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Research paper

High pressure studies of potassium perchlorate

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ABSTRACT

Two experiments are reported on $KClO_4$ at extreme conditions. A static high pressure Raman study was first conducted to 18.9 GPa. Evidence for at least two new phases was observed: one between 2.4 and 7.7 GPa (possibly sluggish), and the second near 11.7 GPa. Then, the X-ray induced decomposition rate of potassium perchlorate $\left(KClO_4 \xrightarrow{h\nu} KCl + 2O_2\right)$ was studied up to 15.2 GPa. The time-dependent growth of KCl and O_2 was monitored. The decomposition rate slowed at higher pressures. We present the first direct evidence for O_2 crystallization at higher pressures, demonstrating that O_2 molecules aggregate at high pressure.

1. Introduction

One critical factor determining the rate and progress of chemical reactions is the ability to rapidly and efficiently deliver mobile oxidants/reactants such as molecular oxygen. Related to this, an outstanding challenge in chemistry pertains to better understanding the rapid production and diffusion of oxygen during detonation conditions inside isolated chambers/shells. During detonation, a shockwave is generated which impresses very high pressures (of the order of 10 GPa) and high temperatures upon reactant molecules [1]. Gaining insight into the mobility of oxygen [2] at extreme conditions of pressure and temperature, therefore, would aid explosives chemistry under extreme conditions due to the critical need for rapid delivery of oxygen as a reactant. Also, understanding how mobile reactants such as hydrogen and oxygen [3], or fluorine and oxygen mix or segregate and react [4] under extreme conditions would be very beneficial for developing novel routes of chemical synthesis.

In this spirit, we have been investigating the X-ray induced decomposition of potassium halates ($KClO_3$ [2,5–8], $KClO_4$ [3,4,9], $KBrO_3$ [9], and KIO_3 [8,9]) into molecular oxygen and potassium chloride using penetrating, highly focused, and highly ionizing white [1,2,4,6] and monochromatic hard X-rays [7,8] from the Advanced Photon Source (APS). For example, we have observed the following acatalytic chemical reaction when irradiating $KClO_4$ (a powerful oxidizer):

$$KClO_4 \xrightarrow{h\nu} KCl + 2O_2 \quad [5,6]$$

The objective of our efforts entailed seeking decomposition reactions that can be photochemically induced to produce mobile reactants such as O_2 [2–9], N_2 [10], H_2 [3,6], Cl_2 [11,12], and most recently F_2 [4,13] inside a diamond anvil cell (DAC) and other sealed chambers, *in situ*. As we have been using $KClO_4$ extensively in our experiments to produce molecular oxygen *in situ* [9], better-understanding its high pressure behavior in its own right would be highly advantageous for our efforts to develop *useful hard X-ray photochemistry* [2–13].

In earlier studies, we observed a strong phase-dependence in the X-ray induced decomposition rate of $KClO_3$ at high pressure [7] which was later theoretically modeled [14]. In that theoretical study, it was ascertained that $KClO_3$ likely decomposes into $KClO_4$ when in the high pressure rhombohedral phase (above 2 GPa) [14] which agreed very well with our experimental X-ray decomposition studies [7]. The presumed reaction is [14]:

$$4KClO_{3(\text{rhombohedral})} \xrightarrow{h\nu} 3KClO_{4(\text{orthorhombic})} + KCl_{(B2)}$$

Thus, to better understand the decomposition mechanisms associated with $KClO_3$ that produce oxygen under extreme conditions, it is important to understand the decomposition of $KClO_4$ under similar conditions. We were also interested in determining if there were any phase transitions associated with $KClO_4$ which might then have phase dependent decomposition rates as well. Potassium perchlorate is an important oxidizer for a variety of chemical reactions including those associated with energetic materials [1] and thus, in some sense, our efforts would aid in better-understanding the production of oxygen in myriad oxidation reactions at high pressure including a better understanding of the performance of this compound during shock wave conditions.

Prior studies have observed that $KClO_4$ decomposes faster than $KClO_3$ [9] and, as such, the former compound can be useful in more

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rapidly delivering oxygen *in situ*. Earlier studies demonstrated that pressure can be a useful mechanism to slow hard X-ray induced decomposition reactions [15,16], offering the potential of chemical control. Yet, $KClO_4$ has been little studied at high pressure and ambient temperature to the best of our knowledge. There is one high pressure study that we are aware of [17] up to 1.5 GPa (beyond our own earlier studies [3,4,9]) which was based on high temperature differential thermal analysis. Another study [18] used the oxidizer to synthesize a superconductor, $(Ca, K)_2CuO_2C1_2$, via high pressure (5 GPa) and high temperature 900 °C. A third study examined the vibrational effects of $KMnO_4$ trapped in a potassium perchlorate matrix up to 2.4 GPa [19] but again, the focus of Refs. [18,19] did not entail any fundamental investigations of $KClO_4$ by itself with pressure.

Solid $KClO_4$ has a orthorhombic unit cell with *Pnma* symmetry [20,21], and with four formula units in the primitive cell. The ClO_4^- and K^+ ions are situated at sites with C_s symmetry [20] at ambient conditions; a = 8.866 Å, b = 5.666 Å and c = 7.254 Å [21]. No phase transitions were observed within the 1.5 GPa pressure range [17]. No phase transitions were observed in the $KMnO_4/KClO_4$ mixture up to 5.5 GPa though this is a different experimental system and thus not directly comparable to pure $KClO_4$ [19].

Therefore, with an aim of better-understanding the high pressure behavior of this very important oxidizer [22] including a determination of how pressure affects the hard X-ray induced decomposition rate, we conducted a static high pressure Raman experiment of $KClO_4$ – the first ever that we are aware of with pressure - and then performed synchrotron X-ray induced decomposition experiments by fixing the X-ray irradiating energy and altering the pressure using a diamond anvil cell (DAC).

2. Experimental

In both sets of experiments, a symmetric-style DAC was employed to pressurize the samples. Stainless steel gaskets were preindented to ~50 μm initial thickness using 300 μm culet diameter, ultralow fluorescence Raman-quality diamonds. Roughly 100 μm diameter holes were drilled into the gaskets via electric discharge machining to contain the samples. The first experiment (Raman spectroscopy) was performed at the Pravica group Raman facility. A Spectra Physics® Ar ion laser tuned to 514.5 nm and set at 100 mW (20 mW at the sample) served as the excitation source. Rayleigh scattered light was removed using a Kaiser optics® 514.5 nm holographic notch filter. Inelastically-scattered Raman light was directed into a Jobin Yvon U1000® spectrometer, dispersing the scattered light, which was then detected via an ISA Instruments Spectrum One® detector. The Raman spectrometer instrumental resolution was ~1 cm^{-1}. Acquisitions typically required 60 s to complete.

The second set of experiments was conducted at the 16 ID-B beamline of the High Pressure-Collaborative Access Team (HP-CAT) at the Advanced Photon Source (APS). Monochromatic hard X-rays (25 keV) were directed to decompose the $KClO_4$ sample at various pressures. The X-ray beam was ~5 μm × 5 μm in dimensions which was much smaller than the diameter of the sample hole (~100 μm). This enabled us to perform multiple experiments using the same sample at different virgin/unirradiated locations within the same sample [7,15,16]. If there were no longer any well-separated and virgin/unirradiated regions (based upon a visual check of the sample under a microscope) then the gasket was emptied, cleaned, reloaded, and repressurized with fresh unirradiated $KClO_4$.

No pressure transmitting medium was used in these experiments to match the conditions of our prior experiments using $KClO_4$ and $KClO_3$.

3. Results (Raman experiment)

The Raman spectra are presented as a function of pressure in Fig. 1. We note in passing that there was no evidence of laser induced damage in our samples over the course of our measurements. The ambient spectrum agrees well with that of prior studies [19,20]. The line near 460 cm^{-1} derives from the ν_2 vibration [19,20]. The modes near 640 cm^{-1} commence with the ν_2 vibration which split in the ordered crystal [19,20]. The peak near 940 cm^{-1} represents the ν_1 vibrational mode with A_1 symmetry [19,20]. Finally, two small peaks near 1090 and 1120 cm^{-1} stem from the ν_3 mode [19,20].

With increase in pressure, many lines shift toward higher energies and broaden, which is typical in many high pressure studies. Near 2.4 GPa, one new peak emerges near 760 cm^{-1}. As pressure was increased to 7.7 GPa, a new peak emerges near 1110 cm^{-1} (see Figs. 1 and 2) as the two peaks near 1130 and 1150 cm^{-1} start merging. The peak near 920 cm^{-1} begins to disappear.

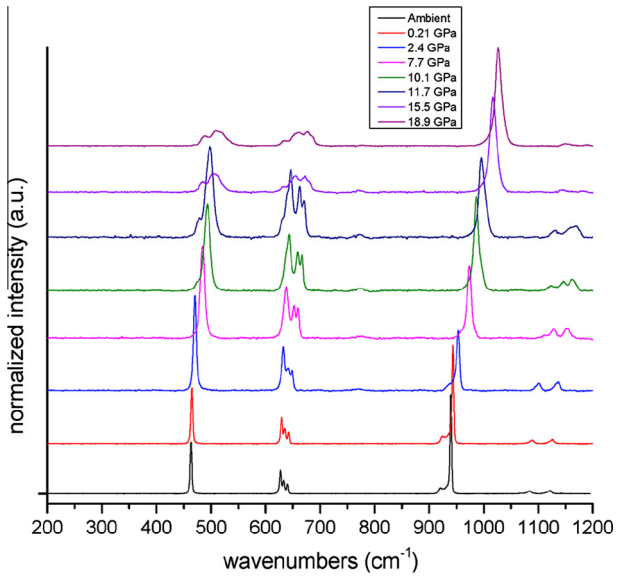

Fig. 1. Raman spectra of $KClO_4$ as a function of pressure in the low wavenumber region (200–1200 cm^{-1}). New peaks emerge in the 2.4. GPa and 7.7 GPa plots suggest a sluggish phase transition that commences near 2.4 GPa and ends around 7.7 GPa. Above 11.7 GPa, some (not all) of the Raman spectral modes are considerably broadened.

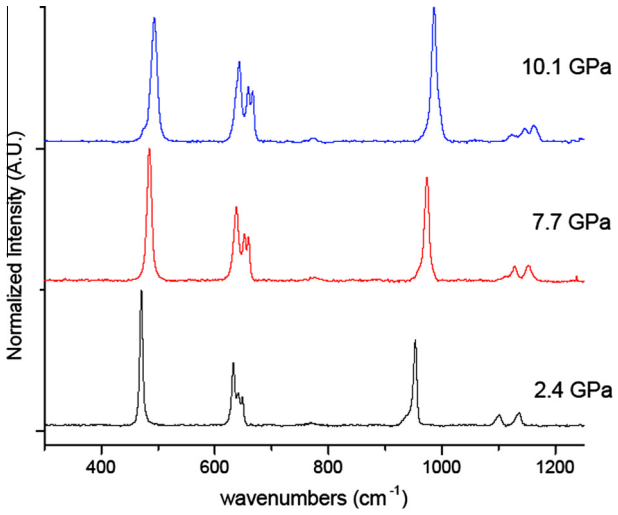

Fig. 2. Selected Raman plots from Fig. 1 better illustrating the new peak that appears near 1120 cm^{-1} in the 10.1 GPa plot.