CHAPTER 6

OPTICAL NONLINEAR STUDIES ON PURE
AND DOPED KAP CRYSTALS

6.1 INTRODUCTION

There is considerable research interest in exploring materials having large nonlinearities. This interest, is driven primarily by the search for materials for all-optical switching and sensor protection applications, concerns both nonlinear absorption (NLA) and nonlinear refraction (NLR). The database for nonlinear optical properties of materials is inadequate for particularly organic or semi-organic, in determining trends to guide synthesis efforts. Thus, there is a need to expand this database (Methods to determine nonlinear coefficients in general and in particular for pure and doped KAP single crystals are discussed).

Nonlinear refraction measurements can be carried out with a variety of techniques including nonlinear interferometry (Moran et al 1975, Weber et al 1978), degenerate four-wave mixing (Friberg and Smith 1987), nearly degenerate three-wave mixing (Adair Chase et al 1987), ellipse rotation (Owyoung 1973), and beam distortion measurements (Williams et al 1984). The first three methods, namely, nonlinear interferometry and wave mixing, are potentially sensitive techniques, but all require relatively complex experimental apparatus. Beam distortion measurements, on the other hand, are relatively insensitive and require detailed wave propagations analysis (Tian et al 1995). A simple ( from the experimental point of view) single beam
Z-scan technique, an application developed by the CREOL group, for measuring the sign and magnitude of \( n_2 \) that has a sensitivity comparable to interferometric methods (Sheik Bahae et al 1989) was used in the present work. The Z-scan technique is based on the principles of spatial beam distortion (Van Stryland et al 1993).

The Z-scan technique is a method which can rapidly measure both nonlinear absorption and nonlinear refraction in solids, liquids and liquid solutions (Sheik Bahae et al 1989, Sheik Bahae et al 1990). The Z-scan method has gained rapid acceptance by the nonlinear optics community as a standard technique for separately determining the nonlinear changes in refractive index and absorption. This acceptance is primarily due to the simplicity of the technique as well as the simplicity of the interpretation. In most experiments the index change, \( \Delta n \), and absorption change, \( \Delta \alpha \), can be determined directly from the data without resorting to computer fitting. However, it must always be recognized that this method is sensitive to all nonlinear optical mechanisms that give rise to a change of the refractive index and/or absorption coefficient, so that determining the underlying physical processes present from a Z-scan is not possible (Gomez et al 2003). A series of Z-scans at varying pulse widths, frequencies, focal geometries etc. along with a variety of other experiments are often needed to unambiguously determine the relevant mechanism.

6.2 PRINCIPLE OF Z-SCAN

The Z-scan technique, based on the principle of spatial beam distortion arising from an optically induced nonlinear refractive index, offers experimental simplicity as well as high sensitivity (Hermann and McDuff 1993). The Z-scan method is an experimental way to obtain data regarding the nonlinear refractive index and nonlinear absorption properties of materials
(Chapple et al 1994). Here nonlinearity simply means the intensity dependent response of the material, which can be used to obtain an optical limiting device, either by nonlinear refraction or absorption (Bridges et al 1995). This method yields both the sign and magnitude of nonlinearity. The value of the nonlinear refractive index can be easily extracted from the experimental data with a minimum of analysis (Van Stryland et al 1993).

In cases, where nonlinear refraction is accompanied by nonlinear absorption, it is possible to separately evaluate the nonlinear refraction as well as the nonlinear absorption in the medium, by performing two Z-scans, one with and one without an aperture (Van Stryland et al 1998). A significant advantage of this technique is that it allows accurate determination of the nonlinear index of refraction without the detailed wave propagation analysis through and beyond the medium, provided that the length of the interacting medium is small compared to the diffraction length of the beam.

In Z-scan technique, the sample is translated in the z-direction along the axis of a focused Gaussian beam, and the far field intensity is measured as a function of sample position. Analysis of the intensity versus sample position Z-scan curve, predicated on a local response, gives the real and imaginary parts of the third order susceptibility. In this technique the optical effects can be measured by translating a sample in and out of the focal region of an incident laser beam. Consequently, increases and decreases in the maximum intensity incident on the sample produces wave front distortions created by nonlinear optical effects in the sample. Moving the sample along a well defined, focused laser beam with varying light intensity in the sample, the Z-scan data are obtained. By varying the aperture in front of the detector, one makes the Z-scan transmittance more or less sensitive to either the real or imaginary parts of the nonlinear response of the material. i.e. nonlinear refractive index and nonlinear absorption, respectively.
6.2.1 Intensity Dependent Refractive Index

The refractive index of a medium is independent of the intensity of light in case of ordinary light sources (Boyd 1992). In the regime of nonlinear optics the index of refraction of material can be altered if a beam of high intensity passes through the medium. The variation of refractive index is given by

\[ n(\omega) = n_0(\omega) + n_{21}(\omega) I(\omega) \]  

(6.1)

In this expression \( n_0(\omega) \) is the fundamental refractive index of a material at any specific frequency \( (\omega = 2\pi f) \), \( n_{21}(\omega) I(\omega) \) is the effective nonlinear refractive index associated with the beam of intensity \( I(\omega) \) and \( n(\omega) \) is the total index of refraction at that frequency. The coefficient \( n_{21}(\omega) \) is not a dimensionless quantity and can be expressed as

\[ n_{21}(\omega) = \frac{12\pi \chi^{(3)}}{n_0^2(\omega)c} \]  

(6.2)

The change in refractive index is sometimes referred to as optical Kerr effect in analogy with the Kerr electro-optic effect in which the change in the refractive index is proportional to the square of the applied electric field. It is present in almost all optical materials. The value of \( n_{21}(\omega) \) is typically of the order of \( 10^{-20} \text{ m}^2/\text{W} \). This effect can lead to self-focusing in laser.

6.2.2 Saturable Absorption

When a high intensity laser beam propagates through a material, the absorption co-efficient \( \alpha \) depends on the intensity \( I \) of the incident laser radiation and is given by the expression
\[ \alpha = \frac{\alpha_o}{1 + \frac{I}{I_s}} \]  \hspace{1cm} (6.3)

where \( \alpha_o \) is the low-intensity absorption co-efficient, and \( I_s \) is a parameter known as the saturation intensity.

### 6.2.3 Two Photon Absorption

In this process, an atom makes a transition from its ground state to an excited state by the simultaneous absorption of two laser photons. The absorption cross section \( \sigma \) describing this process increases linearly with laser intensity according to the relation

\[ \sigma = \sigma^{(2)} I \] \hspace{1cm} (6.4)

where \( \sigma^{(2)} \) is a coefficient that describes two photon absorption.

### 6.3 THEORY FOR Z-SCAN

The Z-scan technique is a simple but very accurate method to determine both nonlinear index of refraction \( n_2 \) and nonlinear absorption coefficient \( \beta \). Nonlinear index of refraction is proportional to the real part of the third-order susceptibility \( \text{Re}[\chi^{(3)}] \) and the nonlinear absorption coefficient is proportional to imaginary part of the third-order susceptibility \( \text{Im}[\chi^{(3)}] \). Basically, the method consists of translating the nonlinear sample through the focal plane of a tightly focused Gaussian beam and monitoring the changes in the far field intensity pattern. For a purely refractive nonlinearity, the light field induces an intensity dependent nonlinear phase and as consequence of the transverse Gaussian intensity profile, the sample presents a lens-like behavior. The induced self-phase modulation has the tendency of defocusing or recollimating the incident beam, depending on its \( z \) position with respect to
the focal plane. By monitoring the transmittance change through a small
 circular aperture placed at the far field position, one is able to determine the
 nonlinear refractive index. Any nonlinear absorption present in the sample
 can be found in a measurement where the aperture is removed (open aperture
 Z-scan). In this case the sample transmittance is measured as a function of the
 intensity, once the sample is scanned through the laser beam focal plane.

6.3.1 Measurement of Nonlinear Parameters

An easily measurable quantity $\Delta T_{p-v}$ (Sheikh Bahae et al 1989) can
be defined as the difference between the normalized peak (maximum)
transmittance $T_p$ and valley (minimum) transmittance $T_v$. The variation of this
quantity as a function of $\Delta \phi$ as calculated for various aperture sizes is found to
be almost linearly dependent on $\Delta \phi$

$$\Delta \phi = \frac{\Delta T_{p-v}}{0.406(1-S)^{0.25}} \quad (6.5)$$

where $\Delta \phi$ is the on-axis phase shift at the focus,

$$S = 1 - \exp \left[ \frac{-2r_a^2}{\omega_o^2} \right] \quad (6.6)$$

is the aperture linear transmittance, with $r_a$ denoting the aperture radius and $\omega_o$
denoting the beam radius at the aperture in the linear regime. And

$$\Delta \phi = k \Delta n \cdot L_{\text{eff}} \quad (6.7)$$

where

$$L_{\text{eff}} = \frac{1 - e^{\alpha L}}{\alpha} \quad (6.8)$$

with $L$ the sample length and $\alpha$ the linear absorption coefficient.
The nonlinear refractive index is

\[ n_2 = \frac{\Delta \phi}{K_l L_{\text{eff}}} \]  

(6.9)

Absorption coefficient is calculated by using the formula,

\[ \beta = \frac{2\sqrt{2}}{I_0} \frac{\Delta T}{L_{\text{eff}}} \]  

(6.10)

The real and imaginary parts of the third-order nonlinear optical susceptibility \( \chi^{(3)} \) are evaluated from the nonlinear refractive index \( n_2 \) and nonlinear absorption coefficients \( \beta \), respectively. The relations are defined as follows:

\[ \text{Re}\chi^{(3)} \text{(esu)} = 10^{-4} \frac{\varepsilon_o c^2 n_o^2}{\pi} n_2 \left( \frac{\text{cm}^2}{\text{W}} \right) \]  

(6.11)

And

\[ \text{Im}\chi^{(3)} \text{(esu)} = 10^{-2} \frac{\varepsilon_o c^2 n_o^2}{4\pi^2} \beta \left( \frac{\text{cm}^2}{\text{W}} \right) \]  

(6.12)

where \( \varepsilon_o \) is the vacuum permittivity, and \( c \) is the light velocity in vacuum.

The absolute value of \( \chi^{(3)} \) was calculated from

\[ |\chi^{(3)}| = \left[ (\text{Re}(\chi^{(3)}))^2 + (\text{Im}(\chi^{(3)}))^2 \right]^{1/2} \]  

(6.13)

\[ \textbf{6.3.2 Z-Scan Characteristic Graphs} \]

The measurement of third order nonlinearity \( \chi^{(3)} \) can be obtained from nonlinear absorption coefficient \( \beta \) (measured by using open aperture
Z-scan) and nonlinear refractive index \( n_2 \) (measured by using closed aperture Z-scan).

The experimental measurements of the third-order nonlinear refractive index \( n_2 \), absorption coefficient \( \beta \) and the nonlinear susceptibility \( \chi^{(3)} \) of KAP crystals using Z-scan technique were carried out with a continuous-wave Nd-YAG laser radiation at 532 nm. Both closed and open aperture Z-scan measurements were made for KAP crystals at an input intensity of 7.824 kW/cm\(^2\). The experiments were repeated for various doped KAP crystals and the third-order nonlinear refractive index is found to be different for different doped KAP crystals.

A plane polarized Gaussian laser beam, propagating in the z-direction, was focused to a narrow waist. The sample was translated along the z-direction and the transmitted intensity was measured through a finite aperture in the far field as a function of the sample position \( z \), measured with respect to the focal plane. As the sample moves through the beam focus (at \( z = 0 \)), self-focusing or defocusing modifies the wave front phase, thereby modifying the detected beam intensity. The schematic set-up of the Z-scan technique is shown in Figure 6.1.

The relation of nonlinear refraction of the sample to the Z-scan transmittance as a function of \( z \) can be understood in the following way. Assume a medium with negative nonlinear refraction index and thickness smaller than the diffraction length of the focused beam. This can be considered as a thin lens of variable focal length. Beginning far from the focus (\( z < 0 \)), the beam irradiance is low and nonlinear refraction is negligible. In this condition, the measured transmittance remains constant (i.e.\( z\)-independent). As the sample approach the beam focus, irradiance increases, leading to self-lensing in the sample. A negative self-lens before
Figure 6.1  Z-scan Experimental Setup
the focal plane will tend to collimate the beam on the aperture in the far field, increasing the transmittance measured at the iris position. After the focal plane, the same self-defocusing increase the beam divergence, leading to a widening of the beam at the iris and thus reducing the measured transmittance. Far from focus \((z > 0)\), again the nonlinear refraction is low resulting in a transmittance \(z\)-independent. A pre-focal transmittance maximum (peak), followed by a post-focal transmittance minimum (valley) is a \(Z\)-scan signature of a negative nonlinearity. An inverse \(Z\)-scan curve (i.e.) a valley followed by a peak characterizes a positive nonlinearity.

6.4 MEASUREMENT OF NONLINEAR OPTICAL PARAMETERS

The \(Z\)-scan experiments were performed using a 532nm second harmonic Nd:YAG laser beam (coherent-compass 215M), which was focused by 3.5 cm focal length lens. The laser beam waist \(\omega_0\) at the focus was measured to be 18.49 \(\mu\)m and the Rayleigh length \(Z_R =1.79\) mm. The schematic of the experimental set up used was shown in Figure 6.1. The set up has a laser, beam steering device, a lens, sample, sample holder and an aperture in far field followed by a detector to detect the variation in the intensity of the beam profile. A 1mm thick slab of pure KAP is translated across the focal region along the axial direction that is the direction of the propagation of laser beam by adjusting the screw in the sample holder. The transmission of the beam through an aperture placed in the far field was measured using photo detector fed to the digital power meter (Field master Gs-coherent). This is known as closed aperture \(Z\)-scan.
For an open aperture Z-scan, a lens to collect the entire laser beam transmitted through the sample replaced the aperture. Experiments were performed on every sample to understand the effect of dopants on the third-order nonlinear refractive index $n_2$.

### 6.4.1 Closed aperture Z-scan

The closed aperture Z-scan is sensitive to both nonlinear absorption and nonlinear refraction. The Z-scan trace is expected to have a minimum transmittance (valley) followed by a maximum transmittance (peak). This corresponds to positive nonlinearity (self-focusing effect). A peak followed by valley corresponds to negative nonlinearity (self defocusing effect). The characteristic curve for pure and alkali metal ions, amino acid, urea, thiourea and chelating agent doped (1 mol% ) KAP single crystals in the closed aperture scheme are shown in Figures 6.2a–6.2h.

### 6.4.2 Open aperture Z-scan

Z-scan with fully open aperture is insensitive to nonlinear refraction. The open aperture Z-scan traces are symmetric with respect to focus ($Z = 0$). If the traces having minimum transmittance, it is called two photon absorption (Bertolotti et al 1992) or if it has maximum transmittance, it is called saturation of absorption (Madhana Sundari and Palanisamy 2006). The characteristic trace of pure and alkali metal ions, amino acid, urea, thiourea and chelating agent doped (1 mol%) KAP single crystals shows that it is due to saturation of absorption (Figure 6.3a–6.3h).
Figure 6.2a  Closed aperture Z-Scan trace for pure KAP crystal

Figure 6.2b  Closed aperture Z-Scan trace for 1mol% Na⁺ doped KAP crystal
Figure 6.2c  Closed aperture Z-Scan trace for 1mol% Rb\(^+\) doped KAP crystal

Figure 6.2d  Closed aperture Z-Scan trace for 1mol% Li\(^+\) doped KAP crystal
Figure 6.2e  Closed aperture Z-Scan trace for 1mol% L-Threonine doped KAP crystal

Figure 6.2f  Closed aperture Z-Scan trace for 1mol% urea doped KAP single crystal
Figure 6.2g  Closed aperture Z-Scan trace for 1mol% thiourea doped KAP single crystal

Figure 6.2h  Closed aperture Z-Scan trace for 1mol% nitrilotriacetic acid doped KAP crystal
Figure 6.3a  Open Aperture Z-scan trace for pure KAP crystal

Figure 6.3b  Open Aperture Z-scan trace for 1mol% Na\textsuperscript{+} doped KAP crystal
Figure 6.3c  Open Aperture Z-scan trace for 1mol% Rb\(^+\) doped KAP crystal

Figure 6.3d  Open Aperture Z-scan trace for 1mol% Li\(^+\) doped KAP crystal
Figure 6.3e  Open Aperture Z-scan trace for 1mol% L-Threonine doped KAP crystal

Figure 6.3f  Open Aperture Z-scan trace for 1mol% urea doped KAP crystal
Figure 6.3g  Open Aperture Z-scan trace for 1mol% thiourea doped KAP crystal

Figure 6.3h  Open Aperture Z-scan trace for 1mol% nitrilotriacetic acid doped KAP crystal
6.5 RESULTS AND DISCUSSION

6.5.1 Observations during the experiment

During the process of scanning when the sample was at different position with respect to the focus, the spot of the transmitted beam was photographed at far away distance from the sample. Figure 6.4(a–d) shows such transmitted beam profiles for pure KAP crystal for 7.824 kW/cm\(^2\) incident beam intensity when the sample was far from the focus, at the focus, out of focus and away from the focus respectively. From the photographs it is clear that the spot has minimum size only when the sample was at focus. The spot size at the focus was measured to be 18.49\(\mu\)m.

6.5.2 Nonlinear properties of pure KAP crystal

The third-order nonlinear refraction \(n_2\) and the nonlinear absorption coefficient \(\beta\) of KAP crystal were determined from the closed and open aperture Z-scan measurements, respectively. Figure 6.2a shows the closed aperture Z-scan data for pure KAP crystal at an incident intensity \(I_0 = 7.824\) kW/cm\(^2\). The peak followed by a valley (normalized transmittance obtained from the closed aperture Z-scan data) indicates that the sign of the nonlinear refraction \(n_2\) is negative i.e., self-defocusing occurs in the crystal.

The measured Z-scan data (open aperture (\(S = 1\))) for pure KAP crystal is shown in Figure 6.3a. The enhanced transmission near the focus indicates that the saturation of absorption takes place at higher intensities. Absorption saturation in the sample at focus enhances the peak and decreases the valley in the closed aperture Z-scan curve and results in distortions in the symmetry of the Z-scan curve about \(z = 0\). The defocusing effect shown in Figure 6.2a is attributed to a thermal nonlinearity resulting from absorption of radiation at 532 nm. Localized absorption of a tightly focused beam
Figure 6.4 Variation in the beam profile corresponding to the sample positions (a) from the focus (b) at the focus (c) out of focus and (d) away from focus for pure KAP crystal

propagating through an absorbing pure KAP crystal medium produces a spatial distribution of temperature in the pure KAP crystal and consequently, a spatial variation of the refractive index, that acts as thermal lens resulting in severe phase distortion of the propagating beam.

The nonlinear absorption coefficient $\beta$ was estimated from the open aperture Z-scan data and is found to be $4.62 \times 10^{-4}$ cm/W. The nonlinear refractive index was calculated as, $n_2 = 1.72 \times 10^{-8}$ cm$^2$/W using closed
aperture Z-scan. The experimental measurements of \( n_2 \) and \( \beta \) was used to determine the real and imaginary parts of the third-order nonlinear optical susceptibility \( \chi^{(3)} \), the obtained values are \( \text{Re}(\chi^{(3)}) = 7.752 \times 10^{-6} \text{ esu} \) and 
\( \text{Im}(\chi^{(3)}) = 8.77 \times 10^{-6} \text{ esu} \) respectively. The absolute value of \( \chi^{(3)} \) was calculated as \( 11.81 \times 10^{-6} \text{ esu} \). The value of \( \chi^{(3)} \) was larger than those of some representative third-order nonlinear optical materials such as organic metal
(Huggard et al 1987) and organic polymers (Jenekhe et al 1990) suggesting that the KAP crystals have a potential application in nonlinear optical devices.

6.5.3 Nonlinear properties of alkali metal ion doped KAP crystals

The graphical representation of the closed aperture Z-scan analysis (Figures 6.2b, 6.2c, and 6.2d) for sodium, rubidium and lithium doped KAP crystals inferred the production of self defocusing effect in the alkali metal ions doped KAP crystals. The value of \( \beta \) and \( n_2 \) of the pure KAP crystals increases on doping with alkali metal ions. The value of \( \beta \) for the doped KAP crystals increases in the order of rubidium \( (4.84 \times 10^{-4} \text{ cm/W}) \), sodium 
\( (5.09 \times 10^{-4} \text{ cm/W}) \) and lithium \( (5.53 \times 10^{-4} \text{ cm/W}) \). The value of \( n_2 \) also increases on doping with alkali metal ions. The value of \( n_2 \) was greater for lithium doped KAP crystal \( (2.09 \times 10^{-8} \text{ cm}^2/\text{W}) \) than that of sodium and rubidium doped KAP crystal. The value of \( n_2 \) for sodium and rubidium doped KAP crystal was calculated as \( 2.03 \times 10^{-8} \text{ cm}^2/\text{W} \) and \( 1.98 \times 10^{-8} \text{ cm}^2/\text{W} \) respectively (Table 6.1). The third-order nonlinear susceptibility \( \chi^{(3)} \) was calculated using the values of \( \beta \) and \( n_2 \). The value of \( \chi^{(3)} \) increases on doping alkali metal ions to the pure KAP crystals. The value of \( \chi^{(3)} \) for the doped KAP crystals increases in the order of lithium \( (14.11 \times 10^{-6} \text{ esu}) \), sodium \( (13.31 \times 10^{-6} \text{ esu}) \) and rubidium \( (12.81 \times 10^{-6} \text{ esu}) \). The lower value of \( \chi^{(3)} \) for rubidium doped KAP crystals may be explained with size effects.
Table 6.1 Nonlinear properties of Pure and alkali Metal ions (Na⁺, Rb⁺, and Li⁺) doped KAP crystals as measured by Z-Scan

| Crystal       | ΔT_p (open) | β × 10⁻⁴ cm/W | ΔT_pν (closed) | |Δφ₀| | n₂ × 10⁻⁸ cm²/W | Im |χ(3) × 10⁻⁶ esu | Re |χ(3) × 10⁻⁶ esu | |χ(3) × 10⁻⁶ esu |
|---------------|-------------|---------------|----------------|---|---|----------------|---|----------------|---|----------------|---|
| KAP           | 0.128       | 4.62          | 0.531          | 1.5945 | 1.72 | 8.77          | 7.752 | 11.81          |
| Na⁺ doped KAP | 0.141       | 5.09          | 0.625          | 1.8768 | 2.03 | 9.67          | 9.149 | 13.31          |
| Rb⁺ doped KAP | 0.134       | 4.84          | 0.610          | 1.8318 | 1.98 | 9.196         | 8.924 | 12.81          |
| Li⁺ doped KAP | 0.153       | 5.53          | 0.643          | 1.9309 | 2.09 | 10.507        | 9.420 | 14.11          |
6.5.4 Nonlinear properties of L-Threonine, urea, thiourea and nitrilotriacetic acid doped KAP crystals

The Figures 6.2 (e – h) represents the closed aperture Z-scan curves for the L-Threonine, urea, thiourea and nitrilotriacetic acid doped KAP crystals respectively. The nature of the curves remains same which indicates the negative nonlinear refraction produced by the doped crystals. The calculated values of $n_2$ for the L-Threonine, urea, thiourea and nitrilotriacetic acid doped KAP crystals were $2.20 \times 10^{-8}$ cm$^2$/W, $2.79 \times 10^{-8}$ cm$^2$/W, $2.67 \times 10^{-8}$ cm$^2$/W, and $2.50 \times 10^{-8}$ cm$^2$/W respectively. The value of $n_2$ increases in the order of urea, thiourea, nitrilotriacetic acid and L-Threonine. The calculated value of $\beta$ increases on doping with L-Threonine, urea, thiourea and nitrilotriacetic acid. The value of $\beta$ ranges from $5.89 \times 10^{-4}$ cm/W to $8.24 \times 10^{-4}$ cm/W for the L-Threonine, urea, thiourea and nitrilotriacetic acid doped KAP crystals (Table 6.2). The real and imaginary values of $\chi^{(3)}$ for L-Threonine, urea, thiourea and nitrilotriacetic acid doped KAP crystals were calculated using the values of $n_2$ and $\beta$. The absolute values of $\chi^{(3)}$, L-Threonine, urea, thiourea and nitrilotriacetic acid doped KAP crystals were $\chi^{(3)}$ determined as $14.95 \times 10^{-6}$ esu, $20.08 \times 10^{-6}$ esu, $18.88 \times 10^{-6}$ esu, and $16.61 \times 10^{-6}$ esu respectively. The urea doped KAP crystal was found to posses more third order nonlinearity.
Table 6.2  Nonlinear properties of Pure, L-Threonine, urea, thiourea and nitrilotriacetic acid doped KAP crystals as measured by Z-Scan

| Crystal                        | $\Delta T_p$ (open) | $\beta \times 10^{-4}$ cm/W | $\Delta T_{p-v}$ (closed) | $|\Delta \phi_0|$ | $n_2 \times 10^{-8}$ cm$^2$/W | Im $[\chi^{(3)}] \times 10^6$ esu | Re $[\chi^{(3)}] \times 10^6$ esu | $[\chi^{(3)}] \times 10^{-6}$ esu |
|-------------------------------|---------------------|-----------------------------|---------------------------|------------------|-------------------------------|---------------------------------|--------------------------------|-------------------------------|
| KAP                           | 0.128               | 4.62                        | 0.531                     | 1.5945           | 1.72                          | 8.77                            | 7.752                          | 11.81                         |
| 1 mol% L-Threonine doped KAP   | 0.163               | 5.89                        | 0.678                     | 2.0360           | 2.20                          | 11.191                          | 9.916                          | 14.95                         |
| 1 mol% urea doped KAP          | 0.228               | 8.24                        | 0.860                     | 2.5825           | 2.79                          | 15.656                          | 12.575                         | 20.08                         |
| 1 mol% thiourea doped KAP      | 0.212               | 7.66                        | 0.822                     | 2.4684           | 2.67                          | 14.55                           | 12.034                         | 18.88                         |
| 1 mol% nitrilotriacetic acid doped KAP | 0.178               | 6.43                        | 0.771                     | 2.3153           | 2.50                          | 12.217                          | 11.268                         | 16.61                         |
6.6 CONCLUSION

The nonlinear properties of pure and 1mol% of alkali metal ions (Na\(^+\), Rb\(^+\) and Li\(^+\)) and L-Threonine, urea, thiourea, and nitrilotriacetic acid doped KAP crystals were measured by Z-scan technique using Nd-YAG (SHG) laser at 532 nm. The peak followed by the valley in the closed aperture Z-scan trace reveals the presence of negative nonlinearity in the both pure and doped KAP crystals. The negative nonlinear refraction \(n_2\) of the pure and doped KAP crystals were calculated. The value of \(n_2\) increases on doping. The value of \(\beta\) was determined using the open aperture Z-scan traces. The value of \(\beta\) of the pure KAP crystal increases on doping for pure and doped KAP crystals. The value of \(\beta\) for the doped KAP crystals increases in the order of rubidium, sodium, lithium, L-Threonine, nitrilotriacetic acid, thiourea and urea. The values of third order nonlinear susceptibility \(\chi^{(3)}\) for pure and doped KAP crystals were calculated using the values of \(n_2\) and \(\beta\). The value of \(\chi^{(3)}\) increases on doping. The value of \(\chi^{(3)}\) is more for urea doped KAP crystals. The value of \(\chi^{(3)}\) for the doped KAP crystals increases in the order of rubidium, sodium, lithium, L-Threonine, nitrilotriacetic acid, thiourea and urea.