

Phase diagram of Ammonium Nitrate

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Abstract. Ammonium Nitrate (AN) has often subjected to uses in improvised explosive devices, due to its wide availability as a fertilizer and its capability of becoming explosive with slight additions of organic and inorganic compounds. Yet, the origin of enhanced energetic properties of impure AN (or AN mixtures) is neither chemically unique nor well understood – resulting in rather catastrophic disasters in the past [1] and thereby a significant burden on safety in using ammonium nitrates even today. To remedy this situation, we have carried out an extensive study to investigate the phase stability of AN at high pressure and temperature, using diamond anvil cells and micro-Raman spectroscopy. The present results confirm the recently proposed phase IV-to-IV' transition above 17 GPa [2] and provide new constraints for the melting and phase diagram of AN to 40 GPa and 400 °C.

1. Introduction

Ammonium Nitrate (AN-NH₄NO₃) is widely used as a nitrogen source in the agricultural industry [3]. Slight additions of organic substances such as fuel oil and inorganic material such as Al powder make AN a powerful secondary explosive [4]. Because of its low price, easy access and strong oxidizing properties AN is regularly used as an improvised explosive device. Hence it is considered as a threat to homeland security and mitigating the threats associated with AN at blast relevant conditions is important. Similar to other explosives AN displays rich polymorphism with six polymorphic forms accessed at ambient pressures (P) from cryogenic temperatures (T) (phases VII [5] → V [6] → IV → III [7] → II → I [8]), a high P-T phase VI [9] and high P ambient T phase IV' [2]. Complexities in phase stabilities however have given rise to ambiguities in proposed transitions of these phases and their transition temperatures [10]. This poses challenges in understanding the phase and chemical changes of AN under various thermal and chemical conditions. The fact that several recent studies of AN [2,3,11] showing great level of diverse results requires the need for further studies.

We have investigated the phase and chemical stabilities of AN at static high P-T conditions in terms of studying the phase diagram and phase stabilities in different environments to gain insights into factors that cause chemical sensitivity and conditions limiting to detonation of AN.

2. Experimental

A small amount of crystalline AN from Sigma Aldrich (99.99% purity) together with a few ruby chips were loaded in a small hole (0.1-0.2 mm in diameter and 0.03-0.1 mm in thickness) of a gasket placed on a membrane diamond anvil cell (m-DAC). The internal pressure was determined from the R₁ shift of ruby luminescence using the pressure calculator program written by James Badro. The high temperatures were achieved by externally heating the m-DAC by wrapping a band heater around it and



the temperatures were measured using a K-type thermocouple that is in contact with one of the diamonds. Spatially resolved Raman spectra were collected using an in house confocal micro-Raman system in backscattering geometry with 514.5 nm excitation line of CW Ar⁺ ion laser.

Polycrystalline AN samples were loaded into stainless steel (SS) gaskets to perform isobaric heating experiments at selected pressures, isothermal compression studies at selected temperatures and temperature ramping experiments crisscrossing the IV-II-VI-VI phase boundaries. These results were then used to establish the new phase boundaries of AN over the pressure-temperature range of 40 GPa and 400 °C. In order to examine the effect of chemical environment on phase transitions we also performed studies of mixtures of AN with n-hexane (mimicking ANFO) and aluminum powders (mimicking Ammonal). ANFO samples were prepared by loading n-hexane into SS gaskets preloaded with a few small pieces of crystalline AN and ruby chips whereas Ammonal samples were prepared by loading AN polycrystals and ruby chips into the hole made in the Al powder packed layer placed on the wall of predrilled SS gaskets. In all these experiments the starting AN phase was confirmed to be in phase IV using Raman characteristics.

3. Results and Discussion

3.1. Phase transitions in AN

3.1.1. Isothermal compression studies at room temperature and elevated temperatures.

The ambient P-T phase IV of AN exhibits intense Raman modes, both internal and external, in agreement with the previous studies [12-14]. Figure 1 shows the pressure-induced Raman spectral changes of phase IV at ambient temperature which signifies the following characteristics. (i) All Raman modes show a blue shift upon compression. (ii) The skewed singlet of $\nu_4(\text{NO}_3^-)$ becomes a doublet above 2 GPa, of which the separation increases with pressure. (iii) New peaks emerge in the low frequency region ($\sim 390 \text{ cm}^{-1}$) above 17 GPa and they become intense with pressure. (iv) The very weak $\nu_2(\text{NH}_4^+)$ mode becomes stronger and more distinct above 17 GPa. The spectral changes that occur above 17 GPa confirm the occurrence of phase IV-IV' transition reported earlier [2]. As the spectral changes associated with this transition are reversible with a small pressure hysteresis ($\sim 16 \text{ GPa}$) with similar results obtained in repeated experiments, this rules out decomposition or other chemical reactions that could explain the observed changes.

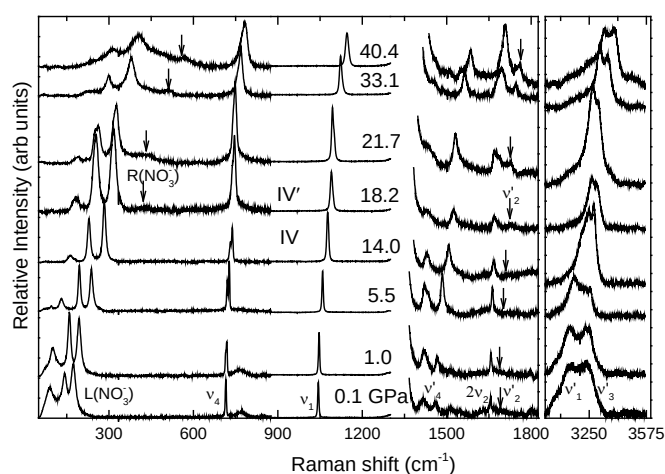


Figure 1. Pressure induced Raman spectra of polycrystal AN at room temperature that shows the phase IV-IV' transition above $\sim 17 \text{ GPa}$. Note that the arrows indicate the changes observed that was the basis for this transformation, L stands for lattice modes, $\nu_{1,2,\dots}$ to NO_3^- modes and $\nu_{1,2,\dots}$ to NH_4^+ modes.

Similar spectral changes were observed at higher temperatures to 300 °C, resulting the onset of IV-IV' phase transition at around 15-18 GPa depending on the temperatures. As expected, the room temperature phase IV transformed to phases II and I when the temperature was elevated above 100 and 200 °C respectively [3,11]. However that starting material did not affect the expected IV-IV'

transition above 15 GPa. Hence this transition is path independent. These results will be discussed later.

3.1.2. Temperature studies at selected pressures.

Temperature induced Raman studies of polycrystal AN during isobaric heating at ~ 1.6 GPa show the previously observed IV-II-I phase transformations at ~ 170 and 200 °C respectively. AN decomposes above ~ 256 °C to N_2 [15], N_2O [16] and H_2O [17] at this pressure, which occurs at the onset of the melt. However, no other phases were observed above 3 GPa upon isobaric heating, before the ambient temperature phases IV (3-15 GPa) and IV' (~ 25 GPa) decomposed. The decomposition temperatures increased to 15 GPa, as expected.

Based on the present and previous studies, we present the phase diagram for AN as shown in figure 2. Our study clearly agrees well with that of Bridgman's early work compared [3,9] to the recent x-ray diffraction studies [11]. However, no spectral evidence was found on both ill-defined phases III and VI, similar to recent x-ray study [11]. Interestingly, we observed a turnover in the decomposition/melt line above 20 GPa, suggesting that the decomposition in phase IV' is preceded by melting, unlike in phases I and IV. Use of relatively weak strengthened SS gaskets for all the experiments limits the present study to 450 °C and 40 GPa.

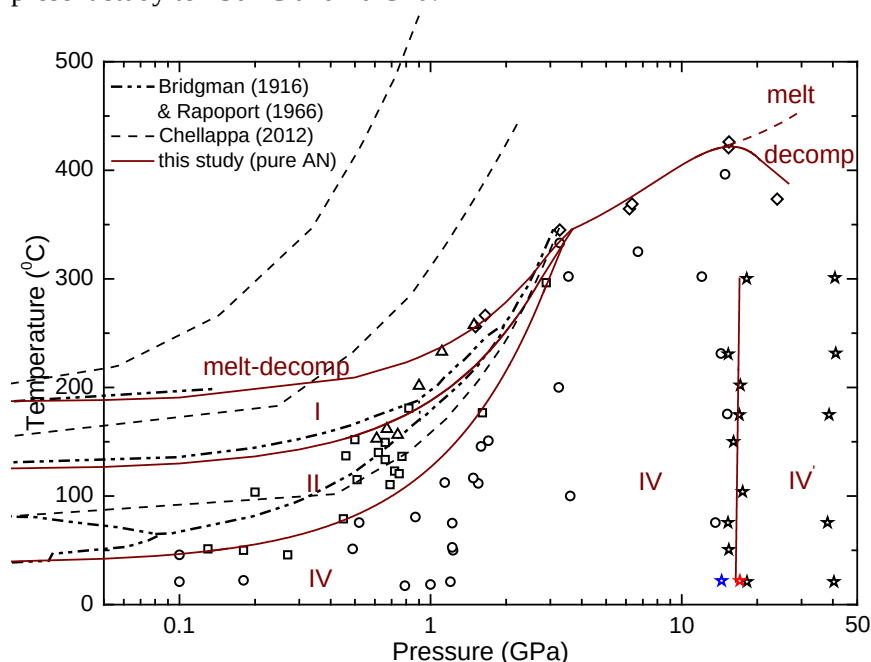


Figure 2. The proposed Phase Diagram of AN. The pressure axis is presented in log scale to account for low pressure transitions. The symbols show selected P-T regions where Raman spectra to the corresponding phases were obtained. Legend: ○-IV, □-II, Δ-I, ☆-IV', ◇-decomposition

The absence of the metastable IV-III transition is due to the low relative humidity in the environment as this transition depends on the moisture content. Differences in AN crystal growth orientations are reported to occur with variations in the preparation methods used, which in turn have an influence on the transition paths and the phase transformations, hence the absence of phase VI. Further compression studies with ANFO and Ammonal at ambient temperature have shown similar spectral characteristics that have been observed for pure AN under similar conditions, confirming phase IV-IV' transition above ~ 15 GPa. This transition is reported to occur because of a subtle difference in the hydrogen bonding network [2], The noticeable decrease observed in the vibrational frequency at the onset of this transition, if phase IV were to prevail, supports the strengthening of intermolecular hydrogen bonding corresponds to phase IV'. Since the environment can influence this transition, lower transition pressures are observed as expected, for ANFO (blue) and Ammonal (red) compared to pure AN as shown in figure 2. The anomaly in decomposition could be due to the structural differences of the phases.

3.2. Chemical effects on phase transitions

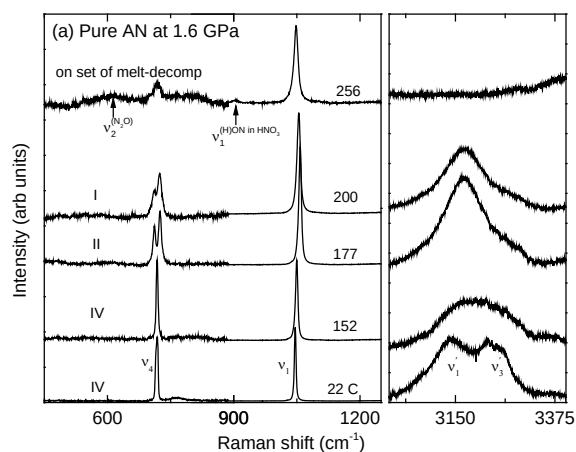
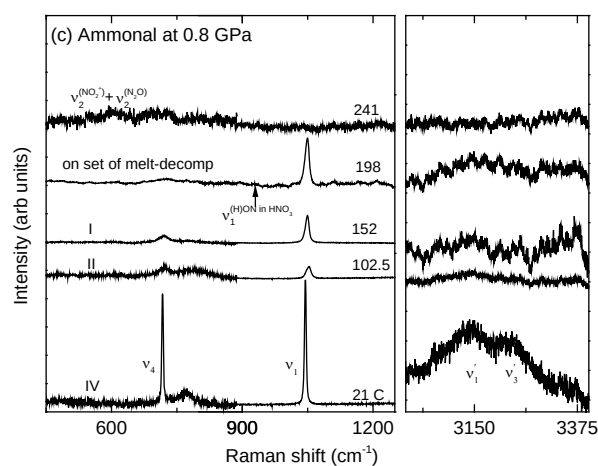
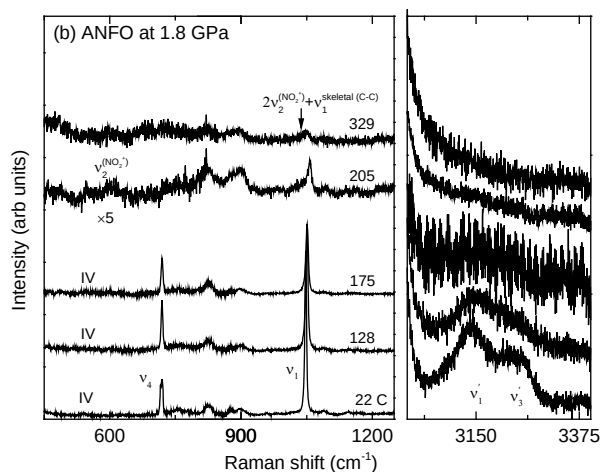


Figure 3. Comparison of Raman spectra of (a) pure AN (b) crystalline AN in n-hexane (ANFO) and (c) polycrystalline AN in Al envelope (Ammonal) in the bending (ν_4) and stretching (ν_1) regions of NO_3^- and stretching ($\nu_{1,3'}$) regions of NH_4^+ .



The Raman spectra of isobarically heated AN crystals in different environments are shown in figure 3. Both pure AN and AN in Ammonal behave similarly in regards to exhibiting similar solid–solid phase transitions before they undergo dissociation with transition temperatures for Ammonal being slightly lower than that of the pure, at comparable pressures. However, AN in ANFO does not show any other transitions before it decomposes. In comparison, both ANFO and Ammonal show relatively weaker Raman features compared to the pure. As expected, the onset of decomposition of AN in both ANFO and Ammonal take place at a lower temperature compared to that of the pure at comparable pressures: $T_{\text{ANFO}}^{1.8 \text{ GPa}} = 205 \text{ }^\circ\text{C}$; $T_{\text{pure}}^{1.6 \text{ GPa}} = 256 \text{ }^\circ\text{C}$; $T_{\text{Ammonal}}^{0.8 \text{ GPa}} = 200 \text{ }^\circ\text{C}$; $T_{\text{pure}}^{0.8 \text{ GPa}}\text{-projected} = 223 \text{ }^\circ\text{C}$. This is identified by the complete disappearance of ν_4 mode along with the appearance of Raman modes corresponding to decomposition. Evidence for NO_2^+ was found in both ANFO and Ammonal, upon decomposition. On the other hand N_2 was only observed upon the decomposition of pure AN. Both N_2O and HNO_3 were observed as decomposition products in both Ammonal and pure AN. All these observations conclude that chemical environment affects the phase transitions and melt-decomposition of AN, possibly by altering the decomposition mechanism.

The addition of sensitizers in AN has shown interesting effects on the phase transitions and chemical decomposition. Because of a great level of heterogeneities in ANFO systems related to morphology, composition and porosity, the predictive capability cannot be accomplished within simple models [18]. Adsorption of organic moiety onto the crystal system can influence decomposition via a low energy path and thereby the decomposition mechanisms. It is also reported that sample

preparation techniques [19] have affected the solid-solid phase transitions at low pressures, hence explain the enhanced thermal stability of phase IV of AN in ANFO. Compared to ANFO, however, Ammonal shows relatively weak sensitivity. Since the size of Al particles and grains as well as the extent of mixing have reported to influence the thermochemical efficiency of initiation mechanism [20] and the possibility of having a limited number of such weak interactions available at defect sites could explain the resemblance to pure AN in Ammonal samples.

4. Conclusion

Our extensive study on AN sheds ample evidence for the presence of phase IV' above 17 GPa at room temperature. We observed that pure AN decomposes at the onset of melting of phase I, whereas phase IV' shows an unusual turnover of the decomposition temperature well below the melting. Our results also showed strong chemical effects on the phase transitions and chemical decomposition of AN.

Acknowledgments

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