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Electrical, mechanical properties of organic- inorganic hybrid of zinc iodide complex with Schiff based ligand

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Abstract: Layered organic-inorganic hybrid Zinc iodide complex were synthesized by reactions in solution. The studies of layered organic-inorganic hybrid materials are very interesting due to their unique electronic structure, electrical and mechanical properties. The mechanical properties of crystals are evaluated by mechanical testing which reveals certain mechanical characteristics. The Vickers hardness number (H_v) was found to increase with load. The Meyer's index number 'n' was calculated from H_v. The frequency dependent dielectric properties of title compound are studied by measuring dielectric constant, dielectric loss and conductivity at different temperatures in the frequency range of 50Hz – 5MHz. The value of dielectric constant and dielectric loss decreases with frequency increases are attributed to Maxwell- Wagner type interfacial polarization
Keywords: Mechanical studies, Meyer index number, Dielectric properties.

1. Introduction:

Hybrid materials were synthesized using well known chemistry of Schiff based ligands [1]. Thiocarbamide molecules are an interesting inorganic matrix modifier due to its large dipole moment and its ability to form and extensive network of hydrogen bonds[2]. Distorted perovskites have reduced symmetry, which is important for the magnetic and electrical properties[3]. The measurement of hardness is very important to fabrication of devices. The microhardness correlates with other mechanical properties such as elastic constant. Dielectric materials with high permittivity are of great importance in microelectronic industry. One of the issues having the direct effect on the dielectric constant is the polarizability of the material. Here,we investigate the electrical and mechanical properties of TZI crystal. Mechanical studies show that the material belongs to soft materials category. Dielectric studies on the sample were carried out using HIOKI 3532-50 LCR Meter in the frequency range 5Hz to 50Hz and temperature range 35ºC to 115 ºC.

1.1 Experimental:

Thiocarbamide zinc iodide (TZI) crystal was synthesized by mixing aqueous solutions of zinc iodide and thiocarbamide in the ratio of 1:2. Preparation of TZI was prepared according to the following chemical reaction

$$ZnI_2 + 2[CS(NH_2)_2] \rightarrow [Zn(CH_4N_2S)_2I_2]$$

Since thiourea has the coordination capacity to form different phases of metal- thiocarbamide complexes, the mixture of the reactants had to be stirred well to avoid co-precipitation of multiple phases. The resulting solution was allowed to stand in air up to the formation of colorless crystals [4].

2. Result and Discussion:

2.1 Mechanical studies:

The mechanical characterization of the TZI crystal was made by microhardness tester (Mututoyo MH 112, Japan) at room temperature. The Vickers indented impressions were approximately square in shape. The length of the two diagonals was measured by a calibrated micrometer attached to the eyepiece of the microscope after unloading. The Vickers hardness number (H_v) was calculated using the standard formula,$H_v = 1.8544\ P/d^2$ -------- (1) Where P is the applied load in kg and d is in mm and Hv is in kg/mm^2.Crack initiation and fragmentation becomes significant beyond 100g of the applied load.

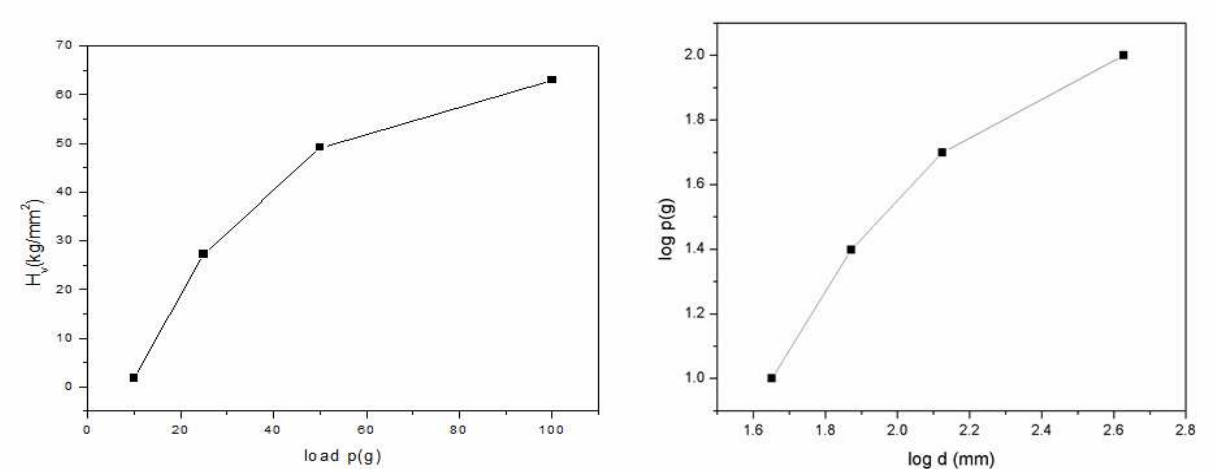

Figure 1(a). Variation of microhardness with load, 1(b) Graph between log P versus log

Figure 1(a) shows the variation of H_v as a function of applied load range from 10g to 100g for the TZI crystal. It is very clear from the figure that H_v value increases with load increases. The Meyer's index number was calculated from the Meyer's law, which relates the load$P = kd^n$ -------(2), $\log P = \log k + n \log d$ ---------(3).Where k is material constant and n is the Meyer's index. In order to find the value of 'n', a graph is plotted for log P against log d (figure 1(b)) which gives a straight line. From the slope of the line the Meyer's index number 'n' was calculated to be 2.5. According to onitsch 'n'should lie between 1 and 1.6 for harder materials and above 1.6 for softer materials. Thus TZI belongs to the soft material category.

2.2 Dielectric properties:

Dielectric study is an important mechanism to explain the origin of dielectric relaxation. Good quailty crystal with perfect planes were chosen for dielectric measurements. Silver paste were appiled on both top and bottom faces to make as the capacitor with crystal as medium. HIOKI 3532-50 LCR Meter were used to carried this experiment.The dielectric constant is calculated from the formula,$\varepsilon' = Ct / \varepsilon_o A$ --------- (4). where C is the capacitance value obtained from analyses, t is the thickness of the crystal, A is the area of thecrystal and ε_o is the permittivity of the free space.The a.c. conductivity is calculated from $\sigma_{a.c} = \omega\ \varepsilon_o\ \varepsilon' \tan\delta$ ---- (5).where f is the appiled a.c. frequency, the activation energy is obtained from the relation$\sigma = \sigma_o \exp(E_a/KT)$ ------- (6). Where K is the Boltzman's constant and T is the temperature.Figure2(a) shows the variations of dielectric constant with log frequency.

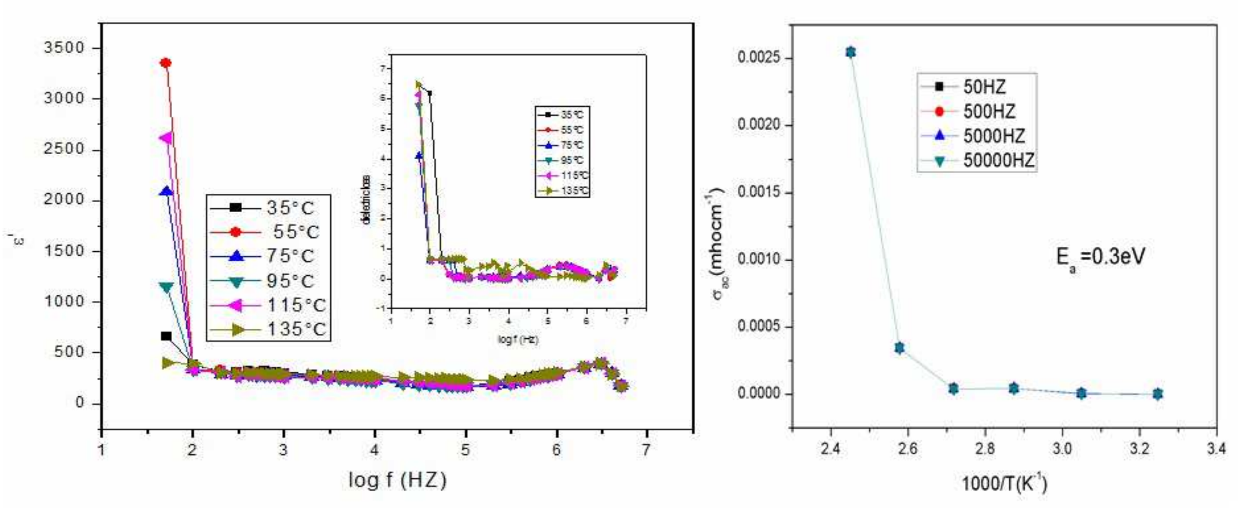

Figure2(a)shows the variations of dielectric constant with log frequency, 2(b) The variation of the dielectric loss with frequency, 2(c)The variation of ac conductivity (σ_{ac}) with temperature.

From the graph,it shows that the dielectric constant is high in the low frequency region and decreases with an increase in frequency. High dielectric constant at low frequencies may be due to the presence of all the four components namely, space charge, orentational, electronic and ionic polarisations. At high frequency dielectric constant decreases gradually. The dielectric loss was also studied for different temperature as afunction of frequency is shown in figure 2(b). Itshows that the dielectric loss decreases with increasing frequency, the low dielectric loss at high frequency indicates the high purity of the crystal. The curve suggest that the dielectric loss is strongly dependent on tne frequency of the applied field.The conductivity gets decreases with increased temperature(shown in fig 2(c)). The activation energies were calculated by curve fitting Eq.6. the activation energy of the crystal is less than 1eV. The low activation energy suggests an intrinsic conduction due to the contribution of space charge. The space charge is created between the sample and electrode.

3. Conclusion:

Electrical and mechanical properties of TZI crystal have investigated. Vickers hardness numbers were calculated for TZI crystal by the application of load and the hardness numbers were found to increase with increase in load. The value of the Meyer's index, n turned to be greater than 1.6 and thus TZI falls in the soft material category. The electricalproperty of TZI was characterized by dielectric studies. An obvious frequency dependance of dielectric response was observed, as is the case for a typical relaxor.

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