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Photoluminescence, Photoconductivity, Thermal, Microhardness and Dielectric Properties of Silver Nitrate Doped Potassium Zinc Phosphate Hexahydrate Single Crystal

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ABSTRACT

Silver nitrate doped potassium zinc phosphate hexahydrate NLO single crystal was grown using conventional solution growth technique. The as grown single crystal was subjected to single crystal X-ray diffraction and it was revealed that crystal belongs to monoclinic system. Photoluminescence spectra was observed at 415 nm and 545 nm due to the π* - n and π- π* transitions. Photoconductivity was measured to understand the internal processes in crystals. The negative conductivity of the as grown crystal may be due to the reduction in number of charge carries in the presences of radiation. Thermal properties of silver nitrate doped potassium zinc phosphate hexahydrate were studied and it was found that the melting point of as grown is 123^0 C. Microhardness of silver nitrate doped potassium zinc phosphate hexahydrate was also studied and concluded that it belongs to soft material. Electrical property of as grown crystal was also carried out.

Keywords : Potassium zinc phosphate hexahydrate, Photoluminescence, Dielectric, monoclinic and microhardness

I. INTRODUCTION

New materials exhibiting non linear optical (NLO) effects have been explored with view to develop opto-electrical devices for example optical modulator and frequency doubling devices [1]. Hence the search for efficient non linear optical (NLO) crystals is in fact that search for the polar crystals in which the macroscopic properties reflect the internal asymmetric molecular relationship. Such a crystal may have an external morphology with hemi hedral faces that have different chemical reactivity and physical properties, such as third order NLO activity in addition to pyro electric, pizzo electric and ferro electric effects [2]-[3]. The unique property of perfect single crystals was employed in the development of device fabrications in semiconductors, optics, photonics, nonlinear optics, light-emitting diodes, faster processors, high- resolution detectors, ferroelectric and piezoelectric applications[4-6]. The numerous applications of the nonlinear optical (NLO) crystals in the vast field of science and technology made the process of search of the new NLO crystals and improvements in the properties of the known crystals a never stopping process. Purely inorganic NLO materials typically have excellent mechanical and thermal properties but often posses relatively modest optical nonlinearities due to their lack of extended π- electrons delocalization. Furthermore inorganic crystals grown from high temperature melts typically have lower damage thresholds and more optical inhomogeneties throughout their bulk due to impurities internal stress and defect resulting from the extremely non-equilibrium growth conditions [7-12]. Zinc potassium phosphate hexahydrate is a molecular ionic crystal. Impurity ions such as transition metal ions are responsible for the modification of many physical properties in the crystals and play a crucial role in fabrication of nonlinear optical devices. In these crystals, acentric frame works are obtained without calling on polarizable chiral entities, while the shielding effect from adequate inorganic anions such as PO_4 group favours the expected polar packing. Recently, development of UV-Vis wavelength technologies has attracted much attention[13-16]. silver nitrate doped potassium zinc phosphate hexahydrate single crystal was grown based on these idea and its structure and functional group optical properties were also reported[17]. In this research article the mechanical, electrical, thermal properties of silver nitrate doped potassium zinc phosphate hexahydrate are presented.

II. EXPERIMENTAL DETAILS

2.1 Crystal growth

Zinc sulfate and Potassium dihydrogen phosphate and potassium zinc phosphate hexahydrate were taken in 1:1 equimolar ratio to dissolve in distilled water at room temperature. The solution was stirred well to get homogeneous solution. A dopant, silver nitrate (70 mg) was mixed in the homogeneous solution while stirring. The solution was kept at room temperature for evaporation and a good quality single crystal of silver nitrate doped potassium zinc phosphate hexahydrate. The as grown crystal was belongs to monoclinic crystal system with space group P2. The cell parameters are a= 6.16 Å, b= 12.20 Å, c= 9.03Å, α= 90°, β= 104.73°, and γ= 90°. The volume of crystal is 655 Å^3 [17].

III. RESULTS AND DISCUSSION

3.1 Photoluminescence

The photoluminescence (PL) spectroscopy is one of the effective tools to provide relatively direct information about the physical properties of materials at the molecular level, including shallow and deep level defects and gap states[18]. Photoluminescence spectra of silver nitrate doped pottasium zinc phosphate hexahydrate was measured using Varian Cary Eclipse Spectrophotometer at ambient temperature. Fig. 1 shows the luminescence spectra of as grown crystal. It is observed from the spectra that as grown crystal exhibited a strong intense beam at 418 nm and 545 nm. This is due to the π* - n and π- π* transitions respectively in the molecules. Energy band gap of high peak intensity was calculated and was found to be 2.28 eV using the relation E_g= 1.24/λ.

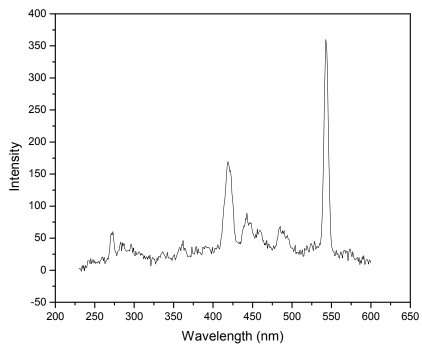

Figure 1. Photoluminescence of silver nitrate doped Zinc pottasium phosphate hexahydrate

3.2 Photoconductivity study

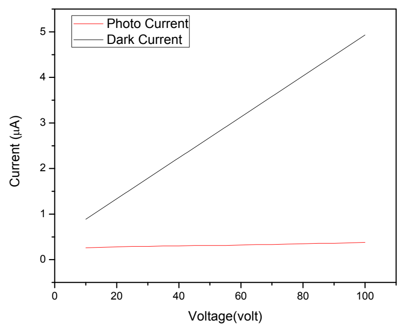

Figure 2. Photoconductivity of silver nitrate doped Zinc potassium phosphate hexahydrate

Photoconductivity serves as a tool to understand the internal processes in crystals and it is also widely used to detect the presence of light and measure its intensity in light – sensitive devices. Photoconductivity is an important property of solids by means of which the bulk conductivity of sample changes due to incident radiation. The photoconductivity of Silver nitrate doped potassium zinc phosphate hexahydrate was measured using KEITHLEY 480 picometer. Initially, the sample was kept away from any other radiation. The dark current (Id) of Silver nitrate doped potassium zinc phosphate hexahydrate was measured by connecting a DC power supply, picometer and the sample in series. The photo current (Id) for the sample was calculated by exposing it to the radiation from a halogen lamp containing iodine vapour by focusing a spot light on the sample with the help of a convex lens. Initially the applied voltage was increased from 100 to 1800 V in steps 200 V and the corresponding dark current (Id) was measured. Figure 2 shows the variation of the dark current (Id) and photo current (Ip) of the sample with applied field. From the graph both the dark current (Id) and photo current (Ip) were seen to increase linearly with the applied field. For same applied field the photo current (Ip) is less than the dark current (Id) which reveal that the negative photoconductivity behaviour of the sample. This negative conductivity may be due to the reduction in number of charge carries in the presences of radiation [19- 21]. The decreases in mobile charge carries during negative photoconductivity were also explained by stock man model. Though the material shows negative photoconductivity for visible light radiation, the material is excited to create more charge carriers for intense beam laser.

3.3 Thermal analysis

Differential scanning calorimetry (DSC) of silver nitrate doped Zinc potassium phosphate hexahydrate is shown in Fig.3. Thermal stability of as grown crystal was measured from room temperature. It is revealed from the DSC graph that there is no endothermic and exothermic peak up to 123.5 °C. A endothermic peak at 123.5 °C may be due to decomposition of the as grown crystal. There is no phase transition observed from this temperature. The melting point of as grown crystal is 123.5 °C.

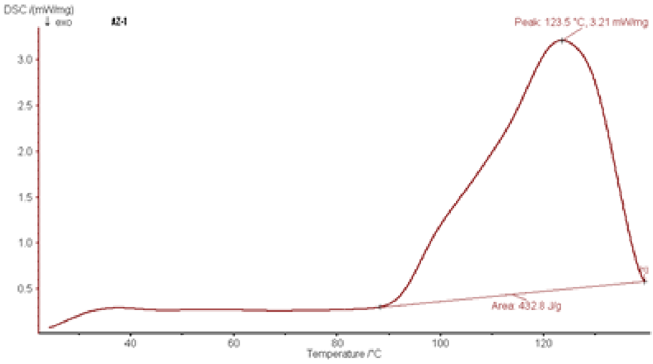

Figure 3. Differential scanning calorimetry (DSC) of silver nitrate doped Zinc potassium phosphate hexahydrate

3.4 Vickers Microhardness

The microhardness of a crystal is an important parameter to define the strength of its material. Mechanical strength of the materials plays a key role in device fabrication. It is a measure of the resistance, the lattice offers to local deformation [22]. Shockley et al and Buckley pointed out that hardness of the crystal is obviously related to the crystal structure of the material (or) in other words, the pattern in which the atom are packed and the electronic factors operating to make the structure stable. Hardness is the only mechanical test that can be employed when the material is not available in substantial quantities. The hardness measurement is treated as an efficient technique of providing information about the elastic, plastic, viscous and fractures properties. Hardness is a measure of the resistance to permanent deformation. We have different methods for measuring hardness of materials. Among various methods, the most common method is the micro indentation and pyramid indenters are found to be best suited for hardness tests. A hardness tester fitted with a diamond pyramid indenter attached to an incident light microscope was used for study. The diamond indenter is in the form of a square pyramid, opposite faces of which make an angle 136^0 with one another. A pyramid indenter is suited for hardness test due to two reasons [23]. (i) The contact pressure for a pyramid indenter is independent of indent size and (ii) pyramid indenters are less affected by elastic release than other indenters. The indenter can be pressed on the sample under a load of 5, 10, 15, etc. gram. The base of the Vickers pyramid is a square and the depth of indentation corresponding to $(1/7)^{th}$ of the indentation diagonal. Hardness is

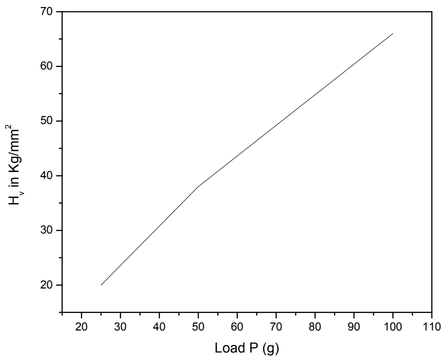

Figure 4. Microhardness of silver nitrate doped Zinc potassium phosphate hexahydrate single crystal

generally defined as the ratio of the load applied to the surface area of indentation. Vickers hardness number (H_v) = load applied/ area of impression

$$H_v = 2p\sin\left(\frac{\alpha}{2}\Big/ d^2\right)$$

Where," p" is the load in kg and "d" is the diagonal length of the indentation mark in mm. α- is the apex angle of the indenter ($\alpha = 136^0$).

$$H_v = 2p\sin\left(\frac{68^0}{d^2}\right)$$

$$H_v = 1.854\frac{p}{d^2}$$

A variation of microhardness number (H_v) with applied load is shown in Fig. 4. It is evidence from the graph that the microhardness of silver nitrate doped Zinc potassium phosphate hexahydrate increases with increase in the applied load. The increases in the microhardness values with increasing load are in agreement with the reverse indentation size effect (ISE). The work hardening coefficient (n) was found to be 2.4. According to Onitsch, if 'n" is greater than 2 the microhardness will increase with an increase in the load. If "n" is less than 2 the microhardness will decrease with an increase in the load. The material is hard, if the value of "n" lies 1 to 1.6. The material is soft, if the value of "n" is greater than 1.6 [24]. Hence, we conclude that silver nitrate doped Zinc potassium phosphate hexahydrate is soft material.

3.5 Dielectric characterization

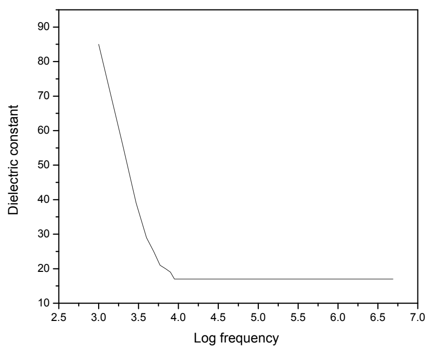

Figure 5. Dielectric constant of silver nitrate doped Zinc pottasium phosphate hexahydrate single crystal

A study of dielectric response gives information about lattice dynamics in the crystal [25]. The dielectric measurement is one of the useful characterizations of electrical response of solids and it gives information about the electric field distribution within the solid [26]. It is the measure of how easily a material is polarized in an external field [27]. Dielectric studies of silver nitrate doped Zinc potassium phosphate hexahydrate was measured using HIOKI 3532-50 LCR HITESTER. The sample was mounted between the copper platform and parallel electrodes. In order to obtain good electric conduct between the crystal and the electrodes, the crystal faces are coated with silver paint. Proper care was taken that the silver paint does not spread to the sides of the crystal. The capacitance and the dissipation factor of the parallel plate capacitor were measured by the copper plate and electrodes having the sample. The dielectric constant and dielectric loss were calculated using the equations (1) and (2) respectively.

$$\varepsilon = \frac{Cd}{\varepsilon_0 A} \text{......(1)}$$

$$\varepsilon' = \varepsilon \tan(\delta) \text{............}(2)$$

Where, C is the capacitance of the parallel capacitor, d is the thickness of the sample. A is the area of the sample and tan (δ)is the loss tangent of the crystal. The observations are made in the frequency range 100 Hz to 100MHz at different temperatures. The measurements were carried out in the temperature range room temperature- 1500. Fig.5 shows the variation of dielectric constant with frequency of silver nitrate doped zinc potassium phosphate hexahydrate. It is observed that the dielectric constant (ε_r) of silver nitrate doped Zinc potassium phosphate hexahydrate crystal decreases with increase infrequency. It was observed that the dielectric constant decreases slowly with increasing frequency and attain saturation at higher frequencies. The high dielectric constant of the crystal at low frequency is attributed due to the presence of all four polarizations such as electronic, dipolar, ionic and space charge polarization [28]. At low frequencies, all these polarizations are active. This behaviour is due to the fact that at lower frequency the dipoles are able to follow the applied field, whereas at higher frequency they are not [29]. At low frequencies the dipoles can easily switch alignment with the changing field. As the frequency increases the dipoles are able to rotate less and maintain phase with the field; thus they reduce their contribution to the polarization [30]. At lower frequencies, space charge polarization is predominant and hence the dielectric constant increases abnormally [31-32]. The lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient [33-34].

IV. CONCLUSION

It was observed from the photoluminescence spectra that as grown crystal exhibited a strong intense beam at 418 nm and 545 nm. This was due to the π^* - n and π- π^* transitions respectively in the molecules. Photoconductivity study revealed that the negative photoconductivity behaviour of the sample. This negative conductivity may be due to the reduction in number of charge carries in the presences of radiation. Thermal stability of the sample was also studied using DSC and melting point of the as grown is 123.5 °C. In this present work mechanical strength of single crystal of silver nitrate doped Zinc potassium phosphate hexahydrate was calculated. Micro hardness indicates that silver nitrate doped Zinc pottasium phosphate hexahydrate NLO single crystal belongs to soft material. The dielectric study indicates that the silver nitrate doped Zinc pottasium phosphate hexahydrate NLO single crystal posses good optical quality with less defects.

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