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Growth, Thermal and Mechanical Studies of Disodium Hydrogen Phosphate(DSHP) Single Crystals

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Abstract - *The single crystals of Disodium Hydrogen Phosphate(DSHP) , an NLO material, were grown by slow evaporation technique. Good optical quality single crystals of size 25X22X10 mm³ were grown in a period of 4 weeks. Thermal properties of the crystal have been investigated using thermo gravimetric (TG), differential thermal analysis (DTA) and differential scanning caliorimetry(DSC). The mechanical strength of the crystal is estimated by Vicker's hardness test.*

Keywords: **single crystals, slow evaporation technique, thermal properties, hardness number, micro indentation**

1.INTRODUCTION

Single crystals are important in science because measurements of the fundamental properties of matter in such a highly ordered state are interpreted more easily than when irregularities in structure are present. Growth of single crystals ranges from a small inexpensive technique to a complex sophisticated process and crystallization time ranges from minutes, hours, days and to months. Crystal growth needs the careful control of a phase change.

In the slow evaporation method the solution loses particles which are weakly bound to other components and, therefore, the volume of the solution decreases. An excess of a given solute is established by utilizing the difference between the rates of evaporation of the solvent and the solute. Normally, the vapour pressure of the solvent above the solution is higher than the vapour pressure of the solute and, therefore, the solvent evaporates more rapidly and the solution becomes supersaturated. It is sufficient to allow the vapour formed above the solution to escape freely into the atmosphere. This method of crystal growth is the oldest and technically it is very simple. For non toxic solvents such as water evaporation is permissible into the atmosphere but for toxic and inflammable solvents precautions are taken to avoid the leakage of solvent vapour in the atmosphere.

Disodium hydrogen phosphate (DSHP) is an interesting and promising inorganic NLO material of phosphate group. It is found that there is a disorder in the phosphate group in the sodium hydrogen phosphates [1, 2]. Thermal analysis is useful in both quantitative and qualitative analyses. Samples may be identified and characterized by qualitative investigations of their thermal behaviour. Information concerning the detailed structure and composition of different phases of a given sample is obtained from the analysis of thermal data.

Thermogravimetry (TG) or thermogravimetric analysis (TGA) provides a quantitative measurement of any weight changes associated with thermally induced transitions. For example, TG can record directly the loss in weight as a function of temperature or time (when operating under isothermal conditions) for transitions that involve dehydration or decomposition. Thermogravimetric curves are characteristic of a given compound or material due to the unique sequence of physical transitions and chemical reactions that occur over definite temperature ranges. TG data are useful in characterizing materials as well as in investigating the thermodynamics and kinetics of the reaction and transitions that result from the application of heat to these materials. The usual temperature range for TG is from ambient to 1200° C in either inert or reactive atmospheres. In TG, the weight of the sample is continuously recorded as the temperature is increased. Samples are placed in a crucible or shallow dish that is positioned in a furnace on a quartz beam attached to an automatic recording balance. Linear heating rates from 5 to 10°C/min are typical. The amount of sample required is from 10 to 300 mg. Computer software allows the computation of $\Delta w/\Delta t$, which is important in kinetic interpretations of reactions and processes.

In differential thermal analysis (DTA), the difference in temperatures between the sample and a thermally inert reference material is measured as a function of temperature (usually the sample temperature). Any transition that the sample undergoes results in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. A plot of the differential temperature, ΔT, versus the programmed temperature, T, indicates the transition temperature and whether the transition is exothermic or endothermic. DTA and TG analyses are often run simultaneously on a single sample.

Differential scanning calorimetry (DSC) is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature.

Micro hardness is a measure of the ability of the substance to resist scratching and/or permanent deformation. Micro hardness studies find wide applications in the study of

material properties of solids [3]. Hardness testing has been widely used to study the strength and deformation in materials. In this, an indentor is forced by a known load into the surface of the material and the hardness is calculated from the size of the indentation mark. Hardness testing has been discussed in detail by Mott [4] and Buckle [5]. Wooster [6], and Westbrook[7, 8]. Vicker's micro hardness test is found to be the most suitable (among various types of hardness measurements available) for the measurement of micro hardness of crystals.

Meyer established a relationship between indentation hardness and plastic and work – hardening capacity of material [9]. The hardness of a material is defined [10] as the resistance it offers to the motion of dislocation, deformation or damage under an applied stress. The most important measurement of hardness is the indentation type. Hardness test methods are used to determine the stress needed to produce plastic flow in the brittle material. It measures the mean contact pressure when a spherical, a conical or a pyramidal indentor is pressed on to the surface of a flat specimen, thus providing a simple and non – destructive means of assessing the resistance of the material to plastic deformation[11-14].

II .Experimental

Single crystals of DSHP was grown from its supersaturated solutions by slow evaporation technique [15,16]. The simplest apparatus for growth by this method is a beaker covered with a few holes in the lid to allow solvent evaporation is shown in figure 1. The rate of crystallization depends on the rate of solvent evaporation which may be governed by changing the total area of the holes. In sophisticated crystallizers, evaporation is controlled by passing air or an inert gas at a controlled rate over the solution. Good control of evaporation rate can also be obtained by using some sort of condenser to allow the removal of condensed solvent at a controlled rate.

Figure 1 Photograph showing the simplest apparatus to grow crystals using slow evaporation technique.

An important step to obtain good quality crystals is the use of high purity chemicals and hence analytical reagent (AR) grade of DSHP was used. The technique followed for the growth of DSHP single crystals was solution method with slow evaporation technique. In accordance with the solubility data, the saturated solution of DSHP was prepared in water at room temperature and maintained with continuous stirring by using a magnetic stirrer for about two hours to ensure homogeneous concentration over the entire volume of the solution. The homogeneous saturated solution was kept in glass vessels covered with perforated filter paper for slow evaporation. Repeated recrystallization was carried out to obtain good quality and transparent crystals of DSHP. Seed crystal technique was also used to harvest large-size crystals of DSHP. A photograph of the harvested DSHP crystal is displayed in Figure 2. The size of the grown crystal was about 25x22x10 mm^3 and it was obtained in a growth period of 25-30 days. TGA, DTA and DSC of DSHP were carried out using 2960 SDT (TA instruments) equipment between 20 to 600°C at a heating rate of 10° C /min in nitrogen atmosphere. The recorded TG, DTA and DSC thermograms of DSHP crystals are displayed in Figures 3, 4 and 5 respectively.

In this test, micro indentation was made on the surface of the crystals with the help of a diamond pyramidal indentor. Hardness is defined as the ratio of the load applied to the surface area of the indentation. Vickers hardness number (H_v) is defined as

$$H_v = 1.8544 \quad P/d^2 \text{ kg/mm}^2,$$

where P is the load and d is the mean diagonal length of the indentation made on the crystal surface. In the present study, micro hardness measurements were done using a Vicker's micro hardness indentor (Leitz Weitzier hardness tester) with a maximum indentor load of 200 g. The indentation impressions on all the crystals grown in the present study (on the flat surface) were square shaped.

III . Result and Discussion

The grown crystals are found to be stable at room temperature, colourless, transparent and have well defined appearance. Since the temperature has not been completely kept constant during the growth of the crystal in the present work, there are some inclusions are found in the grown crystal.

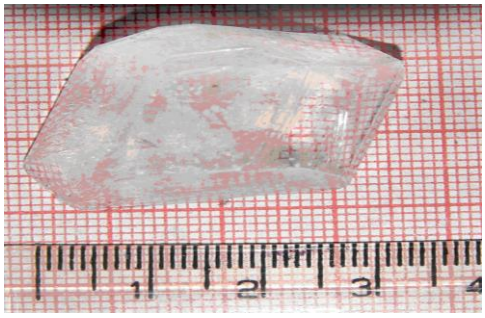

Figure 2: Photograph of the grown DSHP crystal

Thermo gravimetric (TG) analysis of DSHP was carried out using 2960 SDT (TA instruments) equipment between 20 to 600°C at a heating rate of 10° C /min in nitrogen atmosphere.

From TG curve, it is observed that there is an intense weight loss due to water of crystallization and weakly adsorbed water. The latter gives weight loss at lower temperature than the former. The amount of adsorbed water (13.67%) is found to be less than the water of hydration (33.7%). The loss of water below 131.30°C corresponds to release of weakly adsorbed water molecules and the water of crystallization in the sample. The minute weight loss that occurs with the maximum at 351.98°C is assigned to inter molecular condensation of DSHP through OH groups. The resulting residue is found to be thermally stable without any decomposition.

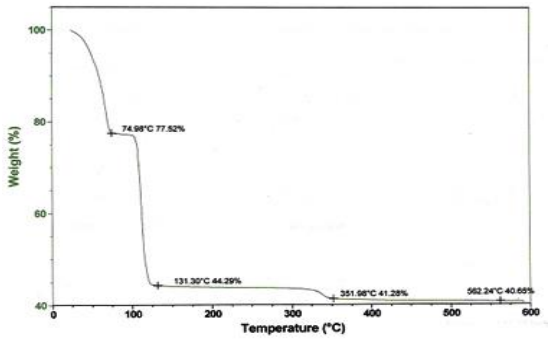

Figure 3: TG thermogram of DSHP crystal

The differential thermal analysis (DTA) of DSHP was carried out using 2960 SDT (TA instruments) equipment again between 20 to 600°C at a heating rate of 10° C/min in nitrogen atmosphere. The endothermic peaks corresponding to 53.48 and 71.14°C of DTA curve indicate the release of weakly adsorbed water molecules. The exothermic peaks at 115.69 and 339.28°C indicate release of water of hydration or crystallization

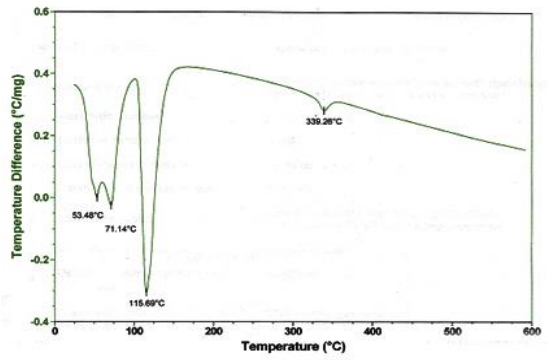

Figure 4: DTA thermogram of DSHP crystal

Assessment of thermal changes by differential scanning calorimetry (DSC) was done using DSC-2920 equipment (TA instruments) between 0 to 200°C at a heating rate of 10°C / min in nitrogen atmosphere. The specimen was placed on aluminum non hermetic pans. The temperature axis was calibrated by indium melting method as per ASTM E 967-03. . DSC curve clearly indicates that the melting point of DSHP crystal is at 35.96°C. The endothermic peaks of DSC curve at 40.78, 51.37 and 94.10°C correspond to release of weakly adsorbed water molecules and above 100°C, the endothermic peaks correspond to release of water of crystallization. All 12 molecules of water from the sample have been released when the temperature is raised to around 200°C.

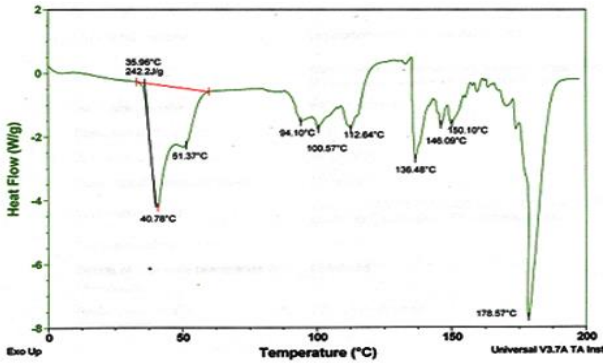

Figure 5: DSC thermogram of DSHP crystal

Micro hardness measurements were made using a diamond pyramid indentor on (010) plane of DSHP crystal. The distance between any two indentations was maintained to be greater than five times that of the diagonal length in order to avoid any mutual influence of the indentations. The loads ranging from 10 to 45 g were used for making indentations, keeping the time of indentation constant at 10 s . Figure 6 shows the load versus Vicker's hardness number for the DSHP crystal.

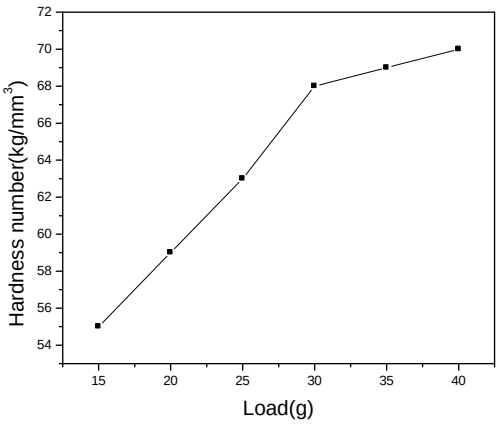

Figure 6: Variation of hardness number with load for the DSHP crystal

From the results it is observed that as the load increases, the hardness is found to increase up to the load of 30 g and remains almost constant beyond that load. This increase in hardness number can be attributed to the work hardening of the surface layers of the crystal. If the load is

increased beyond 45 g, the DSHP crystal is observed to be ruptured.

III Conclusion

Slow evaporation technique was employed in the growth of single crystals of DSHP. The crystals were highly transparent. The thermo gravimetric analysis revealed the condensation of OH groups at 352^{o}C producing a thermally stable product. The DTA curve indicates the release of weakly absorbed water molecules. The DSC curve clearly indicates the melting point of DSHP crystal. Micro hardness studies have been carried out on (0 1 0) face of the conventional solution grown DSHP single crystal.

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