Shock wave-induced optical band gap engineering on pure and dye-doped potassium dihydrogen phosphate crystals

A. Sivakumar[1] · S. Sahaya Jude Dhas[2] · S. A. Martin Britto Dhas[1]

Abstract

At this point in time, there are only a few studies available which deal with the investigation on the effect of shock waves in structural, electrical, thermal, and optical properties of potassium dihydrogen phosphate (KDP) crystal that has been analyzed systematically in the previous publications (Sivakumar et al. in Opt Laser Technol 111:284, 2019; Sivakumar et al. in J Eelectron Mater 47:4831, 2018; Sivakumar et al. in Mater Res Express 6:086303, 2019; Sivakumar et al. in J Electron Mater 48:7868, 2019; Sivakumar et al. in Z. Kristallogr Cryst Mater, 2020, https://doi.org/10.1515/zrki-2020-0017). In this study, the prime interest is to explore the band gap engineering of pure and dye-doped KDP (methylene blue and rhodamine B) crystals by shock waves which would enable to get the deep insight so that better understanding of the relation between shock wave and optical physics could be arrived at and it would pave the way to get acquainted with more knowledge of the material itself. Optical band gap energies are calculated from Tauc plot relations and it is observed that the values of band gap energies are reduced with respect to number of shock pulses for all the test crystals. The reduction of band gap energy is due to the formation of surface defects and oxygen vacancies by the impact of shock waves and this effect is called as Franz–Keldysh effect (Strain Lattice effect). Among the three crystals, RB + KDP crystal is found to be the best such that it could be tuned for the range of band gap energy from 4.89 to 3.3 eV as compared to the other two crystals. Hence, an alternate method is proposed to understand band gap engineering of non-linear optical materials which are suitable for photonic applications.

1 Introduction

Shock wave-induced engineering on analyzing the properties of materials has started to gain significant momentum in such a way that a remarkable attention has been witnessed by the materials science researchers due to the outstanding performance impacted by the shock waves on crystalline and non-crystalline materials. After twentieth century, there has been a rapid increase of shock wave research in materials science division which includes both bulk and nanomaterials. Recent publications provide substantial evidence for the sustained growth with which the field is emerging to be a game changer [1–4]. At the same time, shock wave recovery experiments could supplement with the practical findings that would bridge the communication gap between the materials science and applied physics so that the implications could be better understood and it is recognized to be one of the stand-out research topics in recent years. Therefore from the historical perspective, it is worthwhile to have a strong intention to know how materials would undergo several kinds of deformations, phase transformations when exposed to shock waves, and unearthing the reason for the materials to exhibit such kind of behaviors.

As it is known, non-linear optical (NLO) crystals are the fundamental building blocks of modern technologies and they have potential applications which include second harmonic generation (SHG), high power laser, and electro-optic applications [5–7]. Hence, it is essential to be aware of the fundamental properties and their behaviors at ambient and non-ambient conditions for the materials which are being used in the above-specified applications. Potassium dihydrogen phosphate is one of the elegant and legendary NLO materials for photonic applications due to the outstanding physical and chemical properties [8, 9]. Moreover, KDP crystal is used as the standard material for comparing with the performances of other NLO crystals. Hence, it is one of

✉ S. A. Martin Britto Dhas
  martinbritto@shctpt.edu

1 Department of Physics, Abdul Kalam Research Center, Sacred Heart College, Tirupattur, Vellore, Tamil Nadu 635 601, India

2 Department of Physics, Kings Engineering College, Sriperumbudur, Chennai, Tamil Nadu 602 117, India

the best candidates to be explored on the impact of shock waves so that a valuable addition could be possible for shock wave physics which would in fact be strengthened by the presence of these new findings for this potential non-linear optical material. On these grounds, there have been few works accomplished on KDP crystals supplemented with few experiments so as to understand better about their stability on structural, thermal, electrical, and optical transmittance against the impact of shock waves [10–14]. As per the previous reports, KDP crystal does not undergo any phase transition at shock wave-loaded conditions, whereas it shows slight changes in electrical and optical properties. Dielectric constant is reduced by the impact of shock waves due to the changes occurred in polarized ferro-electrical domains and lattice deformation [11, 12]. Furthermore, it has been also attempted a systematic investigation on the stability of optical transmittance against the shock waves which has revealed that the optical transmittance of KDP crystal is reduced [13]. Interestingly, the observations have come out with a red shift of absorption edge at shock wave-loaded conditions. It has provided a key point with which it is possible to modify the optical band gap energy. Moreover, optical band gap energy makes a significant impact in the second harmonic generation. Hence, it is essential to understand the electronic band pattern and optical band gap energy behavior of photonic materials in order to satisfy the requirements for the advanced optoelectronic and microelectronic applications. There are a large number of publications available to understand the tuning of band gap with respect to dopants and doping concentrations [15–17]. Moreover, during the gamma irradiation, the absorption band undergoes red shift with respect to the energy of the gamma rays due to the formation of color centers in the lattice [18–20].

As per the atomic response theory, harmonic generation of a crystal highly depends on polarized states and unoccupied cations and anions of non-bonding states in the crystal lattice [20]. From the previous works, it has been found that KDP crystal is enforced to modify the polarized dipoles with respect to transient pressure and as a result the dielectric constant is reduced due to the changes occurred in electronic dipoles [11, 12]. In this research article, the investigation of the role of shock waves on KDP crystals in optical band gap engineering is provided with clear evidence in terms of the energy level changes.

2 Experimental section

Optically transparent crystals of pure and doped (methylene blue and rhodamine) potassium dihydrogen phosphate have been grown by slow evaporation method with the dopant concentration of 0.001 M for both the crystals. The grown KDP crystals of dimension $10 \times 10 \times 1$ mm^3 have been utilized for the present band gap engineering experiment.

For the present experiment, table—top pressure-driven shock tube is used to generate shock waves of Mach number 1.7 which has the respective transient pressure and temperature of 1.048 MPa and 644 K. The test crystals are rigidly fixed in the sample holder one after the other and ten periodic shock pulses are applied on each of them. Subsequently, optical transmittance is recorded for control and shocked crystals [14, 21].

3 Results and discussion

3.1 Optical band gap energies

Optical absorption coefficient spectra can provide comprehensive insight of the optical band gap energy according to solid-state band theory. Understanding the changes in band gap energy is very much essential to point out the in-plane compressive stress of the stressed materials. Because of lattice strain conditions, the optical band gap energy is significantly altered and it has been well documented by several researchers [22, 23]. It has been pretty evidently established that optical band gap energy of materials plays a crucial role in electronic device applications. As per the above-specified statements, in this context, it is worthwhile to examine the optical band gap energy of KDP crystals under shock wave-loaded conditions. The observed optical transmittance, surface morphology, and structural properties of KDP crystals have been reported elsewhere [14]. From the XRD results, it has been found that the crystalline nature is reduced with respect to number of shock pulses due to the enhancement of lattice strain and formation of defects. UV–Visible spectroscopic study has been performed so as to understand precisely how shock waves alter the electronic band structure in pure and doped KDP crystals. The measured wavelengths dependent on absorption profiles are utilized to frame the spectral-dependent absorption coefficient of KDP crystals. The obtained band gap energies of control and shock wave-loaded KDP crystals are presented in Figs. 1, 2, and 3. In shock wave-loaded condition, the band gap energies are found to be considerably reduced by the impact of shock waves.

The changes observed in the band gap energy might be due to the red shift of the absorption edge and enhanced localized states in the absorption edge of the test crystal. Moreover, the crystal defects can also induce free electronic localized states in absorption edge. At gamma rays irradiation conditions, band gap energy changes and Urbach tail energy is reduced and these changes have been already well documented [24, 25]. Moreover in the previous article of Triglycine sulfate (TGS), it has been found continuous
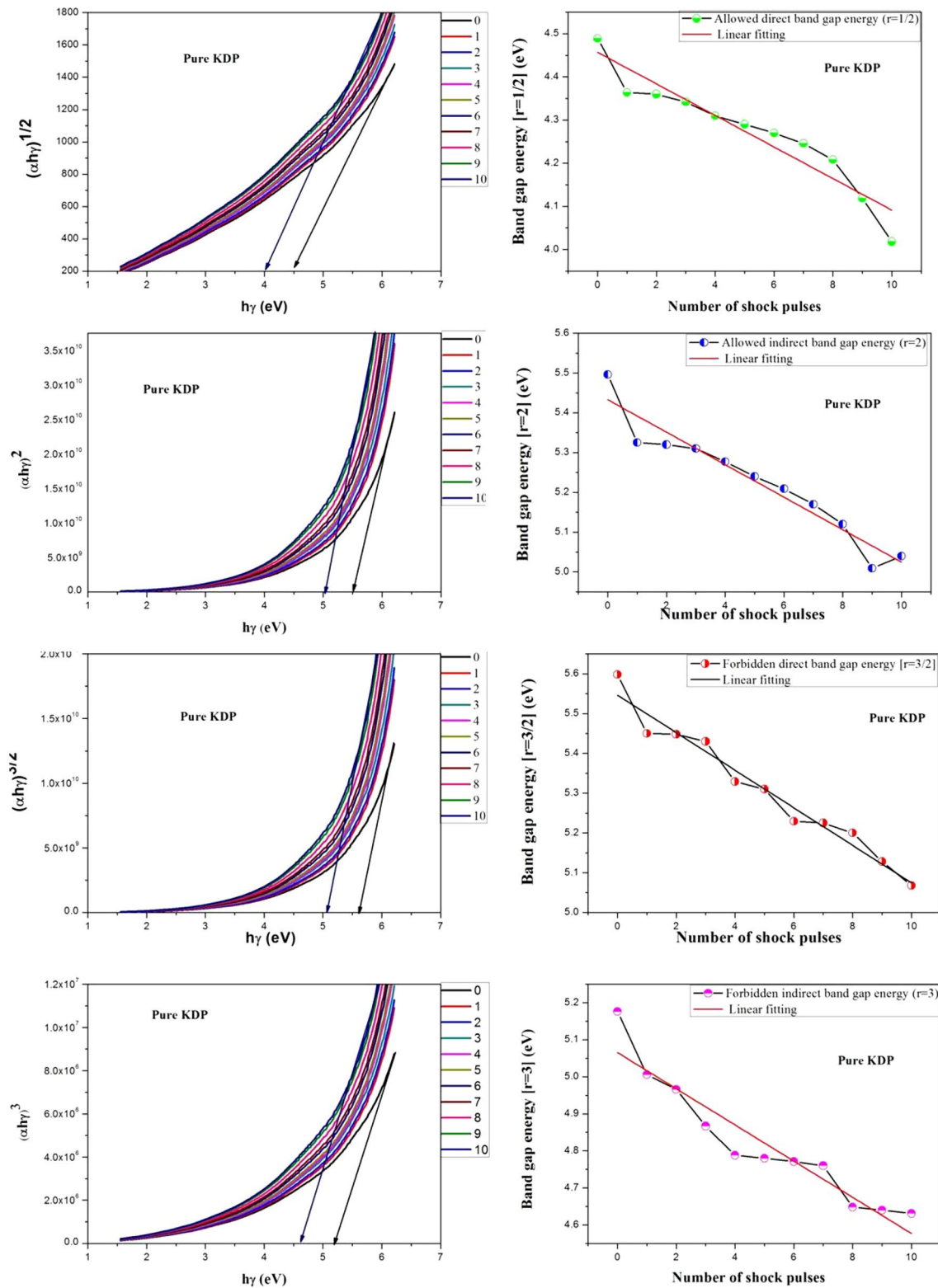
Fig. 1 Direct and indirect band gap energies of pure KDP crystals at control and shock wave-loaded conditions
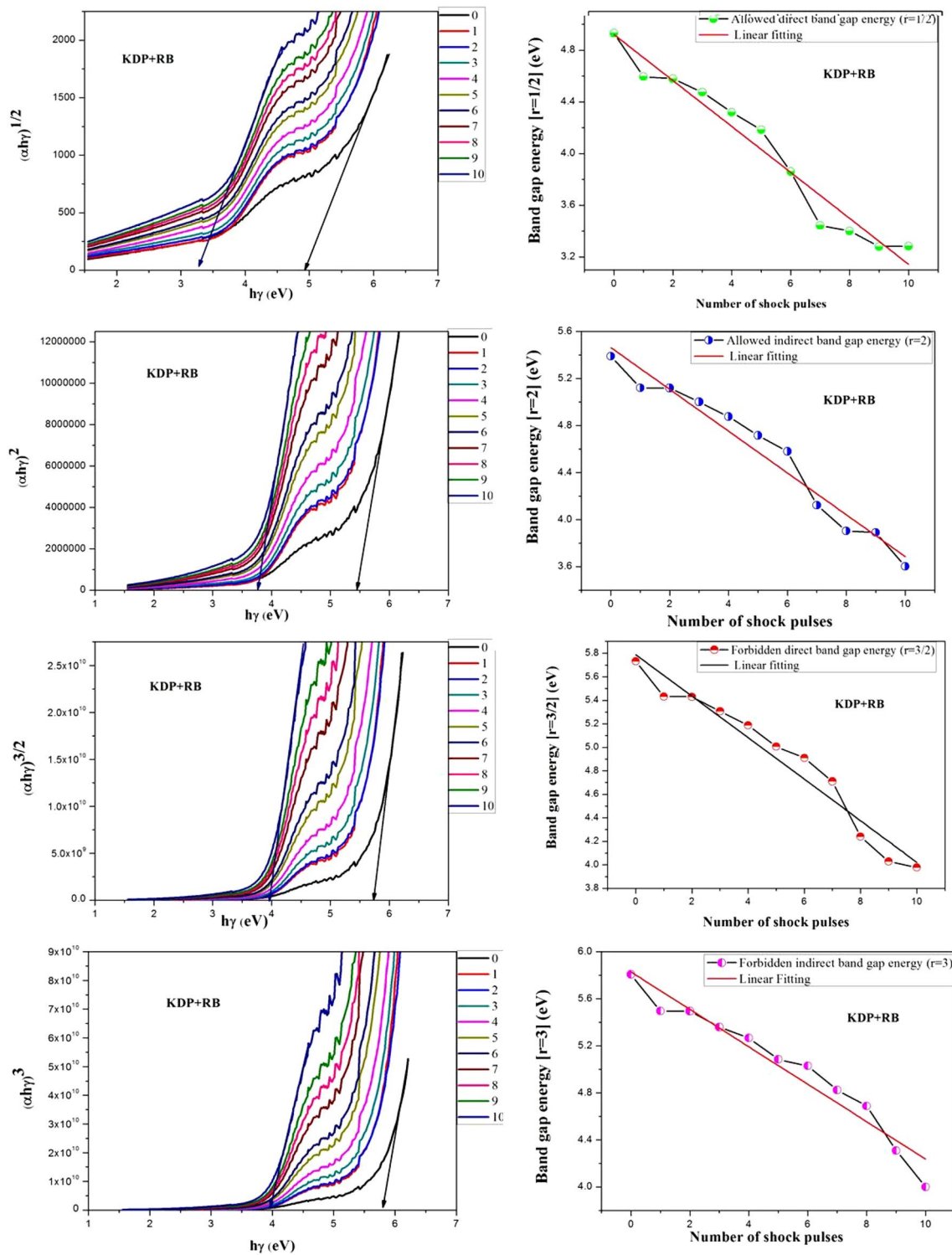
Fig. 2 Direct and indirect band gap energies of KDP+RB crystals at control and shock wave-loaded conditions

reduction of optical band gap energy with respect to number of shock pulses [21]. In the case of Benzil and ammonium dihydrogen phosphate crystals, the optical band gap energy is found to be linearly increased with respect to number of

shock waves [26, 27]. In materials science point of view, at shock wave-loaded conditions, there are several factors possibly involved during the optical band gap changes such as surface defects, absorption edge shift, cumulative effect
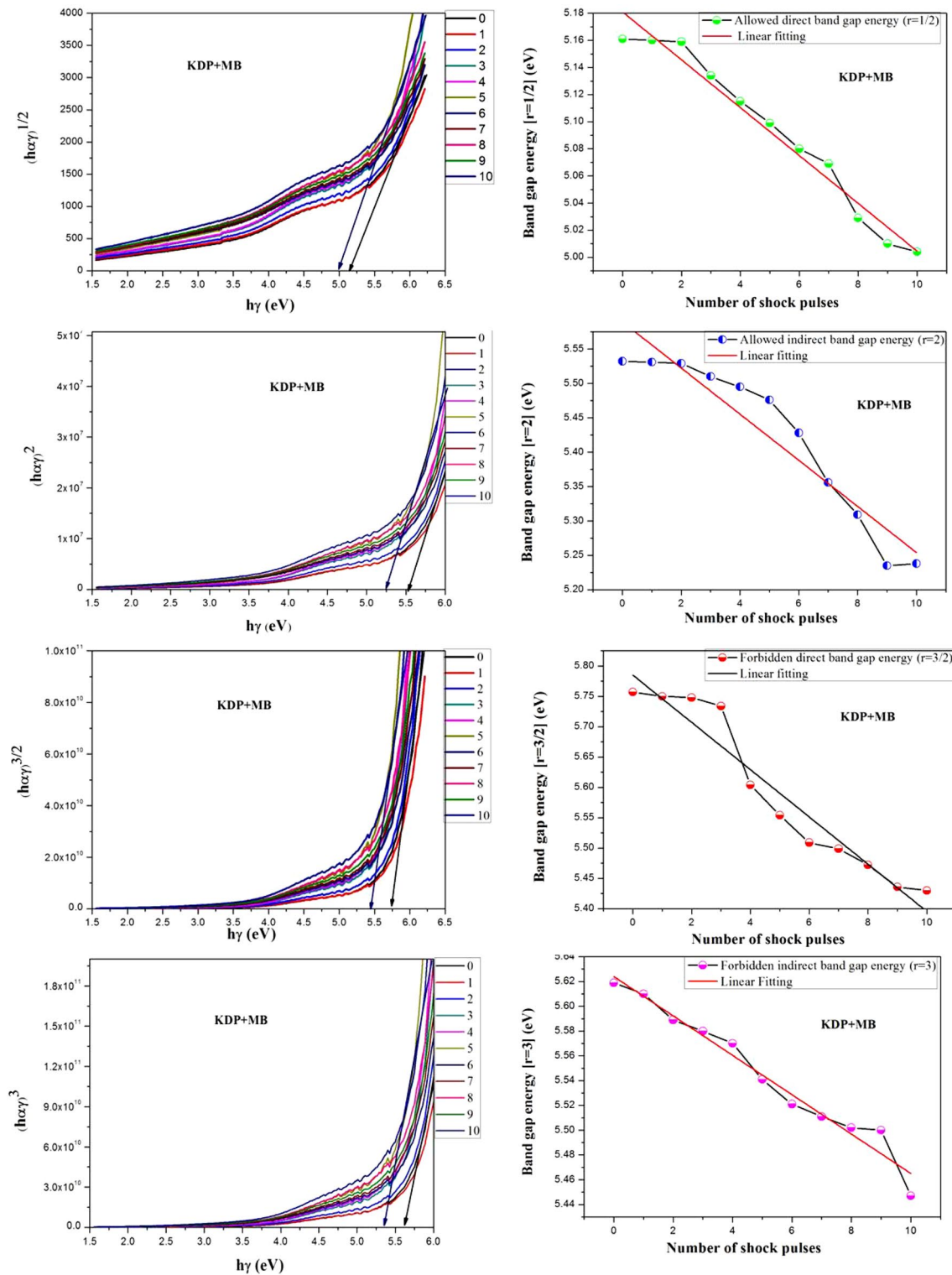
Fig. 3 Direct and indirect band gap energies of KDP + MB crystals at control and shock wave-loaded conditions

of crystal lattice expansion, band shape, band width, density of localized states, and most importantly electron/exciton–phonon interaction of the test materials. All the above said parameters must be taken into the account for the better understanding of band gap changes occurring in materials. The observed band gap energy spectrum of pure KDP crystal is presented in Fig. 1. While looking at the band gap energy spectrum, it is easy to witness visually the linear fitted line

of Tauc plot which is shifted towards the lower energy with respect to number of shock waves. At this point, it is very much essential to consider not only all the above-specified parameters but also the crystalline nature and defect density.

As per previous publications, it has been evidenced that KDP crystal, at shock wave-loaded conditions, undergoes changes so that its sub-micro structural properties are modified in such a way that its dielectric constant is reduced due to the changes occurred in polarized dipoles per unit volume [12]. For the present case also, the same behavior is witnessed by the impact of shock waves such that the lattice disorder might have been enhanced with respect to number of shock waves and as a result, the optical band gap energy is reduced. For pure KDP crystal, the band gap energy is reduced from 4.489 to 4.018 eV for the direct transition ($n = 1/2$). Whereas, if n values are changed as 2, 3/2 and 3, different values of band gap energy could be obtained as presented in Fig. 1. While considering the indirect band gap energy, lattice phonons must be involved in the electronic transition so as to satisfy the law of conversation of energy and momentum [28]. In this case, interaction of the electron/exciton–phonon interaction may be high in shock wave-loaded condition. Because of shock wave transient pressure, the excited electrons may easily move towards the lowest region of conduction band and this effect as called as Franz–Keldysh effect [29, 30]. However in the case of KDP crystal, with respect to number of shock waves, the optical band gap energy is reduced in such a way that the applied shock waves might have enforced interfacial defects, point defects, and oxygen vacancies. Even though the changes are not highly significant, the observed changes should be taken into account so as to understand the shock wave-impacted effects.

Generally, oxygen vacancies and point defects reduce the band gap energy in semiconducting materials and insulating materials [31, 32]. It is well known that KDP crystal is constructed by the three-dimensional hydrogen bonds network. Due to the three-dimensional hydrogen bonds network, the possibilities of formation of oxygen vacancies are high in the case of shocked conditions; because the hydrogen bonds are sensitive to high pressure and high temperature environments [33]. RB and MB-doped KDP crystals also exhibit the similar behavior of reduction of optical band gap energy with respect to number of shock waves. In KDP + RB crystal, the band gap energies are greatly changed for both electron and phonon-based transitions. For example, directly allowed band gap energy is reduced from 4.89 to 3.3 eV and indirectly allowed band gap energy is reduced from 5.5 to 3.6 eV. The corresponding band gap energy spectra are presented in Fig. 2. In this case also, it is proposed the same reason as stated earlier for the change in optical band gap energy with respect to number of shock waves. This large reduction of band gap energies might be due to the higher

concentration of defect centers which have been generated in the crystal system and the enhancement of electronic localized states in the absorption bands of the test crystal. It has been already observed that KDP + RB undergoes high degree of structural disorder and defects at shock wave loaded conditions. Hence, it experiences high number of localized states and reduced optical band gap energies. In addition to that, KDP + MB crystal also shows the similar behavior as that of KDP + RB but the degree of changes are not significant. Control KDP + MB crystal undergoes changes in band gap energy, i.e., from 5.161 to 5.004 eV and the typical band gap energy spectra of both electron and phonon-assisted energies are presented in Fig. 3. These changes are comparatively lower than that of KDP + RB crystal's results. The observed results clearly manifest the uniqueness of RB and MB molecules in the electronic transitions in KDP crystal against the impact of shock waves. Moreover, it is worthwhile to mention that all the obtained linear fits for both the direct and indirect transition probability are not changed by the impact of shock waves.

3.2 Extinction coefficient and reflectance

Extinction coefficient depicts the clear picture of loss of electromagnetic energy with respect to wavelength due to the absorption bands and scattering centers in the test materials. In shock wave-loaded condition, it has been observed that the values of extinction coefficients are linearly increased with respect to number of shock waves for both pure as well as doped KDP crystals and the typical profiles are presented in Fig. 5. From the observed wavelength-dependent profiles, it is clearly delivered that excitation coefficient values are increased with respect to number of shock waves. It is authenticated very much obviously that the amount of loss of incident light is increased with respect to number of shock waves. This light energy loss may be due to the formation of defect centers in the test materials enforced by the impact of applied shock waves. Fundamentally, materials of higher optical transmittance exhibit the lower optical reflection and vice versa for materials of low transmittance. From the present experiment, it has been authenticated that pure and doped KDP crystals have the higher transmittance and lower reflection values. In shock wave-loaded conditions, the optical reflection is significantly affected by the impact of shock waves. The obtained reflection profiles of the test crystals are presented in Fig. 4 which confirms that the amount of reflected light is increased by the impact of shock waves. This enhancement of reflection may be due to the formation of defects and structural disorder in surface of the crystals. Among the all three test crystals, pure KDP crystal suffers a slight change in the reflection values. For the present investigation, the obtained extinction coefficient profiles with respect to wave length for control and shock
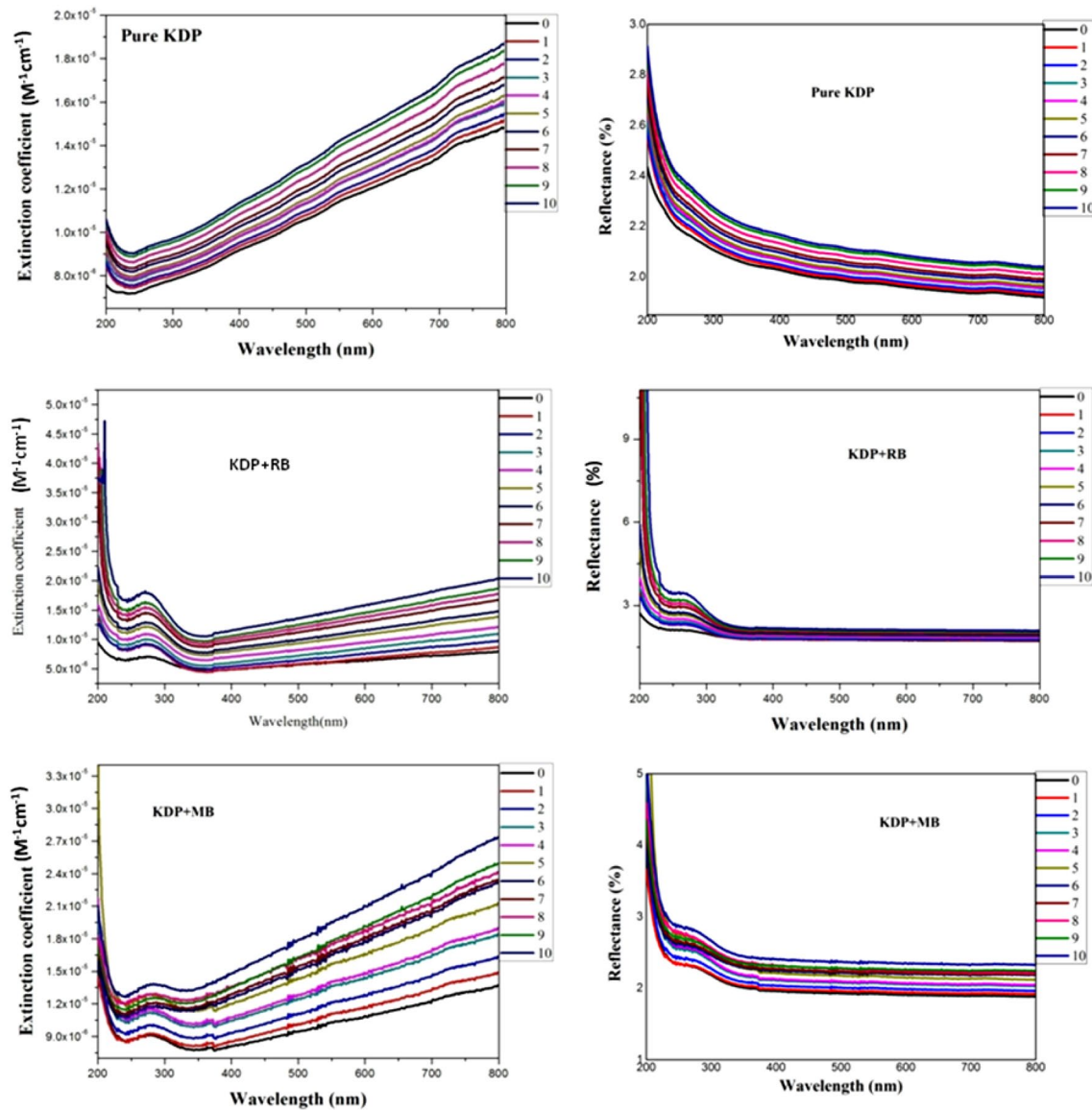
Fig. 4 Extinction coefficient and Reflectance profiles of shock wave-loaded KDP crystals

wave-loaded test crystal are presented in Fig. 4. All the test crystals (Pure KDP, KDP + RB, and KDP + MB) illustrate that the extinction coefficient is strongly dependent on the wavelength of incident light source.

3.3 Optical polarization

Linear optical polarization is a prominent optical property for non-linear optical materials because the harmonic generation of materials is highly associated with polarization in the presence of electrical field of the electromagnetic waves [34]. From the optical constant formulations [27], the optical polarization profiles have been calculated and presented in Fig. 5. From the observed optical polarization profiles, it is

clearly known that before the exposure of shock waves, the test samples have the high optical polarizability with respect to wavelength. But in the case of shock wave applied conditions, it is noticed that there is a considerable reduction of optical polarization with respect to number of shock pulses for all the test samples. But, among the three samples, pure KDP crystal's optical polarization is relatively stable against the impact of shock waves. Since the loss of polarization is comparatively lesser than the other two crystals, for better understanding the loss of optical polarization, it is imperative to correlate the optical polarization with surface defects, dipole orientation, deformation, and structural disorder. As per the previously published article, while shock waves are loaded on KDP crystal, the dipole orientation is encountered
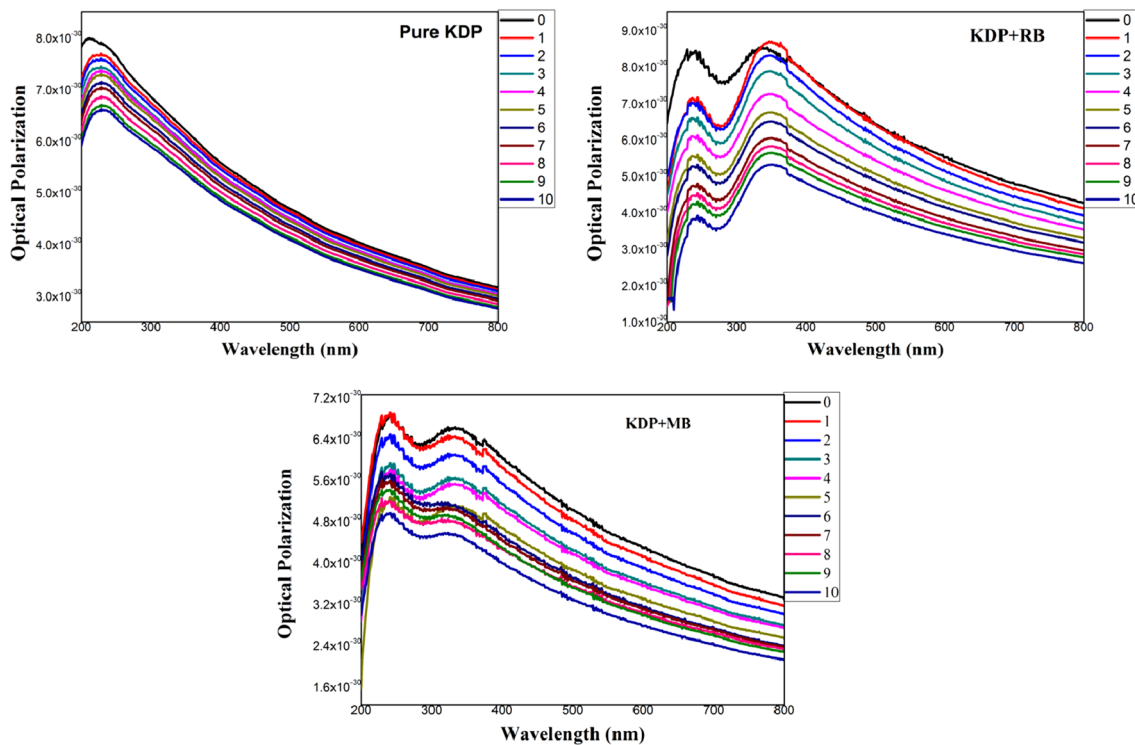
Fig. 5 Optical polarization profiles of shock wave-loaded KDP crystals

with changes by the impact of shock waves and as a result the polarizability (α) is reduced [12]. In this perspective, the harmonic generation signal intensity might have been reduced at shock wave-loaded conditions. On this context, it is proposed that the same behavior could have occurred by the impact of shock waves with which the optical polarization is reduced with respect to the number of shock pulses.

3.4 Correlations between band gap energy and optical polarization

As it is known from the atomic respond theory, the degree of crystalline nature and defects play a non-debatable role in the harmonic generation of the materials. Qiaoling Chen et al. have reported that the intensity of the second harmonic generation signal is enhanced while the particle size is increased for KDP crystal [35]. Also, documented results show that optical band gap and optical polarization are greatly related to each other [26]. So that, it is worthwhile to correlate these two parameters with respect to number of shock pulses to understand better about the optical properties relationship with degree of crystalline nature. Figure 6 clearly shows that the optical polarization and band gap energy are reduced with respect to number of shock waves, which also reveals that the polarizability is reduced while shock waves are exposed on KDP crystals.

The observed results are found to be well corroborated with the previous publication [12].

4 Conclusion

In summarizing the present study, the band gap tuning has been examined with respect to number of shock waves for pure and dye-doped KDP crystals. The present investigation discloses the possibility to tune the band gaps and band edges independently without any additives to KDP crystals. This kind of experiments paves the way for the researchers to catch up with the deep insight through systematic approach while optimizing the materials for applications point of view. Experimentally measured Tauc plot relations are found to be well matched with the linear fit and the observed results are elaborated. KDP + RB shows the maximum reduction of band gap energy from 4.89 to 3.3 eV due to the so-called lattice strain effects, whereas for pure KDP and KDP + MB, only a slight change is enforced by the impact of shock waves. Optical polarization is reduced with respect to number of shock waves for all the KDP samples. But between the three crystals, pure KDP crystal has relatively stable optical polarization against the shock waves.
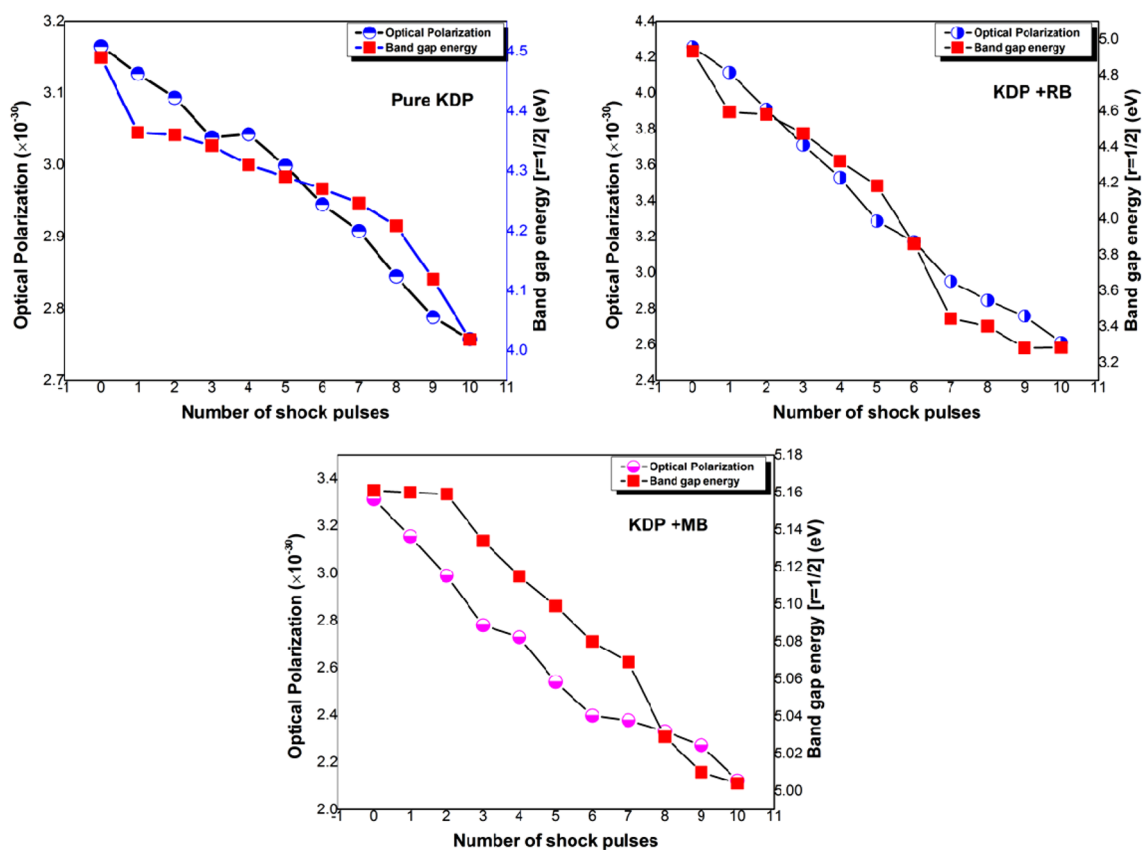
Fig. 6 Correlations between band gap energy and optical polarization profiles of shock wave-loaded KDP crystals

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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