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A Study on Spectral and Morphological Analysis on Unidirectional Neodymium Doped KDP Single Crystal

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Abstract : A nonlinear optical unidirectional $\langle 101 \rangle$ Single crystal of Neodymium doped Potassium dihydrogen orthophosphate (KDP) was grown by Sankaranarayanan-Ramasamy (SR) method. The $\langle 101 \rangle$ oriented seed crystals were mounted at the bottom of the glass ampoule and the crystal of 16mm diameter; 120mm length were grown by SR method. The laser damage threshold was measured using Q-switched Nd:YAG laser (1064 nm) and was found to be 5.456 Gwcm⁻² respectively. The presence of functional groups was examined by Fourier transform infrared (FTIR) analysis. The surface morphology and dislocations along $\langle 101 \rangle$ plane was observed using Scanning electron microscope (SEM) and Transmission electron microscope (TEM).

Keywords : Single crystal growth; Laser damage threshold; FTIR; TEM Analysis.

1. Introduction

Due to various significant applications, the search for NLO materials has continuously attracted attention in researchers since 1961. For a selected NLO material, ultimate aim is to obtain high conversion efficiency. Longer crystal length, smaller the phase mismatching, higher the power density, fast optical response time and larger the nonlinear coefficients will result in the high conversion efficiency [1].

This family of crystals plays a key role in nonlinear optics, and they possess high chemical stability and wide optical transparency [2]. On the other hand, KDP crystal is a famous inorganic Classical Ferroelectric Crystal that has a variety of applications in Laser Technology, Integrated and Nonlinear Optics [3].

The KDP is a widely known compound, wherein applicable NLO properties have made it, an extensively used crystal in frequency converters and modulators. These crystals have high optical quality, operated at high frequencies, can be enormously resistant to Laser radiation harm.

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Attempts were made to dope KDP with inorganic additives to observe the stability of the grown phase and compositional homogeneity of the existing crystal [4-6].

KDP crystals with additives are used in massive scale for many device applications. The KDP crystal doped with rare earth ions can also be used in Scintillators. Several researchers have carried out a lot of studies in pure and doped KDP crystals [7,8]. The aim is to enhance the nonlinear optical efficiency of grown crystals by adding rare earth ions suitable for implementing the crystals in various applications. However, there are no data on the effect of Neodymium on unidirectional crystal growth and various properties of KDP.

Neodymium ions, acts as a laser gain medium, typically emitting 1064 nm light from a particular atomic transition, after being pumped into excitation from an external source. Neodymium doped glass slabs used in extremely powerful lasers for inertial confinement. Neodymium-doped crystals can also be used in substrate crystals for different laser application.

In order to achieve the aim Neodymium is selected as rare earth ion and doped with KDP crystals and the grown crystals are subjected to different characterizations like Laser damage threshold (LDT), FTIR, SEM & TEM analysis.

2. Experimental Procedure

2.1. Crystal growth

A suitable seed crystal having a size of $4 \times 4 \times 4 \text{ mm}^3$ is selected for single crystal growth of $\langle 101 \rangle$ face. The chosen $\langle 101 \rangle$ plane of the seed crystal is mounted in the bottom of the ampoule without polishing the surface. The saturated solution of 1 mol% of Neodymium added KDP solution is prepared at 22°C . The solution is filtered using Whatman filter paper. SR method set up Fig. 1. is arranged to grow the above crystal.

Sankaranarayanan Ramasamy (SR) method is employed to grow Neodymium doped KDP single crystals. The Schematic Diagram of SR method experimental setup is as shown in Figure 1. It consists of temperature controllers, ammeters, transformers, two ring heaters at the bottom and top portions, glass ampoule, sensors and water bath. The growth ampoule is placed inside the water bath. The whole SR method experimental setup is sealed with small pores. The temperature near the heating coils is recorded using Mercury thermometers.

The main points that have to be concentrated in SR method are concentration of the solution, size of the ampoule, selection of seed crystal, seed orientation, mounting, temperature at top and bottom portion, evaporation rate and growth rate.

The saturated solution is first fed into the glass ampoule. For controlled evaporation, the top portion is closed with some opening at the middle using thick plastic cover. In SR method, the growth of the crystal is in particular direction inside a growth ampoule. The growth rate is 2mm/day for the given ampoule of diameter 16 mm. After 70 days of the growth duration, a good quality crystal was harvested with size 120 mm in length and 16 mm in diameter is harvested. The grown crystal is shown in Fig.2(a) &2(b).



Fig. 1. Photograph of experimental setup

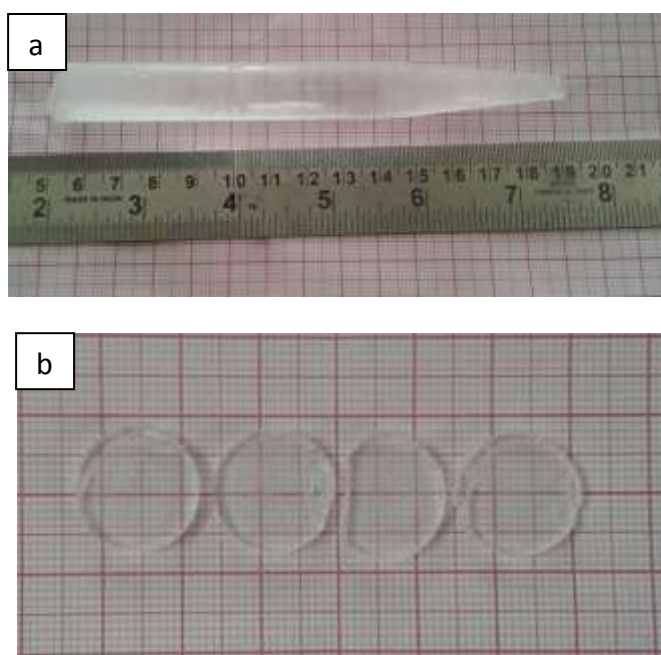


Fig.2a) Neodymium doped KDP <101> crystal grown by SR method b) The cut & polished crystals

3. Results and discussion

3.1 Laser damage threshold measurements

Optical damage in NLO materials might also seriously have an effect on the performance of high-energy laser systems as well as the efficiency of the optical devices. Consequently, excessive-damage threshold is a huge parameter for NLO crystal [9]. LDT measurements are done along the (101) direction for Neodymium doped KDP crystal grown by SR method using Nd:YAG laser. These Nd^{3+} ions permit the crystal to extend light at the laser wavelength through stimulated emission, when energy is furnished to the crystal. The pulse width and the repetition rate of the laser pulse at 1064 nm radiation, are 7 ns and 10KHz respectively.

For this measurement, a beam is focused onto the sample with a lens of 10 cm focal length. The power meter of the input laser beam records the energy density at which the crystal gets damaged. Initially 25mJ is applied up to 60 s, but no damage is observed. But for the energy of 39mJ, a small damage is being seen on the surface of the crystal after 60 s and is shown in Fig. 3.

The LDT is found using the relation (1) [10].

$$\text{Power density } (P_d) = \frac{E}{\tau\pi r^2} \quad (1)$$

Where E is the energy (mJ), τ is the pulse width (ns) and r is the radius of the spot (mm). The calculated damage threshold for the Neodymium doped KDP crystal grown by SR method is 1.909 GWcm^{-2} respectively.



Fig. 3. The Laser damaged crystal image of SR method grown <101> directed Neodymium doped KDP crystal

3.2 Fourier transform Infrared transmission (FTIR) Analysis

Fourier transform infrared transmission (FTIR) spectra of Neodymium doped KDP crystal is carried out in the mid IR region, 400 to 4000 cm^{-1} in order to confirm the presence of functional groups.

The spectrum (Fig. 4.) shows absorption bands at 1389.49 cm^{-1} and 1195.957 cm^{-1} which could be assigned to P=O stretching mode of vibration. The O-H stretching modes have intense broad absorption band between 3404.668 and 2599.816 cm^{-1} . The absorption bands at 2107.848 and 2599.816 cm^{-1} , is assigned to

O-H stretching vibrations. The $(\text{PO}_4)^{3-}$ symmetric bending is at 508.436 cm^{-1} and P-O and $(\text{PO}_4)_3$ plane bending at 454.9164 cm^{-1} . The broad absorption bands appearing at 1739.386 cm^{-1} , 992.1706 cm^{-1} are assigned to P-O-H stretching vibrations. There is a shift in the FTIR spectrum proves the presence of Neodymium in the KDP crystal, when compared with pure KDP reported value [11].

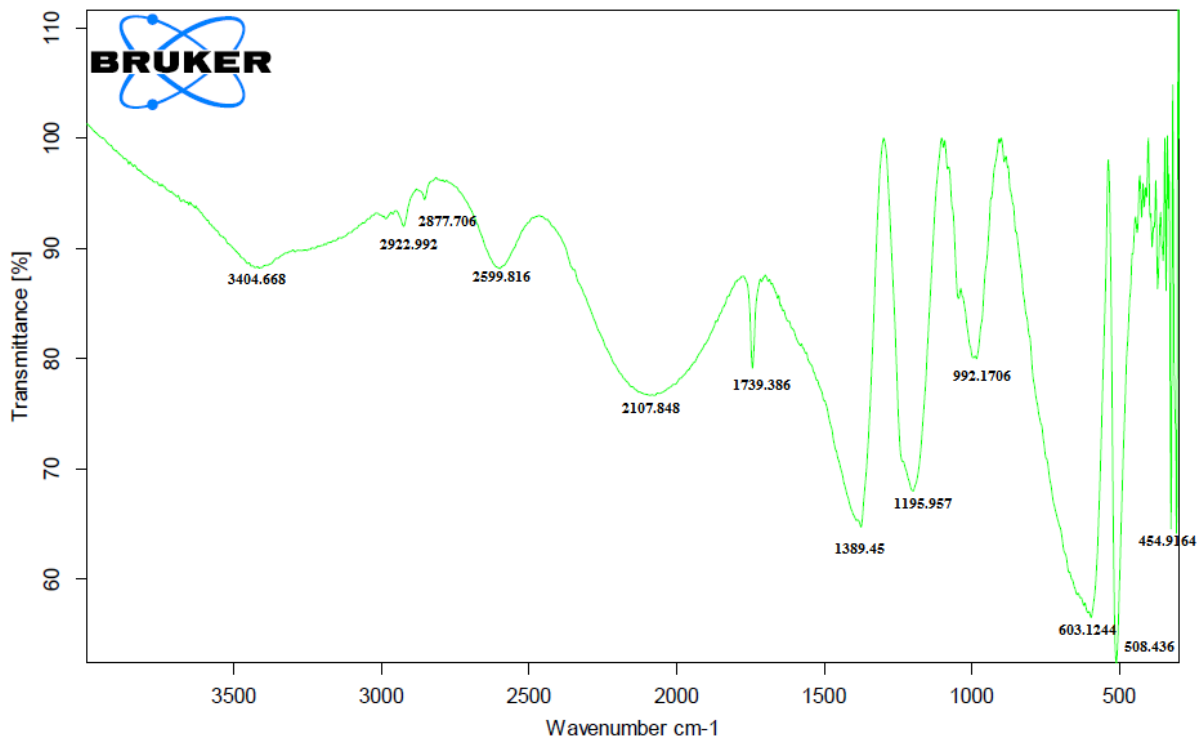


Fig. 4. FTIR spectra of <101> directed Neodymium doped KDP crystal

3.3 Scanning electron microscope (SEM) Analysis

The SEM photograph of the as grown Neodymium doped KDP crystal is recorded along (101) direction. The consequent picture gives the surface morphology of Neodymium doped KDP crystal and is shown in Fig.5 (a) &5 (b).

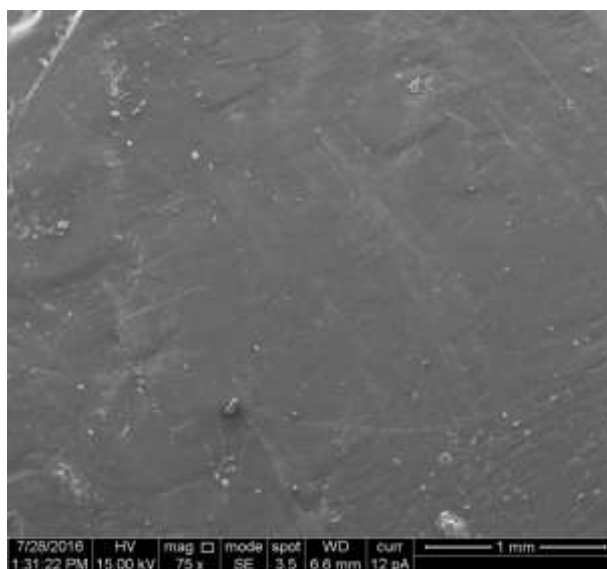


Fig. 5(a) SEM image of the title crystal in 25X magnification

From the SEM photograph, it is observed that, the grown crystal shows smooth surface. Some dislocation networks are discovered at the surface of the growth plane. However, predominant part of the crystal surface is free from dislocation networks and visible inclusions.

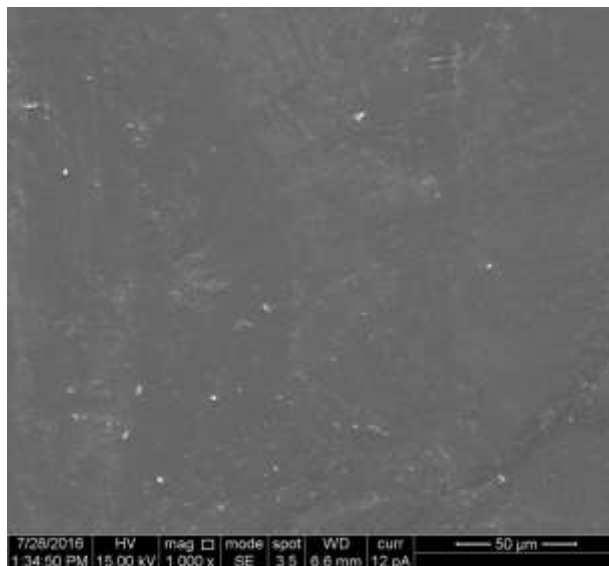
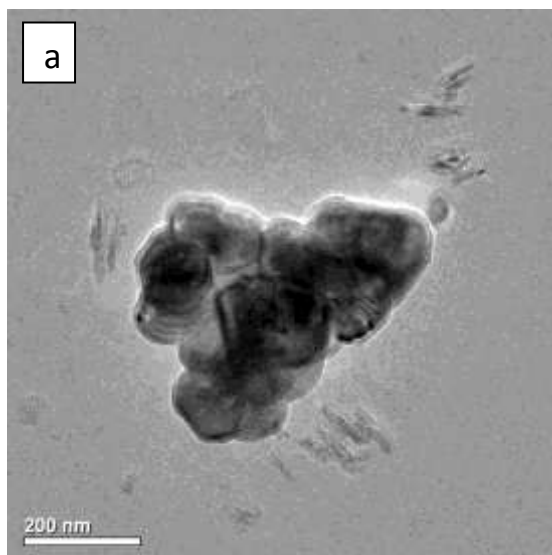


Fig. 5(b) SEM image of the title crystal in 1000X magnification

3.4 Transmission electron microscope (TEM) Analysis



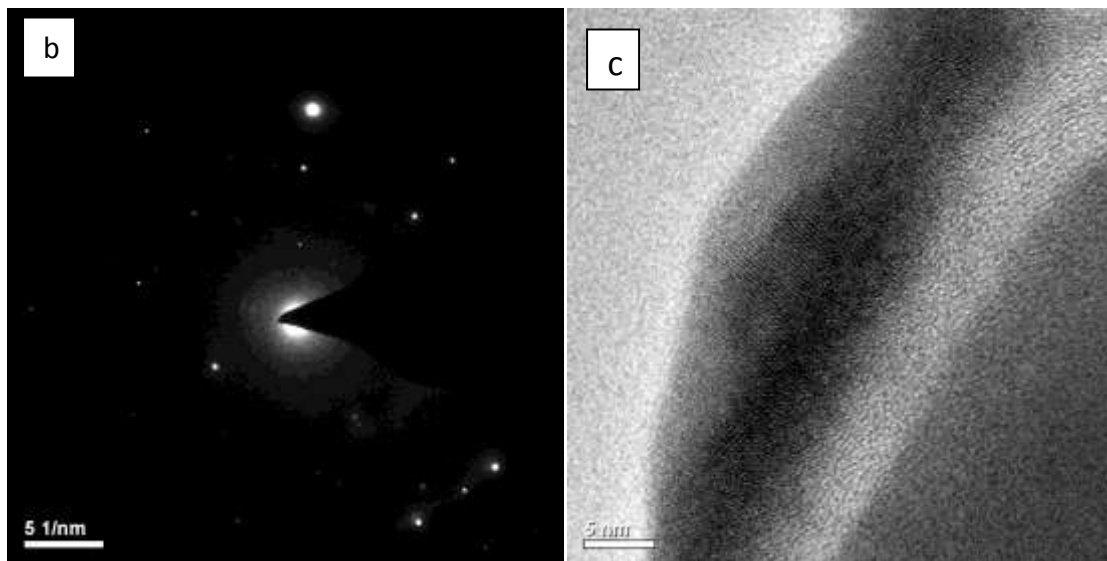


Fig. 6. (a) TEM image (b) SAED pattern and (c) the HRTEM with interplanar spacing of the Neodymium doped KDP crystal by SR method.

Fig. 6. shows the TEM images of crystals grown by SR method. The Tetragonal particles of ~30nm size, is shown in TEM image. The SAED pattern shows the bright spots which indicates that the material is crystalline. The High resolution TEM shows the inter-planar spacing of 2.58 Å.

Conclusions

- A new additive rare earth Neodymium is added to KDP and crystals were grown by SR method. Higher growth rate is achieved in SR method grown crystal.
- The better laser damage threshold value indicates that the grown crystal has high damage resistance and are useful in high power frequency conversion application.
- The presence of various functional groups is confirmed by Fourier transform infrared (FTIR) analysis. The slight shift in the FTIR spectrum confirms the presence of Neodymium inside the KDP crystal.
- The surface morphology and dislocations along $\langle 101 \rangle$ plane is observed using SEM and TEM analysis.

The addition of 1 mol% Neodymium will be useful to grow high-quality, large-size KDP crystals with faster growth rate.

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