Nucleation kinetics, growth, hardness and optical studies of TGSP crystals doped with tartaric acid

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Abstract:

Triglycine sulpho-phosphate (TGSP) doped with tartaric acid salt was synthesized and solubility studies at different temperatures in the range 30-50 ^{o}C were carried out. Induction period was measured for various supersaturation ratios for the undoped and tartaric acid-doped TGSP samples. It is observed that solubility increases with temperature and induction period decreases with supersaturation ratios. The critical nucleation parameters were evaluated based on the classical theory of nucleation. Bulk crystals of undoped and tartaric acid-doped TGSP salts have been grown from the optimized growth parameters. Single crystal XRD studies, UV-visible spectral studies and microhardness studies were performed for the grown crystals and the results are discussed.

Keywords: TGSP crystal; doping; Solubility; Nucleation parameters; solution growth; single crystal; XRD; cell parameters; microhardness; band gap

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1. Introduction

Triglycine Sulpho-Phosphate (TGSP) crystal is a ferroelectric material which could be a suitable material for room temperature infrared detection, environmental analysis monitors, earth observation cameras, astronomical telescopes and other military systems. It is obtained by partial substitution of sulfate ions with phosphate ions in TGS crystal. The ferroelectric transition temperature of TGSP crystal is reported to be at 51 ^{o}C [1]. Relaxation in dielectric properties of pure and gamma ray irradiated TGSP crystals and other properties were studied by Arunmozhi et al [2]. Bhalla et al have studied the pyroelectric properties of pure and doped-TGSP crystals [3]. It is known that presence of impurities during the growth of crystals influences growth kinetics, morphology and quality of the crystals and keeping this in mind, TGSP crystal has been doped with tartaric acid in this work. The aim of the work is to grow single crystals of undoped and tartaric acid-doped TGSP by solution method and to carry out various studies for the harvested crystals. In this work, an attempt has been made to determine the nucleation parameters of tartaric acid-doped TGSP crystals and also to investigate the effect of tartaric acid as the dopant on the structural, optical and mechanical properties of grown crystals.

2. Nucleation phenomena and relevant equations

Nucleation is an initial process of the crystal growth and when few atoms, ions or molecules join together in a supersaturated solution, a cluster or nucleus is formed and the overall excess free energy change between the nucleus and solute in the supersaturated solution is called as Gibbs free energy change (ΔG) and it is sum of surface free energy change and volume free energy change. Once the nucleation occurs in the supersaturated solution, the nucleus grows quickly and a bright sparkling particle is seen. The time interval in which the observation of the first sparkling particle in the undisturbed supersaturated

solution is called the induction period (τ). The expression for the induction period in terms of Gibbs free energy is given by $ln\ \tau = -B + \Delta G / kT$ where B is a constant, k is the Boltzmann's constant and T is the absolute temperature. The Gibbs free energy will be maximum for a certain value of radius (r^*) of nucleus, which is known as critical radius and the corresponding nucleus is called the critical nucleus. Nuclei formed with radius greater than critical radius are stable and its free energy decreases by growing [4, 5]. Supersaturation ratio S is given by $S = C/C_o$ where C is the supersaturated concentration and C_o is the saturated concentration. The induction period can be measured for different values of supersaturation ratio. A plot of $1/ (\ln S)^2$ against $\ln \tau$ forms a straight line and the slope (m) is calculated. After finding the slope (m), the value of interfacial tension (σ) is calculated using the equation $\sigma = (RT/N) [3m/16\pi v^2]^{1/3}$ where R is the universal gas constant, v is the volume of a molecule (v = volume of unit cell / number of molecules per unit cell) and N is the Avogadro's number. The size of the critical nucleus (r^*) and critical Gibbs free energy change (ΔG^*) are given by $r^* = 2 \sigma v N / RT\ ln\ S$ and $\Delta G^* = mRT / [N (ln\ S)^2]$ respectively and the number of molecules in a critical nucleus is found using equation $n = (4/3) (\pi/v) r^{*3}$. The number of crystals produced in the supersaturated solution is expressed as nucleation rate i.e. the number of crystals produced per unit volume per unit time. The nucleation rate (J) can be calculated using the equation $J = A \exp[-\Delta G^*/(kT)]$ where A is the pre-exponential factor (approximately $A = 1 \times 10^{30}$ for solution). The derivations for equations of critical nucleation parameters such as r^*, σ, ΔG^* and n are given the literature [6].

3.Experimental methods

Undoped Triglycine Sulpho-Phosphate (TGSP) salt was obtained by heating the saturated solution of glycine, concentrated sulphuric acid and concentrated ortho-

phosphoric acid in the molar ratio of 3 : 0.8 : 0.2 at 50 ^{o}C . The synthesized salt of TGSP was re-crystallized and the re-crystallized salt was added to 50 ml of doubly distilled water in an air tight container for the measurement of solubility. Solubility study was carried out by gravimetrical method [7]. To obtain the tartaric acid-doped TGSP salt, 1 mole% of tartaric acid was added to the aqueous solution of TGSP salt.

For the measurement of induction period, isothermal method was used at the selected supersaturation ratios viz. 1.4, 1.425, 1.45, 1.475 and 1.5 at the constant temperature of 30 ^{o}C. Using the solubility diagram, the synthesized salt of TGSP was used to prepare supersaturated aqueous solution in a nucleation cell and it was stirred continuously for about 2 hours using a magnetic stirrer to ensure the homogeneous concentration. The nucleation cell was loaded in a constant temperature bath (controlled to an accuracy of 0.01 ^{o}C) and illuminated using a powerful lamp to observe the formation of nucleus. The time interval in which the first speck of particle formed in the supersaturated solution of TGSP is noted and it is called the induction period (τ). Similarly, induction period measurements were performed for the 1 mole% added TGSP sample. Two or three trials were carried out to ascertain the correctness of the results. By knowing the values of induction period, the critical nucleation parameters for pure (undoped) and tartaric acid-doped TGSP samples were determined.

Using the solubility data and the optimized growth parameters, single crystals of undoped and tartaric acid doped TGSP salts were grown by solution method with slow evaporation technique at room temperature (30^{o}C). The optimized growth parameters from the studies of nucleation kinetics were used to grow good quality bulk single crystals. It took about 30 to 35 days to harvest the crystals.

The grown single crystals of undoped and tartaric acid-doped TGSP crystals were subjected to single crystal XRD studies using an ENRAF NONIUS CAD4 diffractometer

with MoK_{α} radiation (λ=0.71073 Å) . UV-Visible transmittance spectra of the samples were recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer in the range 200-1100 nm covering the near UV, visible, near infrared region. The UV-visible transmittance was studied using the cut and polished face of the grown crystals. A crystal of thickness 2 mm has been used in this study. Vickers microhardness studies were carried out on the polished face of the grown crystals of this work at room temperature with the load ranging from 10 g to 50 g using Leitz pyramidal hardness tester fitted with a diamond pyramidal indenter. Three trials were made for each indentation and average value was taken for each load. Time of indentation was kept as 5 seconds for the all trials. Vickers microhardness number (H_v) can calculated using the relation $H_v = 1.8544\ P / d^2$ kg/ mm^2 where P is the load in kilograms, d is the diagonal length of indentation in millimeters (mm) and 1.8544 is a constant of a geometrical factor for the diamond pyramidal indenter [8].

4. Results and discussion

4.1 Solubility, nucleation kinetics and growth

Figure 1 shows the solubility diagram of undoped and tartaric acid-doped TGSP crystals for various temperatures ranging from 30 to 50 ^{o}C. It is observed from the results that the solubility increases with temperature and hence the samples have positive temperature coefficient of solubility. There are three regions in the solubility diagram viz. undersaturated region, saturated region and supersaturated region and using these regions, we can easily prepare saturated and supersaturated solutions of the samples at any temperature in the given range of temperature. It is clear that the solvent is able to accommodate a marginally increased amount of solute for the saturation at the same temperature. Using the solubility diagram, nucleation kinetics studies and the growth of crystals could be carried out in an easy manner at various temperatures.

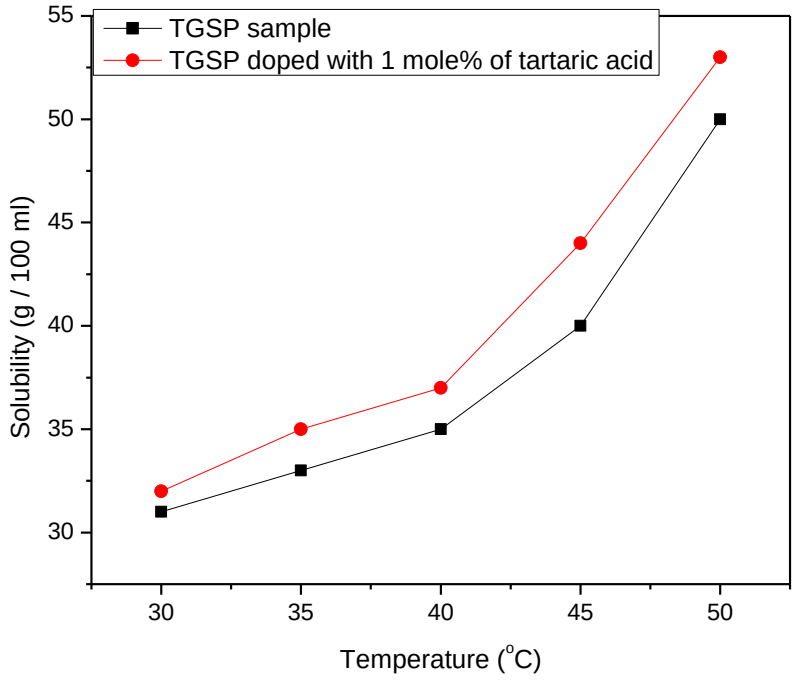

Fig.1: Solubility diagram for pure and tartaric acid-doped TGSP crystals

The variations of induction period (τ) with supersaturation (S) for pure and tartaric acid-added aqueous solution of triglycine sulpho-phosphate (TGSP) are depicted in the figure 2. Induction period decreases as the supersaturation ratio (S) increases for the samples. Since induction period decreases, the rate of nucleation increases as the supersaturated concentration of aqueous solution of TGSP is increased. When TGSP is added with tartaric acid, the induction period decreases and hence nucleation rate increases and this leads to growth of doped crystals faster compared to the undoped TGSP. From the figure 2, plots of $\ln \tau$ against $1/(\ln S)^2$ are approximately linear which explains the classical theory of homogeneous nucleation. From the plots, the slope values (m) are obtained for both samples and the critical nucleation parameters were determined.

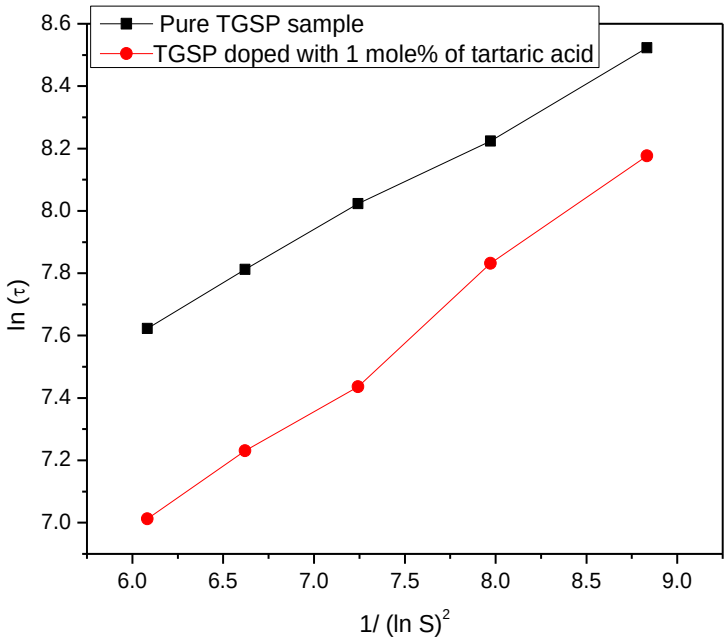

Figure 2: Variation of induction period (τ) with supersaturation ratio (S) for solution of pure TGSP and tartaric acid added TGSP sample

The variations of Gibbs free energy change, radius of critical nucleus and number of molecules in the critical nucleus with the supersaturation ratio (S) are displayed in the figures 3, 4 and 5.

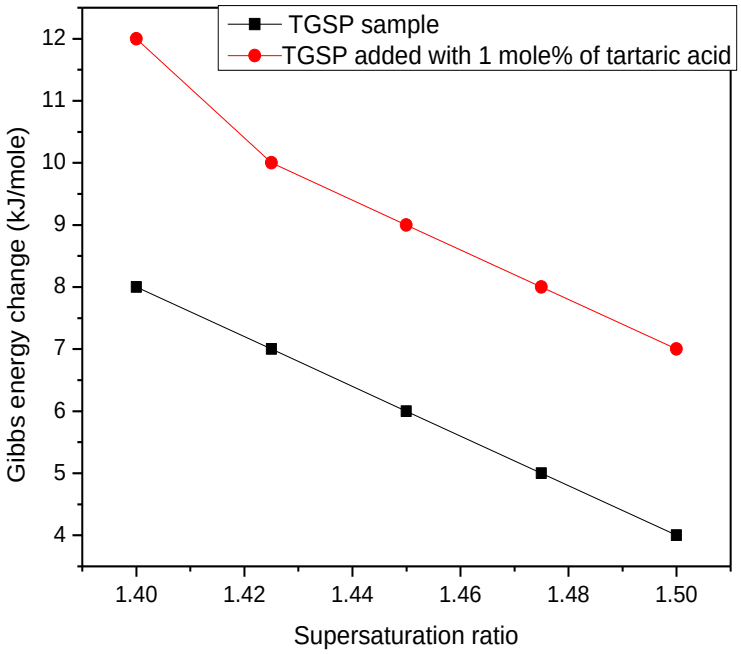

Figure 3: Variation of Gibbs free energy change with supersaturation ratio for solution of undoped TGSP and tartaric acid-doped TGSP samples.

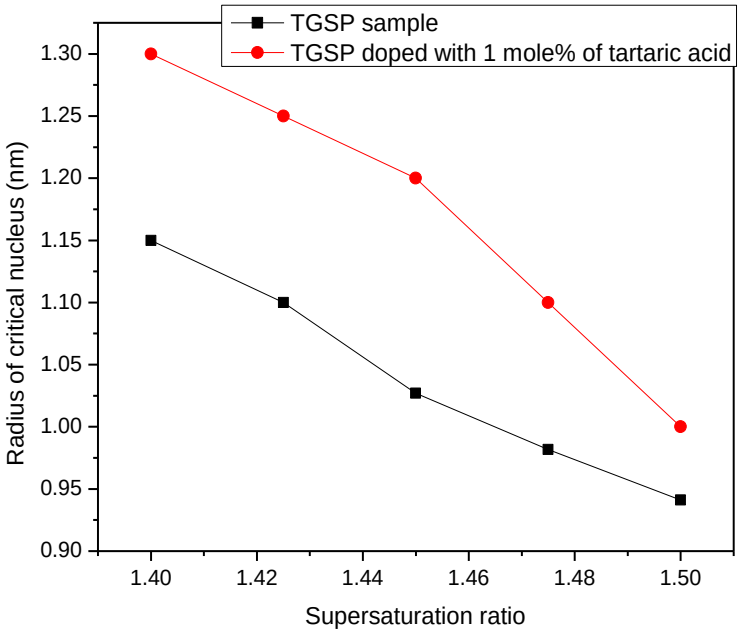

Figure 4: Variation of radius of critical nucleus with supersaturation ratio (S) for solution of undoped and tartaric acid-doped TGSP samples

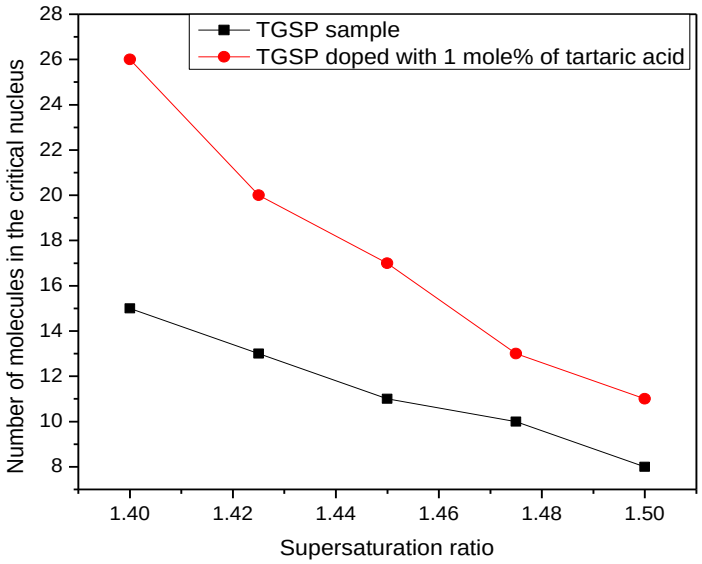

Figure 5: Variation of number of molecules in the critical nucleus (n) with supersaturation ratio (S) for pure and tartaric acid doped TGSP samples.

It is observed from the results that the values of critical nucleation parameters such as radius of critical nucleus, Gibbs free energy change and number of molecules in the critical nucleus decrease with supersaturation ratio and these values increase when TGSP sample is doped with tartaric acid. The supersaturation and presence of impurities in the solution have an important role in controlling the nucleation rate and nucleation parameters during the growth of crystals. Another nucleation parameter viz. interfacial tension of the solid relative to the solution was calculated for undoped and tartaric acid-doped TGSP samples. The obtained values of interfacial tension are 1.88 $x10^{-3}$ and 2.47 $x10^{-3}$ J/m^2. Studies on nucleation kinetics of crystalline samples are carried out in order to have the controlled nucleation rate. Nucleation and crystal growth kinetics in connection with the amount of material available for crystal growth determine the number and volume of crystals produced. The number of crystals produced in the supersaturated solution is expressed as nucleation rate i.e. the number of crystals produced per unit volume per unit time. The variables that affect the nucleation rate are pH, supersaturation, temperature and interfacial tension of the solution. Decrease in induction period and increase in interfacial tension are expected to increase the nucleation rate. In this work, it is observed that there is an increase in interfacial tension when tartaric acid is added to TGSP solution which results in a decrease in the nucleation rate. If the nucleation rate is decreased, spontaneous nucleation can be minimized and large-sized crystals could be grown [9,10]. With the optimized values of growth parameters, the growth of undoped and tartaric acid-doped TGSP crystals have been carried out from aqueous solutions by slow evaporation technique and the grown crystals are found to be transparent and colourless. The harvested crystals are displayed in the diagram 6.

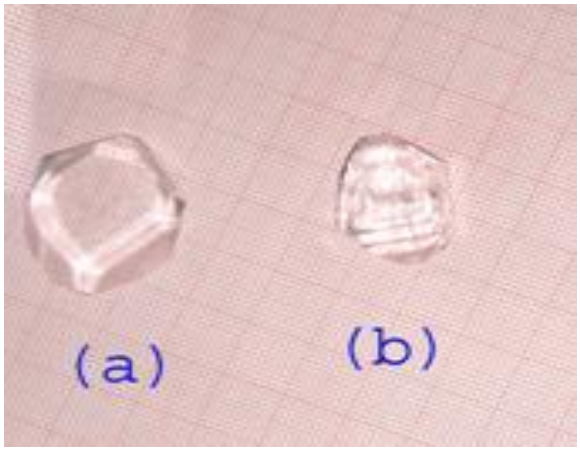

Figure 6: Photograph of (a) undoped TGSP crystal and (b) tartaric acid-doped TGSP crystal

4.2 Structural studies

The grown undoped and tartaric acid-doped TGSP single crystals were subjected to single crystal XRD studies and the unit cell parameters are provided in the table 1. Single crystal XRD analysis indicates that TGSP crystal crystallizes in monoclinic structure with the space group $P2_1$ at room temperature (30 ^oC). The number of molecules per unit cell was found to be 2. It is observed from the results that there is no change of crystal structure when TGSP is doped with tartaric acid.

Table 1: Lattice parameters of undoped and tartaric acid-doped TGSP crystals

Sample	Cell parameters	Volume (Å)^3
Pure TGSP crystal	a= 9.151(2) Å b= 12.732(4) Å , c= 5.778(3) Å α = 90 ^{o}, β= 111.55 (2), γ= 90 ^{o}	626.13(2)
TGSP crystal doped with 1 mole% of tartaric acid	a= 9.199 (3), b= 12.635(1), c= 5.631(2) α = 90 ^{o}, β= 108.35 (2), γ= 90 ^{o}	621.21(1)

4.3 UV-visible spectral studies

The recorded ultra violet-visible (UV-visible) transmittance spectra of pure and tartaric acid-doped TGSP crystals in the wavelength range 200-1100 nm are shown in figure 7. The present experimental study may be assisted in understanding electronic structure of the optical band gap of the crystal. From the transmittance spectra , it is noticed that pure TGSP crystal has a transmittance of more than 90 % in the visible region and the tartaric acid-doped TGSP crystal has lower transmission percentage compared to pure TGSP crystal. In the UV region, a strong absorption is observed at 226 nm for both the samples and this corresponds to the fundamental absorption and UV cut-off wavelength. Absorption in the near ultraviolet region arises from electronic transitions associated within the samples. Using the formula $E_g = 1240 / \lambda$ (nm) , the band gap is calculated to be 5.486 eV. From the results, it is observed that the transmittance for the doped crystal decreases and hence absorbance increases in the entire UV-visible region of the spectra when compared to spectrum of pure TGSP crystal. The increase in the absorbance for the tartaric acid-doped TGSP crystal seems to be due to the presence of dopant (tartaric acid) in the doped crystal.

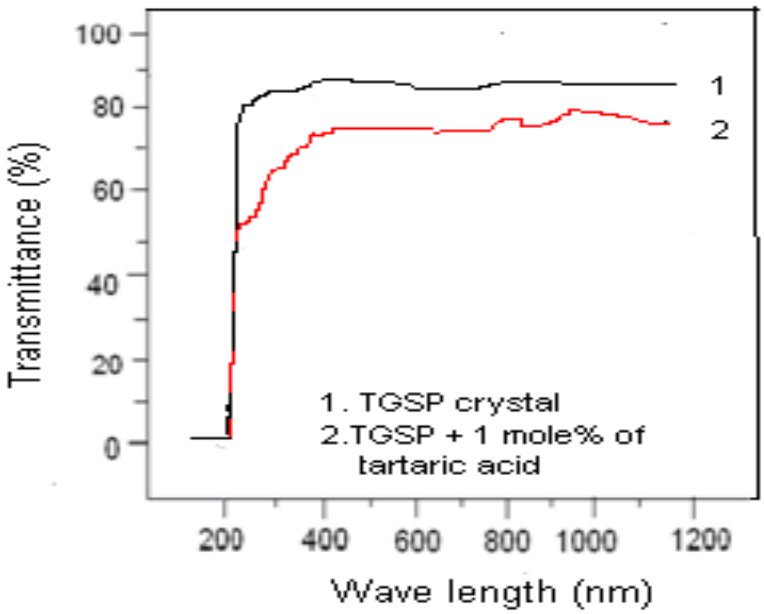

Fig.7: UV-visible spectra for pure and tartaric acid-doped TGSP crystals

4.4 Hardness measurement

The hardness of a material is a measure of its resistance to plastic deformation. The extent to which a material shall deform plastically under an applied stress depends on the strength of intermolecular forces. The permanent deformation can be achieved by indentation, bending, scratching or cutting. In an ideal crystal, the hardness value should be independent of applied load. But in a real crystal, the load dependence is observed and this is due to normal indentation size effect (ISE) [11,12]. Figure 8 shows the variation of hardness number (H_v) with the load for pure and tartaric acid-doped TGSP crystals. At lower loads, hardness is low and it increases with the load upto 50 g. For loads above 50 g, cracks started developing around the indentation mark. It is due to the release of internal stress generated locally by indentation. It is observed from the results that the hardness increases when TGSP crystal is doped with tartaric acid. This may be due to the incorporation of dopant (tartaric acid) in the interstitials of doped TGSP crystal.

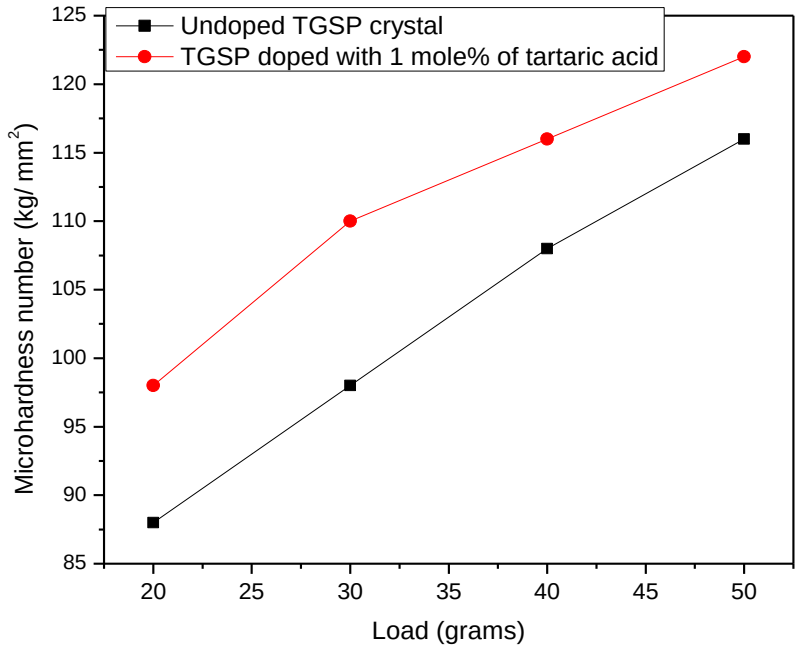

Figure 8: Dependence of hardness number with load for pure and tartaric acid-doped TGSP crystals

5. Conclusions

Solubility and nucleation studies of pure and tartaric acid-doped TGSP crystals were carried out. Induction period measurements were carried out for the samples of this work and it is noticed that the induction period decreases with the supersaturation level. Critical nucleation parameters such as interfacial tension, radius of critical nucleus, Gibbs free energy change and number of molecules in the critical nucleus were calculated. Interfacial tension of the crystal relative to solution was found to increase when TGSP crystal is doped with tartaric acid. Growth of single crystals of undoped and tartaric acid-doped TGSP crystals was carried out by solution method and it is observed that there is a change of morphology of crystal when TGSP crystal is doped with tartaric acid. XRD studies reveal the monoclinic structure of the samples. It is observed from the studies that hardness increases and transmittance decreases when TGSP crystal is doped with tartaric acid.

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