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Synthesis, Characterization and Investigation on Dielectric Properties of Palmierite [$K_2Pb(SO_4)_2$].

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ABSTRACT

Dielectric properties of $K_2Pb(SO_4)_2$ at different temperatures were studied with respect to frequency and the results were discussed. In our present work, $K_2Pb(SO_4)_2$ was synthesized at 80°C using potassium sulphate and lead nitrate of high purity as the starting material. The structural property of the material was studied by X-ray diffraction (XRD). Fourier Transform Infra-Red (FTIR) Spectroscopy was used to identify the functional groups present in the material. The thermal behaviour was analyzed by using TG-DSC studies. UV-Vis Spectroscopy and Photoluminescence studies were carried out to analyze the optical nature of the material.

Keywords: Dielectrics, Palmierite

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INTRODUCTION

Dielectrics are electric insulators which gets polarized on applying an external electric field. As in an electrical conductor, the dielectric materials do not allow the electric charges to flow through it, instead polarization will take place. The electrical properties of a material medium as a function of frequency and temperature can be evaluated by studying its dielectric behaviour. Dielectric analysis can be employed to assess the capability of transferring the electric charge. The analysis of the dielectric properties affords information about electric fields within solid materials. When a dielectric material behaves as a non-conducting material, its dielectric properties can be correlated with electro-optic property of the materials [1]. Materials having low dielectric constant ϵ_r have been used in microelectronic industries as an interlayer dielectric [2]. Ferroelectric, photonic and electro-optic devices need materials fabricated with very low value of dielectric constant at higher frequencies [3].

Palmierite ($K_2Pb(SO_4)_2$) mineral crystallizes in the rhombohedral system with $R\bar{3}m$ space group. This mineral has semi transparency, which is colourless or white. It shows a large birefringence. It occurs as a rare fumarolic sublimate. Palmierite were synthesized from the thermal and the aqueous method by Von Schwartz [4] and Von Saalfeld [5] examined a natural occurring Palmierite mineral from Mount Vesuvius, Italy. Palmierite minerals are related to some other minerals such as Arcanite (K_2SO_4), Barite ($BaSO_4$), Celestine ($SrSO_4$) and Anglesite ($PbSO_4$). In $K_2Pb(SO_4)_2$, cations occupy two crystallographic positions M1 (Pb) and M2 (K). In $K_2Pb(SO_4)_2$, a single SO_4 tetrahedron of AABBC stacking in consecutive layers oriented upside down with respect to each other has been arranged normal to [001]; double triangle-mesh K layers have been positioned between directly superposed tetrahedron layers and single Pb layer between shifted tetrahedron layers [6]. To the best of our knowledge, we were the first to discuss the dielectric property of palmierite mineral. Previously, the crystal structure and chemical composition of palmierite were reported. The interest behind the present work is to scrutinize the dielectric property of the $K_2Pb(SO_4)_2$ as a function of frequency and temperature and to enlighten the dielectric application of this material.

MATERIALS AND METHOD

The synthesis of $K_2Pb(SO_4)_2$ was conducted using K_2SO_4 and $Pb(NO_3)_2$ in 4:1 molar ratio. Potassium sulphate was purchased from M/S. Sisco Research Laboratories Pvt Ltd, Mumbai, and lead nitrate from M/S. Himedia Laboratories PVT LTD, Mumbai. The solutions of potassium sulphate and lead nitrate was prepared individually and filtered. The lead nitrate solution was prepared at room temperature and filtered twice using Whatman filter paper with the mesh size of $11\mu m$. K_2SO_4 solution was prepared at $80^\circ C$ and filtered twice as like before. Then $Pb(NO_3)_2$ solution was added dropwise to the filtered K_2SO_4 solution. The precipitate obtained was stirred for two hours. Then the precipitate was washed with distilled water, mixture of distilled water and methanol (50:50) and finally with methanol.

The as-synthesized palmierite powder was investigated by powder X-RD study, FTIR spectroscopy, TG-DSC analysis, UV-Visible transmission spectroscopy, PL spectroscopy and Dielectric studies.

RESULT AND DISCUSSIONS

X-RD Analysis

The X-RD pattern of the sample was recorded on an XPERT-PRO X-ray diffraction instrument using $CuK\alpha$ (1.5406\AA) radiation at 40 kV and 30 mA. The X-RD pattern in fig (1) recorded for the synthesized sample was well in agreement with literature values [7] and ICDD data no: 291015 which confirms that the synthesized powder was $K_2Pb(SO_4)_2$ and it belongs to the rhombohedral structure with the space group $R\bar{3}m$ of hexagonal scalenohedral class. The sharp peaks observed shows that the material synthesized was highly crystalline. The lattice parameters and volume of the unit cell was given in table (1)

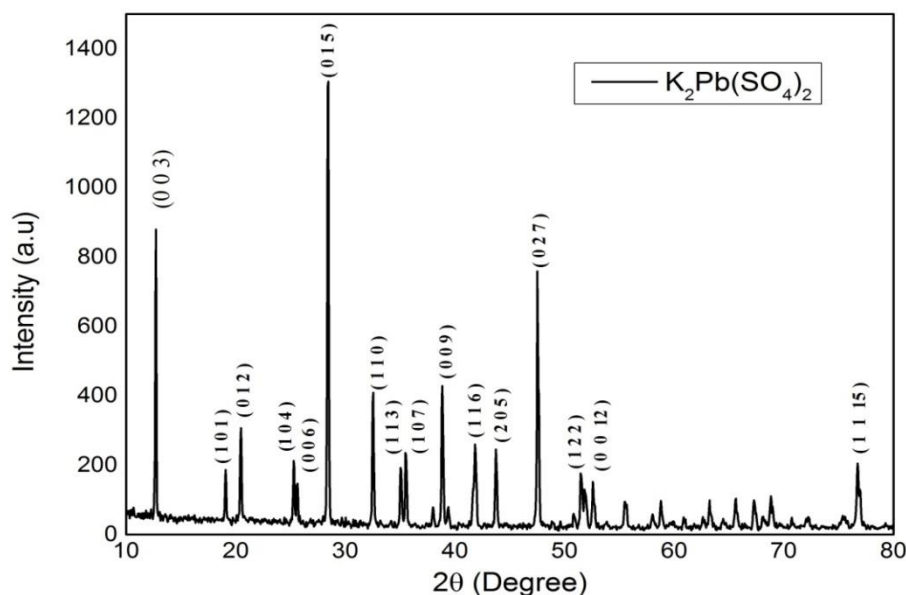


Fig 1: Powder XRD Pattern for Palmierite [K₂Pb(SO₄)₂].

Table 1: Lattice parameters and volume of the unit cell

Lattice Parameters	Theoretical Value	Literature Value	Calculated Value
a (Å)	5.495	5.497	5.509
c (Å)	20.849	20.864	20.894
V (Å ³)	545.19	545.98	549.14

From the value of d-spacing obtained, the lattice parameters 'a' and 'c' are calculated using the formula

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (1)$$

The volume of the unit cell was calculated from

$$V = \frac{\sqrt{3}a^2c}{2} \quad (2)$$

FTIR Analysis

"Perkin Elmer" spectrometer was used to record the FTIR spectrum in the region of 400 - 4000 cm⁻¹ using a KBr pellet technique. Fig 2 shows the FTIR spectrum of K₂Pb(SO₄)₂ - Palmierite material. In general, the frequency from 400-1400 cm⁻¹ acts as the fingerprint region of the material. Normally, T_d symmetry was found in free SO₄²⁻ ion. It has 4 fundamental vibrations at 981 cm⁻¹(non degenerate ν₁ mode), 451 cm⁻¹ (doubly degenerate ν₂ mode), at 1104 cm⁻¹(triply degenerate ν₃ asymmetric mode) and at 613 cm⁻¹ (triply degenerate ν₄ symmetric mode)[8]. The peak at 447 cm⁻¹ corresponds to doubly degenerate (ν₂) symmetric bending of SO₄²⁻ mode. The sharp, distinct peak at 617 cm⁻¹ and the absorption at 1080 cm⁻¹ were attributed to triply degenerate (ν₄) asymmetric bending and triply degenerate symmetric stretching (ν₃) of SO₄²⁻ ions respectively.

The presence of nitrate ions was detected in the precipitation which was confirmed from the low absorption peak appeared at 1378 cm⁻¹. This peak may also be responsible for the presence of N-O stretching vibrations. The peaks at 1610 cm⁻¹ and 3443 cm⁻¹ were due to O-H bending and O-H stretching respectively,

which confirms the presence of water molecules in the as-prepared samples even after repeated washing with organic solvents followed by atmospheric drying.

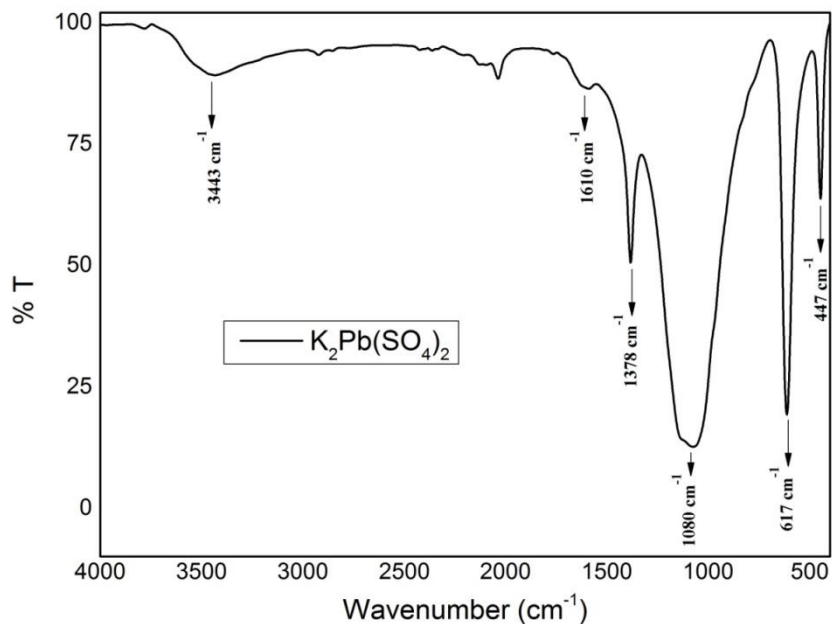


Fig 2: FTIR spectra for Palmierite [$K_2Pb(SO_4)_2$].

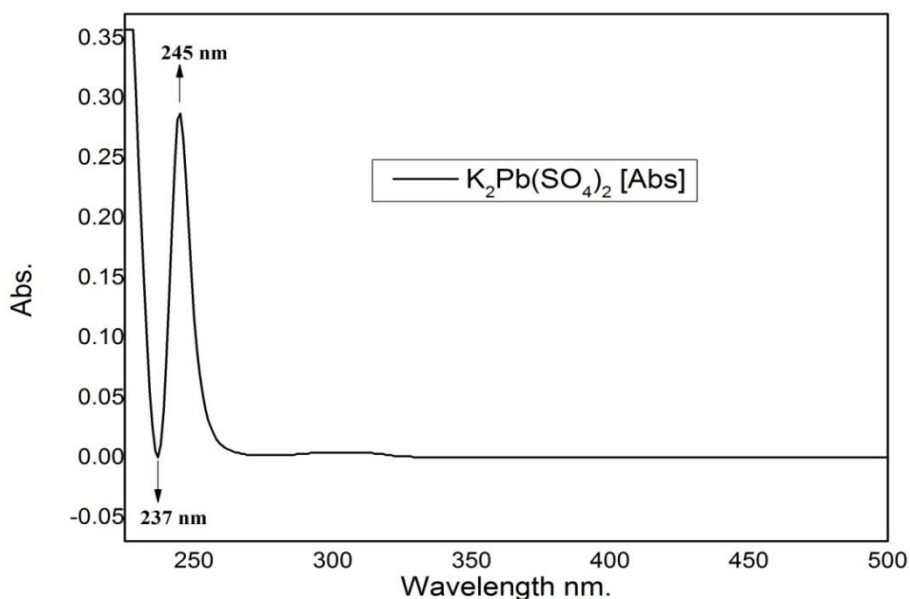


Fig 3: UV-Vis spectrum of Palmierite [$K_2Pb(SO_4)_2$].

UV-Vis Spectra

The optical transmittance range and the absorption band/cutoff are the important parameters to tailor the material for specific device applications. From the recorded spectrum in fig (3), it was evident that $K_2Pb(SO_4)_2$ has an absorption maximum at 245 nm. After 245 nm, the absorption started decreasing and above 266 nm, the $K_2Pb(SO_4)_2$ attains 100% optical transparency which represents the cutoff wavelength. The estimated band gap energy of the synthesized material was found to be 4.67eV which generally falls in the insulating region.

PL Spectroscopy

The room temperature photoluminescence properties of $K_2Pb(SO_4)_2$ were studied using the Cary Eclipse instrument of Savitzky-Golay type with a scanning rate of 600 nm/min at a data interval of 1 nm of averaging time 1 ns. PL emission of $K_2Pb(SO_4)_2$ was studied at the excitation wavelength of 245nm. The PL emission spectrum in fig (4) shows a single emission peak in the blue-green range (490 nm). The single and sharp emission peak indicates that the synthesized material is highly free from impurities and surface defects.

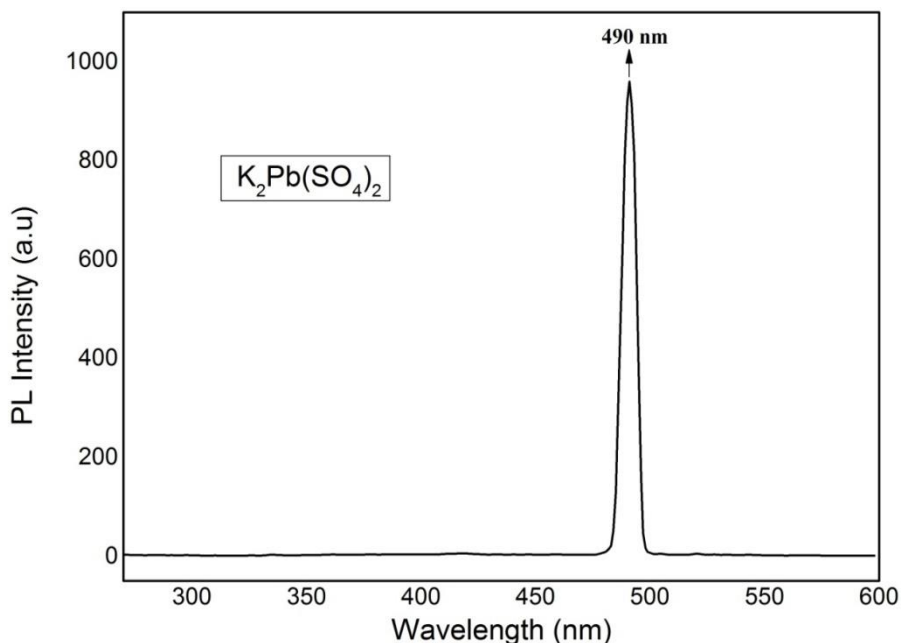


Fig 4: Room temperature PL emission spectrum of Palmierite [$K_2Pb(SO_4)_2$].

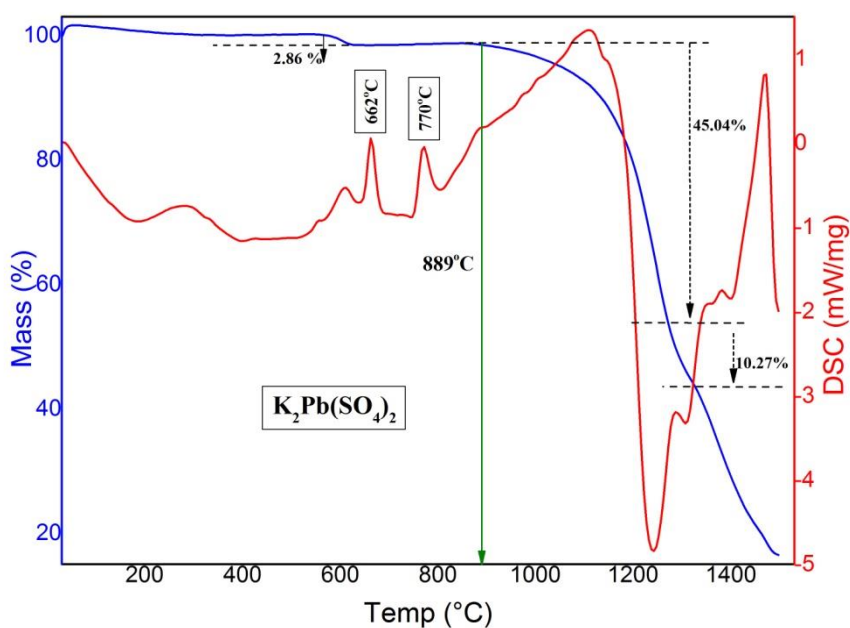


Fig 5: TG-DSC Analysis of Palmierite [$K_2Pb(SO_4)_2$].

TG-DSC Analysis

TGA and DSC studies of $K_2Pb(SO_4)_2$ were carried out at NETZSCH Technologies India Pvt Ltd, Chennai. The heating rate was 10K/min with flowing N_2 gas using Al_2O_3 crucible. Fig (5) shows the TG-DSC spectra of palmierite - $K_2Pb(SO_4)_2$.

Initially, it seems that the mass of the substance increases of 101.71% up to 250°C, which may be due to the presence of residuals. From RT to 600°C, a mass loss of 2.9% was noticed, which was expected because of the evaporation of water molecules present in the sample as moisture. From the TG curve, it was clear that the material maintains a thermal stability until 889°C. From there, the decomposition of the molecules takes place. The gradual decomposition of the molecules present in it was indicated from the slope in the TG curve.

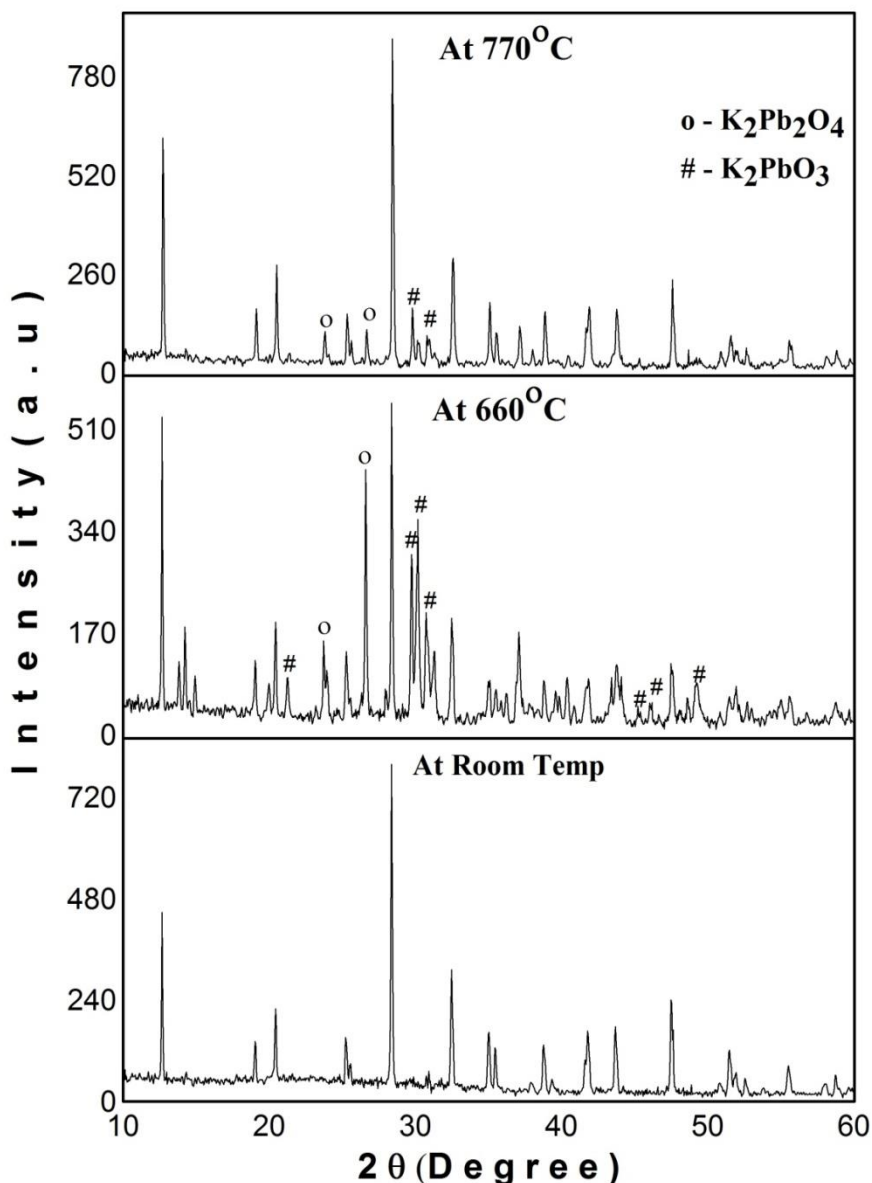


Fig 6: Powder XRD patterns of $K_2Pb(SO_4)_2$ at RT and annealed at 660 and 770°C

The decomposition can be split into three regions. Region 1: from 890°C to 1272°C, region 2: 1272°C to 1330°C and region 3: 1330°C to 1496°C. The weight loss in the temperature range between 890°C and 1272°C was found to be 45.04% that may be due to the evolution of PbO , which the weight loss was calculated to be 46.75% ($= \frac{223.19}{477.44} \times 100$). The 10.27 % weight loss was witnessed in the temperature range of

1272-1330°C. This value was consistent with the theoretical weight loss of 10.07% ($= 48.06/477.44 \times 100$) by assuming the evolution of SO. Above 1330°C, the fall in weight loss, increased drastically in the TG curve due to decomposition caused by the evolutions of the remaining molecules (K₂SO₄ and O₂).

Two exothermic peaks were obtained in the DSC curve at 662°C and 770°C without any change in the TG curve. It may be attributed to the possible structural changes happened due to oxidization in the material as evident from the recorded powder XRD on the samples annealed at 660 and 770°C (Fig.6).

Dielectric Studies

HIOKI 3532 LCR HITESTER was used to measure the temperature dependent dielectric constant and dielectric loss of K₂Pb(SO₄)₂ in the frequency range of 100Hz-5MHz. A silver paint coated pellet of thickness 0.97 mm and 121 mm² cross-sectional area was prepared in order to confirm good electrical contact between the material and the electrodes. Fig (7) shows the change in dielectric constant with respect to the change in frequency and temperature. The dielectric constant (ϵ_r) is calculated using the formula

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \tag{3}$$

Where C is the capacitance, A is the area, d is the thickness and ϵ_0 is the absolute permittivity of free space ($8.854 \times 10^{-12} \text{ Fm}^{-1}$).

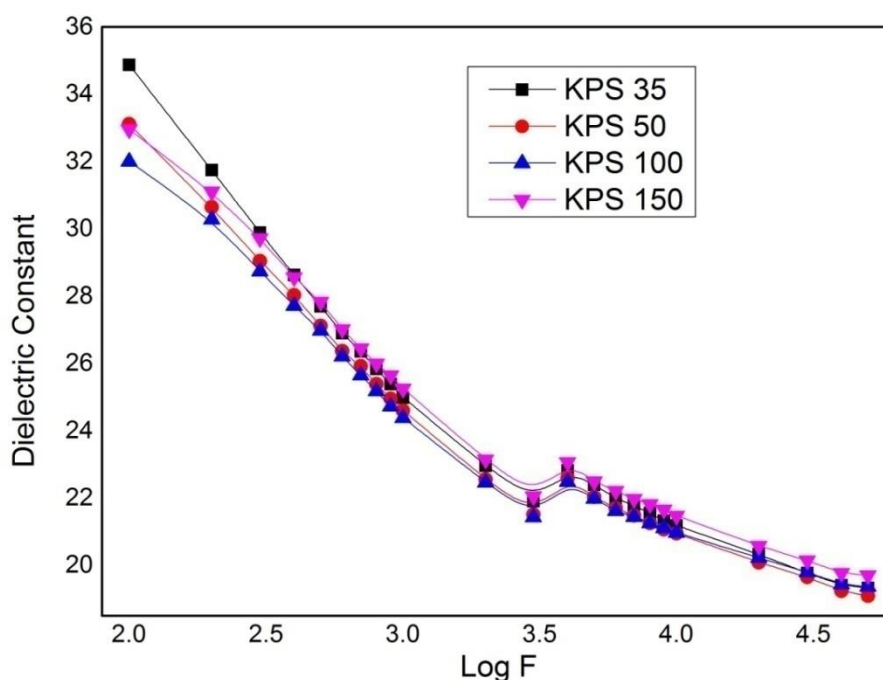


Fig 7: Dielectric constant of K₂Pb(SO₄)₂ as a function of frequency

From the graph, it was evident that the dielectric constant decreases with the increase in frequency in all temperatures. That was a normal dielectric behaviour of many materials. At the low frequency range, there was a drastic fall in the dielectric constant. At 5 kHz, a sudden increase in the dielectric constant was observed, and later it gets decreased with the increase in frequency. The decrease in dielectric constant at low frequency was very rapid and it slowed at high frequency region.

As per the literature, ionic, electronic, orientation and space charge polarization are four main contributions for the polarization in a material. The contribution of electronic polarization over the decrease in dielectric constant was quite less. Space charge and orientation polarization are responsible for the high value of dielectric constant at low frequency. The dielectric constant was very high at lower frequency region, and it slowly reduces at the high frequency region. This behaviour can be explained by Maxwell-Wagner type

relaxation [9]. According to Maxwell-Wagner model, the material with inhomogeneous structure consists of insulating grain boundaries which separates the well conducting grains. On applying an external electric field, migration of charge carriers takes place into the grains and get accumulated on the grain boundaries. So, large polarization and high value of dielectric constant was produced in this process. The polarization rises because of the displacement of ions in the applied field direction which is caused by the electronic exchange of the number of ions in the material.

The grain structure and porosity causes inhomogeneity in the system. The polarizability of species gets decreased with increase in frequency, thus the dielectric constant also decreases with frequency and then reaches a constant value which was attributed due to the fact that after reaching a certain frequency of applied external electric field, the different transition metal ions cannot bind according to the applied external field [10]. The polarizability of metal ions was found to lag behind the applied external electric field as the frequency was increased. At high frequencies, the dipoles will not obey with the varying external field and the polarization becomes free from frequency. Orientational polarization, material expansion, the presence of impurities and defects could be the reason behind the change of dielectric constant with temperature.

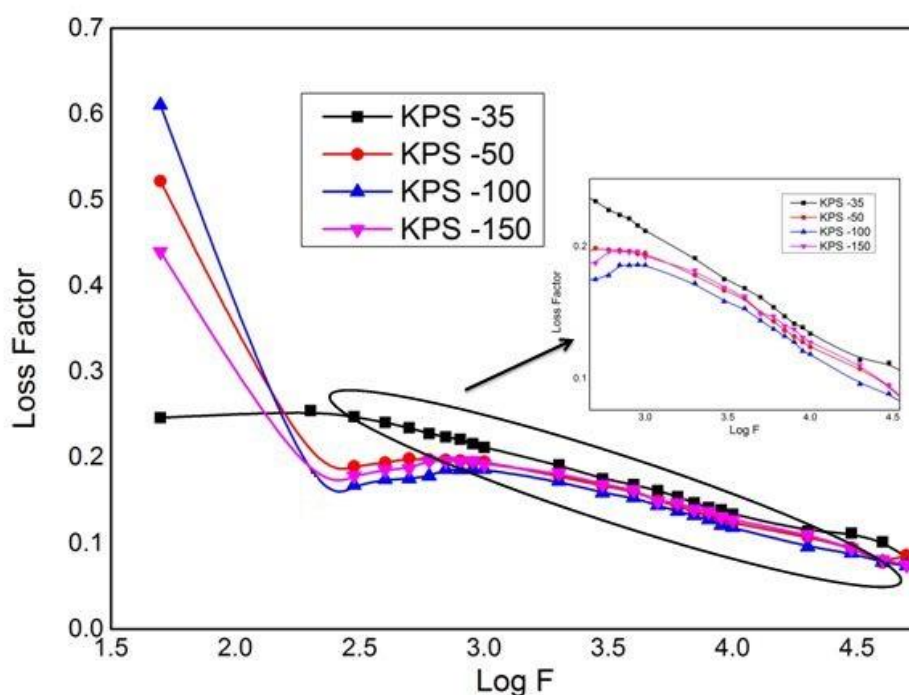


Fig 8: Dielectric loss of $K_2Pb(SO_4)_2$ as a function of frequency

From fig (8) it was clear that in all temperatures, the dielectric loss decreases with the increase in frequency which is in the pattern as similar as dielectric constant. Thus, it was confirmed that the dielectric loss absolutely depends on the applied frequency. Space charge polarization was responsible for the decrease in dielectric loss at a low frequency. The characteristics of low dielectric loss at high frequencies may be attributed to the purity of the material, having negligible defects with good optical quality and thus it could be useful in the design of optical devices [10].

At higher temperature, behaviour of loss may be due to macroscopic distribution of charges. According to Schokley - Read mechanism, the surface electron has been captured by the impurity ions in the bulk matrices at lower and middle frequencies and at higher temperatures, which in turn cause the surface charge polarization at the surfaces. With increasing temperature, this process also gets increased.

The synthesized sample can be used in various electro - optic devices and their applications because of its low dielectric constant and dielectric loss with high frequency and also it offers that the sample possesses an enhanced optical quality with lesser defects[10].

CONCLUSION

Palmierite - $K_2Pb(SO_4)_2$ was synthesized and a bulk solid mass was prepared by sintering it at 850°C . The structural studies confirmed that $K_2Pb(SO_4)_2$ belongs to the rhombohedral system with space group $R\bar{3}m$. The functional groups present in the as-prepared sample was identified with FTIR spectra studies. The optical studies revealed that the sample was free from impurities, and the calculated band gap energy shows that the material falls under insulator category. The thermal stability of $K_2Pb(SO_4)_2$ was studied from TG-DSC analysis. The dielectric studies at different temperatures confirmed that at high frequencies, the material has a low value of the dielectric constant and dielectric loss and is independent of the temperature.

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