Available online at www.elixirpublishers.com (Elixir International Journal)

Crystal Research

Elixir Crystal Research 101 (2016) 44041-44043

ISSN: 2229-712X

Optical, thermal mechanical and NLO properties of mono,di,tri valent metal ion doped KAP crystals

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ARTICLE INFO

Article history:

Received: 21 October 2016;
Received in revised form:
10 December 2016;
Accepted: 21 December 2016;

Keywords

Crystal growth,
Nonlinear optical materials,
Solution growth.
TG/DTA ,
FTIR,
Optical properties,
SHG efficiency,
UV-Vis.

ABSTRACT

Semi-organic nonlinear optical crystal Pottasium hydrogen phthalate (KAP) crystals doped with mono, di, trivalent metal ion(Ag^+,Ca^{2+},Cr^{3+}) doped separately were grown by slow evaporation solution growth technique. The crystal system and lattice parameters were confirmed from the powder X-ray diffraction analysis. Fourier transform infrared (FTIR) studies confirm the various functional groups present in the grown crystal. The transmittance of electromagnetic radiation is studied through UV-Visible spectrum. The mechanical property of grown crystals has been analyzed by Vicker's microhardness method. The thermal behaviour of the grown crystals has been investigated by DTA and TGA analysis. SHG efficiencies were measured using Kurtz powder technique. The NLO efficiency of these crystals was measured and Ca^{2+} doped KAP have the highest SHG value than all other crystals.

1.Introduction

The metallic ion dopants (Fe^{3+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, etc.) in the KAP crystals are reported to induce significant changes in optical, ferroelectric and non linear optical behaviours [1-3]. Kejalakshmy et. al [1] have reported that the metal ion (Cr and Fe) doped KAP crystals serve as good electro-optic modulator. Monica Enculescu [5, 4] has studied the effect of rhodamine 6G, coumarine 6 and polyvinylpyrrolidone (PVP) on KAP crystals using solution growth method. It was reported that the dopants enhance the second harmonic generation (SHG) efficiency of KAP. Parthiban et al. [3] also reported that the Zn^{2+} doping into KAP crystals improves its SHG efficiency. Murugakoothan et al. [6] have investigated the effect of impurities like potassium dihydrogen orthophosphate, urea and L-arginine phosphate on KAP crystals and concluded that the urea doping yields high mechanical stability and optical transmission than other dopants.

In this background, the goal of present work was set to the growth and characterisation of a series of KAP crystals with different cations (trivalent, divalent and monovalent).

2. Experimental

Pure and doped KAP crystals were grown by slow evaporation method in room temperature with double distilled water as solvent. Recrystallised salt of KAP (Merck) was used in this work. Initially saturated KAP solution was prepared by using double distilled water as solvent at room temperature. The saturated solution was filtered by micro filter paper of 0.1μm porosity. The mono,di,tri valent impurities Ag^+, Ca^{2+}, Cr^{3+} were selected as additives in the form of Agcl, $CaCl_2$ and $K_2Cr_2O_4$. The various cationic impurities were added with pure KAP solution with 0.1M% of each. The final solution was again stirred well and filtered each separately.

The pH values of the pure and doped KAP solutions were found to be 4. After three days, tiny crystals were seen at the bottom of the beakers and they were used as seed crystals. Transparent and good quality seed crystals were tied with separate nylon thread and these seed crystals were placed inside the respective mother solutions for the even growth of all faces of the growing crystals. Crystals were allowed to grow for about 10 days at room temperature without disturbing the vessels containing solutions and were harvested. The pH values of the final solutions after the completion of the growth were found to be 4.0 as that of initial saturated solution. The grown crystals were shown in fig: 1.

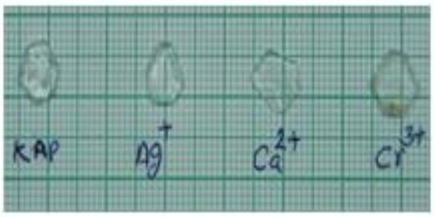

Fig 1. As grown Pure KAP, Ag^+, Ca^{2+} and Cr^{3+} doped KAP crystals

3. Results and discussion

3.1. Powder X-ray diffraction studies

The crystals of pure and doped KAP crystals were crushed into fine powder and subjected to powder X-ray diffraction studies using Shimadzu Model XRD- 6000 diffractometer to determine the lattice parameters and crystal structure. The powdered samples were scanned in the range 10-60° at a scan rate of 2°/min. The powder X-ray diffraction (XRD) patterns of the crystals were shown in the figure 2. The sharp and well defined peaks at specific 2Θ values indicate the high crystalline nature of the crystal.

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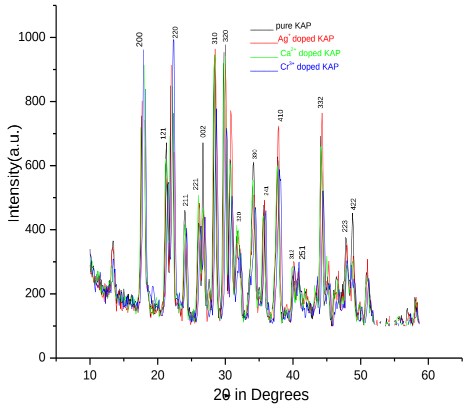

Fig. 2 powder X-ray diffraction (XRD) patterns of pure and doped KAP crystals.

3.2 Thermal analyses

Thermogravimetric analysis was carried out between 50° to 1000°C in nitrogen atmosphere using Universal V4.3A TA instrument (SDT Q600 V8.3 Build 101) with the heating rate of 20°C/min. The TGA curves of pure and Ag^+, Ca^{2+} and Cr^{3+} doped KAP are shown in Fig.3. The silver doped KAP crystals have lowest mass loss when compared to all other crystal.

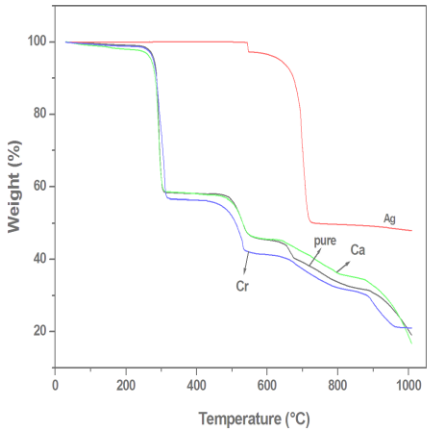

Fig 3.TGA curves of pure and doped KAP crystals

3.3 FTIR analyses

FTIR spectra were recorded in transmittance and absorption mode using the instrument Lambda 35 make Perkin Elmer (Spectrum RX1). The results are shown in Fig. 4. The various vibrational assignments are shown in Table 2. Absorption peak in the region less than 900 cm^{-1} appears due to C-H bending vibrations. The asymmetric and symmetric stretching modes of –C-O vibrations were at present at around 1570 cm^{-1}, and 1380 cm^{-1} respectively. Aromatic ring group appears in the frequency range 1600-1500 cm^{-1}. C-H stretching vibration appears between 2480 and 2810cm^{-1}. The C=C mode of vibrations was present at 3000 cm^{-1}. It illustrates that the strong hydrogen bonding interaction of C-OH group and corresponding C-OH in plane and out of plane bands are occur as weak band at

1475 cm^{-1} and 950 cm^{-1} [7]. The low sharpness of multiple bands in this region is taken as evidence for the exchange of acid proton by divalent impurities.

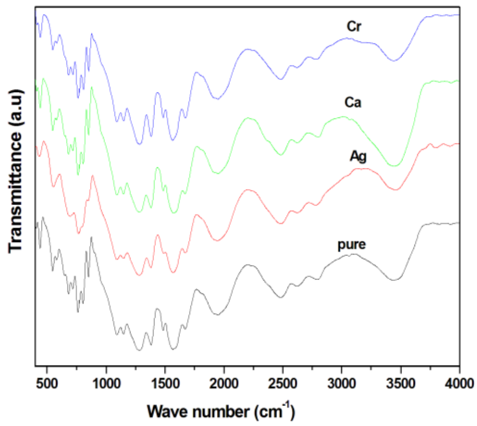

Fig. 4 FTIR spectrum of pure and doped KAP crystals.

3.4 Dielectric studies

Dielectric studies of pure and doped KAP crystals were carried out on (010) faces of the crystals using Hioki 3532-50 LCR Hitester. The samples were coated with graphite on opposite faces and the coated crystal was placed between two copper electrodes for further measurements. The capacitance was measured at various frequencies ranging from 100 H_Z to 5 MHz. The dielectric constant is calculated using the relation $\varepsilon_r = Cd/\varepsilon_0 A$, where C is the capacitance, d is the thickness, A is the area and ε_0 is the absolute permittivity of the free space [2]. The dielectric constant and dielectric loss is studied as a function of frequency at 40°C.. Fig. 5 and 6 reveals that the dielectric constant decreases as the frequency increases for all the investigated samples. The values are high at the low frequency region. This could be attributed to the fact that all the four polarizations such as space charge, orientational, electronic and ionic polarization contribute initially to the dielectric nature of the samples. Its low values at high frequencies may be due to the loss of importance of these polarizations.

Among the four samples, Ag^+ doped KAP has lowest dielectric constant and Ca^{2+} has the highest dielectric constant in the entire frequency region. These results confirm that the metal ion doping has strong influence on the physical properties of KAP.

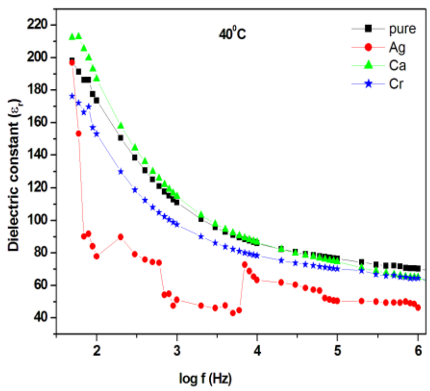

Fig 5.dielectric constant verses frequency measured at 40°C for pure and doped KAP crystals.

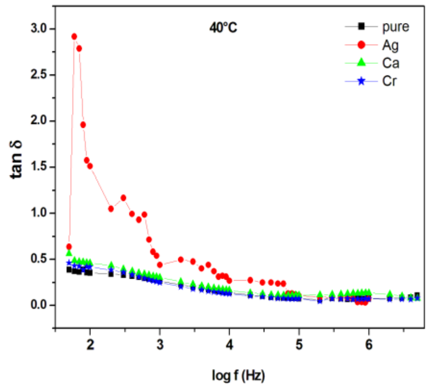

Fig 6. dielectric loss verses frequency measured at 40°C for pure and doped KAP crystals

3.5 Vickers microhardness studies

Microhardness measurements were carried out using Shimadzu tester. The indentations made at several points with the applied load of 25, 50 and 100 gm

loads for pure and metal ion doped KAP crystals (Fig. 7). Hardness values were calculated from the formula, $H\upsilon=1.8544\ P/d^2$ kg/mm^2, where Hυ is the Vicker's microhardness number in kg/m^2 value, P is the applied load in gram, and d is the average diagonal length of crystal in micrometer. The results indicate that the hardness value is higher in the case of Cr doped KAP.

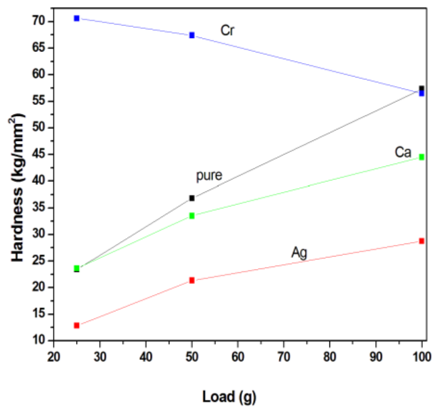

Fig 7. Hardness number versus load.

3.6 SHG measurements

The second harmonic generation conversation efficiency of the samples was measured using Kurtz powder technique. A Q switched Nd:YAG laser beam of wave length 1064 nm was used within an input energy of 5.02 mJ/pulse and the pulse width of 8 ns the depletion rate being 10 Hz. The SHG radiations of 532 nm (green light) emitted were collected by a photo multiplier tube (PMT-Philips Photonics model 8563) and the optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 3052). The SHG efficiencies of pure KAP, Ag-KAP, Ca-KAP and Cr-KAP were found to be 39%, 33%, 52% and 30% respectively as that of KDP. Ca-KAP crystals showed significantly higher conversion efficiency when compared to the other doped KAP crystals.

4. Conclusions

Pure and mono,di,tri valent metal ion doped KAP crystals were grown using slow evaporation solution growth method. The crystal system and lattice parameters were confirmed from the powder X-ray diffraction analysis. Fourier transform infrared (FTIR) studies confirm the various functional groups present in the grown crystal. The decomposition temperature of as grown crystals was measured using TGA measurements. There is appositive influence of NLO, dielectric and hardness values of Ca^{2+} doped KAP crystal.

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