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Phase transitions induced by shock compression on a gypsum mineral: X-ray and micro-Raman analysis

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As a part of systematic researches of phase transitions induced by shock compression in phosphates, silicates, germanates and sulfates, in this article we report preliminary results obtained from shock recovery experiments on powders of a gypsum mineral. The shock experiment was performed in a light gas gun until a pressure close to 14 GPa reached. The experimental techniques employed to analyze the shock effects on recovered samples were: Scanning Electron Microscopy (SEM), X-ray Powder Diffraction (XRD) and Micro-Raman Spectroscopy (MRS). The SEM observations show a high plasticity in the impacted sample composed mainly by gypsum and bassanite quantified by Rietveld analysis of the XRD. The results indicate the partial dehydration of gypsum as a result of impact. The MRS analysis suggests the presence of micro-mixtures of gypsum, bassanite and anhydrite heterogeneously distributed throughout the recovered sample.

Keywords: gypsum; shock compression; light gas gun; X-ray diffraction; micro-Raman

1. Introduction

Shock wave compression of condensed matter makes it possible to achieve a number of chemical and phase transformations in unusually short times.[1] For several years, this approach has proved to be useful in such branches of science as the Earth and Planetary Sciences in order to understand the physicochemical processes involved in the genesis of minerals in the upper mantle and crust, or during impact processes of comets and meteors with the earth and other planets or satellites within the solar system.[2] From the experimental point of view there are two different ways of dealing with the problem: one is to look for the presence of minerals with physicochemical properties originated by high pressures and temperatures in the material ejected during the impact of meteors on the earth, by using several spectroscopic techniques.[3–5] The other one is to try to reproduce impact effects on these minerals form dynamic compression experiments through explosive techniques or by means of propellant or light gas gun devices.[6–8]

On the other hand, to understand the origin and the mineral composition of the Earth's crust, it is also necessary to investigate the mechanisms that underlie the formation of new minerals from phase transformations induced by meteor impacts. In order to simulate this type of transformations, dynamic shock compression experiments must be carried out on mixtures of the most common minerals found on the earth surface, and then, the recovered shocked samples

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have to be analyzed through various spectroscopic techniques, such as X ray, infrared, Raman and others (*e.g.* see the abstracts of the 46th Lunar and Planetary Science Conference sess. 613, 2015).[9]

As a part of systematic researches undertaken in our laboratory on silicates, carbonates, sulfates and phosphate minerals submitted to shock waves, in this paper we are reporting some results of phase transitions induced on shocked gypsum powders ($CaSO_4 \cdot 2H_2O$).

2. Methods

A shock experiment on powders of the above-mentioned gypsum was carried out using the one stage light gas gun at the High Pressure Laboratory of the Instituto de Física at the Universidad Nacional Autónoma de México.[10] The propellant gas employed was helium. The projectile and target design were described elsewhere.[11] With this arrangement, it is possible to perform planar shock-waves experiments by impacting a stainless steel plate against a target, which consists of three stainless steel capsule chambers hermetically sealed. Each chamber contains a specific volume cavity to locate a powdered compound or mineral under study, in this case gypsum, that was tested together with powders of wollastonite and tricalcium phosphate mineral. For the experiment, we employed a stainless steel plate of 106 g with a thickness of 3.46 mm. The plate was mounted on the nose of a nylon projectile (impact 2000), and was accelerated to reach a velocity of 829 m/s. By the impedance matching method, the peak pressure was estimated to be of the order of 14 GPa in the target.

The tested powder specimens of $CaSO_4 \cdot 2H_2O$ were prepared by crushing a fragment of a gypsum single crystal from Naica mines (Cave of Swords) located in the north of Mexico,[12] which was obtained by courtesy of Servicios Industrales Peñoles, the owner of the mine. The crushed samples for the experiment were fragments of irregular shapes and micrometric sizes ($< 50\,\mu m$). Before the shock experiment, the pristine powders were pre-compacted up to a density of 2.08 g/cm^3 corresponding approximately to 90% of the theoretical density of the gypsum (2.32 g/cm^3).

X-ray powder diffraction (XRD) of the recovered sample was measured at room temperature by means of a Bruker D8 Advance diffractometer; Cu $K_{\alpha 1}$ radiation and goniometer with a lynxeye detector. The data were collected from 20° to 110°, with a step size of 0.019°, and operating conditions of 35 kV and 25 mA in the X-ray generator. Scanning electron microscopy (SEM) observations were performed using JEOL JSM 5600 LV microscope. Micro-Raman spectra (MRS) were measured with Thermo Smart Raman spectrometer ($\lambda = 532$ nm), with a spatial resolution of 2–3 μm. Light was focused on the sample with an optical microscope (50 × objective), which also collected the scattered light onto the spectrometer. Laser power density on the sample surface was of the order of 0.2 mW/cm^2.

After the impact, the recovered sample with flat cylindrical shape was divided into two equal sections along their diameter; one of them was used for the XRD analysis and the other one was observed by SEM along the fractured surface. Different parts of the upper and lower faces as well as the fractured surface were analyzed using Raman microscopy.

For performing the quantitative phase analysis, the structural information for each one of the identified phases was obtained from the ICSD databank (ICSD, 2013). Cell parameters, crystal symmetry and atomic coordinates were introduced in the Rietveld program General structure analysis system,[13] using the experiment graphical user interface, EXPGUI (Toby, 2001).[14] Modified pseudo-Voigt function was chosen to generate the peak shape of the diffraction reflections. The refined parameters were: zero point and scale factors, cell parameters, half-width, atomic coordinates and isotropic thermal coefficients for each phase. The atomic coordinates

were fixed during the refinement. The background was modeled using shifted Chevyschev polynomial fitting 60 selected points with 18 refined terms.

3. Results and discussion

3.1. *SEM observations*

The SEM micrograph taken at different regions of the recovered sample shows highly deformed zones accompanied by slip bands, and apparently melted material (Figure 1). This severe strain detected in the sample of gypsum is the result of the extreme conditions of pressure and temperature to which it was subjected during the impact. High levels of plasticity on gypsum have been also detected [7] on shocked mixtures of calcite, silicate and gypsum.

3.2. *XRD analysis*

Before and after the shock experiment, the sample was subjected to an analysis by XRD (Figure 2) showing clearly the dehydration of gypsum and formation of bassanite.

It can be seen that the starting crystal structure of $CaSO_4{\cdot}2H_2O$ was preserved after the precompression, which agrees with evidence obtained by other researchers on gypsum compressed at moderate pressure and low temperatures ($T < 70°C$) (see Figure 1 of the article of Mirwald, 2008).[15] By contrast, the quantitative phase analysis by Rietveld refinement of the XRD corresponding to the impacted powder (Table 1) shows the presence of gypsum, $CaSO_4{\cdot}2H_2O$, and β-bassanite, $CaSO_4{\cdot}0.5H_2O$, both in proportions near to 50-weight %.

Numerous studies support the hypothesis that gypsum dehydration follows the sequence gypsum → basanite → anhydrite, when it is quasistatically heated up to 400°C in different environments.[16,17] Some others show that this dehydration sequence is fulfilled, when the gypsum sample is also subjected to high pressures. For instance, gypsum samples subjected to stresses up 3.0 GPa and at low strain rate regime ($10^{-4}\,s^{-1}$ to $10^{-5}\,s^{-1}$) in the temperature interval 80–300°C,[15] or samples subjected to compression in a diamond anvil cell up to 25 GPa and 360°C [18] have been reported to show complete dehydration. Our X-ray analysis of the

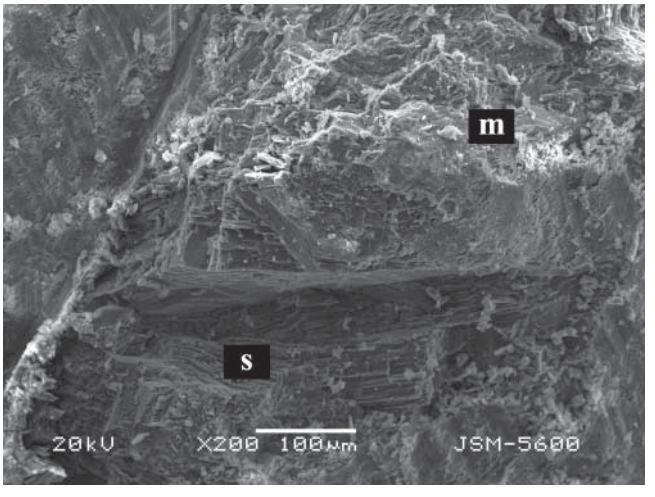

Figure 1. Micrograph taken on an area of fractured surface of recovered gypsum sample. Slip bands and apparently melted material are observed (labeled as s and m, respectively).

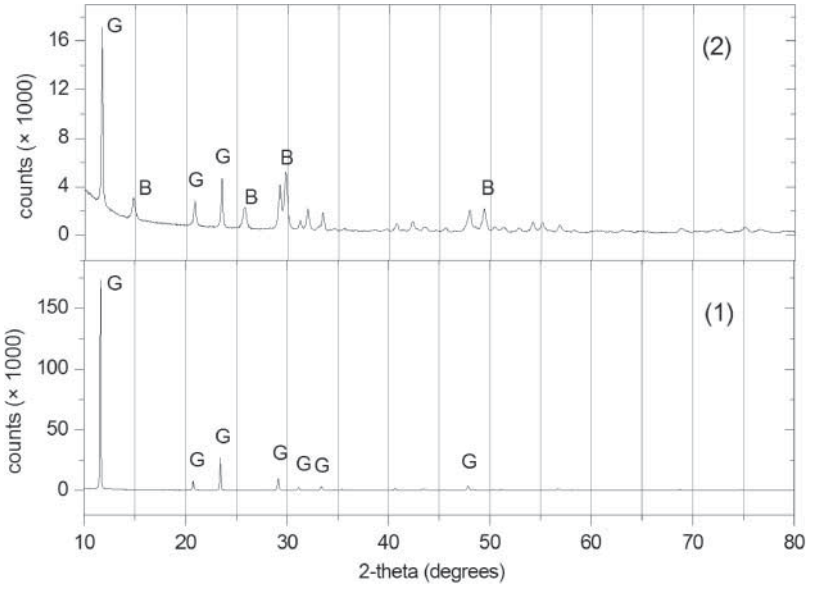

Figure 2. X ray diffractograms before (1) and after (2) shock compression experiment.

Table 1. Crystallographic data and quantitative analysis of phases present in the impacted sample.

Phase	Gypsum	Bassanite
Chemical formula	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 0.5H_2O$
ICSD/PDF files	27876/33–311	73262/24–1068
Crystal system	Monoclinic	Trigonal/rhombohedral
Space group	I 2/*c* (No. 15)	P 3_1 2 1 (No. 152)
Z	4	3
Cell parameters (Å/°)	$a = 5.705(2)$ $b = 15.255(5)$ $\beta = 118.52(1)$ $c = 6.545(3)$	$a = 6.946(2)$ $c = 6.352(2)$
V (Å^3)	500.5(5)	265.4(3)
Weight content (%)	50.3(4)	49.7(4)

Note: Global reliability factors: $R_{wp} = 0.088$, $R_p = 0.062$, $\chi^2 = 5.231$.

gypsum sample compressed dynamically does not indicate the presence of a detectable amount of anhydrite ($CaSO_4$) or any of their high pressure and temperature polymorphs.[19] Therefore, it seems that the impact only caused the partial dehydration of the gypsum, notwithstanding the extreme conditions of pressure and temperature to which it was subjected.[11] In general, it is observed that the phases generated by the shock waves appear heterogeneously distributed along the impacted sample.[1] Some of them can be detected only in very small quantities using microscopic analysis techniques.[20]

3.3. *MRS analysis*

Since the MRS analysis technique enables very precise detection of the distribution of small quantities of different phases in the cases of ceramic materials and minerals submitted to physic-ochemical transformations, in the present research we used this looking for possible new phases generated at high pressures and temperatures into the gypsum mineral studied.

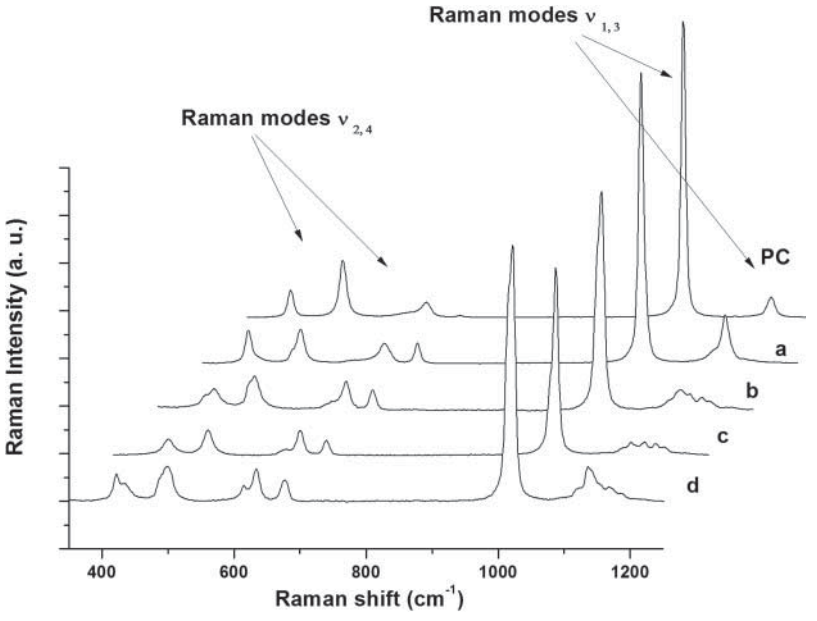

Figure 3. Raman Spectra taken at different points of fractured face of recovered sample. The PC spectrum corresponds to the pre-compressed sample.

In Figure 3, we show Raman spectra of pre-compressed gypsum powders before the impact. The spectra shape coincides with that reported for gypsum from Cave of Swords at Naica, México (RUFF data base, 2015).[21] On the other hand, the peak positions assigned by us in the 400–1200 cm^{-1} interval, matches with those reported by Buzgar et al.[22] for the internal vibration modes of SO_4 group on gypsum mineral exited with a λ of 532 nm. The most intense peak, centered at 1010 cm^{-1}, corresponds to the ν_1 symmetric stretch vibration mode of SO_4 group, the peak at 1143 cm^{-1} corresponds to ν_3 asymmetric stretch vibration mode and the doublets at 416, 495 cm^{-1} and 622, 674 cm^{-1} corresponds to the ν_2 symmetric bending and ν_4 asymmetric bending vibrations, respectively.

The Raman Spectra along 200–1200 cm^{-1} interval (Figure 3) were taken at four different sites of fractured face of the shocked sample, together with the spectrum of pre-compressed powders. The spectra labeled as (a) and (d) in Figure 3 were taken at the edges of the fractured face, and the spectra labeled as b and c correspond to two middle zones of the fractured face.

Clearly, there are marked differences in the Raman features of the spectra of Figure 3. A plausible interpretation of this result is that the impact process caused a series of phase transformations in heterogeneous way along the sample. This assumption can be better supported if we analyze in detail the differences between the peaks associated with the symmetric stretching mode ν_1 of SO_4 group.

In Figure 4 we have shown the deconvolution of peak labeled as (b). The shape of this band can be matched with three Lorentzian-shape peaks centered at 1010, 1015 and 1019 cm^{-1}. According to the studies by Raman spectroscopy performed by Buzgar et al.(2009) [22] in anhydrous and hydrated sulfates, the position of these peaks could correspond to gypsum, bassanite and anhydrite, respectively.

This result seems to confirm that in the impacted sample, at least, a third crystalline phase anhydrite coexists with gypsum and bassanite in such small amounts that could not be detected by XRD. Recently, an analysis by Raman spectroscopy performed by Bell & Zolensky [23]

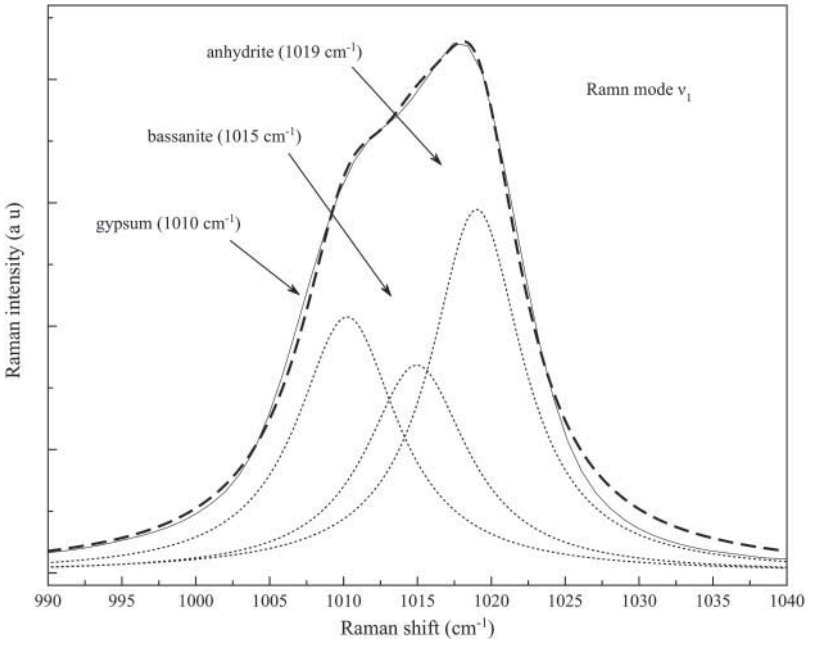

Figure 4. Deconvolution of peaks assigned to ν_1 Raman mode of the spectrum labeled as (b) in Figure 3.

suggested the transformation of gypsum to anhydrite during the dynamic compression of mixtures of the synthetic compounds $CaSO_4 \cdot 2H_2O$ and SiO_2.

The process of transformation of gypsum to bassanite and bassanite to anhydrite as a function of pressure has been analyzed in great detail through X-ray diffraction, Raman Spectroscopy and FTIR Spectroscopy in compression experiments using diamond anvil cells at high temperatures;[18,24] in contrast, there are very few studies of this kind of transformations under shock loading experiments. In this work we have presented some preliminary results related to such transformations. Within the second part of this research, we will carry out a more detailed analysis of the distribution and identification of the phases generated on the gypsum mineral, through shock loading experiments. In order to accomplish this fully, we will employ additional micro-analysis techniques. Finally, it is necessary to continue the study of the transformations of natural minerals subjected to impact processes to understand many aspects of the structure and composition of the earth crust. In particular, sulfur minerals are of great interest because of the catastrophic effects that can cause the decomposition and evaporation of those minerals, when natural ore deposits are impacted by some meteor, as has been suggested in the case of the Chicxulub impact.[25]

4. Conclusion

We investigate the shock effects on gypsum powders using SEM, XRD and MRS. The SEM analysis indicates that gypsum is highly plastic under dynamic compression. The XRD results show the partial transformation of the gypsum to bassanite induced by the shock compression. The MRS analysis suggests the heterogeneous distribution of mixtures of phases in the recovered sample, possibly anhydrite, basanite and gypsum.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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