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Investigation of SR method grown <101> directed Praseodymium doped KDP crystal and its Single crystal Xrd, LDT, thermal, mechanical, Etching, FTIR, SEM & TEM analysis

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Abstract : *An nonlinear optical unidirectionnel <101> single Crystal of Praseodymium doped potassium dihydrogen orthophosphate (KDP) was grown by Sankaranarayanan-Ramasamy (SR) method. The <101> oriented seed Crystal were mounted at the bottom of the glass ampoules and the Crystal of 16 mm diameter, 150 mm length were grown by SR method. The unit cell parameters were confirmed by single Crystal X-ray diffraction analysis and it belongs to Tetragonal system with a space group of* I42d. *The laser damage threshold (LDT) was measured using Q-switched Nd:YAG laser (1064nm) and was found to be 5.546 Gwcm^{-2} respectively. Its thermal stability has been studied using Vickers Microhardness tester and it exhibit higher hardness value. Chemical etching represent the distribution of structural defects in grown crystal. The presence of functional groups was examined by Fourier transform infrared (FTIR) analysis. The surface morphology and dislocations along <101> plane was observed using Scanning electron microscope (SEM) and Transmission electron microscope (TEM).*

Keywords: *Etching studies, Laser damage threshold, Mechanical properties, Single crystal growth, TEM*

I. Introduction

With the advanced research approach on efficient nonlinear optical material (NLO) is intensively studied for various optical device applications. Potassium dihydrogen orthophosphate (KDP) is a best known NLO material and has been used for second harmonic generation for high pulse energy, laser frequency conversion, low repetition (<100 Hz) rate lasers, electro-optical modulation and Q-switching applications [1-3].

As a result, significant efforts have been made to find novel and efficient NLO materials. The study of the crystallization behavior of KDP and the factors influencing its structural properties is still of great interest. The most important factor which influences the growth rate, the surface morphology of crystal is impurities [4,5]. An impurity can suppress, enhance or stop the growth of crystal completely. Modern technical tasks like high power laser systems have a great demand for very large size crystals. The use of special additives is an effective way to accelerate the growth rate. The beneficial effect of additives on the growth process and properties of crystals has been applied in recent years [6-8]. Several researchers have carried out a lot of studies in pure and doped KDP crystals [9,10]. However, there are no data on the effect of Praseodymium on unidirectional crystal growth and various properties of KDP. The most efficient additives are reagents with metal ions that have the same properties as that of bulk solutions which can change the properties of solution such as viscosity, surface tension, etc. without deteriorating the optical qualities of crystals. Praseodymium is used as catalyst in a wide variety of metallurgical applications, in lasers, masers, in industrial glass production, as polishing agent and still in electronic and thermoelectric components. It is valued for its magnetic, electrical, chemical and optical properties. Hence Praseodymium is selected as additive in the KDP solution and doped KDP crystals were grown from the aqueous solution with SR method and the grown crystals are subjected to different characterizations like micro hardness, chemical etching, thermal analysis (TG/DTA), single crystal xrd analysis, Laser damage threshold (LDT), FTIR, SEM & TEM analysis.

II. Experimental Procedure

2.1. Crystal growth

A suitable seed crystal having a size of 4x4x4 mm3 was selected for single crystal growth of <101> face. The chosen <101> plane of the seed crystal was mounted in the bottom of the ampoule without polishing the surface. The saturated solution of 0.1 mol% of Praseodymium added KDP solution was prepared at 27^{0}C. The solution was filtered using Whatman filter paper.

The apparatus consists of glass container of size 30x30x30 cm^3 and ampoule of inner diameter 16 mm using two ring heaters. The ampoule was kept in the glass water bath to maintain constant ambient temperature. The filtered Super saturated solution was poured carefully into the ampoule without disturbing the seed crystal. The ring heaters are positioned one at the top and another at the bottom of the growth ampoule.

The growth was initiated with a suitable temperature provided by the ring heater at the top region of the saturated solution under equilibrium condition. The temperature difference between the top and bottom ring heaters of the growth ampoule was carefully maintained to control the nucleation. In the present work, the temperature around the top and bottom of the ampoule was maintained at 32^{o}C and 27^{o}C respectively. Under this condition highly transparent crystal growth was seen. The growth rate was 2mm/day for the given ampoule of diameter 16 mm. After 75 days of the growth duration, a good quality crystal was harvested with size 150 mm in length and 16 mm in diameter was harvested. The grown crystal is shown in Fig.1(a) & 1(b).

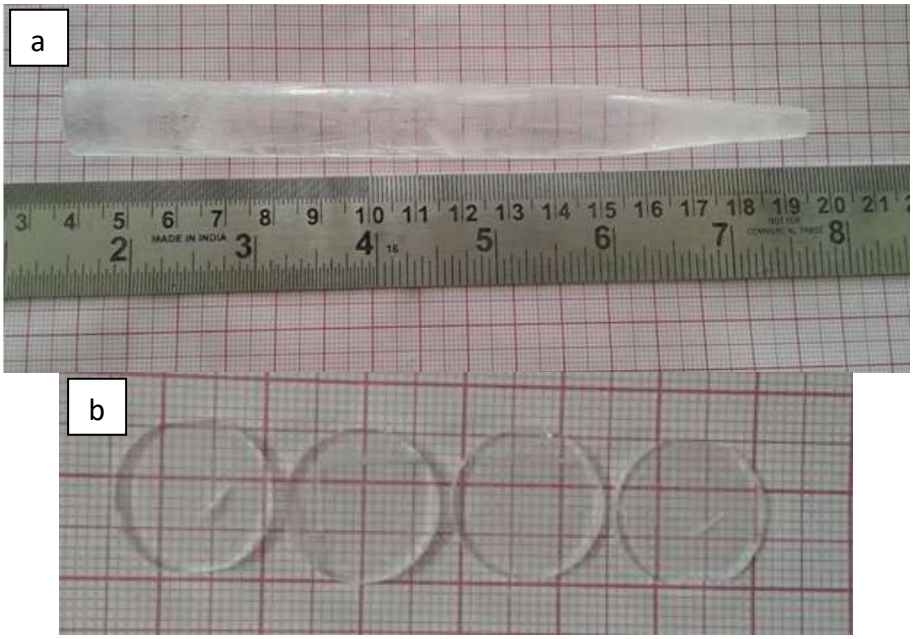

Fig.1 a) Praseodymium doped KDP <101> crystal grown by SR method b) The cut & polished crystals

III. Results and discussion

3.1 Single crystal XRD Analysis

The Praseodymium doped KDP crystals were subjected to single crystal X-ray diffraction analysis using Bruker Smart Apex Duo single crystal X-ray diffractometer to determine the lattice parameters and space group. The title compound crystallizes in Tetragonal system with space group I42d. From the XRD data, the obtained lattice parameter values are found to be a=b=7.235Å, c=6.37Å, α=β=γ=90° and cell volume V= 365.4Å^{3}. It is observed that there is no change in the phase structure (unit cell) of the doped crystal, however, the lattice parameters and cell volume of the grown crystal has been slightly modified compared to KDP due to the lattice strain produced by the dopant. The obtained cell parameters are in good agreement with the data given by Xu and Xue [11].

Hardness of a crystal is due to the resistance offered by a solid to the movement of dislocation, practically which is caused by scratching or indentation [12,13]. Due to the application of mechanical stress by the indenter, dislocations are generally at the region of the indentation.

Vickers hardness studies have been carried out using Future Tech Micro hardness tester FM-800. The indentation hardness was measured as the ratio of applied load to the surface area of the indentation. The grown crystal of Praseodymium doped KDP by SR method was selected for micro hardness studies. Indentations were carried out using Vickers indenter for varying loads. For each load (p), several indentations were made and the average value of the diagonal length (d) was used to calculate the micro hardness of the crystals. Vickers micro hardness number was determined using the relation (1).

$$Hv = \frac{1.8544p}{d^2} \quad \text{---------- (1)}$$

Where, 1.8544 is a constant of a geometrical factor for the diamond pyramid. The load Vs. hardness value of Praseodymium doped KDP crystal by SR method are shown in Fig. 2. It is observed that hardness increases up to a load of 100g, above which cracks start developing which may be due to the release of internal stress generation with indentation. Higher hardness value for SR method grown Praseodymium doped KDP crystal indicates greater stress required to form dislocation thus confirming greater crystalline perfection.

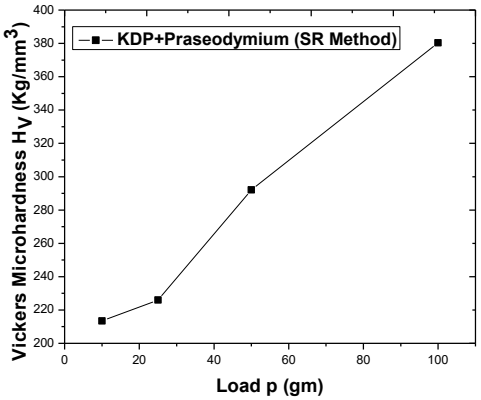

Fig. 2. Plot of micro hardness study for grown crystal

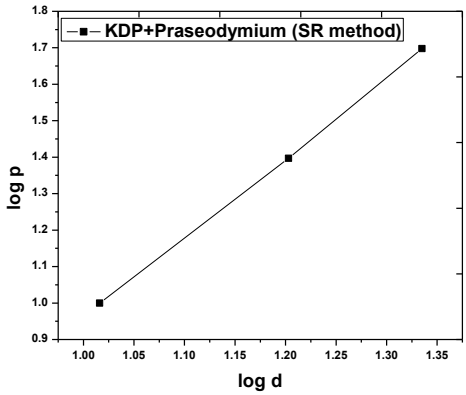

Fig.3. log p versus log d plot of grown crystals

The log P Vs. log d plot are also plotted and are shown in Fig. 3. The plots are found to be nearly straight line. From the slope of the best fitted lines, the work hardening co-efficient or Meyer indices (n) were obtained. The Meyer's law [14] is expressed in relation (2).

$$P = K_1 d^n \text{ --------- (2)}$$

Where K_1 is the material constant. According to Onitsch and Hanneman 'n' should lie between 1.0 and 1.6 for hard material and above 1.6 for soft ones [14]. The value of 'n' obtained for <101> face of SR grown Erbium doped KDP crystal was 2.22. The 'n' value observed in the present study is more than 1.6. This indicates that the grown crystal belong to soft material category.

3.3 TG-DTA analysis

To analyze the thermal stability and to confirm the weight loss of the Praseodymium doped KDP (SR method) crystal, the Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out using PL-STA 1500 thermal analyzer at a heating rate of 20^0C min^{-1} to 1000^0C in nitrogen inert atmosphere. The Thermo gram TGA trace are shown in Fig. 4(a). Although the TGA trace appears nearly straight up to the temperature of 200^0C, a careful examination of Thermo gram indicates that short weight loss is at temperature near 200^0C, it may be due to physically absorbed water, which is in good agreement with the reported work [15]. The DTA curve of praseodymium doped KDP (SR method) crystal are shown in Fig. 4(b). It is found that there is an endothermic peak at 40^0C, which may correspond to the so called high temperature phase transition.

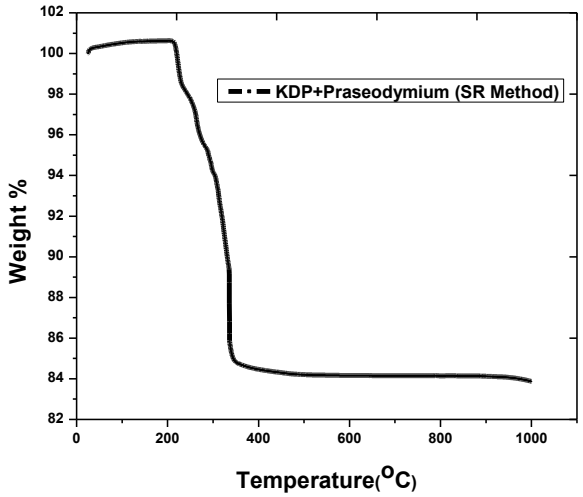

Fig. 4(a). TGA curve of Praseodymium doped KDP (SR method) crystal

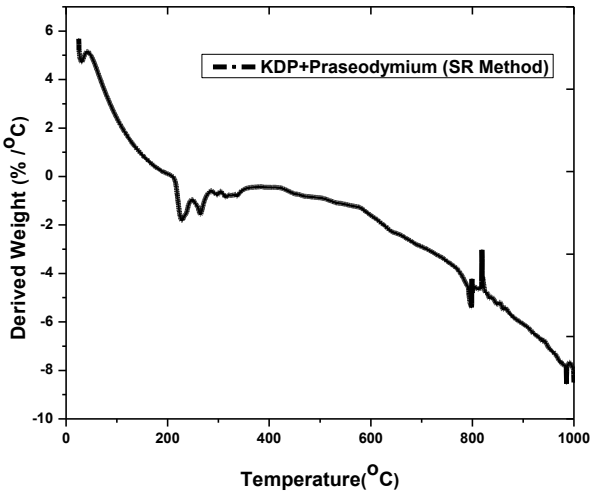

Fig. 4(b). DTA curve of Praseodymium doped KDP (SR method) crystal

3.4 Chemical etching studies

The nonlinear efficiency of the NLO material mainly depends on the quality of the grown crystals because the segregated impurities and dislocations which occur during growth results in the distortion of the optical beam to be processed . So, it is very essential to study the micro structural imperfections or crystal defects in the grown crystals. The etching technique is the simplest characterization technique that can be best employed to study the defect structure of a single crystal [16]. However the success of this technique lies in the efficiency of the chemical etchant to sense the dislocation sites selectively. Subsequently, etch pits are formed at the dislocation centers on those faces at which the additives are found. Etching study are made on <101> plane of Praseodymium doped KDP crystal grown by SR method with water as an etchant for 10s. Water is a superior etching solution for revealing dislocation etch pits and is insensitive to surface orientation as it produced pits almost on all surfaces. The etched surface was soaked with good quality filter paper and examined under an optical microscope in reflection mode. Fig. 5(a). shows the surface of the SR method grown crystal before etching, which reveal the as grown crystals have smooth layered surface. Fig. 5(b). shows the etch pattern on the <101> plane of SR grown Praseodymium doped KDP crystal surface after 10s etching. The etch pattern shows well defined small and big rock like patterns. The shape of the etch pits varies with different etchants because the morphology of etch pits is connected with the nature of chemical complexes present in the solution [17]. To utilize the single crystals for NLO applications, it is essential to grow single crystals with less dislocation [18].

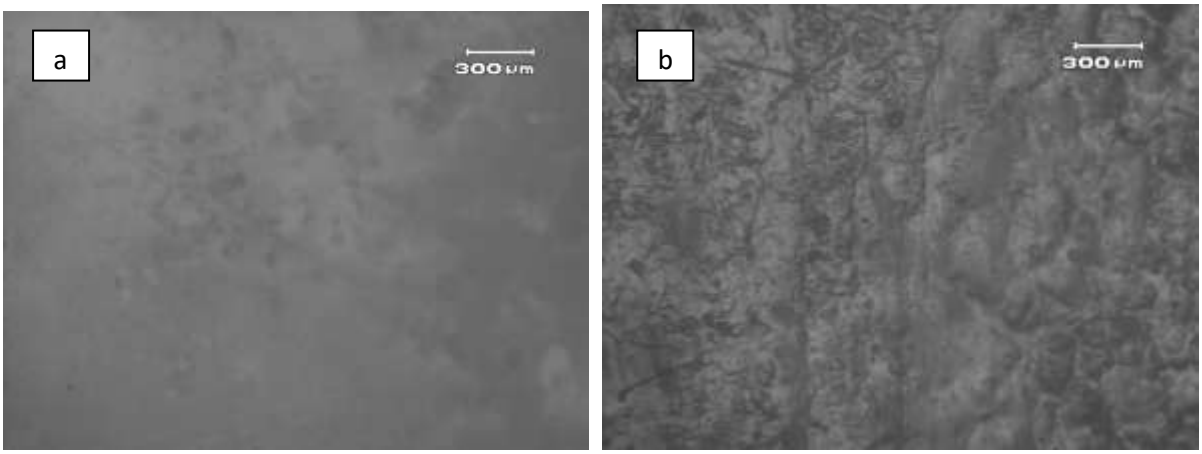

Fig. 5(a). shows the surface of the grown crystal before etching
Fig. 5(b). shows the etch pattern on the <101> plane of SR grown Praseodymium doped KDP crystal

3.5 Laser damage threshold measurements

Optical damage in NLO materials may severely affect the performance of high-power laser systems as well as the efficiency of the optical devices based on nonlinear processes. Hence, high-damage threshold is a

significant parameter for NLO crystal. Two main mechanisms that cause laser-induced damage in the wide band gap dielectric materials are dielectric break down and thermal absorptions [19]. Laser damage threshold measurements are carried out along the <101> direction for SR method grown Praseodymium doped KDP grown crystals using an actively Q-switched diode array side pumped Nd:YAG laser. The pulse width and the repetition rate of the laser pulses were 7ns and 10KHz, respectively, at 1064nm radiation. For this measurement, a beam was focused onto the sample with a 10cm focal length lens. Experiments were performed by keeping the positions of the lens and crystal plate as fixed and increasing the laser pulse energy until a whitish spot was seen at the surface of the crystal. During laser radiation, the power meter records the energy density of the input laser beam by which the crystal gets damaged. Initially 25mJ was applied up to 60 s but no damage was observed and when applying 30mJ after 60 s a small damage was seen on the surface. The Laser damaged crystal image are shown in Fig. 6.

Fig. 6. The Laser damaged crystal image of SR method grown <101> directed Praseodymium doped KDP crystal

The laser damage threshold was calculated using the expression (3) [20].

$$\text{Power density } (P_d) = E/\tau\, \pi r^2 \text{ ---------- (3)}$$

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 SR method Praseodymium doped KDP crystal are 5.456 $Gwcm^{-2}$ respectively.

3.6 Fourier transform Infrared transmission (FTIR) Analysis

Fourier transform infrared transmission (FTIR) spectra of Praseodymium doped KDP crystal was carried out in the mid IR region, 400 to 4000 cm^{-1} in order to confirm the presence of functional groups. The spectrum (Fig. 7.) shows absorption bands at 1395.626 cm^{-1} and 1200.074 cm^{-1} which could be assigned to P=O stretching mode of vibration. The O-H stretching modes have intense broad absorption band between 3748.429 and 2601.875 cm^{-1}. The absorption bands at 2111.965 and 2601.875 cm-1, is assigned to O-H stretching vibrations. The $(PO_4)^{3-}$ symmetric bending is at 512.23 cm^{-1} and P-O and $(PO_4)_3$ plane bending at 459.033 cm^{-1}. The broad absorption bands appearing at 1694.1 cm^{-1}, 1000.404 cm^{-1} are assigned to P-O-H stretching vibrations. There is a shift in the FTIR spectrum proves the presence of Praseodymium in the KDP crystal, when compared with pure KDP reported value [21].

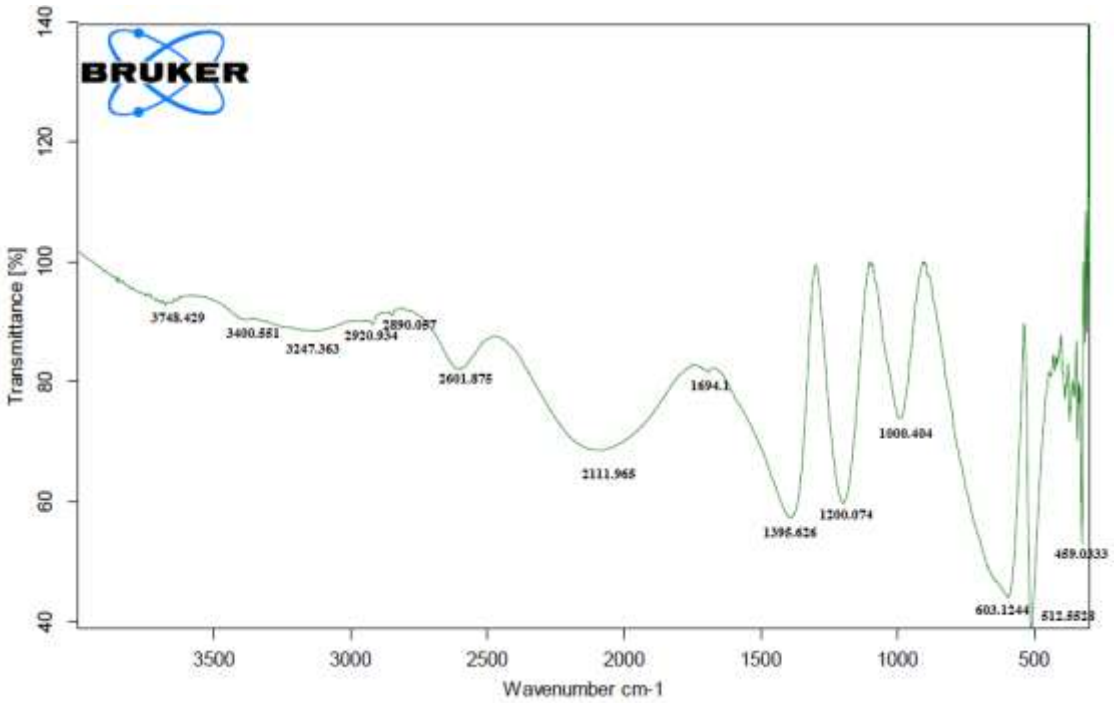

Fig.7. FTIR spectra of <101> directed Praseodymium doped KDP crystal

3.7 Scanning electron microscope (SEM) Analysis

The SEM image of the as grown Praseodymium doped KDP crystal was recorded along <101> plane. The resultant image are shown in Fig. 8(a) & (b). A few dislocation networks are observed on the surface of the growth plane. However, major part of the crystal surface is free from dislocation networks and visible inclusions.

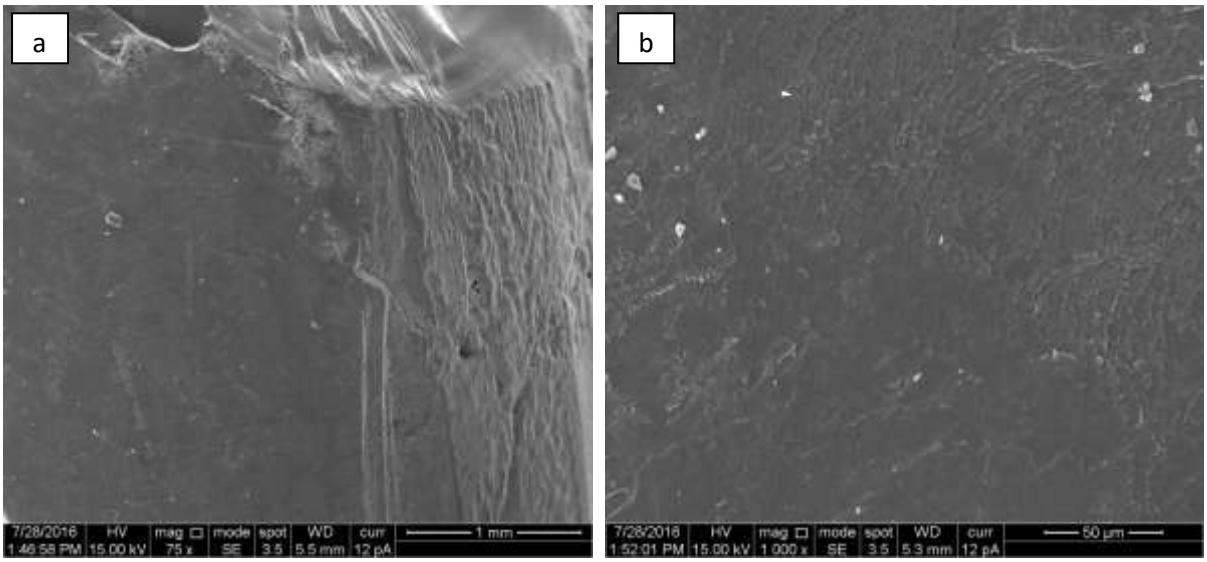

Fig. 8(a) SEM image of the title crystal in 25X magnification
Fig. 8(b) SEM image of the title crystal in 1000X magnification

3.8 Transmission electron microscope (TEM) Analysis

Fig. 9. shows the TEM image, SAED pattern and the HRTEM images of Praseodymium doped KDP crystals grown by SR method. The TEM image shows the almost Tetragonal particles of ~20nm size, which combined together to form a flakes shape of SEM image. The SAED pattern shows the well-defined circles corresponds to the Miller indices of single crystal XRD results. The HRTEM shows the planes with inter-planar spacing.

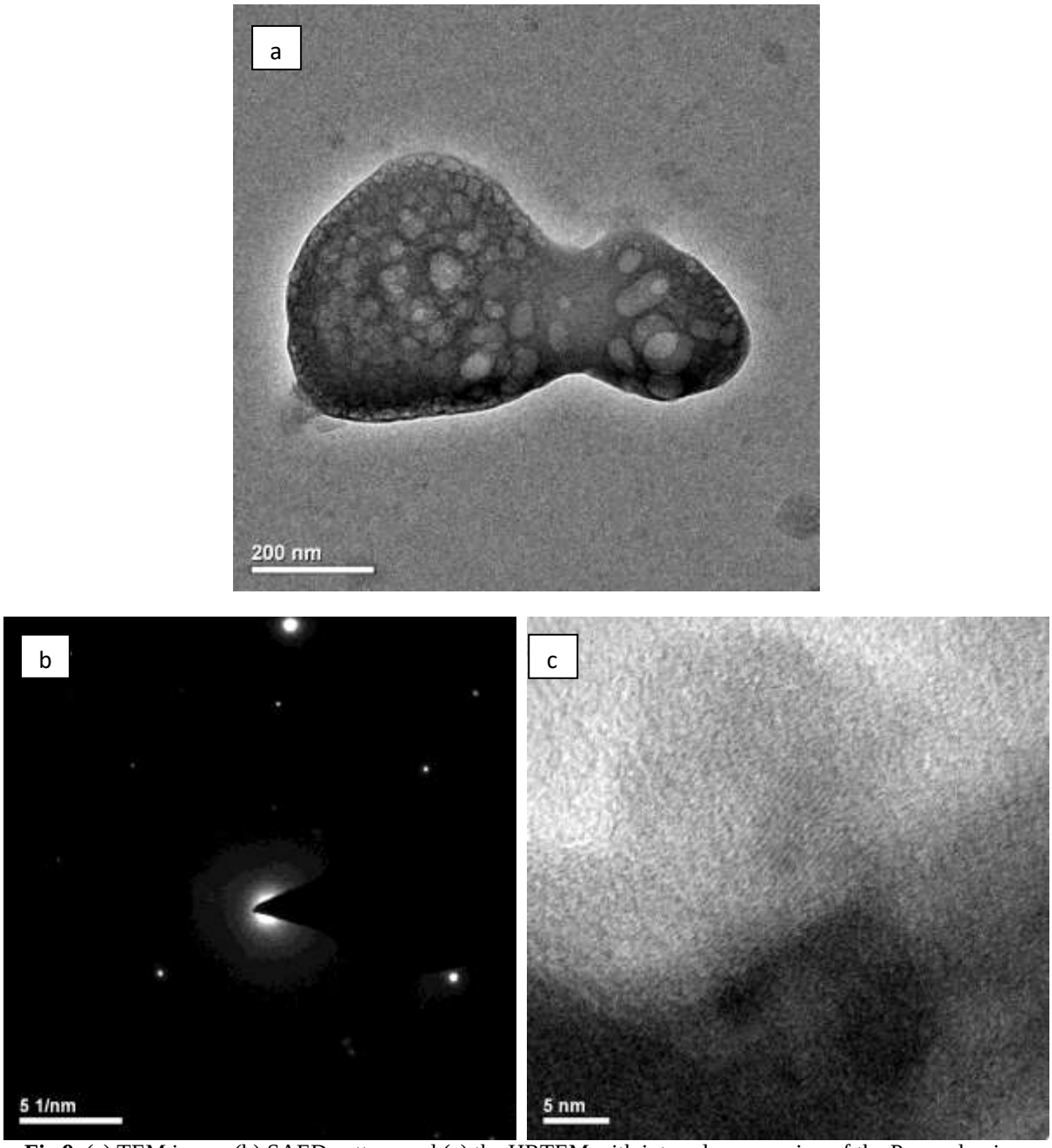

Fig.9. (a) TEM image (b) SAED pattern and (c) the HRTEM with inter planar spacing of the Praseodymium doped KDP crystal by SR method.

IV. Conclusion

1. A new additive rare earth Praseodymium was added to KDP and crystals were grown by SR method. Higher growth rate is achieved in SR method grown crystal.
2. The unit cell parameters a=b=7.235Å, c=6.37Å, α=β=γ=90° and cell volume V= 365.4Å^3 were confirmed by single crystal X-ray diffraction analysis and it belongs to Tetragonal system with a space group of I42d.
3. The Vickers Micro hardness number, H_V for the SR grown Praseodymium doped KDP crystal was calculated by application of load in the range of 10 g-100 g.
4. The value of Meyer's index for SR grown Praseodymium doped KDP crystal was 2.22 respectively. It suggests that the grown crystal belong to soft material category.
5. TGA indicates that short weight loss is at temperature near 200^{0}C. DTA indicates that there is an endothermic peak at 40^{0}C, which may correspond to the so called high temperature phase transition.
6. Chemical etching studies represent the distribution of structural defects in grown crystal.

7. The better laser damage threshold value indicates that the grown crystal has high damage resistance and are useful in high power frequency conversion application.
8. The functional groups was examined by Fourier transform infrared (FTIR) analysis. The shift in the FTIR spectrum proves the presence of Praseodymium in the KDP crystal.
9. The surface morphology and dislocations along <101> plane was observed using Scanning electron microscope (SEM) and Transmission electron microscope (TEM).
10. The addition of 0.1 mol% Praseodymium will be useful to grow high-quality, large-size KDP crystals with faster growth rate.

Acknowledgements

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