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Microwave measurements of dielectric constants of SnI_2 and SnI_4

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The bulk dielectric parameters at microwave frequencies (8.95 GHz) for tin-di-iodide (SnI_2) and tin-tetra-iodide (SnI_4) have been determined using Looyenga's formula. It has also been investigated under different conditions such as particle size, packing fraction and temperature of the powders. It has been observed that the dielectric constant of SnI_2 is greater than that of SnI_4 materials. The temperature dependence of dielectric parameters in these materials indicated the presence of dissociation processes causing the fall in dielectric constants. An attempt has been made to understand these results and the implications are discussed.

1. Introduction

A study of the dielectric properties of solids gives a good insight into the electric field distribution in them. At microwave frequencies, the bulk dielectric constant of a solid is generally obtained from powder measurements and the dielectric properties of powder correlated with bulk materials, because in most cases bulk materials in the form of sufficiently large crystals are frequently not available in the size required for dielectric studies. Van Beck [1] has reviewed different procedures that are used for correlating the dielectric properties of powder with those of bulk materials. It has been shown that Looyenga's equation [2] is the best relation for correlating the dielectric constant of powder and bulk materials.

Tin-di-iodide (SnI_2) and tin-tetra-iodide (SnI_4) are of considerable interest, particularly in basic studies of their phase transformation and of their electronic optical and other pertinent characteristics, particularly SnI_4 as this molecule is simple in terms of symmetry and structure [3]. SnI_2, a layered luminescence semiconductor [4], has high colour rendering when used in an electric arc lamp [5]. As far as the authors are aware, dielectric constants of SnI_2 and SnI_4 have not been reported in the literature. In this paper we report dielectric constants of SnI_2 and SnI_4 at various packing fractions, particle sizes and temperatures using Looyenga's equation.

2. Experimental methods

The single crystals of SnI_2 and SnI_4 were grown in the laboratory using the gel technique [6]. The crystals were crushed, powdered and passed through different sieves to obtain fine powders. Measurements of dielectric constants for the SnI_2 and SnI_4 powders were carried out in the X-band of a microwave bench operating at 8.95 GHz. The dielectric constants were calculated using the method of Dakins and Works [7].

A known quantity of powders of SnI_2 and SnI_4 were packed in wave guide cells. The cell was a piece of a wave guide of cross-section 0.9 in. x 0.4 in. and 2.4 in long, and having a fixed short circuit brazed at its one end. Different packings were obtained by pressing the powder in the cell using a close-fitting plunger, operated by a hydraulic press. The compression applied to the powders not only involves a decrease in voids between the particles but also compresses the solid particles themselves. It has been observed that the

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compressibility of SnI_4 is very similar to that of a nylon. Care was taken to keep the upper surface of the powder horizontal in the wave guide.

In order to achieve maximum accuracy for dielectric measurement, the length of the powder sample was kept to approximately odd multiples (in practice usually first or third multiple) of quarter wavelengths, the approximate wavelength λ_p being determined from preliminary measurement of permittivity ϵ_p. λ_p and ϵ_p are related by the expression:

$$\epsilon_p = \lambda_0^2 \left(\frac{1}{\lambda_p^2} + \frac{1}{\lambda_c^2} \right), \quad (1)$$

where λ_0 is the free space wavelength and λ_c is the cut-off wavelength. Determining ϵ_p, using an arbitrary sample length, λ_p can be determined. The sample length is now readjusted to about $\lambda_p/4$ or its odd multiple, to measure accurate values of ϵ_p. The maximum length of the powder sample was not more than a centimetre in the present investigation.

The nominal accuracy of measurement in the present method [8] for permittivity is ± 3%. The dielectric values are reported after performing the experiment three times at a given packing fraction, at room temperature. The values were quite consistent and reproducible. No dielectric loss was observed at this microwave frequency for these powder materials. The experiments are first carried out on the known sample (KCl) to test the performance of the experimental method.

The variation of dielectric constants with temperature were studied for SnI_2 (packing fraction: 0.654) and SnI_4 (packing fraction: 0.865). An oil bath was used and the temperature was measured with a chromel–alumel thermocouple (± 2° C). The position of the first minimum with an air-filled wave guide cell was noted at different temperatures and any necessary correction was made for the shift in minimum with the sample in the cell at different temperatures, while calculating the dielectric constants.

2.1. Method of calculation

Samples were dried sufficiently before investigation, and dielectric parameters were measured at room temperature (28° C). The bulk dielectric constants of SnI_2 and SnI_4 materials were estimated using Looyenga's equation:

$$\epsilon_p^{1/3} - 1 = \delta \, (\epsilon_s^{1/3} - 1) \quad (2)$$

TABLE I Dielectric parameters calculated for the bulk from measurements on powders (average particle size 150 μm). Measurements are at 8.95 GHz

Substance	Packing fraction, δ	Dielectric constant of powder, ϵ_p	Dielectric constant of bulk material, ϵ_s
KCl	0.587	2.750	4.78
	0.631	2.906	4.72
SnI_2	0.584	11.230	30.30
	0.637	12.240	28.80
SnI_4	0.764	16.18	27.00
	0.875	19.70	25.50

where ϵ_s represents the dielectric constant of the bulk material and ϵ_p is the dielectric constant of the powder sample at packing fraction δ.

The dielectric constants of powder materials (ϵ_p) of SnI_2 and SnI_4 are determined by the method of Dakins and Works and using Equation (2) the bulk dielectric constants (ϵ_s) of materials are calculated.

3. Results and discussion

The experimental data at microwave frequencies 8.95 GHz for the SnI_2 and SnI_4 samples of average particle size 150 and 50 μm are reported in Tables I and II, respectively. The following observations are noted from the tables.

(1) The dielectric constants of the powder depend upon the particle size and packing fraction.

(2) The dielectric constant for fine powder is low and this may be attributed to surface effects and associated considerations as suggested by Goswami [9].

(3) The dielectric constants ϵ_s for SnI_2 are greater than for SnI_4 materials.

The variation of bulk dielectric constants (ϵ_s) with temperature is shown in Figs 1 and

TABLE II Dielectric parameters calculated for the bulk from measurements on powders (average particle size 50 μm). Measurements are at 8.95 GHz

Substance	Packing fraction, δ	Dielectric constant of powder, ϵ_p	Dielectric constants of bulk material, ϵ_s
KCl	0.562	2.59	4.63
	0.609	2.72	4.50
SnI_2	0.532	9.05	29.82
	0.608	11.30	28.26
SnI_4	0.710	13.60	25.70
	0.771	15.10	24.50

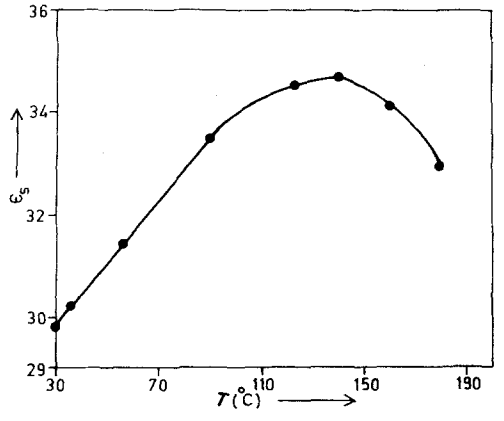

Figure 1 Variation of dielectric constant, ϵ_s, of SnI_2 with temperature at a frequency of 8.95 GHz for an average particle size of 150 μm.

2 for SnI_2 and SnI_4, respectively. In the figures we find three stages of variation in ϵ_s: (i) a slow rise, (ii) a rather fast rise; and (iii) a fall in the value of ϵ_s.

The dielectric constant of a material is composed of the following contributions: electronic, ionic, dipolar, interfacial, lattice and space-charge polarizations. For molecular crystals, such as SnI_4, the total macroscopic polarizability is the sum of the electronic polarizability and lattice polarizability [10]. The dipolar orientational effect can sometimes be observed in materials even up to 10^{10} Hz, while ionic and electronic polarizations always exist below 10^{13} Hz. The Debye mechanism may not be convenient to explain the temperature dependence of dielectric constants of SnI_2 and SnI_4 materials owing their high values -30 for SnI_2 and 25 for SnI_4. The space-charge contribution will depend on the purity and perfection of crystals. The crystal defect can only

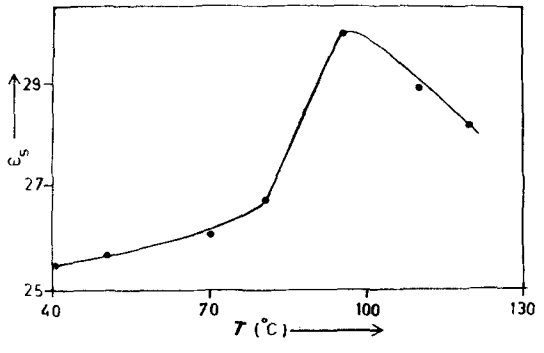

Figure 2 Variation of dielectric constant ϵ_s of SnI_4 with temperature at a frequency 8.95 GHz for an average particle size of 150 μm.

increase with temperature, making the space-charge polarization dominant, hence ϵ_s increases with temperature. This is supported by our studies on the variation of d.c. electrical conductivity with temperature, reported elsewhere. Further rapid increase of ϵ_s with temperature may be due to the creation and destruction of dipoles as suggested by Rao and Smakula [11]. The fall in the value of ϵ_s with increasing temperature for SnI_4 may be attributed to the dissociation of SnI_4 as Pringsthein [12] has noted that iodine atoms in SnI_4 are tetrahedrally arranged around the tin atoms. At high temperatures, the amplitude of oscillation becomes sufficiently great that the two iodine atoms can approach each other so closely that they can be separated in a single act from the parent as an excited iodine molecule.

For SnI_2, the variation in values may be understood in a general way by assuming a barrier fomation due to a thermally generated space-charge layer on the surface of the sample, a consequence of the migration of defects acting as a deep donor. At elevated temperature, the leakage of charge carriers across the barrier becomes more prominent [13] and permittivity (ϵ_s) decreases. Keeping in mind that the single crystals of SnI_2 exhibit anisotropy in the dielectric properties, it may be mentioned that the results of a study on pellets correspond to an average of the properties measured in various directions.

The following conclusions may be drawn from this study.

(1) Dielectric constants (ϵ_p) of SnI_2 and SnI_4 powders are measured using the method of Dakins and Works.

(2) Looyenga's formula is found to be satisfactory for determining the bulk dielectric constants of SnI_2 and SnI_4 (in the microwave region).

(3) The dielectric constants ϵ_p and ϵ_s depend upon particle size and packing fraction of the materials.

(4) The dielectric constants of SnI_2 are greater than those of SnI_4 materials.

(5) The fall in values of dielectric constants at higher temperature is attributed to the dissociation of materials in the case of SnI_4, while, in the case of SnI_2, it may be due to the leakage of charge carriers across the surface barrier.

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