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PHYSICS

STUDIES ON GROWTH AND VARIOUS PROPERTIES OF TRIGLYCINE SULFATE (TGS) CRYSTALS DOPED WITH COPPER SULPHATE

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Abstract

Pure and copper sulphate-doped Triglycine Sulfate(TGS) salts were synthesized and single crystals of the synthesized salts were grown from aqueous solutions by slow evaporation technique. The structural studies on the grown crystals were carried out by single crystal XRD analysis and found that the grown crystals crystallize in monoclinic structure. The FTIR spectra have been recorded in the range 500-4000 cm⁻¹ and the functional groups of the grown crystals have been identified. UV-Visible spectra show that the grown crystals have wide optical transparency in the entire visible region. Atomic absorption study reveals the presence of copper in the doped TGS crystals. Density of the samples have been measured by floatation method. The dielectric studies for the pure and copper sulphate-doped TGS crystals have been performed by measuring the dielectric parameters like dielectric constant and dielectric loss at a constant frequency of 1000 Hz with the temperatures ranging from 30 to 75 °C and this study reveals an increase of dielectric constant and loss when TGS crystal is doped with copper sulphate. Microhardness studies have been carried out to analyse the mechanical strength of the samples.

Key Words: TGS; Crystal growth; Doping; XRD; FTIR; Band gap; Ferroelectric materials, Curie point; microhardness

Introduction

Triglycine Sulfate (TGS) crystal is a useful ferroelectric material founded in 1956 and has low dielectric constant and large pyroelectric coefficient. It finds applications in the fabrication of pyroelectric vidicon tubes, capacitors, transducers, sensors and also it is used in the infrared detection techniques as commercial products^{1,2}. TGS crystal shows a ferroelectric phase transition at the Curie point(49 °C). Below the T_c, TGS possesses the polar point symmetry of group 2 of the monoclinic system, spontaneous polarization arises along the b-axis and above T_c, it possesses the non-polar point group 2/m of the monoclinic system^{3,4}. It is observed that undoped TGS crystals have some disadvantages over doped TGS crystals such as high mobility of ferroelectric domains at room temperature, easy depolarization by electrical, mechanical and thermal means, microbial contamination with time during the growth and low Curie point etc^{5,6}. Many organic and inorganic dopants have been used by researchers in order to overcome these disadvantages and to achieve effective internal bias to stabilize the domains and desired pyroelectric and ferroelectric properties⁷⁻¹⁰. Many metallic ion dopants such as Fe³⁺, Cr³⁺, Mn²⁺, Ni²⁺ have been added to modify the properties of TGS crystals¹¹⁻¹³. Rare earth metal ions such as La, Ce and Nd modified the morphology and coercive field values¹⁴. In this work, copper sulphate has

been introduced into the lattice of TGS crystal to alter various physical and chemical properties. The objectives of present work are to investigate the effect of the dopant (copper sulphate) on the growth, structural, optical, mechanical and dielectric properties of TGS crystals.

Methods and Techniques

Synthesis, solubility and Growth

Commercially purchased Analar Reagent (AR) grade glycine, copper sulphate and concentrated sulphuric acid (H₂SO₄) were used for synthesis and growth. Glycine and H₂SO₄ in the molar ratio of 3: 1 were dissolved in de-ionized water and the solution was heated at low temperatures (below 50°C) to obtain synthesized salt of undoped TGS.

1 mole % of copper sulphate was added to the solution of TGS and it was heated at 45°C to obtain the copper sulphate-doped TGS salt. The purity of the synthesized salts of undoped and copper sulphate-doped TGS was improved by successive re-crystallization. The re-crystallized salt of TGS was added to 50 ml of de-ionized water in an air tight container for the measurement of solubility in the temperature range 30-50°C. Solubility study was carried out using a hot plate magnetic stirrer and a digital thermometer

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(accuracy is ± 0.1 °C). Here the temperature was controlled using a voltage regulator attached to the magnetic stirrer. Initially, the solution was kept at 30 °C and stirred continuously using the magnetic stirrer for about 2 hours. After attaining the saturation, the solubility was determined

gravimetrically¹⁵. The same procedure was followed for other temperatures and for copper sulphate-added TGS salt. The solubility curves for pure and copper sulphate-added TGS salts are displayed in the figure 1.

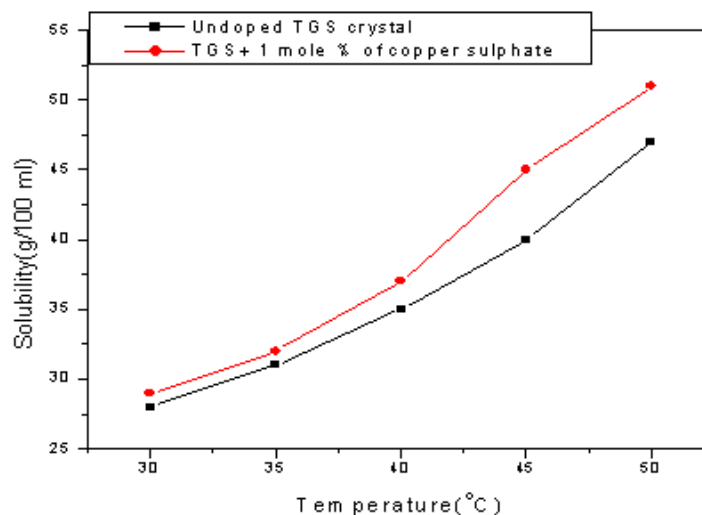


Fig.1: Solubility curves for pure and copper sulphate-added TGS salts

From the results, it is observed that solubility increases with temperature for the samples and it is found to be more in copper sulphate-added TGS salts than that for the pure TGS sample. Hence it is clear that in the case of doped sample, the solvent is able to accommodate a marginally increased amount of solute for the saturation at the same temperature. Solubility data is necessary to prepare the saturated solution of the sample at a particular temperature.

Solution method with slow evaporation technique was adopted to grow the single crystals of the synthesized salts of undoped and copper sulphate-doped TGS. In accordance with the solubility data, the saturated solutions were prepared and were constantly stirred for about 3 hours using a magnetic stirrer and were filtered using 4 micro Whatmann filter papers. Then the filtered solutions were kept in borosil beakers covered with porous papers and the beakers were kept in constant temperature water bath. The grown crystals were harvested after a period of 30 days and they are displayed in the photograph (Fig.2). It is noticed that the pure (undoped) TGS crystal is colourless and transparent. But the copper sulphate-doped TGS crystal is observed to be slightly blue in colour and this indicates the introduction of the dopant (copper sulphate) into the lattice of TGS crystal. There are morphological alteration in the TGS crystal when it is doped with

copper sulphate. This is due to adsorption of impurity onto the surface of the crystals during the growth¹⁶.

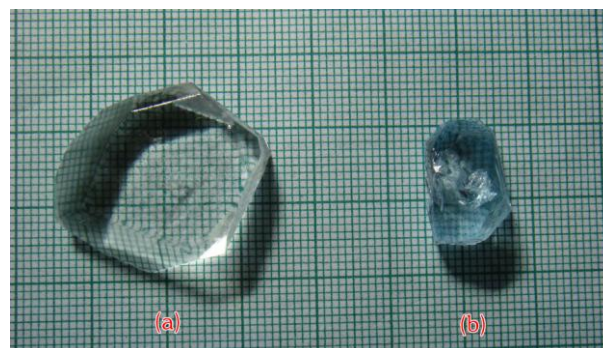


Fig.2: Harvested crystals of (a) undoped and (b) copper sulphate-doped TGS crystals

Instrumentation

Single crystal X-ray diffraction (XRD) studies were carried out on the grown pure (undoped) and copper sulphate-doped TGS crystals by employing a Nonius CAD-4 / MACH single crystal X-ray diffractometer, with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature (30 °C). The FTIR spectra of the samples were recorded using JASCO FI-IR 460 spectrometer by KBr pellet technique in the range 500-4000 cm^{-1} . Atomic absorption study for copper sulphate-doped TGS crystal was carried out using an atomic absorption spectrometer (Model: AA 6300).

A Varian Cary 5E UV-Visible-NIR spectrophotometer was used for spectral transmission studies. A crystal thickness of about 2 mm was used for transmission studies. The floatation method was employed for the precise determination of density of a crystal. The liquids like bromoform (density: 2.69 g/cc) and carbon tetrachloride (density: 1.59 g/cc) were used for the experiment. A small piece of crystal is kept in a specific gravity bottle and the denser liquid bromoform and the rarer liquid carbon tetrachloride are poured in the specific gravity bottle so that the crystal neither sinks nor floats. When the sample is attained in a state of mechanical equilibrium, the density of the crystal would be equal to the density of mixture of liquids. The density was calculated using the relation $\rho = (W_3 - W_1) / (W_2 - W_1)$ where W_1 is the weight of the empty specific gravity bottle, W_2 is the weight of the specific gravity bottle with full of water and W_3 is the weight of the specific gravity bottle with full of the mixture of bromoform and carbon tetrachloride¹⁷.

Dielectric measurements for the samples were carried out using the parallel plate capacitor method¹⁸ at various temperatures ranging from 30 to 70 °C and at 1000 Hz using an Agilent 4284A LCR meter. The sample cleaved perpendicular to the polar axis (b-axis)

was used. Opposite faces of the sample crystals were coated with good quality graphite to obtain a good ohmic contact. The dimensions of the crystals were measured using a traveling microscope (LC = 0.001 cm). The dielectric constant (ϵ_r) of the crystal was calculated using the relation $\epsilon_r = C d / \epsilon_0 A$ where C is the capacitance of the capacitor with crystal, d is the thickness and A is the area of cross section of the crystal.

Results and discussion

Structural properties

The grown crystals were subjected to single crystal XRD analysis to find the crystal structure. From the data, it is observed that pure and copper sulphate-doped TGS crystals crystallize in monoclinic system and the unit cell parameters are listed in table 1. The obtained values of lattice parameters for the pure TGS crystal are found to be in good agreement with the reported literature¹⁹. It is observed that the lattice parameters slightly increase when TGS is doped with copper sulphate. The space group and number of molecules per unit cell for the grown pure and copper sulphate-doped TGS crystals were found to be $P2_1$ and 2 respectively.

Table 1: Lattice parameters for pure and copper sulphate-doped TGS crystals

| Parameters | Samples | |
|----------------|-----------------------|-----------------------|
| | Pure TGS crystal | TGS: copper sulphate |
| Crystal system | Monoclinic system | Monoclinic system |
| Space group | $P2_1$ | $P2_1$ |
| a | 9.398 Å | 9.412 Å |
| b | 12.634 Å | 12.695 Å |
| c | 5.784 Å | 5.835 Å |
| α | 90° | 90° |
| β | 109.55° | 111.43° |
| γ | 90° | 90° |
| V | 652.27 Å ³ | 664.73 Å ³ |
| Z | 2 | 2 |

Optical properties

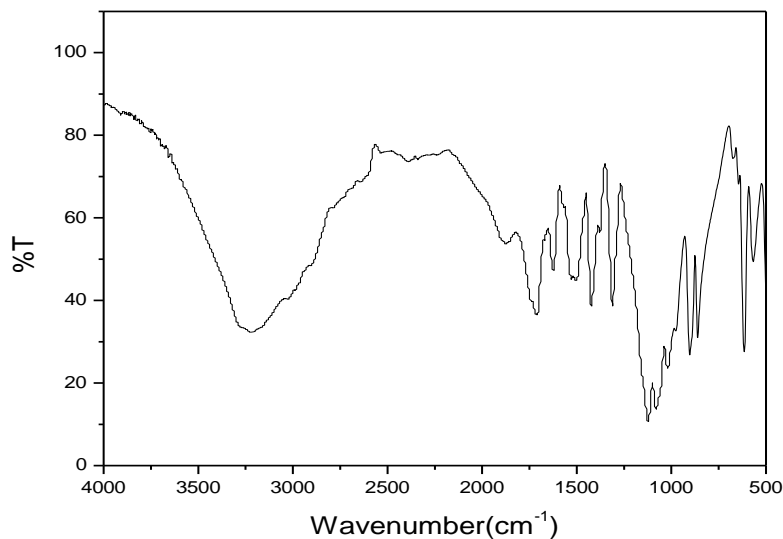
FTIR studies

FTIR spectra of pure and copper sulphate-doped TGS crystals are presented in the figure 3. The broad band between 2200 and 3800 cm^{-1} in the spectra indicate stretching frequencies of superimposed O-H and NH_3^+ modes. Multiple combination and overtone bands of CH_2 have been observed in the region 2300-2500 cm^{-1} . The NH_2 asymmetric stretching vibrations appear between 3200 and 3500 cm^{-1} and NH_2 symmetric stretching vibrations occur between 2800-3200 cm^{-1} . The absorption in the region 1700-1650 cm^{-1} is assigned to C=O stretching of COOH group. The peaks between 1610 and

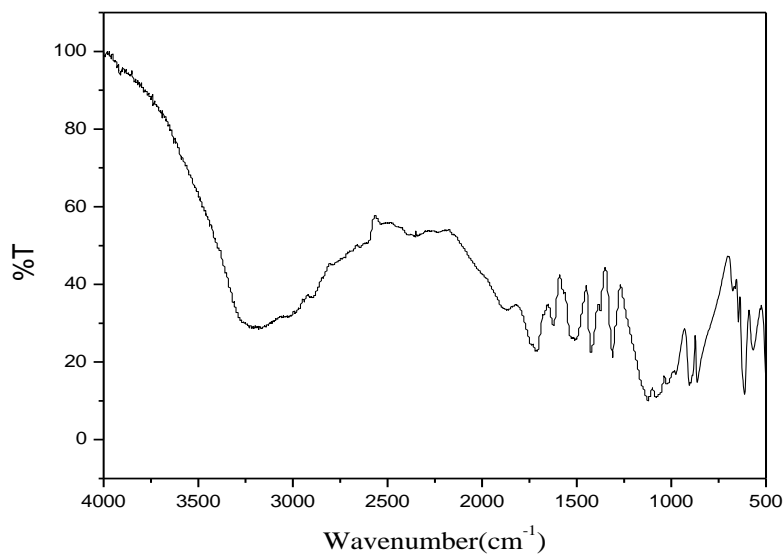
1450 cm^{-1} in the FTIR spectra can be assigned to COO- vibrational mode. It is noticed here that some of NH_2 vibrations overlap with C-N and SO_4 vibrations. The strong peak region 1120-1150 cm^{-1} in the samples is attributed to C-N stretching vibrations. The strong absorption in the range 1020 -1130 cm^{-1} is evidently due to the sulphate part of the molecule. The peaks observed at 615, 570 and 502 cm^{-1} are due to NH_3^+ oscillation. Since the functional groups of pure and copper sulphate-doped TGS crystals are identical, FTIR spectra appear similar for the samples. The assignments for the absorption bands/peaks of the FTIR spectra are given in accordance with the data reported in the literature²⁰. It is

noticed that some of bands of spectra of the copper sulphate-doped TGS samples are either broadened or

narrowed and this indicates the presence of copper sulphate in the doped TGS crystal.



(a)



(b)

Fig.3: FTIR spectra of (a) pure TGS crystal and (b) copper sulphate-doped TGS crystal

UV-visible transmittance studies

UV-visible transmittance studies are assisted in understanding electronic structure of the optical band gap of the crystals. The study of the absorption edge is essential in connection with the theory of electronic structure, which leads to the prediction of whether the band structure is affected near the band extreme. From the transmittance spectra (Fig.4), it is noticed that pure

TGS crystal has a transmittance of more than 95 % in the visible region. Copper sulphate-doped TGS crystal has lower transmission percentage compared to pure TGS crystal. A strong absorption is observed at 228 nm for pure TGS crystal 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 $E_g = 1240 / \lambda$ eV (Here λ is in nm) , the band gap is calculated to be 5.438 eV. The observed behaviour of the spectra and band gap value found in this work are in good agreement with UV-Visible spectral data of TGS crystal reported in the literature²¹. From the results, it is observed that the transmittance for the copper sulphate-doped crystal decreases and hence absorbance

increases in the entire UV-Visible region of the spectra when compared to spectrum of pure TGS crystal. From the results, it seems that the cut-off wavelength for copper sulphate-doped TGS crystal is slightly less compared to that of pure TGS crystal and this is due to formation of impurity levels below the conduction band.

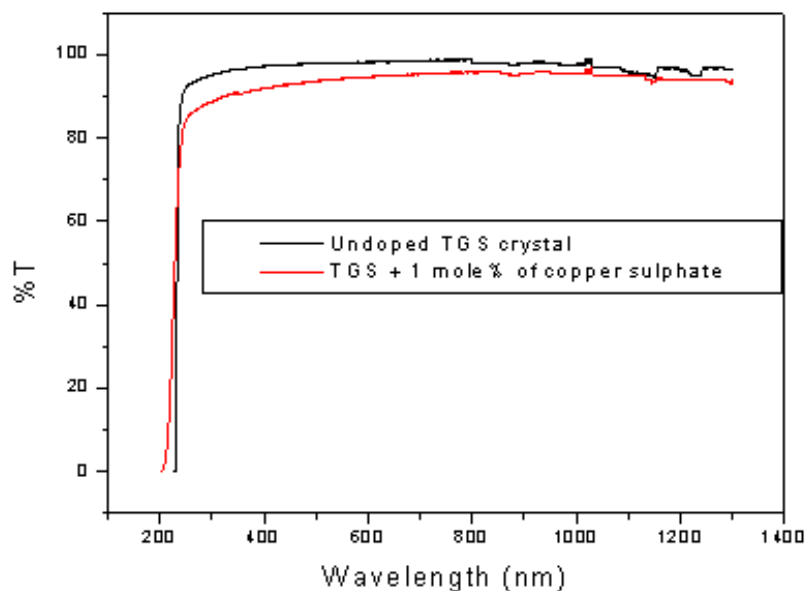


Fig.4: UV-visible transmittance spectra for undoped and copper sulphate-doped TGS crystals

Atomic absorption studies

Atomic Absorption Spectroscopic (AAS) study for the copper sulphate-doped TGS crystal was carried out to confirm the presence of copper in the lattice of the crystal. From the results, it is observed that the concentration of the impurity (copper metal content) was found to be 840 ppm. Even though 1 mole % of copper sulphate was used in the solution of TGS during the growth, it is observed from the AAS study that only low concentration of copper has been incorporated into the lattice of the doped-TGS crystal.

Measurement of density

Floatation method was used to measure the density of the grown crystals. The obtained values of density for pure and copper sulphate-doped TGS crystals are 1.664 g/cc and 1.727 g/cc respectively. It is noticed that the density of TGS crystal is found to increase when it is doped with copper sulphate. This may be due to incorporation of dopant in the interstitial positions of the sample. If the dopant occupies the crystal interstice, mass increases and hence density increases. The density was also calculated from the crystallographic data using the relation $\rho = (M.Z)/(N.V)$ where M is the molecular weight of

the material used, Z is the number of molecules per unit cell, N is Avogadro's number and V is the volume of the unit cell. It is found that the measured value of density for pure TGS crystal by floatation method and value of density obtained from crystallographic data are comparable.

Dielectric properties

Variation of dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) of the pure and copper sulphate-doped TGS crystals at 1000 Hz and at different temperatures are displayed in the figures 5 and 6. The Curie point, T_c for the samples was observed to be 49°C. The dielectric constant is small at low temperature, which increases with temperature and rises sharply up to the Curie point. Above T_c , the dielectric constant decreases suddenly and obeys Curie_Weiss law. The dielectric loss of the samples shows the same behaviour. The rapid increase of dielectric constant and loss may be due to the space charge polarization of thermally generated carriers. It is observed that there is no change in the Curie temperature and there is only increase of dielectric constant and loss observed when TGS crystals are doped with copper sulphate. The increase in dielectric constant and loss for

copper sulphate-doped TGS crystals may be due to frittering of domains due to incorporation of impurities in the lattice. Referring the figure 5, the value of dielectric

loss ($\tan \delta$) at room temperature is low and this indicates that the grown TGS crystal is of high quality²².

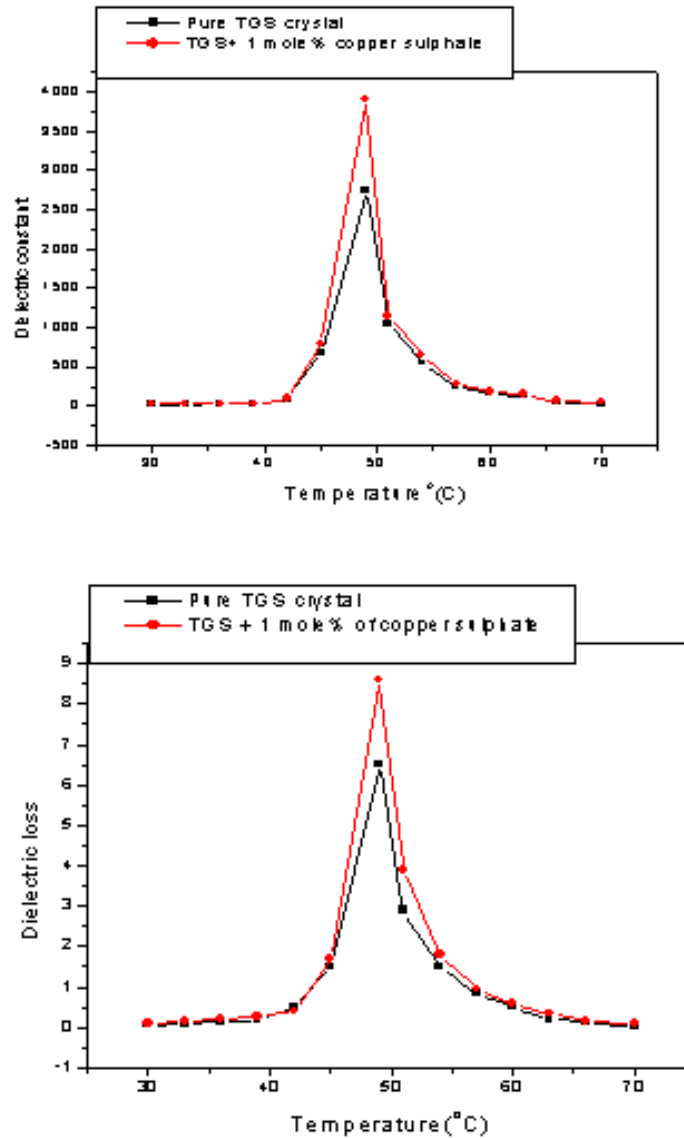


Fig.5: Variation of dielectric constant with temperature for pure and copper sulphate-doped crystals at 1000 Hz; Fig.6: Variation of dielectric loss with temperature for pure and copper sulphate-doped crystals at 1000 Hz

Mechanical properties

Variations of microhardness number (H_v) with the load (P) for pure and copper sulphate-doped TGS crystals are shown in the fig. 7. At lower loads, hardness is low and it increases with the load up to 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. In this study, hardness number(H_v) increases with load for the samples. This can be explained qualitatively on the basis of depth of penetration of the

indenter²³. For small loads, only a few surface layers are penetrated by the indenter. The measured hardness is the characteristics of these layers and H_v increases with load in this region. With increase in load, the overall effect is due to surface as well as inner layers of the sample. From the results, it is observed that the hardness of TGS crystal increases when it is doped with copper sulphate. This increase in the hardness of doped TGS crystals can be attributed to the incorporation of impurities in the lattice of crystals. The incorporation of impurities in the lattice most

probably enhances the strength of bonding with the host

material and hence the hardness increases.

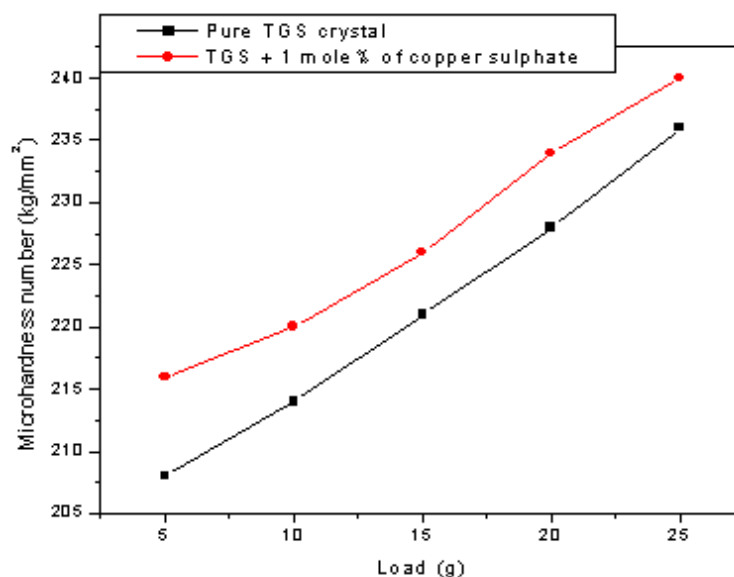


Fig.7: Variation of microhardness number with the load for pure and copper sulphate-doped TGS crystals

Conclusions

Undoped pure and copper sulphate-added TGS salts were synthesized and solubility studies were carried out for the prepared samples in de-ionized water in the temperature ranging from 30 to 50 °C. In accordance with the solubility data, saturated solutions were prepared for growing pure and copper sulphate-doped TGS crystals by slow evaporation technique. The grown pure TGS crystal is observed to be colourless while copper sulphate-doped TGS crystal is observed to be slightly blue in colour. Morphological alterations have been observed when TGS crystals are doped with copper sulphate. XRD studies reveal the monoclinic structure of the grown crystals. Density of copper sulphate-doped TGS crystal is more compared to that of pure TGS crystal. Atomic absorption study confirms the presence of copper ions in the lattice of doped TGS crystal. It is observed from dielectric studies that there is no change of Curie point and increase of dielectric parameters when TGS crystals are doped with copper sulphate. Mechanical property of the grown crystals has been studied by microhardness test and noticed that there is an increase of microhardness number when TGS crystal is doped with copper sulphate.

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