



Impact of Shock Waves on Molecular and Structural Response of Potassium Dihydrogen Phosphate Crystal

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The physical properties of potassium dihydrogen phosphate powder samples have been investigated before and after shock loading. The optical transmittance and bandgap energy were derived by ultraviolet (UV) diffuse reflectance spectroscopy (DRS). The molecular and structural stability of the test crystal after shock loading were confirmed. Test crystals were exposed to 50 and 100 controlled shock pulses with corresponding Mach number of 2.2 then probed by Fourier-transform infrared (FTIR) spectroscopy and powder x-ray diffraction analysis. FTIR spectra showed no considerable changes in the molecular bands of the crystal after shock loading. XRD analysis illustrated the appearance of a few secondary peaks after 50 and 100 shock pulses but retaining the original crystal phase, which may be due to orientation defects and microdistortions of the crystal caused by the impact of shock waves.

Key words: Shock waves, KDP crystal, microdistortions, orientation defects

INTRODUCTION

Shock wave recovery experiments on crystalline materials have opened the door to a new era of major breakthroughs in materials science research based on analysis under strong pulsating energy. It is well known that similar molecules can form dissimilar periodic structures via polymorphism, which depends upon the crystallization environment. Various new phases can be created in materials by application of high-pressure, high-temperature, or very low-temperature conditions, motivating researchers to analyze and understand the fundamental mechanisms of crystallization and solid-state transformation of such crystal structures.^{1–5} High-pressure polymorphism has great practical importance for understanding the structural stability of molecules under extreme conditions, which can lead to the emergence of new phases with different structural and physical

properties. Besides, standardization of polymorphism is one of the remaining problems in crystal engineering, molecular devices, and biomimetic systems.^{4–7} In general, hydrogen bonds play a critical role in the formation and performance of crystal structures and their related physical properties for the above-mentioned applications. Moreover, hydrogen bonds have a major influence on properties such as the nature of the material, its structural stability, bond energies, force constant under critical conditions, etc.^{8,9} Furthermore, it has been observed that the angles between the planes and axes of molecules change under pressure.¹⁰ Consequently, investigation of the structural stability of materials under critical conditions has now become a hot research topic with the aim of industrial applications. To determine the functionality and applicability of high-stability materials, application of shock waves has proved to be an interesting tool to understand material properties under extreme pressure and temperature conditions.

In general, shock waves result in nonlinear pressure phenomena produced by the sudden

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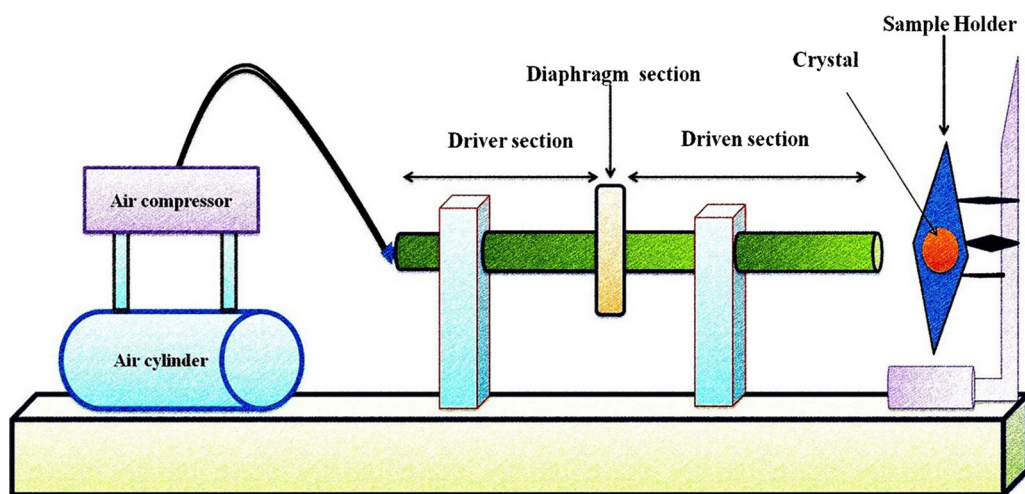


Fig. 1. Schematic of experimental setup.

discharge of large amounts of energy within the span of a few microseconds. Their impact results in very high levels of dynamic pressure and temperature, which interact with the material and thereby change its physical properties. This has raised a lot of curiosity among physicists and chemists for the study of the behavior of solid, liquid, and gaseous materials in high-pressure and high-temperature environmental conditions and the resulting modifications of their properties. Shock waves can be generated in laboratory conditions by using shock tubes, which can produce shock waves with both low and high Mach number. Normally, shock tubes can produce waves with well-defined temperatures and pressures that cover the broad regions of interest for engineering and scientific applications (temperatures from 500 K to 5000 K).^{11–15} However, little research has been published on the influence of shock waves on metals and crystals (in bulk to nanoform), dealing with the impact of shock waves on atomic sites both theoretically as well as experimentally.^{16–21}

At present, nonlinear optical (NLO) materials are of paramount importance due to their dominant contributions to innovations in fields such as microelectronics, optoelectronics, telecommunication, frequency converters, high-power lasers, etc. Among the prevalent NLO materials, potassium dihydrogen phosphate (KDP) is an outstanding material that is predominantly used for the mentioned applications. Moreover, literature reveals that it exhibits three crystal systems, viz. tetragonal, orthorhombic, and monoclinic, of which the tetragonal system is generally found at ambient conditions.^{22–27} Numerous researchers have reported the effect of hydrostatic pressure on the electrical properties, ferroelectric behavior, thermal stability, thermal decomposition, and elastic constants of this material.^{28–31} The structural response of as-grown KDP crystal after shock loading has been investigated, revealing that its crystal system is stable,

although the intensity of the peaks suffers a slight reduction.¹ However, performance of the same experiment on powder samples with a higher number of shock pulses can provide further understating of its structural behavior, although this has not been reported in literature to date. Therefore, in the work presented herein, the molecular and structural stability of KDP crystal after 50 and 100 shock pulses was investigated.

EXPERIMENTAL PROCEDURES

Crystals were grown using potassium dihydrogen phosphate (KDP) as solute and deionized water as solvent, allowing the saturated solution to crystallize by slow evaporation. After a couple of weeks, bulk-size transparent crystals were harvested. The best, optically transparent KDP crystal was chosen for this shock impact study. Fine-grained crystal powder was subjected to shock waves with Mach number of 2.2 generated by a semiautomatic pressure-driven shock tube developed at our research center. Each shock pulse emanating from the tube had a transient pressure of 2.0 MPa and transient temperature of 925 K. The sample was divided into three parts, one being kept as control and the other two being subjected to loading with 50 and 100 shock pulses, respectively. The control and shock-loaded samples were characterized by ultraviolet (UV) diffuse reflectance spectroscopy (DRS), Fourier-transform infrared (FTIR) spectroscopy, powder x-ray diffraction (PXRD) analysis, and NLO measurements to understand the impact of the shock waves on the test material. Figure 1 shows a schematic of the experimental setup.

RESULTS AND DISCUSSION

UV-DRS Analysis

The optical transmittance spectrum of the KDP crystal before and after shock loading were recorded

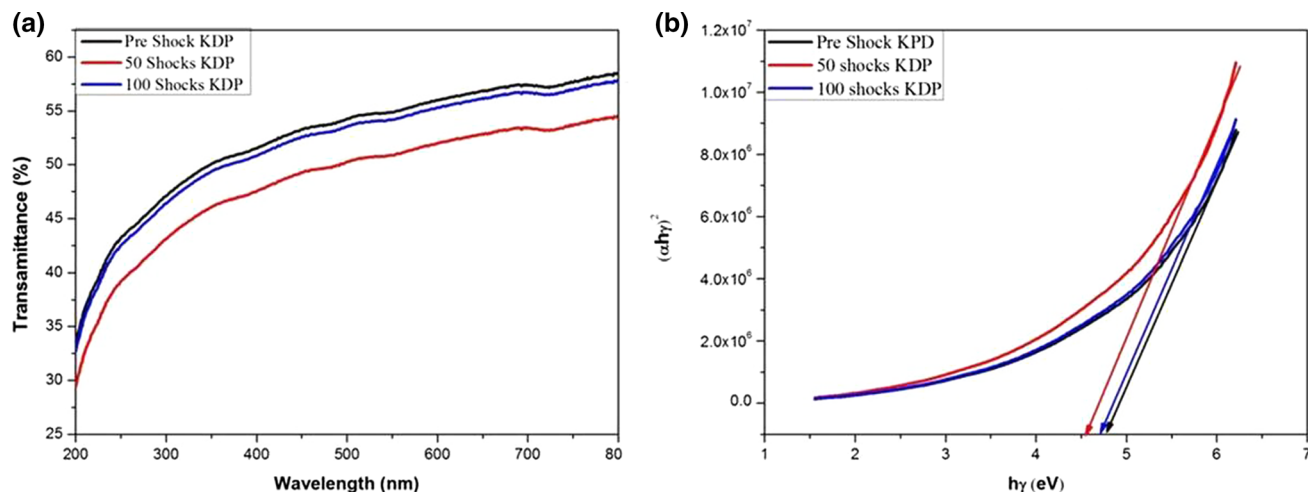


Fig. 2. (a) Optical transmittance spectra and (b) band gap energy of control and shocked KDP crystals.

by UV-DRS in the wavelength range from 200 nm to 800 nm (Fig. 2a). The maximum transparency (58%) was observed at 800 nm for the crystal before shock loading, which showed a transparent window across the entire visible and near-IR region, a behavior that is highly suitable for optoelectronic applications.²⁶ The transmittance was slightly reduced for the crystal subjected to 50 shock waves, but increased after 100 shock waves. This effect may be due to grain size changes or defect formation under shock loading.

The optical bandgap energy of the KDP crystal samples before and after loading with 50 and 100 shocks was calculated using Tauc plots (Fig. 2b), yielding values of 4.79 eV, 4.55 eV, and 4.70 eV, respectively. The lower optical bandgap energy after 50 shocks may be due to formation of defects.

FTIR Spectroscopy

Vibrational spectroscopy is a sensitive tool, typically used to explore the nature of chemical bonding in a material. It provides understanding of the effects of pressure on chemical bonds, especially internal molecular structures.^{32,33} It is well known that high pressure can affect the structure, chemical bonds, surface, and performance of materials. Therefore, application of shock pressure is one of the approaches available to identify new classes of materials with high performance. FTIR spectra of KDP crystal before and after shock loading were captured in the mid-IR region from wavenumber of 4000 cm^{-1} to 400 cm^{-1} using a PerkinElmer FTIR spectrometer. Comparison of the obtained IR vibrational assignments for the KDP crystal before shock loading with reported standard values reveals excellent agreement.^{34–37} Dynamic high-pressure impacts can play a dual role in lattice relaxation. During high-pressure loading of a material, structural stress is generated in the lattice, which in turn affects the lattice relaxation process.³² When the

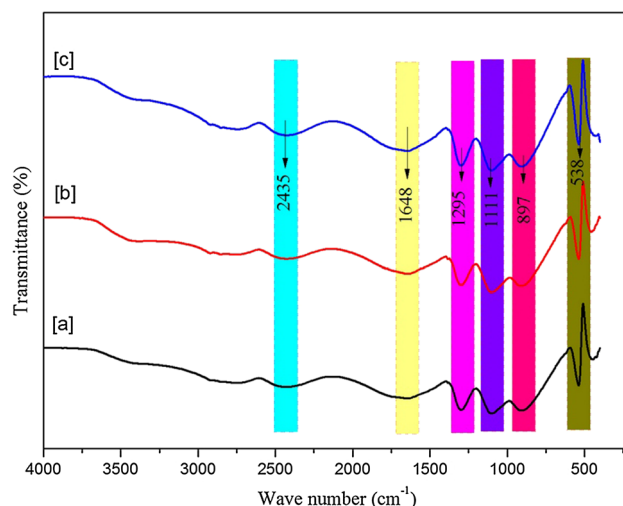


Fig. 3. FTIR spectra of KDP crystals (a) before shock loading, and after (b) 50 and (c) 100 shocks.

pressure is relatively low, the amount of stress generated in the lattice is also lower. However, high pressure can initiate more intermolecular chemical reactions in the decomposition process or induce atomic bonds to break up.³² The IR spectra of the samples after loading with 50 and 100 shocks are shown in Fig. 3, and the tentative modes of vibrations are presented in Table I. Interestingly, these results show that the peaks of the KDP crystals before and after shock loading were identical. Moreover, there was no considerable change in the position or nature of the peaks observed before and after shock loading, despite the relatively high shock wave pressure applied. This confirms that the molecular structure of the crystal was stable after application of 100 number of shocks in this transient pressure range. This excellent molecular stability of the crystal may be due to the very strong O=P–OH stretching and P=O stretching in

Table I. Tentative FTIR vibrational assignments of KDP crystals before and after shock loading

Wavenumber (cm ⁻¹)		Vibrational assignment
Before shock loading	After 50 and 100 shocks	
2435	2435	P–O–H bending of KDP (VW)
1648	1648	O=P–OH stretching (VS)
1295	1295	P=O stretching of KDP (S)
1111	1111	P=O stretching (S)
897	897	P–O–H stretching of KDP (S)
538	538	OH–P–OH bending vibration (S)

VW, very weak; VS, very strong; S, strong.

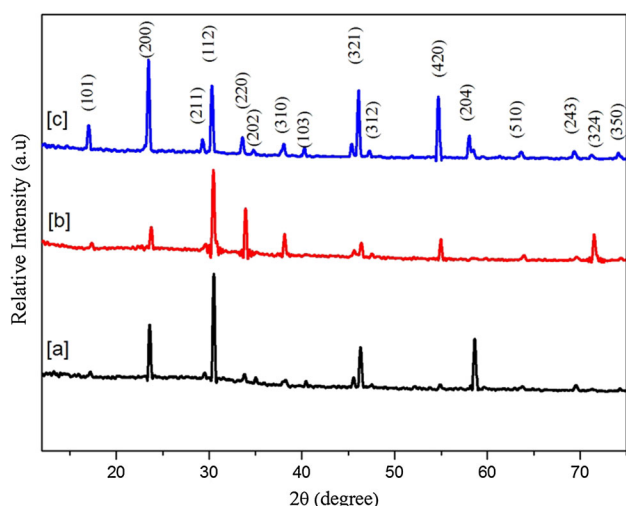


Fig. 4. PXRD patterns of KDP samples (a) before shock loading, and after (b) 50 and (c) 100 shocks.

KDP. Moreover, the observed results clearly reveal that no chemical decomposition effects occurred due to the high-enthalpy shock waves. These results indicate that KDP crystal has highly stable chemical bonds and extremely intense intermolecular attractive forces, suggesting that it could be an effective candidate for use in extreme conditions such as high pressure and high temperature, or in high-power laser applications.

PXRD Analysis

Powder XRD is a superior tool to distinguish between crystal polymorphs and physical phases in a material. PXRD patterns of the KDP crystal before and after shock loading were recorded using a Rigaku MiniFlex II over the diffraction angle range from 0° to 90° (Fig. 4). The crystalline planes (*hkl*) observed for the KDP crystals before and after shock loading matched very well with literature.^{37–39}

The diffraction patterns indicate that, before shock loading, the KDP crystal belonged to the tetragonal system, showing signals from (200), (112), (312), and (204) planes. The diffraction peaks showed only a slight change after shock loading. However, a remarkable observation is that, new crystal planes were observed, corresponding to planes (200), (112), (220), (310), (312), (420), and (324) after 50 shocks and (101), (200), (211), (112), (220), (202), (310), (103), (321), (312), (420), (204), (150), (243), (324), (350), (305), and (260) after 100 shocks. The majority of the signals observed before shock loading were also observed after shock loading, with no great peak shifts observed in diffraction angle. Hence, the original peak positions were considerably stable to shock wave loading, whereas their intensity was greatly affected. After 50 shocks, crystalline peaks corresponding to planes such as (220), (310), and (420) exhibited a slight increase in intensity compared with before shock loading.

Moreover, the signal corresponding to crystalline plane (204) completely disappeared after application of 50 shocks, but reappeared after 100 shocks. On the other hand, the signal corresponding to crystalline plane (324) was absent before shock loading, appeared after 50 shocks, but disappeared again after 100 shocks. After 100 shocks, the signals corresponding to planes such as (101), (211), (103), (204), and (243) exhibited great enhancement due to growth orientation caused by the shock waves. Overall, this structural analysis reveals that some of the planes underwent rapid enhancement while others underwent rapid diminishment. This orientation change effect may occur due to microdistortions, orientation defects, and structural dynamics in the lattice planes resulting from the impact of shock waves.^{7,40} For better understanding, it is essential to calculate the crystallite size and lattice strain values of the crystals before and after shock loading using the relations for standard structural properties.⁴¹ The calculated values are presented in Table II. The sample subjected to 50 shock waves showed lower crystallite size compared with that

Table II. Structural properties of control and shock-loaded KDP crystal

S. no	Parameter	Control	After 50 shocks	After 100 shocks
1	Crystalline size (nm)	31	20	31
2	Dislocation density ($\times 10^{15}$ lines/m ²)	1.0405	2.5	1.0405
3	Residual lattice strain (10^{-3})	1.226	1.838	1.226

before shock loading as well as that subjected to 100 shocks. The crystallite size distributions of the KDP samples before and after shock loading clearly show that the sample subjected to 50 shocks exhibited high structural complexity, whereas the original range was recovered after 100 shocks. As for the crystallite size, the residual lattice strain was also higher after 50 shocks compared with the other two cases. This effect may be due to fission of a few single crystallites, splitting into two or more crystallites and thereby reducing the net crystallite size after 50 shocks, but without modifying the original crystal system of the material. Furthermore, when a greater number of shock pulses was applied, the number of crystalline planes also increased in the crystal system. It is clearly seen that, as the number of shocks was increased, the microdistortions and crystalline orientation defects also increased, and a few planes in the crystalline system were enhanced. Based on the discussion above, it is clear that the title crystal exhibits good structural stability and shock resistance.

NLO Studies

The nonlinear optical (NLO) properties of a crystal can be established using the Kurtz–Perry powder technique. KDP crystals before and after 100 shocks were ground to fine powder and packed into a capillary tube. The fundamental beam from a Nd:yttrium aluminum garnet (YAG) laser (wavelength 1064 nm, repetition rate 10 Hz, pulse width 10 ns, energy 1.2 mJ/pulse) was made to pass through the samples after reflection by an IR reflector. Second-harmonic generation (SHG) by the crystals was confirmed by the emission of intense green radiation (532 nm). SHG signals were observed from both samples, at 22 mV and 25.3 mV, respectively. The NLO efficiency of the shock-loaded KDP crystal was found to be 1.15 times higher compared with the KDP crystal before shock loading. Interestingly, after shock loading, the KDP crystal showed slightly higher efficiency compared with before shock loading. This higher efficiency might be attributable to growth of a few planes during shock loading.

CONCLUSION

Application of shock waves to crystals is a fruitful approach to investigate and develop new structural models. The impact of 50 and 100 shock waves on

KDP crystal and its molecular structure stability was investigated in this work. The optical transmittance was reduced after 50 shocks but increased again after 100 shocks. FTIR spectroscopy confirmed that the shock waves did not affect the functional groups in the KDP samples. PXRD profiles obtained after shock loading confirmed the stability of the crystallographic planes and also demonstrated that some new planes were created due to microdistortions and orientation defects after shock loading, albeit without altering the original crystal system of the KDP crystal. Kurtz–Perry powder measurements revealed that the KDP crystal exhibited 1.15 times higher NLO efficiency after shock loading. Based on the results presented herein, it can be asserted that KDP crystal exhibits good structural stability and shock resistance, thus representing an effective and appropriate candidate for fabrication of moving and vibrating devices as well as high-temperature molecular devices.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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