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Effect of Ferric (Fe^{3+}) Ion Dopant on the Dielectric Properties of Potassium Hydrogen Phthalate Single Crystals for Electrical Devices

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Abstract

Using a slow evaporation process, single crystals of potassium hydrogen phthalate (KHP) were developed. Ferric (Fe^{3+}) ion in the form of $FeCl_3$ (0.15 mol %.) was introduced in the solution as a dopant. The dielectric constant, dielectric loss, ac conductivity, dc conductivity, and activation energies of the pure and Fe^{3+} ion doped KHP crystals grown have been determined. Materials with such frequency-dependent electrical properties make excellent prospects for microelectronic applications. Heating devices generally use crystals having high dielectric constants at low frequencies. A low dielectric constant in the higher frequency range indicates that the crystals have improved optical quality with fewer flaws, demonstrating the materials' aptitude for NLO applications. According to the impedance analysis, the conductivity response is good at lower frequencies (100Hz). Hence, low-frequency insulators can also be made from these materials.

Keywords: *Semiorganic crystal; Solution growth; Doping; Dielectric properties; Conductivity*

1. Introduction

Nowadays, a great deal of research and development is being done on dielectric materials in the form of crystals. Microelectronics, lasers, microwaves, computing, military, radio, and electrical devices are only a few of the many industrial applications for these materials. These days, the main topics of dielectric research, both in theory and in practice, are ferroelectrics, piezoelectrics, pyroelectrics, and multi-ferroelectric materials. Comprehensive studies on H-bonded single crystals are leading to the development of new materials for device applications. The exploration of H-bonded single crystals in detail has also spurred the development of novel materials for use in devices [1].

The exceptional mechanical properties, high resistance to laser-induced damage, large non-linear optical co-efficient, and low angular sensitivity of semi-organic crystals make them a popular choice for device fabrication. [2, 3]. Semi-organic potassium hydrogen phthalate (KHP) crystal, with the chemical formula K

($C_6H_4COOH.COO$), is used in the production of crystal analyzers for long-wave X-ray spectrometers. These crystals also show pyroelectric, elastic, nonlinear optical, and piezoelectric properties [6–8]. Upon crystallization, KHP exhibits the subsequent unit cell properties: a = 9.605 Å, b = 13.331 Å, c = 6.473 Å, and α = β = γ = 90° [9, 10]. It exists in an orthorhombic system with the space group Pca21. KHP crystal has a polarity, which allows it to exhibit molecular and ionic properties with a broad range of uses. [11]. The KHP's well-defined cleavage (010) plane is better suited for all kinds of surface morphological investigations. [12]. KHP single crystals are good monochromators and show promise as materials for both qualitative and quantitative X-ray examination of light elements in the long and medium spectrum areas, such as Fe, Al, Mg, F, Si, and so forth [13, 14]. KHP crystals have recently been employed as substrate materials to manufacture highly orientated conjugated polymer films with strong non-linear susceptibility [15, 16].

When Fe^{3+} ions are present in low concentrations (ppm range), potassium hydrogen phthalate (KHP) grows spirally in the (010) plane. [17]. The electro-optical properties and refractive index studies of pure, Fe^{3+}, and Cr^{3+} ion doped KHP crystals have been studied for the purpose of device design [18]. Non-linear optical (NLO) properties and growth features of ferric ions doped KHP were found to have quality single crystals [19]. The effect of the Fe^{3+} ion dopant on the dielectric characteristics of the KHP crystal has been investigated in this investigation.

2. Crystal Growth

Single crystals of potassium hydrogen phthalate (KHP) were produced via a slow evaporation technique. The high-purity salt (E-Merck) was used to make the saturated solution of KHP in compliance with the previously published solubility data (12.5gm/100ml at 30 °C) [20]. A recrystallization process was used to eliminate impurities from the KHP crystal. Ferric (Fe^{3+}) ions in the form of $FeCl_3$ (0.15 mol%) were used as a dopant. The saturated solutions of pure and Fe^{3+} ion-doped KHP were stirred for around 10 hours in order to attain homogeneity. Deionized water with a resistivity of 18.2 MΩ.cm was utilized as the solvent to extract contaminants and a syringe filter with holes the size of 0.45 µm was employed for filtration. Transparent, flawless single crystals were harvested after three to four weeks of solvent evaporation. Figures 1(a) and 1(b) display pure and doped KHP (1FKHP) crystals. The crystals were gathered and briefly dipped in the n-hexane solution to prevent them from growing further or etching.

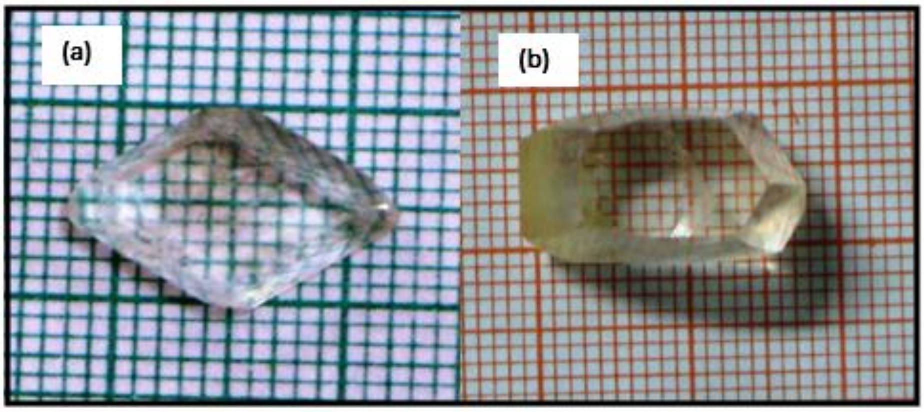

Figure. 1 As grown crystal of (a) pure KHP, (b) 0.15 mol% $FeCl_3$ doped KHP crystals

3. Results and discussions

3.1. Dielectric Studies

An essential tool for determining a material's electrical conductivity is the dielectric measurement. High-quality pure and Fe^{3+} doped KHP single crystals were used for the dielectric measurements, which were performed at different temperatures using the HIOKI 3532-50 LCR HITESTER in the frequency range of 50 Hz to 1MHz. After that, the selected crystals were polished with glycerol solution and flattened using a diamond saw. Silver paste has been applied on both sides to form a capacitor in which the crystalline substance serves as the dielectric medium. The relationship can be used to evaluate the dielectric constant.

$\varepsilon_r = C.d/\varepsilon_o.A$

Where d is the thickness in mm, C is the capacitance in F, A is the area in mm^2 and ε_0 is the absolute permittivity of free space.

3.1.2. Dielectric constant (ε_r) and dielectric loss (tanδ)

The dielectric loss and dielectric constant for pure and Fe^{3+} ion doped KHP single crystals change with frequency at 353 K, as shown in Figures 2 and 3. A material's dielectric constant is influenced by space charge, dipolar, ionic, and electronic charge polarisations [21]. The relationship between the dielectric constant and loss is inverse for the applied frequency. This illustrates the behaviour of dielectric materials with increase in frequency [22]. Materials act in this way due to a polarisation mechanism that is comparable to the conduction process. The graph (Figure 2) shows that as frequency increases, the dielectric constant decreases until it approaches a constant value. This is because once the electric field frequency reaches a certain threshold, the dipoles cease to respond and begin following the ac field [23]. As per the principle of Miller, low values of dielectric constant observed at upper ranges of frequencies are an indicator of the possibility of improving the SHG coefficient [24]. Doped KHP crystals show a decrease in dielectric constant with the rise in frequency, just as pure KHP crystals do. It is observed that pure KHP crystal has a lower dielectric constant than KHP with 0.15 mol% $FeCl_3$. Crystals having a large value of the dielectric constant in the range of lower frequencies are preferred for heating components [23]. Figure 3 shows that the crystalline samples had reduced dielectric loss in the range of high frequencies, indicating that the materials have fewer flaws and better optical quality. These are the welcoming traits of the materials employed in the fabrication of NLO-based devices. [25]. Dielectric loss is proven to be significant, frequency-dependent and to have an effect similar to that of the dielectric constant in the ionic crystalline system [26, 27].

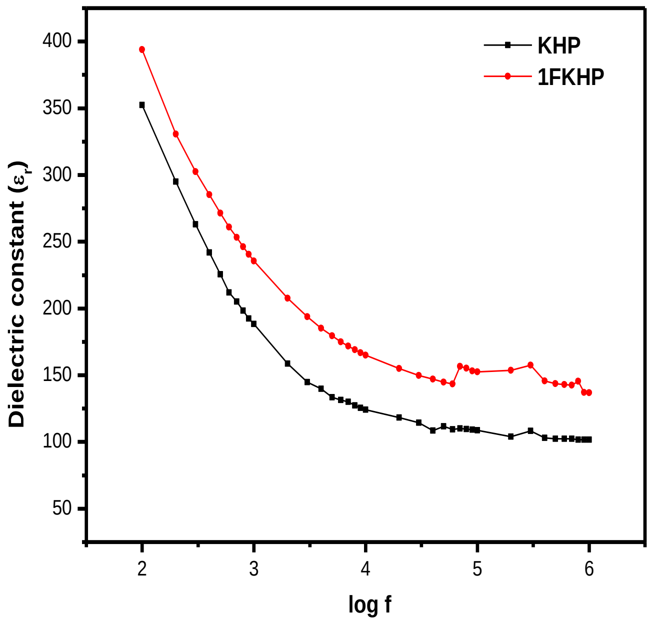

Figure. 2 Variation of dielectric constant with frequency at 353K for pure and $FeCl_3$ doped KHP crystal

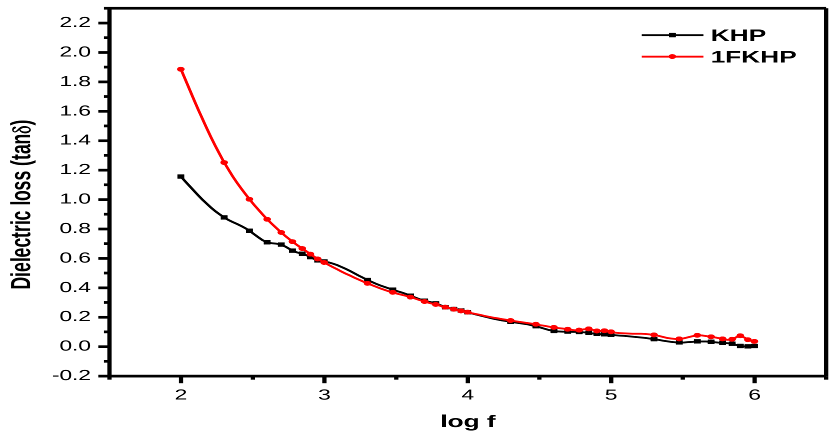

Figure. 3 Variation of dielectric loss with frequency at 353K for pure and $FeCl_3$ doped KHP crystal.

3.2 Electrical Conductivity

The ac electrical conductivity (σ_{ac}) was calculated using the formula,

$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan\delta$

Where ε_o is the permittivity of free space, ε_r is the relative dielectric constant, ω is the angular frequency (=2πf) and tanδ is the dielectric loss.

For both pure and Fe^{3+} ion-doped KHP crystals, the variation in a.c electrical conductivity at 353 K as a function of frequency is shown in Figure 4. An increase in the conductivity behavior of pure KHP crystal has been seen upon the introduction of the Fe^{3+} ion. Conductivity increases at higher frequencies, indicating a decrease in space charge polarisation.

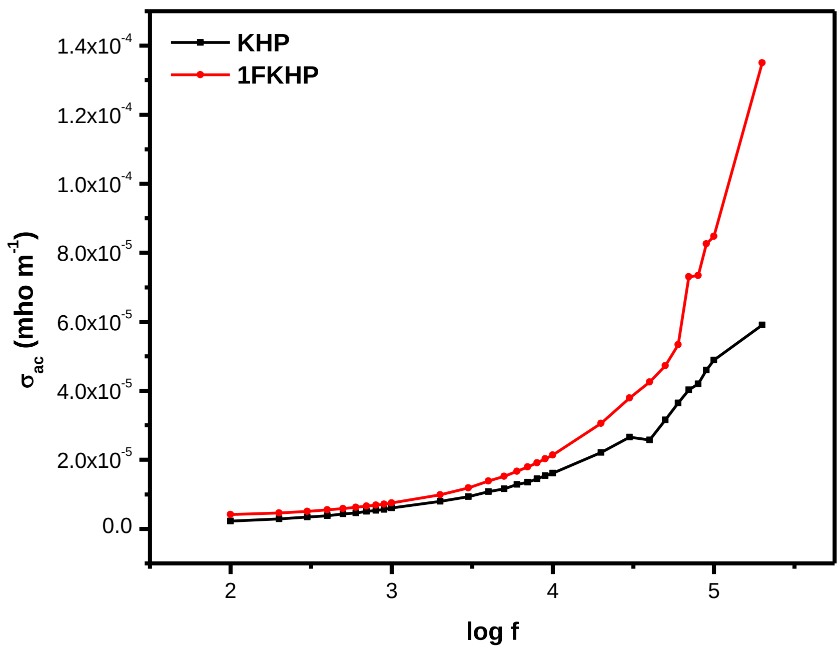

Figure. 4 Ac conductivity curve of pure and $FeCl_3$ doped KHP crystal

The ac activation energy was determined by applying the Arrhenius equation.

$\sigma_{ac} = \sigma_0 \exp [-E_\alpha / kT]$

Where σ_0 is the pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant and T is the temperature. The a.c electrical conductivity of ionic crystalline materials usually shows a frequency-independent plateau at lower frequencies and dispersion at greater frequency ranges.

3.3. Impedance analysis

The temperature and frequency of application have a big influence on the materials' physical and structural properties. Impedance analysis is a helpful technique for the experimental assessment of a material's electrical properties [28]. Through the use of a Princeton Applied Research VERSA STAT-2 Channel Using an impedance analyzer at room temperature, complex impedance spectroscopy was used to examine the materials' electrical impedance. The cut and polished pure and doped KHP crystals with roughly equivalent thicknesses of 1 mm have been selected for this purpose.

3.3.1. Real part impedance

The high resistance and capacitances of the crystal cause the component of the real part to vary, as shown in the plot of the real part of impedance (Z_{re}) vs frequency for a pure and Fe^{3+} ion-doped KHP crystal (Figure. 5) [29]. According to the real component of the analysis of impedance (Z_{re}), both pure and doped materials exhibit a gradual increase in impedance as frequency rises. Impedance decreases at frequencies greater than 10 Hz. In the frequency range from 100 Hz to 1 MHz, the real part impedance of all crystals becomes virtually constant. According to this real-part study, all of the materials might begin conducting electricity at roughly 100 Hz. The plateau area indicated on the plot demonstrates the existence of the relaxation process in the crystalline material. These stationary species and/or the existence of electrons at lower temperatures may be the cause of this relaxation process [28].

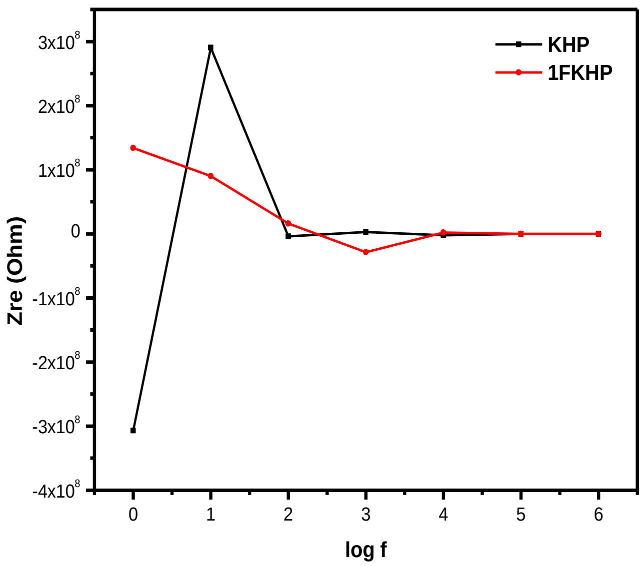

Figure. 5 Real part impedance (Z_{re}) curves for pure and 0.15 mol % $FeCl_3$ doped KHP crystal.

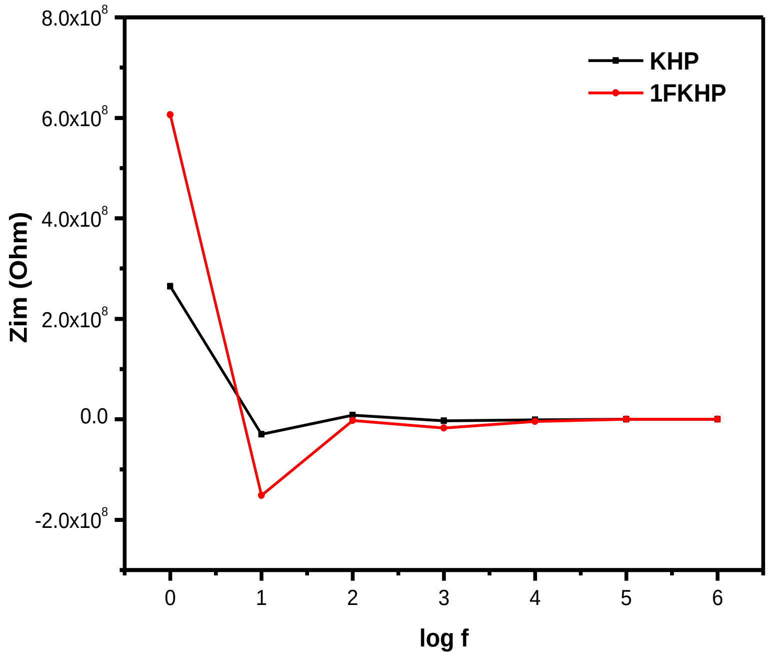

Figure.6 Imaginary part impedance (Z_{im}) curves for pure and 0.15 mol % $FeCl_3$ doped KHP crystal.

The materials' potential increase in ac conductivity is evident by the fact that the real part of the impedance (Z_{re}) decreases as frequency increases [30]. The (Z_{re}) curves for the real part of the magnitude for the doped and pure KHP crystals are mixed for frequencies higher than 100 Hz. This could be because space charge polarisation has been released due to a drop in the material's barrier properties, which could be the cause of the material's increased ac conductivity at higher frequencies [31].

3.3.2. Imaginary part impedance

At lower frequencies, the impedance of Fe^{3+} ion-doped KHP crystals decreases, as shown by the study. As frequency increases, the imaginary fraction of impedance (Z_{im}) falls at lower frequencies, as Figure. 6 illustrates. Conduction starts at lower frequencies since the impedance of all materials becomes constant between 10 Hz and 1 MHz.

4. Conclusion

Research has been done on the impact of ferric (Fe^{3+}) ion doping on the electrical conductivity properties of potassium hydrogen phthalate (KHP) single crystals. Heating equipment uses crystals that have a high dielectric constant at low frequencies. The ability of the materials for NLO applications is demonstrated by the low dielectric constant in the higher frequency range, which shows that the crystals have better optical quality with fewer defects. Based on the impedance analysis, the conductivity response is shown to be good at lower frequencies (100Hz). As such, low-frequency insulators can be made from these materials.

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