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Raman analysis of an impacted $\alpha$-GeO$_2$–H$_2$O mixture

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Through a Raman analysis, we detected polymorphism at high pressure on mixtures of $\alpha$-GeO$_2$ microcrystalline powder and water under impact experiments with a single-stage gas gun. The Raman measurements taken from recovered samples show two vibrational modes associated with water-related species. After the impact, the size of the $\alpha$-GeO$_2$ crystallites was approximately 10 times higher showing molten zones and a lot of porous faces. Raman examination showed some unknown peaks possibly associated with other GeO$_2$ polymorphs detected by X-ray diffraction experiments and perhaps stabilized in the porous of the $\alpha$-GeO$_2$ crystallites.

Keywords: phase transformation; shock waves; germanium dioxide; polymorphism

1. Introduction

The study of chemical reactions and phase transformations occurring at high pressures and temperatures is an interesting topic in fields such as earth and planetary sciences as well as materials science. Concerning the first two cases, particular importance has been given to the phenomena of forming minerals which appear during the impact processes of meteors with earth or planets and, also, the physicochemical processes occurring between minerals inside the earth mantle [1]. In the case of materials science, two main motivations are focussed for the research of this kind of transformations: one of them deals with the basic physical and chemical principles of materials working at high pressure/temperatures, while the other is concerned with the rise of new materials having novel physical properties and potential technological applications [2].

In general, from the experimental point of view, two techniques are used to induce chemical reactions and phase transformations at high pressures and temperatures: the static compression method and the shock compression method. In the first method, the pressure is applied to the sample gradually by using devices such as diamond anvil cells, where the hydrostatic pressure can reach as high as 100 GPa. Simultaneously, the sample can be heated in a controlled manner using, e.g. Nd-YAG kind of laser. In these experiments, the detection of the phases that formed during the compression process is done in situ, using different techniques such as Raman spectroscopy (RE)
and X-ray synchrotron diffraction, which are the most commonly used. The latter allows a more
detailed analysis of phase transformations induced by pressure and temperature applied in such a
small region corresponding to the small size of the samples, only a few tens of microns \[3\]. In the
shock compression method, high pressure pulses (microseconds in duration) are applied to the
sample by using explosives or projectiles traveling at speeds between 1 and 10 km/s and impact
the samples encapsulated in metal containers. In the latter case, gas guns of one or two stages have
been used; these are loaded with pressurized gases (He and H) that are released abruptly to acceler-
ate the projectiles \[4\]. Other devices have been recently developed that speed up magnetically
metal projectiles that reach velocities somewhat higher than 20 km/s \[5\]. Whether using explo-
sives or projectile accelerator devices, the shock compression method can induce physicochemical
changes on the sample, in time scales at the peak pressure state (shock-induced processes) or can
result in the generation of highly activated materials that significantly enhanced their chemical
reactivity during post-shock thermal treatments (shock-assisted processes) \[6\]. To estimate the
peak shock pressure and mean temperature on the metal bulk containers, numerical models have
been developed for a specific experimental setup in the case of experiments with explosives \[7,8\].
In experiments with projectiles, the peak shock pressure on the metal container is calculated by
applying the impedance match method \[4\] and the mean bulk temperature is measured directly
by spectroscopic techniques \[9\] or estimated from high pressure/temperature equation of state
of impacted materials. This methodology, together with the microstructural analysis of sam-
ple recovered after impact, allows having an overview of the conditions under which there are
phase transformations and chemical reactions in the materials under study. Although considerable
progress has been made to explain from a theoretical framework mechanism that gives rise to
phase transformations and chemical reactions for mixtures of powders of geophysical and tech-
nological interest \[10\], it is still necessary to verify whether the models developed can be applied
to other systems, as for example porous samples of rare-earth oxides or of elements of group IV.

Recently, our group has initiated a systematic study of phase transformations that occur in oxides
porous samples of type XO$_2$ (X = Ge, Sn, Pb), which were recovered after being subjected to
impact processes by the use of one-stage gas gun. These compounds have the advantage that
there is enough information in the literature concerning the phases that are generated in them,
when they are subjected to high pressures in diamond cells. In particular, the GeO$_2$ exhibits
a large variety of amorphous and liquid phases under pressure \[11\]. In a previous work, we
have reported fusion processes, phase transformations and grain growth in a recovered sample
of mixtures of microcrystalline $\alpha$-GeO$_2$ powders and water, submitted to high pressure planar
shock waves \[12\]. After impact, 88% of the sample is $\alpha$-GeO$_2$, and the remaining (12%) was
found to be transformed to other polymorphs. The amounts of the other phases reported were:
6.0% of monoclinic GeO$_2$ (S.G. P2$_1$/c); 4.9% of CaCl$_2$-type GeO$_2$ (S.G. Pnmm); and 1.1% of
rutile-type GeO$_2$ (S.G. P4$_2$/mnm). This quantitative phase analysis was performed by Rietveld
refinement using conventional X-ray powder diffraction measurements on the recovered sample
\[12\]. All these phases have already been reported qualitatively by different authors, but from static
pressure experiments \[13\]. These results indicate that the shock waves cause the sample to reach
temperatures as high or higher than the melting point of $\alpha$-GeO$_2$ ($T \geq 1389$ K), and pressures at
least equal to the transition of rutile-type GeO$_2$ to CaCl$_2$-type GeO$_2$ ($P \geq 26$ GPa).

The aim of the present research is to report additional data on these phase transformations by
performing Raman, and scanning electron microscopy (SEM) measurements.

2. Methods

A series of shock experiments on mixtures of deionized water and microcrystalline alpha-GeO$_2$
powders were carried out using the one-stage light gas gun installed at the High Pressure
Laboratory of the Instituto de Física at the Universidad Nacional Autónoma de México [14].

The propellant gas that was employed in all cases was helium. The projectile and target designs are described elsewhere [12]. With this arrangement, it is possible to perform planar shock-wave experiment by impacting a stainless steel plate against a target which consists of three stainless steel capsule chambers hermetically sealed. Each chamber contains a specific amount of microcrystalline powder of $\alpha$-GeO$_2$. In order to promote particle interactions during shock-loading conditions, less dense samples were prepared, mixing $\alpha$-GeO$_2$ powders (Sigma-Aldrich 99.99%) with different proportions of deionized water. For the experiment, we employed a plate of 106 g with a thickness of 3.46 mm. The plate was mounted on the nose of a nylon projectile (impact 2000) accelerated to a projectile velocity of 829 m/s; under these conditions, by impedance matching, the peak pressure was estimated to be 14 GPa in the target. SEM observations were performed on a JEOL JSM 5600 LV microscope. Raman spectra were measured with a Renishaw Ramascope 2000 spectrometer by employing a 514.5 nm argon laser line, with a spatial resolution of 1–2 $\mu$m. Light was focussed 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$^2$. X-ray powder diffraction of the recovered sample was measured at room temperature in a Bruker D8 Advance diffractometer; Cu Ka$_1$ radiation, and goniometer with a LynxEye detector. The data were collected from $2\theta = 7 - 110^\circ$, with a step size of 0.019$^\circ$ and operating conditions of 35 kV and 25 mA in the X-ray generator [12].

3. Results and discussion

Figure 1(a,b) shows at the same amplification, SEM images of powders of the $\alpha$-GeO$_2$ phase before and after the shock event, respectively. Before impact, the $\alpha$-GeO$_2$ phase shows rhombohedrally faceted crystallites of 1 $\mu$m size. In Figure 1(b), the sample appears with molten zones in faceted crystals showing [100] and [101] forms with size around 10 $\mu$m. It seems that this is due to collisions between particles induced by the shock event. From those figures, it is evident that the impact induced the growth of microcrystals of tens of microns. Moreover, a most detailed SEM analysis of the recovered sample shows zones characterized by partially molten-particle aggregates (Figure 2(a)) and zones with well-crystallized grains (Figure 2(b)). This complex process leads to a heterogeneous distribution of particles of different sizes and, as it will be discussed later, to different high pressure phases associated with GeO$_2$ as well as to chemical reactions between microcrystalline powders of $\alpha$-GeO$_2$ and the added water of the mixture. All this is a consequence of localized pressure gradients and elevated temperatures induced on the sample by the shock pressure. This type of transformations is similar to other previously reported for low-density porous materials [15,16]. In order to detect the distribution of phases generated by the shock waves in the sample, a detailed Raman analysis in different zones was performed.

By analyzing different points of the sample before impact, we obtain the characteristic Raman spectrum of the $\alpha$-GeO$_2$ phase (Figure 3(a)), where the inset is an image obtained by optical microscopy that corresponds to the analyzed zone. However, when measuring the powder of the sample recovered, significant variations on the shape of the Raman spectra were found (Figure 3(b)). In this figure, four Raman spectra are plotted and the inset image shows a cluster of microcrystals at which these Raman spectra were taken at four different points. Besides the characteristic bands corresponding to the $\alpha$-GeO$_2$ phase, some additional peaks appear, and their presence, intensity and position differ in each spectrum. For some faceted crystallites, we obtained spectra with a combination of narrow and broad bands (Figure 3(c)) what was interpreted as due to the presence of a $\alpha$-GeO$_2$ crystallite (narrow bands) with amorphous GeO$_2$ (broad bands) which could have been formed and stabilized in the porous part of the faceted crystallite (inset SEM image) after the change produced by the shock wave. This kind of spectra has been observed
Figure 1. (a) Panoramic SEM image of $\alpha$-GeO$_2$ sample before impact. (b) Sample after impact appears with high degree of molten zones with crystallites of dimensions bigger than those from starting $\alpha$-GeO$_2$ obtained after impact.

by other researchers on samples of crystalline $\alpha$-GeO$_2$ powders submitted to static compression and released in the range from 8 to 20 GPa [17]; and from experiments in which monolithic powders of $\alpha$-GeO$_2$ were amorphized by impact [18]. This kind of spectra has been observed by other researchers on samples of crystalline $\alpha$-GeO$_2$ powders submitted to static compression and released in the range from 8 to 20 GPa [19] and from experiments in which monolithic powders of $\alpha$-GeO$_2$ were amorphized by impact [17]. The Raman spectrum plotted in Figure 4(a) corresponds to the inset image of $\alpha$-GeO$_2$ crystal (signaled with an arrow) with well-defined faces. The crystal forms typically observed in $\alpha$-GeO$_2$ crystals are represented also in the inset image in which it is possible to appreciate the characteristic rhombohedral symmetry. This Raman spectrum presents well-defined bands which belong to $\alpha$-GeO$_2$ with other additional peaks marked with arrows in Figure 4(a). The description of the spectrum is as follows: a double degenerate modes of E symmetry split in transverse optic (TO) and longitudinal optic (LO) modes of $\alpha$-GeO$_2$ are localized at the values 121 (TO + LO), 165 (TO + LO), 210 (TO), 325 (TO and a shocking $A_1$ mode), 517 (LO), 589 (LO) 855 (TO), 962 (TO), 989 (LO) cm$^{-1}$ and the symmetric shocking $A_1$ modes at 262, 442, 880 cm$^{-1}$ being the peak at 442 cm$^{-1}$, a very intense band that characterizes
Figure 2. (a) Sample after impact appears with high degree of molten zones similar to those shown in Figure 1(b). (b) Sample after impact appears with low degree of molten zones. Faceted crystals of $\alpha$-GeO$_2$ showing typically $\{100\}$ and $\{101\}$ forms with size around 10 $\mu$m can be seen.

This polymorph [18,20,21] accompanied by a peak and a shoulder at 370–390 cm$^{-1}$, assigned to other E symmetry (LO) and (TO) modes of $\alpha$-GeO$_2$ by Scott [20]. It is worthy to note that three additional peaks have been detected; a broad band between 700 and 800 cm$^{-1}$, at higher frequencies, above 1150 cm$^{-1}$, an unassigned peak to any known GeO$_2$ phase, and other broad band at 1200–1700 cm$^{-1}$. A deconvolution of the broad band between 700 and 800 cm$^{-1}$ (Figure 4(b)) gives two bands; one at 741 and the other at 771 cm$^{-1}$. According to the Raman active modes for rutile-type GeO$_2$ given by $\Gamma = A_{1g} + B_{1g} + B_{2g} + E$, the band at 741 cm$^{-1}$ could be assigned to the active Raman mode $A_{1g}$ [22]. In this case, the change in the Raman shift corresponding to the $A_{1g}$ mode from 701 cm$^{-1}$ to a higher value could be a consequence of the pressure applied during the impact [18,22]. These and other bands for different GeO$_2$ polymorphs, which have been characterized by RE [18–22], are summarized in Table 1. The band localized at 771 cm$^{-1}$, has a position closer to the one reported for a peak assigned to the stretching mode of the Ge–OH complex (769 cm$^{-1}$) in GeO$_2$ gels [23]. Since in our experiment, the sample of $\alpha$-GeO$_2$ under shock compression was mixed with water, it is reasonable to expect that water species appear in
Figure 3. (a) Representative Raman spectrum of the $\alpha$-GeO$_2$ obtained by analyzing different points of the sample before impact. Inset figure is an image obtained by optical microscopy that corresponds to the analyzed zone. (b) Raman spectra obtained from the recovered sample. Significant variations on the shape of the bands can be seen. The inset image shows a cluster of microcrystals for which these Raman spectra were taken at four different points. (c) Representative Raman spectrum for some faceted crystallites is presented in the inset image. Narrow and broad bands were interpreted as due to the presence of a $\alpha$-GeO$_2$ crystallite (narrow bands) with amorphous GeO$_2$ (broad bands), which could have been formed and stabilized in the porous part of the faceted crystallite after the change produced by the shock wave.

Under shock pressure, it has been proposed that the water molecule transforms according to the following dissociations reactions [24–26]:

\[ 2\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_3\text{O}^+ \]  
\[ \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+ \]  

So, the presence of hydroxyl (OH$^-$), hydronium (H$_3$O$^+$) and protons (H$^+$) during the impact event, gives the possibility for chemical reactions between microcrystalline $\alpha$-GeO$_2$ (or polymorphs) and water. This could be the origin of the hydrous-species encountered in this work in a single micro-crystal (Figure 4(a)). After deconvolution, two bands can be appreciated in Figure 4(c). One of them, centered at 1592 cm$^{-1}$, could be assigned to the E anti-symmetric vibrational mode of hydronium ion H$_3$O$^+$, possibly adsorbed at the surface of $\alpha$-GeO$_2$ [27,28],
Figure 4. (a) Raman spectrum corresponding to the inset image of α-GeO₂ crystal (signaled with an arrow) with well-defined faces. The crystal forms typically observed in α-GeO₂ crystals are also represented in the inset image in which it is possible to appreciate the characteristic rhombohedral symmetry. (b) The deconvolution of the broad band between 700 and 800 cm⁻¹ gives two bands: one at 741 and the other at 771 cm⁻¹. The band at 741 cm⁻¹ could be assigned to the active Raman mode A₁g for rutile-type GeO₂ [22]. (c) Deconvolution of two bands can be appreciated: one of them, centered at 1592 cm⁻¹, could be assigned to the E anti-symmetric vibrational mode of hydronium ion H₃O⁺, possibly adsorbed at the surface of α-GeO₂.

Table 1. Active modes of vibration (cm⁻¹) observed in RE for GeO₂ polymorphs. The symmetry mode corresponding for each Raman shift is written below its value.

<table>
<thead>
<tr>
<th>GeO₂ polymorph</th>
<th>Raman shift (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Quartz-type GeO₂ [9–11]</td>
<td>973 960 881 860 593 516 444 330 263 212 166 123</td>
</tr>
<tr>
<td>Rutile-type GeO₂ (at 0.1 MPa) [12]</td>
<td>E_LO  E_TO  A₁  E_TO  E_LO  E_LO  A₁  A₁, E_TO  A₁  E_TO  E²  E⁵</td>
</tr>
<tr>
<td>CaCl₂-type GeO₂ (at 34.2 GPa) [12]</td>
<td>1012 815 155</td>
</tr>
<tr>
<td></td>
<td>B₁g  A₁g</td>
</tr>
</tbody>
</table>

whereas the other peak, centered at 1512 cm⁻¹, could not be assigned to other vibrational modes of the hydronium or others hydrous-species within the GeO₂ matrix.

The experimental design described in this and in the previous work [12], allows studying the effect of shock waves in three chambers impacted simultaneously, in such a way that the same impact conditions can be ensured on porous oxide samples of different densities. The analysis of the recovered samples, by means of some common techniques such as X-ray powder diffractometry, SEM, micro-RE and others, allows to determine the type of physicochemical changes
induced by the shock compression. In order to detect the pressure and temperatures generated during and/or after the impact on complex systems such as mixtures of reactive compounds, it could be used as temperature and pressure sensors, ceramic oxides as those of group IV, knowing in advance that all of them show the following phase transformation sequence [29]:

\[
\alpha-\text{GeO}_2 (P3_2 2) \rightarrow \text{rutile-type}(P4_2/mnm \text{ at } 7 \text{ GPa}) \rightarrow \text{CaCl}_2\text{-type} \\
(Pnnm \text{ at } 26 \text{ GPa}) \rightarrow \alpha-\text{PbO}_2\text{-type} (Pbcn \text{ at } 44 \text{ GPa}) \rightarrow \text{pyrite-type} (Pa-3 \text{ at } 70 \text{ GPa})
\]

Following this experimental procedure, it is possible to explore interaction processes between particles of different sizes and/or hardness, in microcrystalline or nano-crystalline, of the same phase or of different phases and of course, chemical reactions between solid–solid, solid–liquid or other kind of reactive powder mixtures as has been pointed out by Bastanov [30]. Our group has started a systematic research work to explore the possible application of this kind of oxides as a high pressure–temperature sensors on impact experiments.

4. Conclusions

The Raman analysis performed in this investigation, allowed us to detect crystalline and crystalline-amorph mixed phases on impacted samples of \(\alpha-\text{GeO}_2\). We detected a complex and heterogeneous distribution of those phases on the recovered sample. The Raman spectra of individual micro-crystals (tens of microns) showed all bands associated with longitudinal and traverse optic modes of \(\alpha-\text{GeO}_2\) together with additional bands. The bands at 395, 1150 and 1500 cm\(^{-1}\) could not be assigned to any known species of GeO\(_2\) or other hydrous-species within GeO\(_2\). The bands at 471 and at 441 cm\(^{-1}\) were assigned as follows: the former to the stretching mode of the GeO-OH in the crystal network and the second to the active Raman mode A\(_{1g}\) of rutile GeO\(_2\) (400 cm\(^{-1}\)), shifted to a higher frequency, possibly due to the effect of impact pressure. Our analysis shows that the impact also induces chemical reactions between microcrystalline powders and the water of the mixture, allowing the formation of hydrous species into the amorphous or crystalline structures of GeO\(_2\). SEM observations unequivocally show grain growth with partially melted crystalline and well-defined crystalline zones on impacted samples of \(\alpha-\text{GeO}_2\).

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References

The structure of amorphous, crystalline and liquid GeO

M. Micoulaut, L. Cormier, and G.S. Henderson,

Phonon spectra of quartz isomorphs

W. Dultz, M. Quilichini, J.F. Scott, and G. Lehman,

Structural studies of gels and gel-glasses in SiO

S.P. Mukherjee and S.K. Sharma,

Ferroelastic phase transition in rutile-type germanium

J. Haines, J.M. Léger, C. Chateau, R. Bini, and L. Ulivi,

Shock-wave properties and high-pressure equations of state of geophysically important materials

M. Boslough and R.A. Graham,

Shock-induced chemical

M.B. Boslough and R.A. Graham,

Submicrosecond shock-induced chemical reactions in solids: First real-time

M. Madon, Ph. Gillet, Ch. Julian, and G.D. Price,

The vibrational spectrum of the hydronium ion in hydronium perchlorate

B. Desbat and P.V. Huong,

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V.B. Prakapenka, L.S. Dubrovinsky, G. Shen, M.L. Rivers, S.R. Sutton, V. Dimitriev, H.P. Weber, and T. Le Bihan,

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Grain growth and phase transformations

I. Rosales, C. Thions-Renero, E. Martinez, L. Bucio, and E. Orozco,

Shock compression of liquid hydrazine

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Spontaneous Raman scattering from shocked water

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K.S. Vandersall and N.N. Thadhani,

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V.B. Prakapenka, L.S. Dubrovinsky, G. Shen, M.L. Rivers, S.R. Sutton, V. Dimitriev, H.P. Weber, and T. Le Bihan,

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