Pressure–Temperature Phase Diagram of Diglycine Perchlorate

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Abstract

Perchlorates (-ClO_4^-) are widely recognized for their strong oxidizing nature and diverse structural chemistry. Organic perchlorates exhibit weak intermolecular interactions that play a decisive role in modulating their physical properties and energetics, often contributing to exothermic behavior during synthesis, handling, and applications. This necessitates a detailed understanding of their dissociation mechanism and phase behaviour, which is still a gap area in this class of materials. Here we present our studies on diglycine perchlorate (DGPCl), a model organic perchlorate, carried out in two steps. First, the complete thermal dissociation mechanism of DGPCl was understood using a variety of techniques including vibrational spectroscopy, mass spectrometery (MS), differential scanning calorimetry and synchrotron XRD. Subsequently, using simultaneous high-pressure–high-temperature (HP-HT) investigations, we could successfully construct its PT-phase diagram, providing a comprehensive understanding of the phase behavior of this model compound. For these systematic studies in the range 1atm – 20 GPa and 30 – 400°C, a resistive heated symmetric diamond anvil cell, with type IIa diamond anvils was used to measure infrared and Raman spectra.

At ambient conditions, DGPCl crystallizes in a triclinic lattice (phase I), stabilized by O-H---O and N-H---O H-bonds, with significant ambiguity in the reported thermal behaviour [1, 2]. Our studies show a reversible melting transition near 130°C (phase II), followed by an irreversible transition at 170°C forming colored intermediate liquid phase (phase III). Above 220°C, it decomposes via evolution of gases, namely H_2O, CO_2, HCN, HCl, CO, CH_4, N_2O and NO. The gases have been identified using high-resolution rotational-vibrational spectroscopy and MS [3]. Our studies further reveal that the remnant residue (phase IV) comprises of ammonium perchlorate (AP- a highly potent oxidizer) along with carbon (a potential fuel), leading to an exothermic dissociation enthalpy of ~405 kJ mol^{-1} above 260°C. Using room temperature (RT)- HP studies, we further note that DGPCl shows multiple phase transitions leading to the formation of AP above 6 GPa without heating.

The PT – phase diagram of DGPCl, being reported for the first time for this class of compounds, constructed using HP-HT spectroscopic studies is shown in Fig.1a. For visual interpretation and to monitor gas evolution, we repeated the HP-HT studies under an optical microscope (see Fig.1b). DGPCl shows a sluggish melting behaviour, with completion shown by the melting line. The H-bonds get strengthened in the melt phase, as infered from CH, OH, NH vibrational modes. Unlike RT-HP studies, heating at HP reveals the formation of an unique combination of AP and AN in the intermediate phase in addition to an imine complex, just prior to dissociation, as shown in Fig.1c. We find that all the DGPCl modes are replaced by new ClO_4, NH_4, NO_3 modes and entirely different lattice region for temperatures higher than 240°C. Complete details of various phases of DGPCl and its energetics under varying P-T conditions, and comparison of its phase diagram with the most widely used oxidizer- AP, will be discussed.

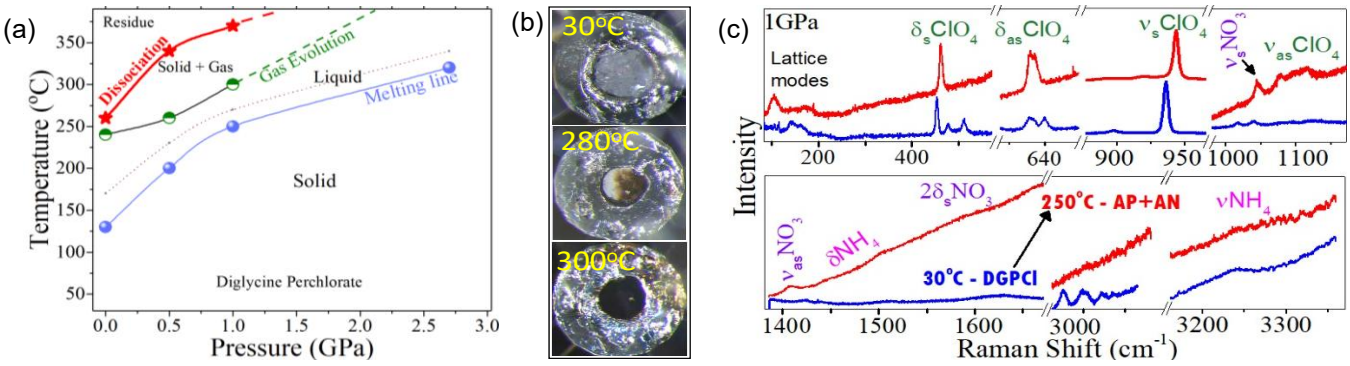

Fig.1(a) Constructed P-T phase diagram of DGPCl, (b) Micro-photgraphic images at 1GPa, (c) Raman spectra at 1GPa-30°C & 250 °C, changes in baseline and vibrational modes suggest melting and conversion to AP – AN complex, respectively.

References:

1. L. Panicker et al., J. Chem. Crystallogr. 41, 147 (2011).

2. M.S. Kumar et al., J. Nonlin. Opt. Phys. Mater. 28, 1950023 (2019).

3. H. Kumawat et al., Inorg. Chem. 64, 892 (2025).