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Research Article

COMPARATIVE STUDIES OF UNDOPED AND ZINC SULFATE DOPED MAGNESIUM IODATE CRYSTALS

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ABSTRACT

Undoped and zinc sulfate doped magnesium iodate crystals have been grown by solution method using the double distilled water as the solvent. The reactants used here are magnesium sulfate, iodic acid and zinc sulfate and the grown crystals were harvested after a period of nearly one month. The grown crystals were subjected to XRD studies, LDT studies, UV-visible spectral studies, micro hardness studies, SHG and dielectric studies. Both undoped and zinc sulfate doped magnesium iodate (ZSMI) crystals are found to be crystallizing in monoclinic crystal structure. The transmittance is observed to be decreasing when magnesium iodate crystal is doped with zinc sulfate. The hardness is found to be increasing due to doping of zinc sulfate into the lattice of magnesium iodate crystal. The NLO properties like SHG efficiency have been enhanced when magnesium iodate crystals are doped with zinc sulfate and the obtained results are analyzed and reported.

Keywords: Magnesium Iodate; Doping; Solution Method; Slow Evaporation Technique; Characterization; XRD; Microhardness; SHG; Dielectrics

1. INTRODUCTION

Organic nonlinear optical crystals have some drawbacks like low hardness, low thermal stability and low mechanical strength but inorganic NLO crystals have high melting point and high degree of chemical inertness. The phenomenon of Second Harmonic Generation (SHG) in an inorganic crystal quartz was first reported in 1961, which led to the development of recent NLO materials such as inorganic systems, semiconductors and inorganic photorefractive crystals and these are covalent and ionic bonded in which the optical nonlinearity is considered as the bulk effect [1-4]. Metal iodates are the inorganic crystals and they are studied for nonlinear optical property due to the presence of a lone pair on iodine in the iodate group, which favors the acentric structure formation with remarkable thermal stability [5-7]. Metal iodates like potassium iodate, sodium iodate, lithium iodate etc are the useful inorganic NLO materials [8-10]. Bergman *et al*. have reported the studies of many iodate and chlorate samples [11]. Geneva Sequirea Roche *et al.* have grown the picric acid added potassium iodate crystals recently [12].

In this paper, a comparative study is made for undoped and zinc sulfate doped magnesium iodate crystals and the aim of the work is to analyze the effect of zinc sulfate on various properties of magnesium iodate crystals.

2. MATERIAL AND METHODS

2.1. Crystal growth

AR grade chemicals like magnesium sulfate, zinc sulfate and iodic acid were purchased and used without any further purification. Magnesium sulfate and iodic acid were taken in the molar ratio of 1:1 and the calculated amounts of the chemicals were dissolved in double distilled water, stirred well using a hot-plate magnetic stirrer and the saturated solution was prepared. The solution was heated at 50°C for three hours for the synthesis of the sample. Then, the solution was cooled and filtered using the Whatmann filter papers and the filtered solution was taken in a growth vessel covered with a perforated paper. The growth vessel containing the solution was kept in vibration-free place and due to slow evaporation of the solvent, the undoped magnesium iodate crystals were harvested after the growth period of

30-35 days. Zinc sulfate doped magnesium iodate (ZSMI) crystals were prepared by adding 1 mole% of zinc sulfate into the aqueous solution of magnesium iodate. The grown crystals of undoped and zinc sulfate doped magnesium iodate are shown in the fig. 1.

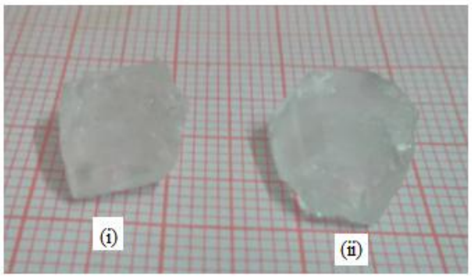

Fig.1: Harvested crystals of (i) undoped and (ii) zinc sulfate doped magnesium iodate crystals

3. CHARACTERIZATION

3.1. XRD studies

X-ray diffraction (XRD) is based on the principle of Bragg's law 2d sin ø = n λ where ø is the Bragg's glancing angle, d is the interplanar spacing, n is the order of diffraction and λ is the wavelength of X-rays. When X-rays fall on a crystalline sample, X-ray diffraction takes place. Here the crystal is considered as a three dimensional grating because the atoms or molecules are regularly arranged in the crystal in a three dimensional manner. It is mentioned here that the value of the interplanar spacing is of the same order of wavelength of X-rays and hence when the Bragg's law is satisfied, X-rays are diffracted. By measuring the intensity of the diffracted X-rays from the different planes of the crystal, crystal structure can be solved [13, 14]. In this work, a single crystal X-ray diffractometer (Bruker-Nonius MACH3/CAD4) was used to find the lattice parameters and crystal structure. The obtained lattice parameters of the samples are provided in the table 1.

Single crystal XRD analysis indicates that the grown crystals crystallize in monoclinic structure. The space group of the both the samples are observed to be $P2_1$ and this space group is a non-centrosymmetric space group. Hence second harmonic generation (SHG) of laser light can be produced from the grown crystals of undoped and zinc sulfate doped magnesium iodate.

Table 1: Values of lattice parameters and space group of undoped and zinc sulfate doped magnesium iodate crystals

Lattice parameters	Undoped Magnesium iodate	ZSMI crystal
a (Å)	10.952(3)	10.958(4)
b (Å)	5.186(2)	5.190(3)
c (Å)	10.898(4)	10.936 (3)
α, β and γ	90°, 98.57(5)°, 90°	90°, 98.63(2)°, 90°
Crystal System	Monoclinic,	Monoclinic,
Space group	$P2_1$	$P2_1$
Volume of unit cell	612.06(3) $Å^3$	614.92(2) $Å^3$

3.2. Linear optical studies

Linear optical parameters like transmittance, absorption coefficient, extinction coefficient and optical band gap of undoped and zinc sulfate doped magnesium iodate (ZSMI) crystals have been calculated using the optical transmittance spectra. A UV-visible spectrophotometer was used to record the UV-visible transmittance spectra of the samples in the wavelength range 190-1100 nm and the recorded spectra are shown in the fig. 2. The result indicates that sample crystals have high optical transmittance in the visible region and the transmittance is slightly decreased when magnesium iodate crystal is doped with zinc sulfate. At 295 nm, there is a sudden decrease of transmittance is observed for the samples and the wavelength at which a sharp fall of transmittance and high absorbance observed in the UV region is called the UV cut-off wavelength or the fundamental absorbance. The transmittance of about 75% in the entire visible region and low UV cut-off wavelength are the interesting parameters for the grown crystals and hence these crystals are the suitable for the NLO and opto-electronic applications. The linear optical absorption coefficient of the samples was calculated using the formula $\alpha = (2.303/d)* \log (1/T)$ where d is thickness and T is the transmittance of the crystal. The calculated values of absorption coefficient of undoped and zinc sulfate doped magnesium iodate (ZSMI) crystal are presented in the fig. 3.

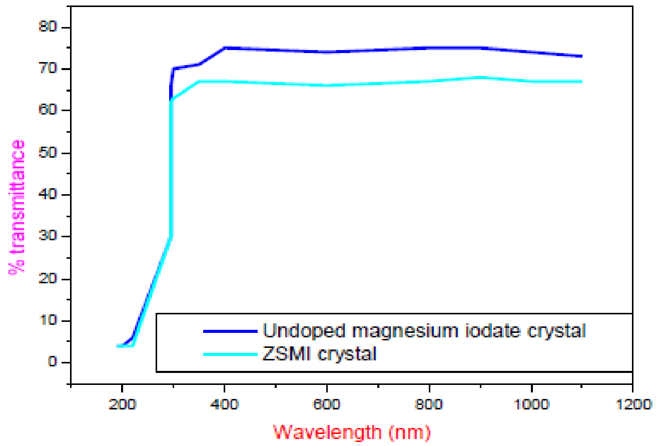

Fig.2: Optical transmittance spectra of undoped and zinc sulfate doped magnesium iodate crystals

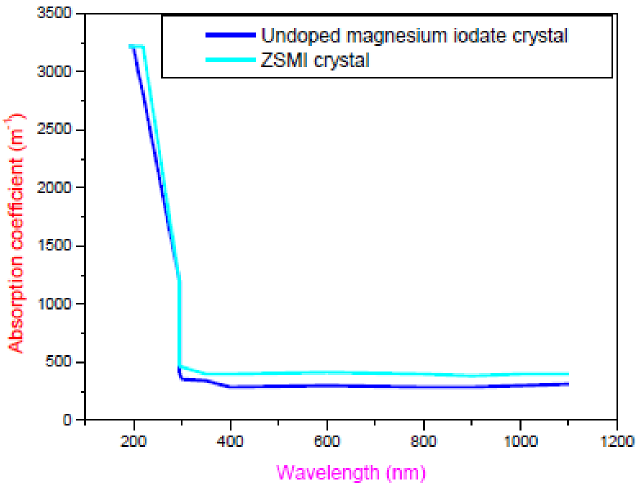

Fig.3: Plots of Linear absorption coefficient versus wavelength for undoped and zinc sulfate doped magnesium iodate crystals

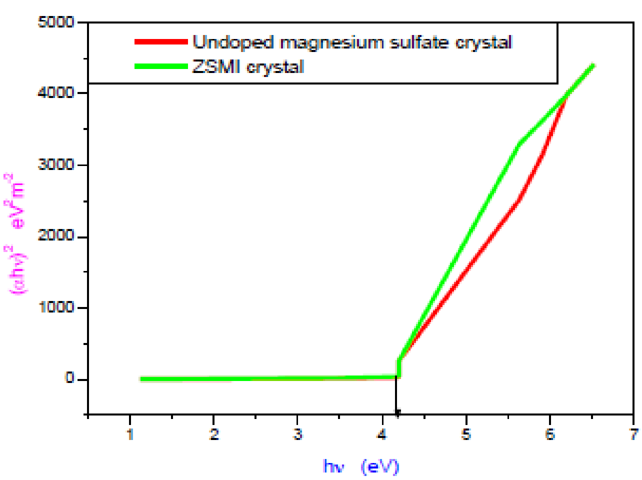

Fig. 4: Tauc's plots for undoped and zinc sulfate doped magnesium iodate crystals

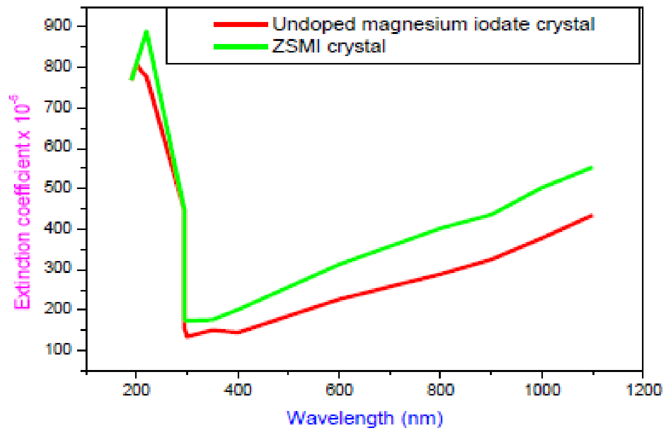

Fig.5: Plots of extinction coefficient versus wavelength for undoped and zinc sulfate doped magnesium iodate crystals

It is observed that the absorption coefficient is low in the visible-NIR region and it is high at the wavelength of 295 nm. Using the Tauc's equation [15], the values of optical band gap of the samples are obtained. Tauc's relation is given by $\alpha h\nu = A(h\nu - E_g)^{1/2}$ where E_g is the optical energy gap, A is a constant and α is the linear absorption coefficient, ν is the frequency of light and h is the Planck's constant. Using this relation, Tauc's plots for undoped and zinc sulfate doped magnesium iodate are drawn and the plots are presented 4. The values of optical band gap for the samples are found to be 4.20 eV and since the cut-off wavelength of the samples is the same, the optical band gap is observed to be the same. The extinction coefficient of the sample crystals was calculated using the relation $K = \alpha\lambda/4\pi$ where α is the linear absorption coefficient and λ is the wavelength of the light. The plots of wavelength dependence of extinction coefficient for samples are shown in the fig. 5. The result indicates that the extinction coefficient increases with increase of wavelength in visible-NIR region for both undoped and zinc sulfate doped magnesium iodate crystals. It is noticed that absorption coefficient is high in the UV-region. Since the extinction coefficient of these crystals is low of the order of 10^{-5}, the crystals of undoped and zinc sulfate doped magnesium iodate are the useful optical materials with little loss of energy when UV-visible-NIR light is passed through the samples.

3.3. Microhardness studies

There are many hardness tests like Brinell test, Vickers test and Knoop test etc. In this work, Vickers hardness test was adopted to find the mechanical parameters of the grown crystals was studied using SHIMADZU HMV-2T microhardness tester. It was originally known as the 136° diamond pyramidal hardness test because of the shape of the indenter. The indentations were made on the polished crystal for the loads of 25 g, 50 g, 75 g and 100 g. The indentation time was kept for 10 seconds for all the loads. As the load is increased beyond this limit, cracks developed on the smooth surface due to the internal stress generated locally by the indentation. The average value of indentation length (d) is obtained for different applied loads for both the samples and the corresponding plots are shown in the fig. 6.

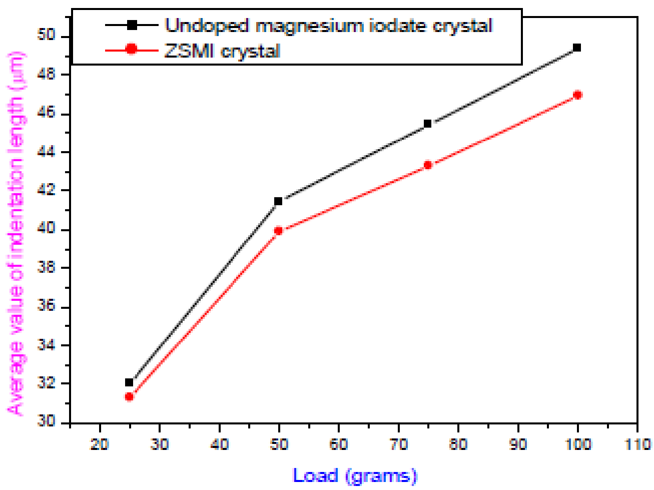

Fig.6: Plots of average indentation length versus the applied load for undoped and zinc sulfate doped magnesium iodate crystals

The Vickers hardness number (H_v) is computed using the relation $H_v = (1.8544\ P)/d^2$ where P is the indentation load in kg and d is the mean diagonal indentation length in mm. The plots of hardness number versus applied load for the crystals of undoped and zinc sulfate doped magnesium iodate (ZSMI) are presented in the figure 7.

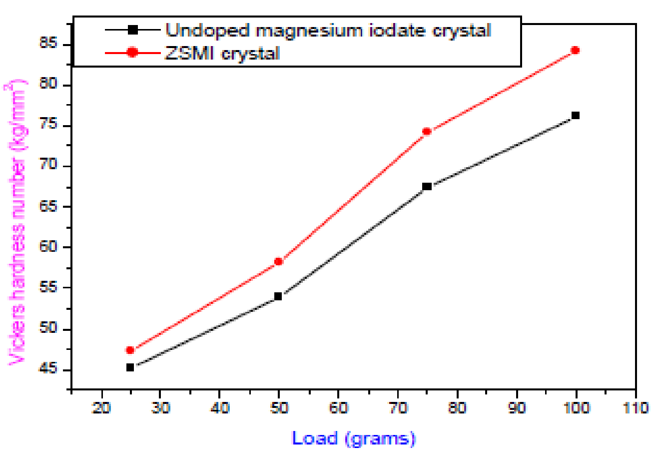

Fig.7: Plots of Vickers hardness number versus the applied load for undoped and zinc sulfate doped magnesium iodate crystals

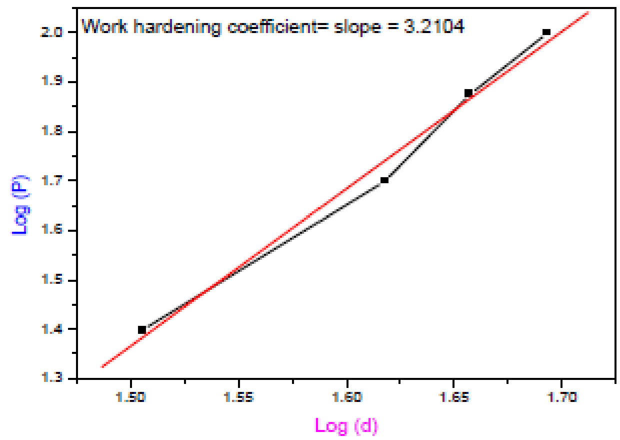

Fig.8: Plot Log (P) versus Log (d) for undoped magnesium iodate crystal

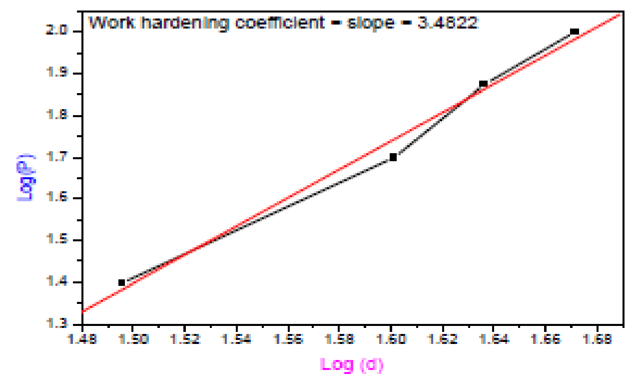

Fig. 9: Plot Log (P) versus Log (d) for zinc sulfate doped magnesium iodate ZSMI) crystal

It is observed that hardness number increases with increase of the applied load for both the samples. Since the hardness increases with increase of load, the crystals have the reverse indentation size effect (RISE). Meyer's plot is drawn using the relation $P = a\ d^n$ where, a is a constant and n is work hardening coefficient of the sample. The values of work hardening coefficient of the grown crystals are obtained from the Meyer's plots (Figs.8 and 9) and the obtained values are 3.2104 and 3.4822 respectively for undoped magnesium iodate and zinc sulfate doped magnesium iodate crystals. According to theory of microhardness, $1.0 \leq n \leq 1.6$ for hard materials and $n > 1.6$ for soft materials and it is concluded that these crystals belong to the soft category of materials. The values of depth of indentation in the grown crystals are determined using the relation $h = d/7.006$, where d is average indentation length. The plot of depth of indentation versus applied load for the sample is shown in the figure 10. The results indicate that the depth of indentation in the samples is very low and hence samples have more hardness and mechanical strength. Comparatively, the hardness and work hardening coefficient of ZSMI crystal is more than those of undoped magnesium iodate crystal. The average indentation length and depth indentation of ZSMI crystal are observed to be less in comparison with that of undoped magnesium iodate crystal. Hence, ZSMI crystal has better mechanical properties than that of undoped magnesium iodate crystal.

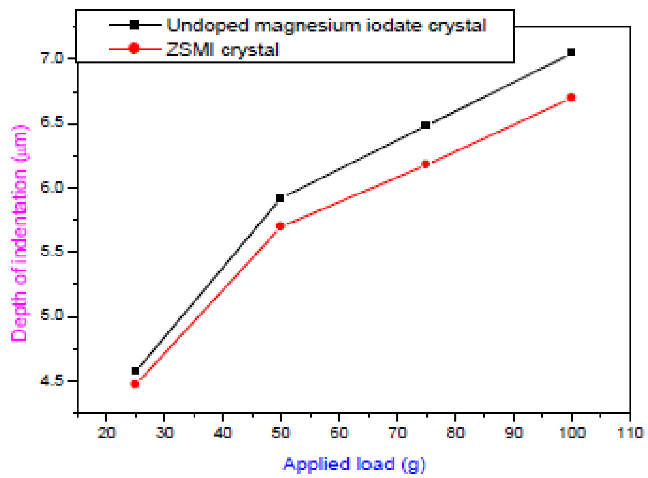

Fig. 10: Plots of depth of indentation versus the applied load for undoped and zinc sulfate doped magnesium iodate crystals

3.4. LDT studies

Laser damage threshold (LDT) value is a parameter which indicates the tolerance to laser damage on a crystal. LDT value of grown crystals was measured using the Q-switched Nd-YAG laser (λ= 1064 nm) and duration of the pulse is 10 ns. The laser damage occurring on the surface of the sample is observed with the help of scattered radiation of laser from its surface. A sharp reduction in the intensity of the transmitted laser beam gives the indication of the laser damage in the sample. The LDT value was calculated using the relation $P = E/\pi\tau r^2$ where E is the energy in mJ, τ is the pulse width in ns and r is radius of the spot in mm. The calculated values of LDT for the grown crystals of undoped magnesium iodate and zinc sulfate doped magnesium iodate (ZSMI) are 0.521 GW/cm^2 and 0.644 GW/cm^2 respectively. Hence, in terms of laser damage, ZSMI crystal is better in comparison with undoped magnesium iodate.

3.5. Second harmonic generation

The study of the interaction of high intense laser beams with various material media resulted in the observation of many new optical phenomena. This prompted a large number of experimental and theoretical investigations. Laser sources can provide sufficiently high light intensities to modify the optical properties of materials. This interaction of light waves can result in the generation of optical fields at new frequencies, including optical harmonics of incident radiation or sum or difference frequency signals. In short, light of one or more frequencies impinges on a sample and light at a different or several different frequencies emerges. A simple example is Second Harmonic Generation (SHG), where the wavelength of the light that emerges is exactly half of the incident beam. The second harmonic generation is a nonlinear optical processes, in which photons interacting with a nonlinear material are effectively combined to form new photons with twice the energy and therefore twice the frequency and half the wavelength of the initial photons. The SHG emission from the samples was checked by Kurtz- Perry powder technique and here a pulsed Nd: YAG laser with the input wavelength of 1064 nm was used [16]. It is powder technique and so the samples are ground to powder of grain size 400-500 µm and subjected to measurement of SHG. It is noticed that there is an emission of green radiation with a wavelength of 532 nm from the samples. The second harmonic generation signal of 21.59 mJ/pulse was observed for undoped magnesium iodate crystalline sample for an input energy of 0.70 J/pulse. But SHG signal of 23.42 mJ/pulse was observed from ZSMI crystalline sample. Also, from the reference KDP sample, SHG signal of 8.9 mJ/pulse was obtained. The data in connection with SHG studies of the samples are given in the table 2. The results indicate that SHG efficiency of ZSMI crystal is more than that of undoped magnesium iodate crystal.

Table 2: Obtained data in connection with SHG studies for undoped and zinc sulfate doped magnesium iodate (ZSMI) crystals

Sample Code / Name of the Sample	Output Energy (mJ / pulse)	Input Energy J/pulse	Relative SHG efficiency (with respect to KDP)
Undoped magnesium iodate	21.59	0.70	2.426
ZSMI crystal	23.42	0.70	2.631
KDP crystal (Reference sample)	8.90	0.70	1

3.6. Dielectric studies

To understand the dielectric behaviour, measurement of dielectric parameters like dielectric constant and dielectric loss factor of the samples was carried out at different frequencies and temperatures for undoped and zinc sulfate doped magnesium iodate (ZSMI) crystals. The variations of dielectric constant and dielectric loss of the samples are carried out at various frequencies. This study was performed using an LCR meter. The grown crystals were cut, polished and silver electroded and the values of capacitance with the sample (C_o) and capacitance without sample (C) have been measured. The dielectric constant was determined using relation $\varepsilon_r = C/C_o$. The dielectric loss is the energy loss in a dielectric material and it was measured directly from the LCR meter. The variations of dielectric constant and dielectric loss with frequency for undoped and zinc sulfate doped magnesium iodate (ZSMI) crystals are shown in the figs. 11 and 12.

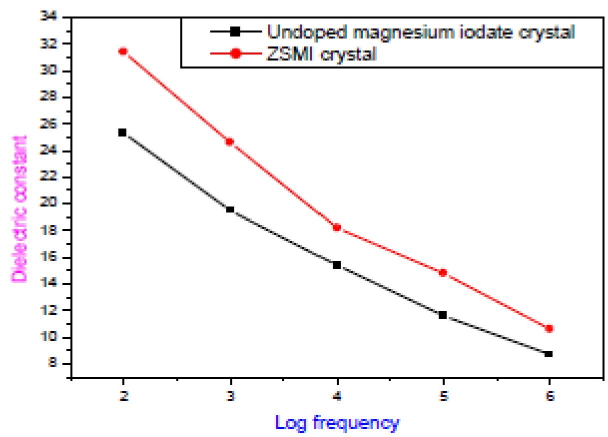

Fig.11: Variation of dielectric constant with frequency for undoped and zinc sulfate doped magnesium iodate (ZSMI) crystals

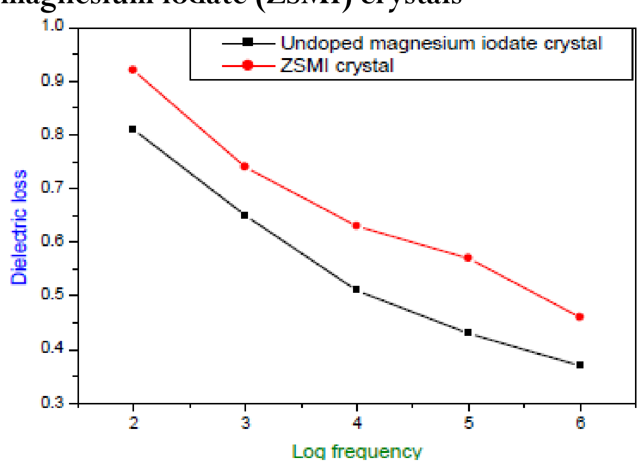

Fig.12: Variation of dielectric loss with frequency for undoped and zinc sulfate doped magnesium iodate (ZSMI) crystals

It is observed from the results that the dielectric constant and dielectric loss for both the samples decrease with increase of frequency. The high values of dielectric constant at low frequencies may be due to presence of space charge polarization and its low value may be due to the reduction of polarizations at higher frequencies. As the frequency is large, the relaxation time for dipoles in the crystal is less and hence the dipoles will not get enough time to orient themselves in the direction of electric field and this leads to reduction of polarization in the high frequency region [17, 18]. When magnesium iodate crystal is doped with zinc sulfate, the dielectric constant and loss are observed to be increasing and this is due to increase of charged species in the ZSMI sample.

4. CONCLUSIONS

Undoped and zinc sulfate doped magnesium iodate crystals were grown by slow evaporation method at room temperature. From single crystal XRD studies, it is confirmed that the crystals crystallize in monoclinic structure and the crystal structure is not changed due to doping of zinc sulfate into magnesium iodate crystal. Optical transmittance of ZSMI crystal is observed to be less when compared to that of the undoped magnesium iodate. The optical band gap of both the samples is found to be 4.22 eV. The linear optical parameters like absorption coefficient and extinction coefficient of the samples were determined at different wavelength values. LDT value is found to be more for ZSMI crystal compared to that of undoped magnesium iodate crystal. Dielectric constant and dielectric loss have been measured for the samples at different frequencies. Since SHG value is more for zinc sulfate doped magnesium iodate (ZSMI) crystal compared to that of undoped magnesium iodate crystal, the doped sample is the better candidate for NLO applications.

5. ACKNOWLEDGEMENT

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