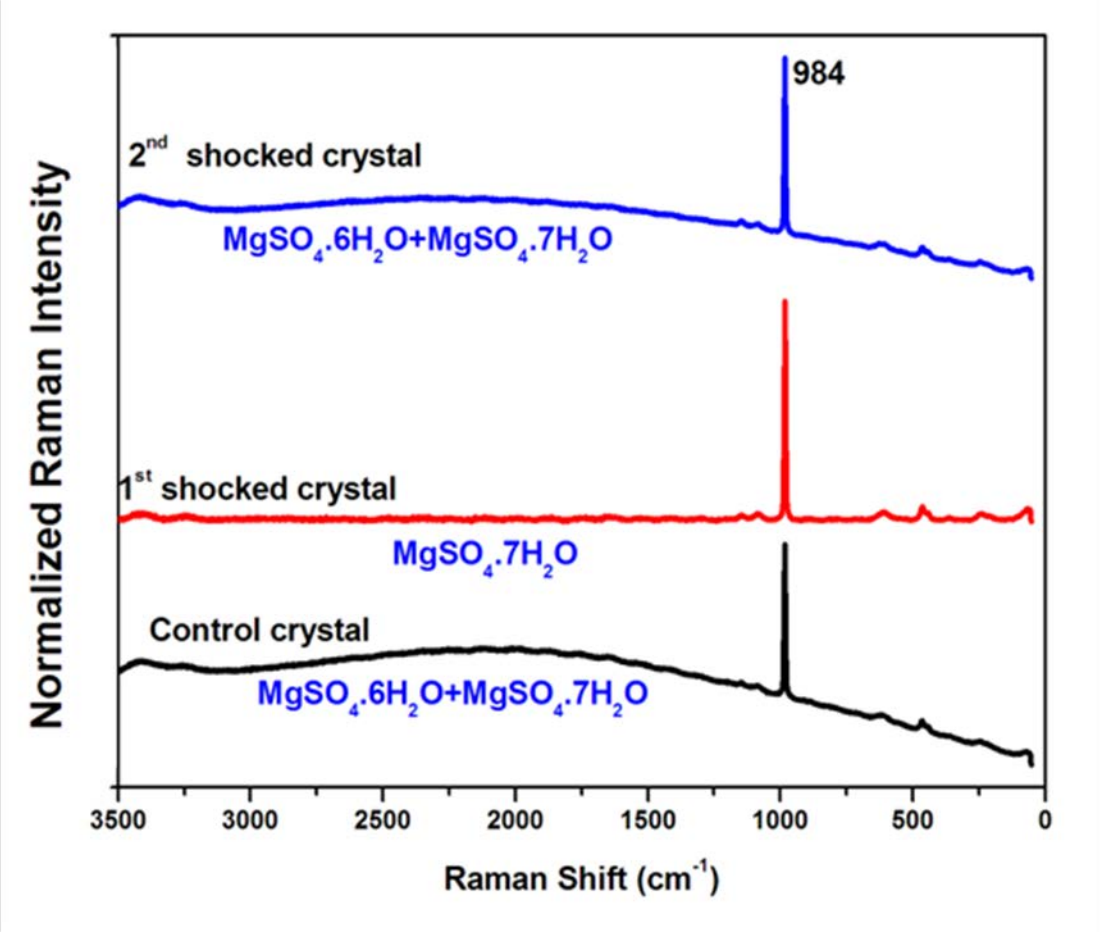

Fig.5 Raman spectra of the control and shocked crystals

As per the previous publications, $MgSO_4.7H_2O$ has the characteristic peaks at 983 cm^{-1} (ϑ_1 $-SO_4$), 3322 cm^{-1} (ϑ_1 $-H_2O$) and 3458 cm^{-1} (ϑ_3 $-H_2O$) bands. Based on the XRD results of the present experiment, the control crystal has mixed phase of $MgSO_4.7H_2O$ and $MgSO_4.6H_2O$ such that the observed Raman spectra also justify the XRD results through the vibrational modes

of water molecules so that the corresponding zoomed version of the Raman spectra are presented in Fig.6. The tetrahedral coordination of SO_4 position is almost similar for $MgSO4.7H_2O$ and $MgSO_4.6H_2O$ crystal structures and hence we cannot suspect significant changes in the SO_4 tetrahedral wherein the SO_4 band should move towards the higher wavenumber region during the de-hydration process expect in $MgSO_4.6H_2O$.[37] But, in the case of the vibrational modes of water molecules, one can see considerable changes in the Raman spectra since the lattice water and pore water transformation has the significant contribution in the formation of the mixed phase. As seen in Fig.6b, the water molecules identified in Raman bands have less Raman intensity and high full-width half-maximum (FWHM) values. It may be due to the contribution of the enhancement of pore water in the crystal than that of the lattice water due to the incomplete de-hydration process. In addition to that, the strong interaction between lattice water molecules is reduced during such kinds of incomplete de-hydration process.[35,36]

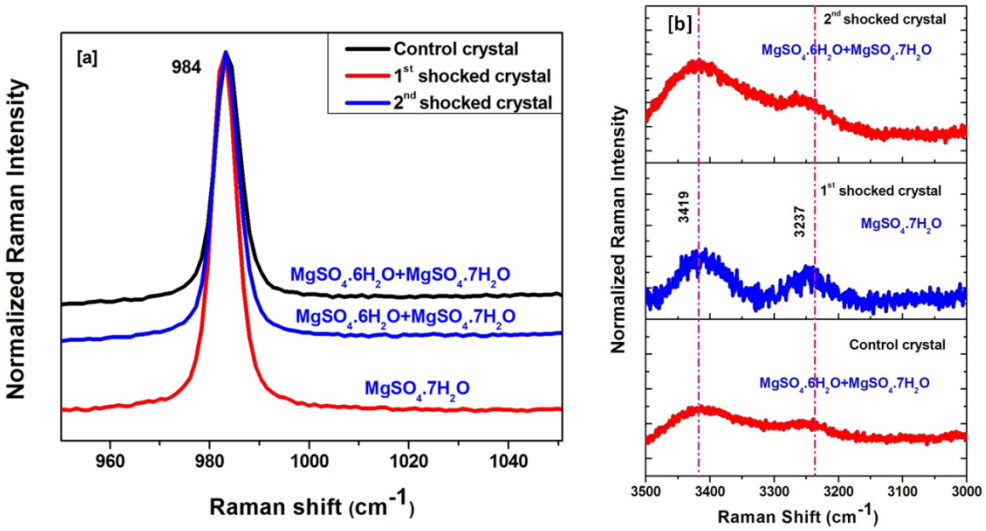

Fig.6 Zoomed versions of Raman spectra of the control and shocked crystals (a) SO_4 band (b) H_2O bands

So that, the Raman bands of water molecule have less intensity. Followed by the Raman bands of water molecules, SO_4 tetrahedral Raman band also shows the possible difference while compared to the pure single phase of $MgSO_4.7H_2O$ crystal structure. As seen in Fig.6a, the control crystal's SO_4 band (984 cm^{-1}) has high full-width half-maximum values compared to that of $MgSO_4.7H_2O$ crystal structure. During the mixed phase formation, the

partial $MgSO_4.6H_2O$ structure molecules are pulled to the (SO_4) tetrahedral to stay at lower wavenumber side so that the resultant slight changes can be obtained in full-width half-maximum since the actual positions of SO_4 tetrahedral for $MgSO_4.6H_2O$ (984.1 cm^{-1}) and $MgSO_4.7H_2O$ (984.3 cm^{-1}) crystal structures do not have the great differences.[37] At shocked conditions, considerable amount of changes have been noticed in symmetric stretching mode of the sulfate tetrahedral and in the vibrational modes of water molecules. At 1st shocked condition, the SO_4 Raman band showcases less FWHM compared to the control crystal and it is one of the signatures for the existence of the single phase with higher structural order and similar results are also noticed in the XRD results. But the position of the SO_4 Raman band has not changed. On the other hand, highly visible changes have been noticed in the vibrational modes of water molecules both in (ϑ_1 $-H_2O$) and 3458 cm^{-1} (ϑ_3 $-H_2O$) bands in particularly their intensities which may be due to the phase transition occurring from mixed phase to single phase of $MgSO_4.7H_2O$ crystal structure. The increment of Raman intensity may be due to the transition of some water molecules from pore water states to lattice water states. At this stage, the interaction of lattice water molecules are significantly increased so that strengthening of the hydrogen bonding is increased. Hence, the Raman bands have higher intensity at 1st shocked condition and the obtained phase transitions results are well corroborated with the XRD results. It could be noted that there is no significant dehydration process and formation of pure phase of lower hydrate structures occurred at shocked conditions even though it has enough transient temperature and pressure. At second shocked condition, revert of mixed phase is confirmed due to the existence of the higher value of FWHM for SO_4 (984 cm^{-1}) band water molecules of 3458 cm^{-1} and 3237 cm^{-1}. As seen in Fig.6a and b, the band patterns of SO_4 and water molecules are similar. For better understanding of the FWHM values of the control and shocked crystals, we have provided a clear picture about the values with respect to the number of shocks and it is presented in Fig.7.

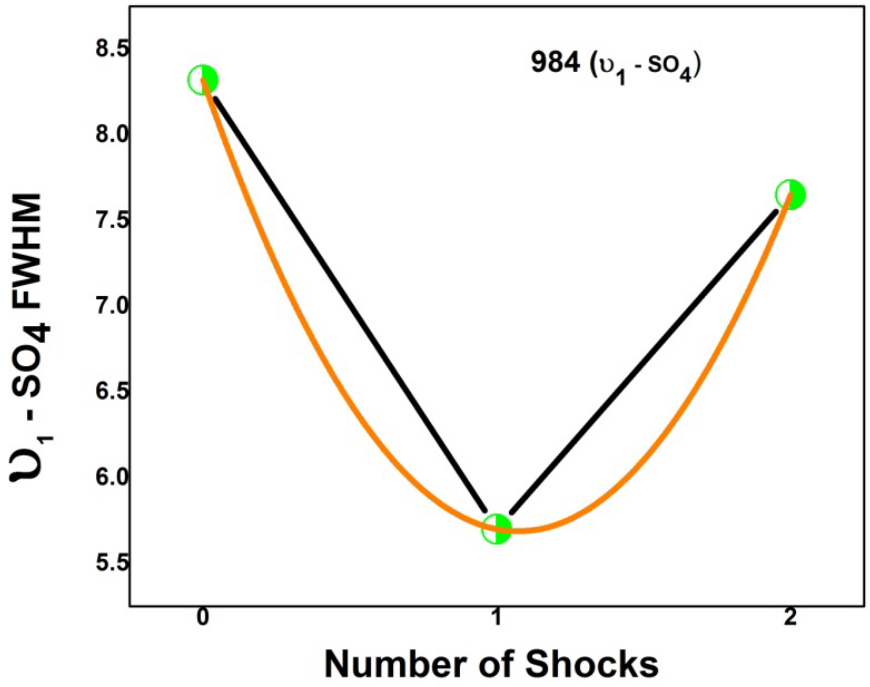

Fig.7 ϑ_1 –SO_4 tetrahedral FWHM values of the control and shocked crystals

UV-DRS spectral Analysis

Assessment of optical transmittance for the optically transparent crystals is another important parameter which can give the possible information to draw the convincing conclusion about the crystallographic phase transitions.[25] Herein, the ultra-violet diffused reflectance spectrometer (UV-DRS) has been utilized to measure the optical transmittance of the control and shocked crystal and the observed optical transmittance profiles of the crystal are presented in Fig.8. As seen in Fig.8, the control mixed phase crystal has transparent window in the entire visible region. But, the percentage of the optical transmittance is quite low such that the value of the optical transmittance is 17% at 600 nm. The value is quite convincing even though it is optically transparent crystal, since the test crystal has the mixed phase it obviously has several grain boundaries which belong to $MgSO_4.7H_2O$ and $MgSO_4.6H_2O$. Hence, it is quite obvious that the net values of the optical transmission are significantly reduced. At first shocked condition, the optical transmittance spectrum is significantly changed and the value of the optical transmittance has remarkably increased such that the transmittance value is found to be 47 % at

500 nm. This is may be due to the formation of single phase $MgSO_4.7H_2O$ crystal. At this stage, the light scattering centers are significantly reduced so that the amount of propagation of light has increased giving rise to enhanced optical transmittance.

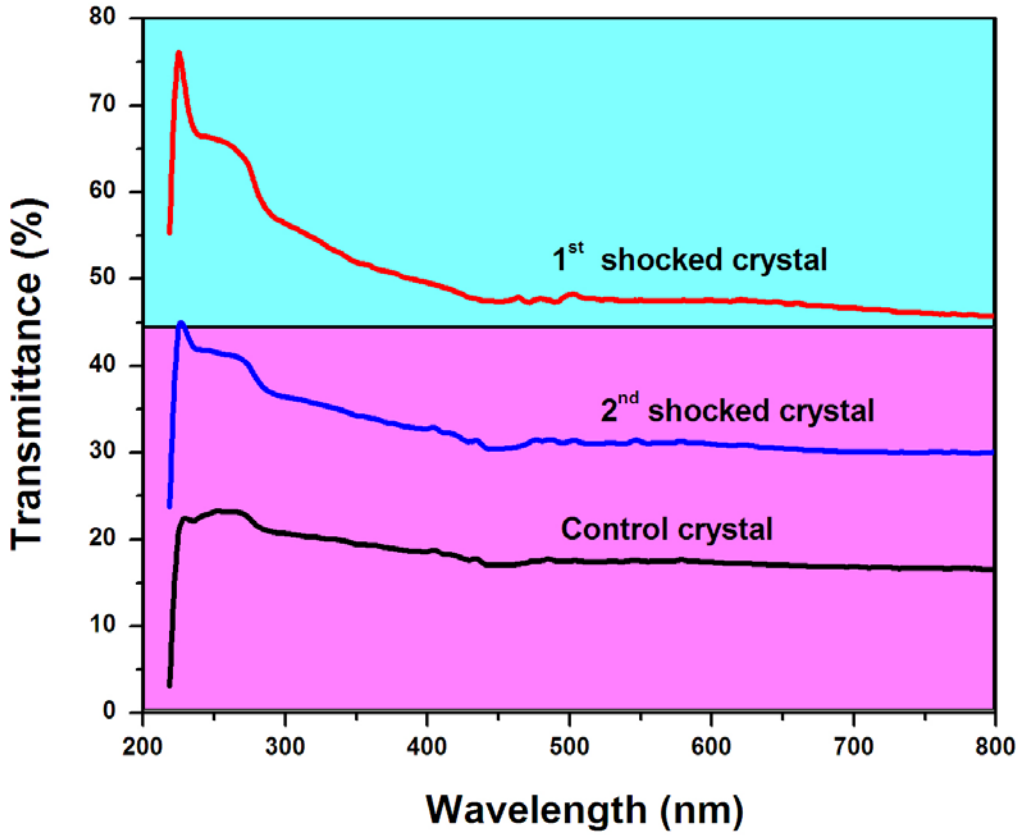

Fig.8 Optical transmittance spectra of the control and shocked crystals

It could be noted that the optical transmittance profile of the 1st shocked crystal is well-matched with the previous reports of $MgSO_4.7H_2O$.[44] At second shocked condition, the percentage of optical transmittance is reduced due to the formation of mixed phase which supports the XRD and Raman results. The optical transmittance percentage of the crystals at 600 nm with respect to the numbers of shock pulses is displayed in Fig.9. Based on the optical transmittance analysis, it provides the possible supporting evidence for the observed changes in the XRD and Raman measurement with respect to the number of shock pulses.

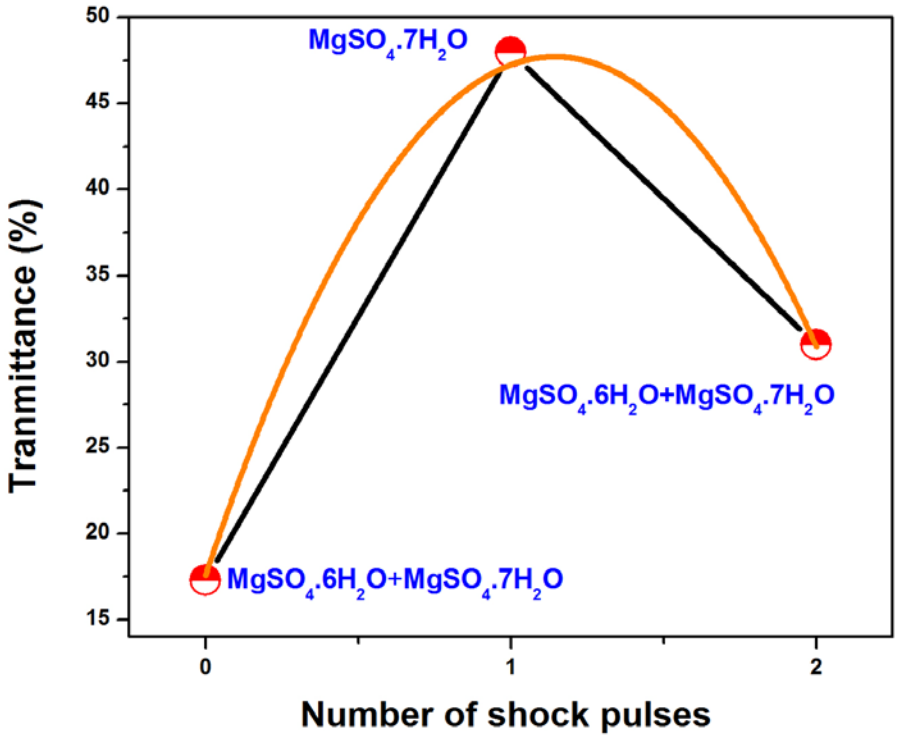

Fig.9 The optical transmittance percentage of the control and shocked crystals at 500 nm

Conclusion

In summary, we have systematically demonstrated the switchable phase transitions of hydrated magnesium salt with respect to the number of shock waves and the results have been evaluated by XRD, Raman and UV-DRS techniques. The XRD results evidently demonstrate that the $MgSO_4.7H_2O$ + $MgSO_4.6H_2O$ has been phase transformed to $MgSO4.7H_2O$ crystal at the first shocked condition due to the dynamic re-crystallization and changes in the pore water to lattice water states and the mixed phase is retrieved at the second shocked condition. The Raman spectral analysis gives the clear picture about the water molecules states which are considerably changed from pore water states to lattice water states due to the order-disorder process of tetrahedral (SO_4) with respect to the number of shock pulses and it gives direct correlation for understanding the switching behavior of the test crystal. UV-DRS spectral analysis also provides the possible substantiation to justify the XRD and Raman results so that switching of optical transmittance percentage with respect to the number of shock pulses could also be achieved. It could be noted that all the three different types of analytical techniques provide the similar

authentication with respect to the numbers of shock pulses. Hence, we strongly claim that the test samples have undergone switchable phase transitions and such kinds of materials are highly deserved for applications in sensor, phase shifters, resistive memories and flash memories. Innovative theoretical insights into unlocking the truth behind such shock impacted switching behavior of materials with respect to the number of shock pulses would be extremely valid so that it is reserved for the continual activity which will be in progress for this extended future course of research work. We strongly believe that the present shock wave recovery experiment would provide the new beginning for bringing out many more experiments on hydrate salts of planets so that new structural concepts could emerge at shocked conditions.

Compliance with ethical standards

None

Conflict of interest

The authors declare that they have no conflict of interest**.**

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Dynamic Shock Waves Induced Switchable Phase Transition of Magnesium Sulfate Heptahydrate

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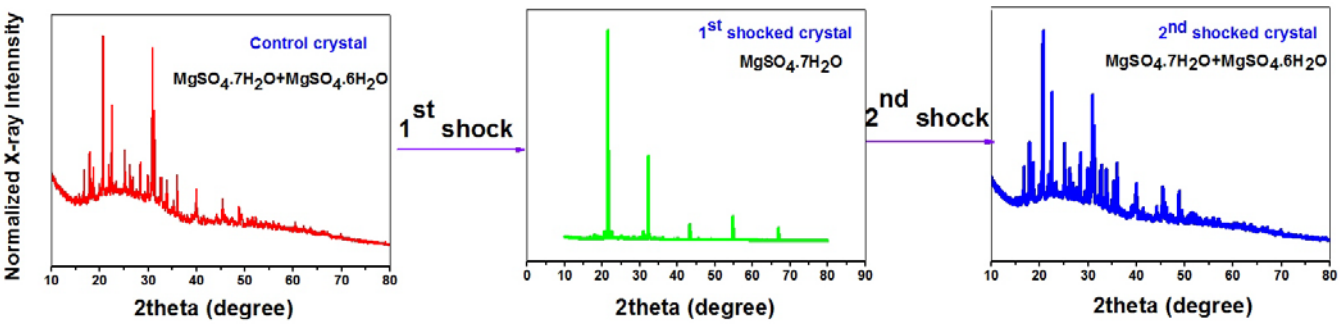
TOC Graphic Image



Synopsis

Dynamic Shock wave induced reversible phase transformation of $MgSO_4.7H_2O$ is achieved at ambient condition due to occurrence of dynamic re-crystallization. The phase transition is evidenced by XRD and Raman spectroscopy.