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## Dielectric and optical behaviors for pure potassium sulfate and doped with copper and iron

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### Abstract:

Dielectric measurements were carried on pure and doping potassium sulfate with copper and iron ions samples at 1wt.% and 3wt.% for both of copper and iron. The dielectric constant ( $\epsilon'$ ) decreases exponentially from 2.8 to 1.5 as frequency increase for both dopant which is attributed to the space charge and structural distortion. The dielectric loss ( $\epsilon''$ ) for Cu dopant decrease gradually with frequency. The same behavior for 1%Fe dopant while its 3%Fe doping started from 0.27 then decrease exponential. Band gaps for all samples almost constant around 6 eV.

**Keywords:** doped  $K_2SO_4$ , dielectric constant, loss tangent, LCR Meter, optical measurements.

### السلوكيات العزلية والبصرية لكبريتات البوتاسيوم النقية والمطعمة بالنحاس والحديد

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### الخلاصة:

تم اجراء القياسات العزلية لكبريتات البوتاسيوم النقية والمطعمة بالنحاس والحديد ب نسبة 1wt.% و 3wt.% لكلا من النحاس و الحديد. ثابت العزل الكهربائي ( $\epsilon'$ ) يقل اسياً من 2,8 الى 1,5 بزيادة التردد لكلا التشويب والذي يعزى الى شحنه الفراغ والتشويه التركيبي ، ان عامل الخسارة ( $\epsilon''$ ) لحالة التطعيم بالنحاس لكلا النسبتين يقل تدريجياً مع التردد ويسلك نفس السلوك في حالة 1wt.% للحديد بينما في حالة 3wt.% تبدأ من 0,27 ويقل اسياً ، اما فجوة الطاقة لكل النماذج تبقى ثابتة تقريبا حوالي 6 إلكترون-فولط

**الكلمات المفتاحية:** كبريتات البوتاسيوم المطعمة ، ثابت العزل ، عامل الفقد ، جهاز LCR ، القياسات البصرية .

### Introduction:

The dielectric constant and optical properties are very important parameters for any nonlinear optics materials; due to that it is use as a wide transparency window [1].

Potassium sulfate  $K_2SO_4$  belongs to the orthorhombic system with space group Pnma (primitive mirror plan) and lattice parameters  $a=7.476\text{Å}$ ,  $b=10.071\text{Å}$  and  $c=5.763\text{Å}$ . It transforms upon heating at  $587^\circ\text{C}$  into hexagonal structure with  $a=5.921\text{Å}$  and  $c=8.182\text{Å}$  and is called as  $\alpha$ - $K_2SO_4$  while the orthorhombic phase is called as  $\beta$ - $K_2SO_4$  [2]. The phase transition behavior of pure potassium sulfate by dielectric and electrical conductivity high temperatures were studied [3].

The ability of a dielectric material to store electric energy under the influence of an electric field, results from the field-induced separation and alignment of electric charges. Polarization in its four mechanisms occurs when the electric field causes a separation of the positive and negative charges in the material. The larger the dipole moment arms of this charge separation in the direction of a field

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and the larger the number of these dipoles, the higher the material's dielectric permittivity. In the presence of electronic, ionic and dipolar polarization mechanisms, the average induced dipole moment per molecule  $P_{av}$  will be the sum of all the contributions in terms of the local field (effective field) acting on each individual molecule [4]. The loss tangent ( $\tan \delta$ ) is the ratio of the loss or resistive current to the charging current in sample. Also it is known that there is strong correlation, between the conduction mechanism and the dielectric constant behavior (Polarization mechanism) [5].

Due to useful applications of doping, it is worthy to work on doping of  $K_2SO_4$ . Doping is possible if a suitable host can be found. The cupric ion and iron ion doped in the  $K_2SO_4$  crystal, but the degree of application of the data to the pure  $(Cu;Fe)_2SO_4$  system depends very highly on the nature of the host. [6], Recently the crystal structure and characterizations of  $K_2SO_4$  doped as crystal described was studied [7]. In the present study, the investigations are focused on dielectric constant and its loss factor and optical properties of doped  $K_2SO_4$  compound at room temperature.

### Experimental details

The details concerning the crystal growth of potassium sulfate crystal doped with copper and iron along with their structural, morphology and its DSC can be found in [7]. in which, the crystal were grown by slow evaporation techniques according to the required weight percentage of the starting materials ( $K_2SO_4$ ,  $CuSO_4 \cdot 5H_2O$  and  $FeSO_4 \cdot 7H_2O$ ) by sensitive balance with 4-digit type (KERN) for doping of 1wt.% & 3wt.% for each of  $CuSO_4 \cdot 5H_2O$  and  $FeSO_4 \cdot 7H_2O$ , As the molecular weight of potassium sulfate equals 174.2 g / mol, and for 1M solution 17.42g required to dissolve in 100 ml of double distilled water and the required amount of the dopants are calculated as follow;

For pure  $K_2SO_4 = 17.42$  g is considered as 100% and its 1% of it is 0.1742 g.

While the required percentage of the dopant sample were calculated according to proportional,

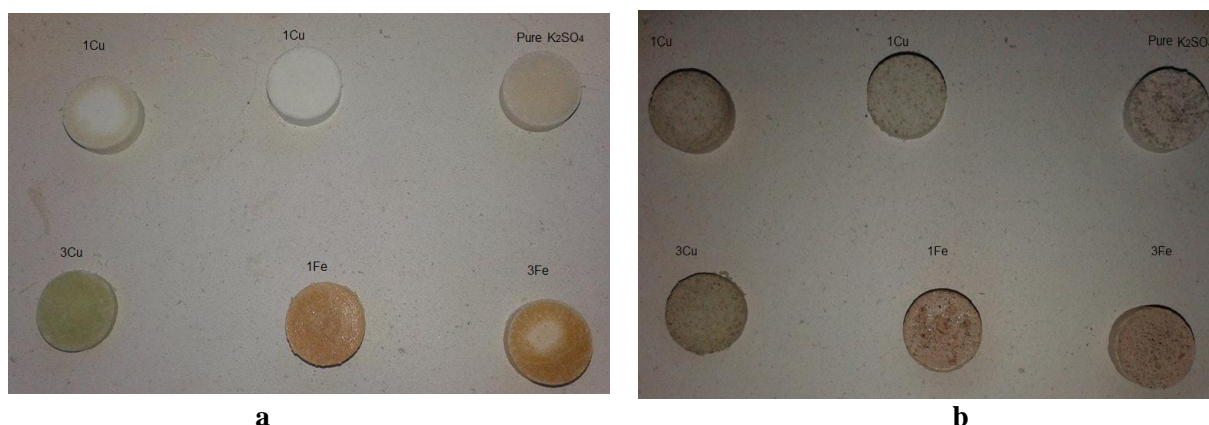
$$\begin{array}{lll} X=17.24g(99\% K_2SO_4) & X=17.42*99/100 \% & 17.42gm/100 = X/ 99 \% \\ X=16.89g(97\% K_2SO_4) & X=17.42*97/100 \% & 17.42gm/100 = X/ 97 \% \end{array}$$

So,

$$1\% = 17.42 \text{ g} - 17.24 \text{ g} = 0.18 \text{ g for } (CuSO_4 \cdot 5H_2O \text{ \& } FeSO_4 \cdot 7H_2O)$$

$$3\% = 17.42 \text{ g} - 16.89 \text{ g} = 0.53 \text{ g for } (CuSO_4 \cdot 5H_2O \text{ \& } FeSO_4 \cdot 7H_2O)$$

In this work, the starting materials were the crystal supplied from the author of ref [7], and milling it by the Vortex mixer for about 1/2 hour to obtain very fine powder then pressed into pellets with 1cm in diameter and (0.49) cm in thickness, using stainless steel cylindrical die under hydraulic pressure of 3Mpa, The prepared samples were shown in Figure-1a Then it sintered in the furnace at 450°C for 4 hours at heating rate 2°C/min, then cooled to room temperature and presented in Figure-1b. Preparation of pure and doped samples are characterized.



**Figure 1-** photograph of the prepared samples (a) before sintering, (b) after sintering at 450°C

The capacitance were measured at room temperature using LCR meter model (GW INSTEK, LCR-8105G, Precision LCR-Meter, 20 Hz - 5 MHz, GPIB, RS-232, Taiwan).

A sample is placed between the two parallel copper electrodes [8]. The dielectric constant for all samples were recalculated in frequencies ranging from (1KHz to 1MHz) by measuring the capacitance (C). The values of the real and imaginary parts are calculated according to the equations. [9]:

$$\epsilon' = Cd / A\epsilon_0 \quad (1)$$

$$|\tan \delta| = \epsilon'' / \epsilon' \quad (2)$$

Where d is the thickness of the pellet, A is the area of the electrode,

$\epsilon_0$  is the permittivity of free space =  $8.85 \times 10^{-12}$  F/m

$\epsilon'$  = Real part of dielectric constant; C= Capacitance of the Pellet in

$\epsilon''$  = The imaginary part of the dielectric constant or dielectric loss

Optical spectra was recorded by UV-Visible 1800 (Shimadzu) spectrometer with performing wavelength ranging from 200 to 1100 nm. The samples are obtained by dissolving their crystals in distilled water and shake stirrer by hand until a homogenous solutions were obtained. When the light is incident on a material, optical phenomena such as absorption, transmission and reflection takes place. The absorption spectrum occurs when the energy of the photon which is incident on the material is equal or larger than the energy gap of the materials then the electronic transitions takes place from valence bands to the conduction bands. These transitions may be either direct or indirect and the absorption coefficient can be calculated according to the following relations.

If the light intensity ( $I_0$ ) incident on a surface of thickness (t) it will transmitted from the surface according to the expression:

$$I(t) = I_0 e^{-\alpha t} \quad (3)$$

where  $\alpha$  is the absorption coefficient of the material which depends on the wavelength of light and is given in  $\text{cm}^{-1}$  [10]. The absorption coefficient ( $\alpha$ ) of material depends on optical absorbance (A) and thickness of the sample (t) which is equal to the path length (L) of the examination solution, which is evaluated by using eq. (4), [11]:

$$\alpha = 2.303A/t \quad (4)$$

which is equal to (1cm) thickness of the quartz tube.) L) is the path length of the light (cm)

Transmittance (T) is given by the intensity of the transmitting rays from the sample (I) to the intensity of the incident rays ( $I_0$ ) ( $T = I/I_0$ ), and can be calculated by:

$$T = \exp[-2.303A] \quad (5)$$

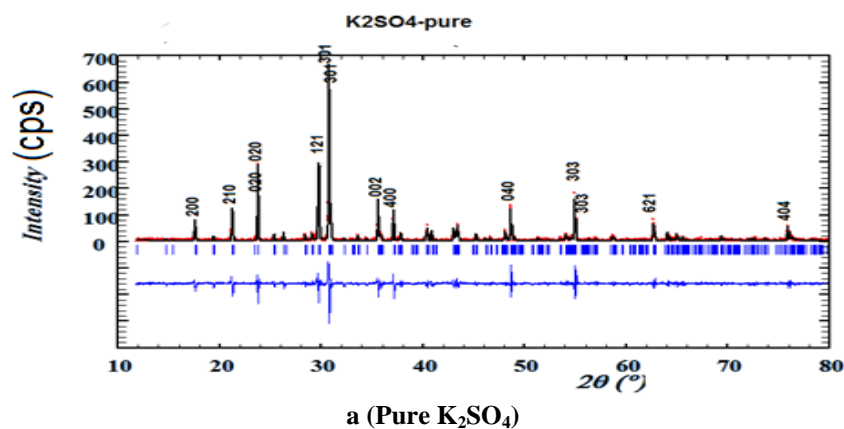
Reflectance can be obtained from absorption and transmission spectra in accordance with the law of conservation of energy by the relation

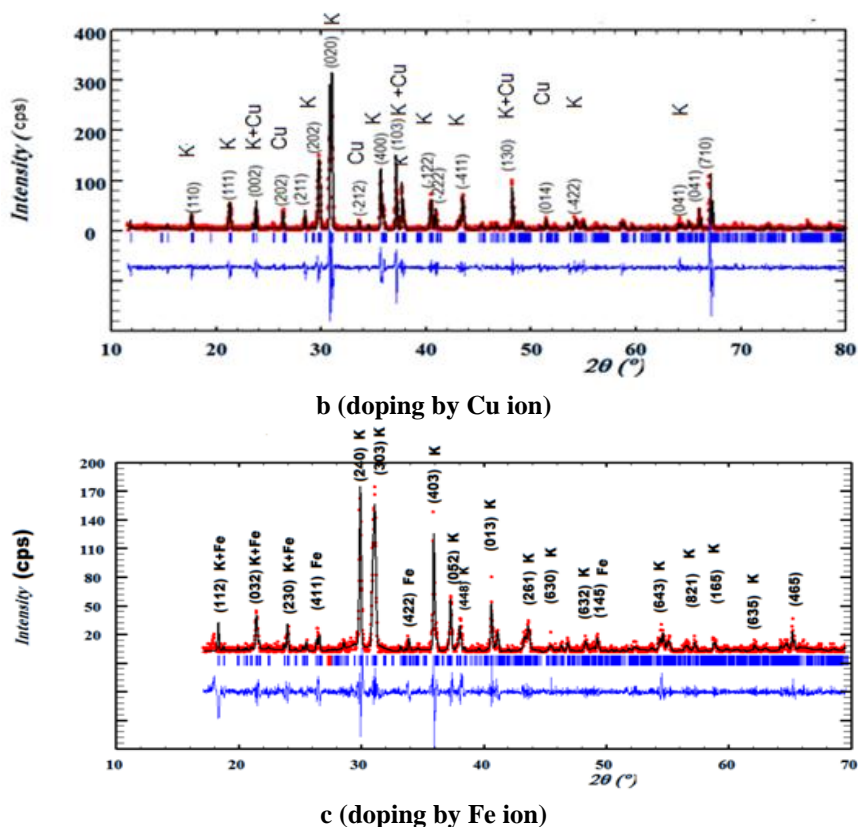
$$R + T + A = 1 \quad (6)$$

The optical band gap ( $E_g$ ) is obtained from the transmission spectra by plotting  $(\alpha h\nu)^{1/r}$  versus  $h\nu$  with r values equal to 1/2, 3/2, 2, and 3. The linear portion was best fitted with  $r=1/2$ , which indicates a transition of direct type. Where h is the Planck's constant and  $\nu$  the frequency of the incident photon [12].

### Results and Discussion

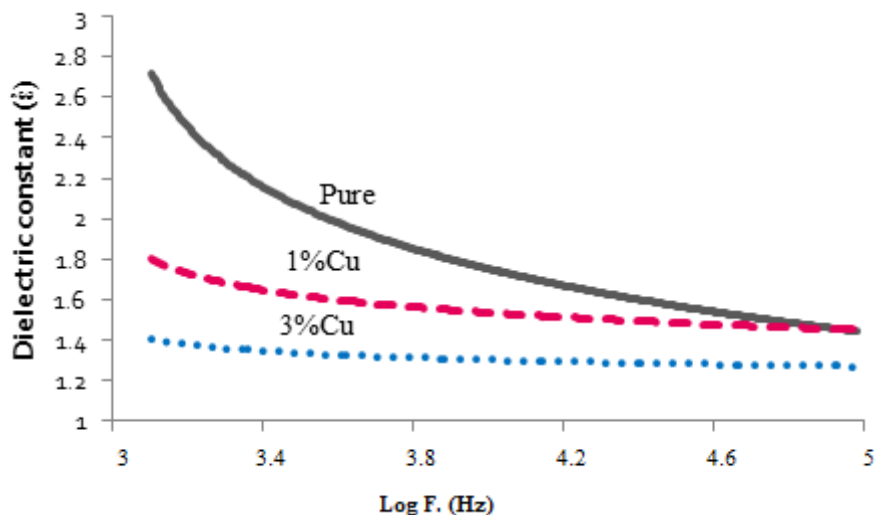
The structural characterization of all the samples was carried out by XRD at room temperature. Their crystalline phases were identified by comparison with reference data from the cards (JCPDS) [6]. In the case of dopants, it is noted the appearance of potassium sulfate peaks in the same locations with small shift from their positions, as well as the appearance of additional peaks refer to the dopants materials. Due to that the cell parameters are changed and resulted in the distortion of octahedron of the structure [6, 7]. The recorded diffraction pattern of pure  $\text{K}_2\text{SO}_4$  and doping crystals by Cu & Fe respectively, is shown in the Figures-2a, -2b, -2c [7].





**Figure 2-** (a,b,c) Refinement the X-ray diffraction pattern for Pure  $K_2SO_4$  and doping by Cu & Fe ions [7]

Figures-3,-4 and Figures-5,-6 presented the dielectric constant and dielectric loss at different frequencies of the prepared samples. It can be seen that these parameters decrease gradually with increasing frequency. This behavior can be explained on the basis of polarization mechanism.



**Figure 3-** Variation of dielectric constant vs. Log Frequency for  $K_2SO_4$  doped Cu ions

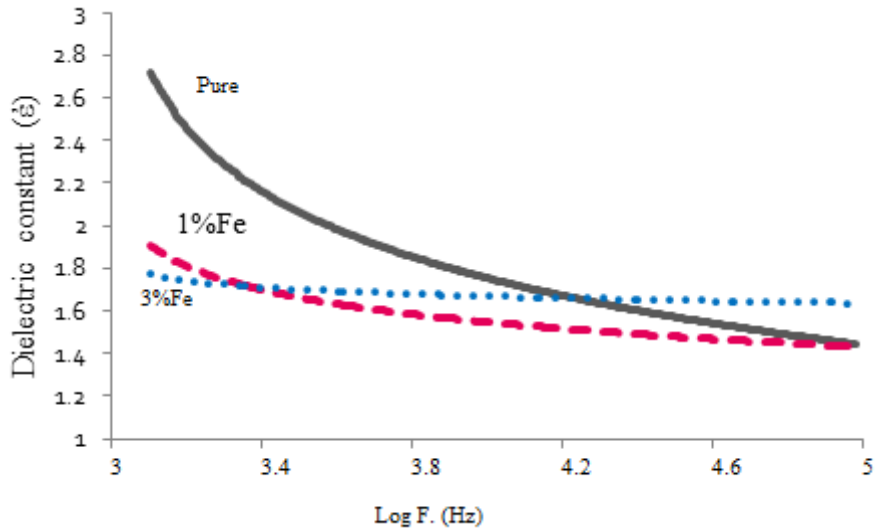


Figure 4- Variation of dielectric constant vs. Log Frequency for  $K_2SO_4$  doped Fe ions

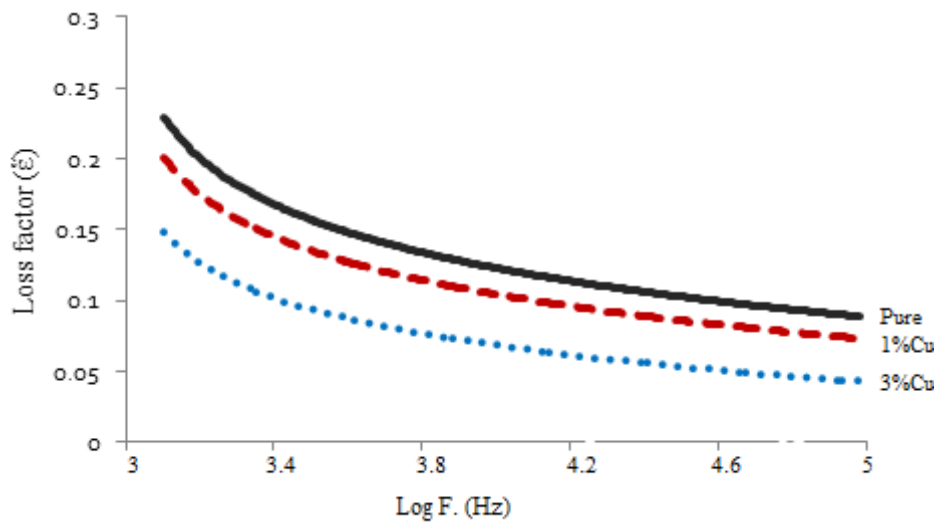


Figure 5- Variation of dielectric loss factor vs. Log Frequency for  $K_2SO_4$  doped Cu ions

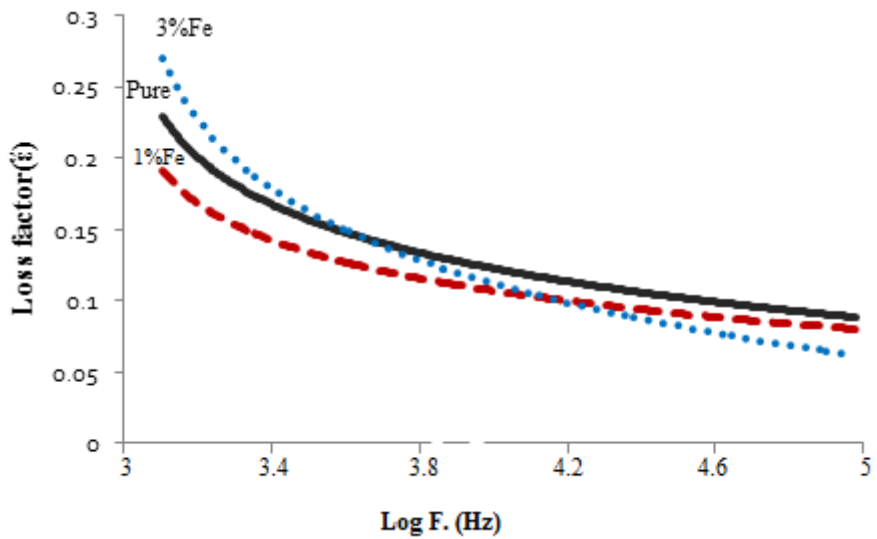
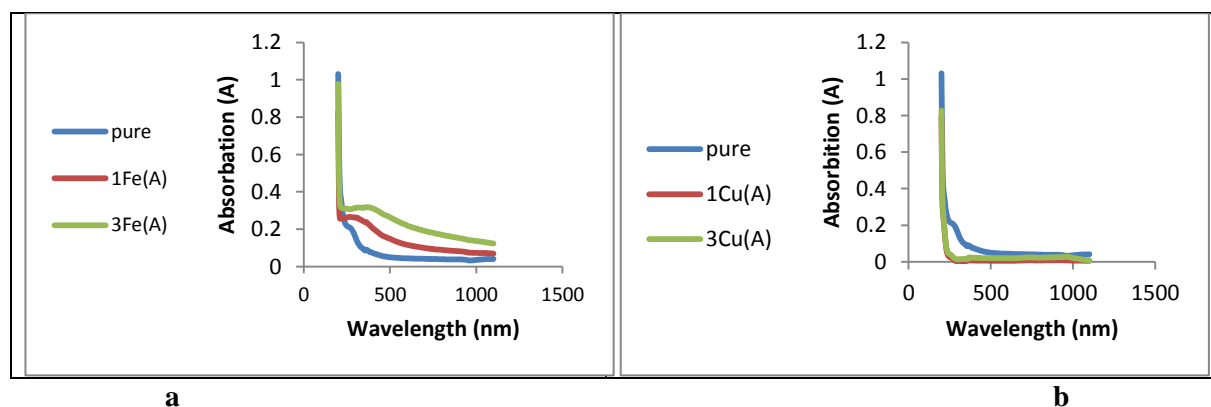


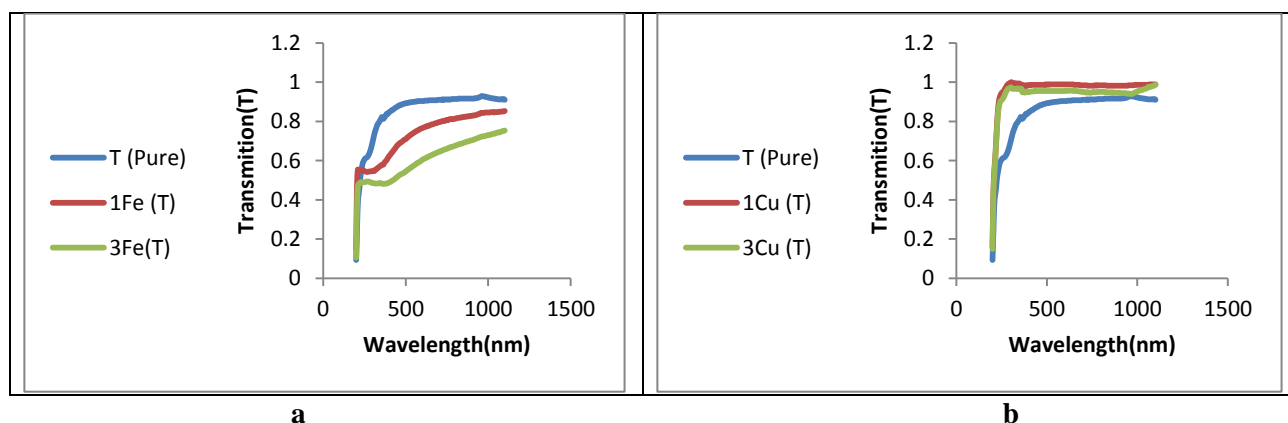
Figure 6- Variation of dielectric loss factor vs. Log Frequency for  $K_2SO_4$  doped Fe ions

The larger value of dielectric constant at lower frequency was attributed to the impedance of the charge carriers motion at the electrodes ,this results from the space charge and macroscopic distortion [13].While its low value at higher frequencies due to the fact that at higher frequencies the ionic and electronic polarizations are actives [14].The same behavior appeared for  $K_2SO_4$  doped with urea and explained it's according to Miller rule, the lower values of dielectric constant are a suitable parameter for enhancement of second harmonic generation coefficient [15].The small dielectric constant for all dopants samples at low frequency may be due to content of polarizable  $Fe^{2+}$  ions in the octahedral site of the structure. The influence of dopants clearly appeared in the behavior of the dielectric constant and loss factor. As an increase of dopant rates, the dielectric constant decreases gradually for cases of dopants with iron and copper ions. It can be noted that the case of dopants by 3wt.% of iron ion measurements dielectric constant appears with constant value almost at all frequencies. That is due to the balance between polarization parameters non alignments according to frequency change. So, it clear value from its lower than the other cases. At 3%Fe dopant, it is noted that the loss factor is larger value at low frequencies and decreases gradually to the lowest value at high frequencies with showed to the other samples , that is due to the relation  $\tan\delta = \frac{\epsilon''}{\epsilon'}$ .

The UV-Visible spectra of pure  $K_2SO_4$  and doped with copper and iron ions samples are shown in Figures-7 , -8 and -9 respectively The spectrum gives information about the structure of the molecule because the absorption of UV and Visible light involves promotion of the electron from the ground state to higher states [1].The samples show absorption in the entire visible region. The lower cut off wavelength is 385 nm this transparent nature in the visible region is a desirous property for the material used for nonlinear optics applications. In general majority of the sulfate show continual optical transmission from UV to near IR wavelength range.

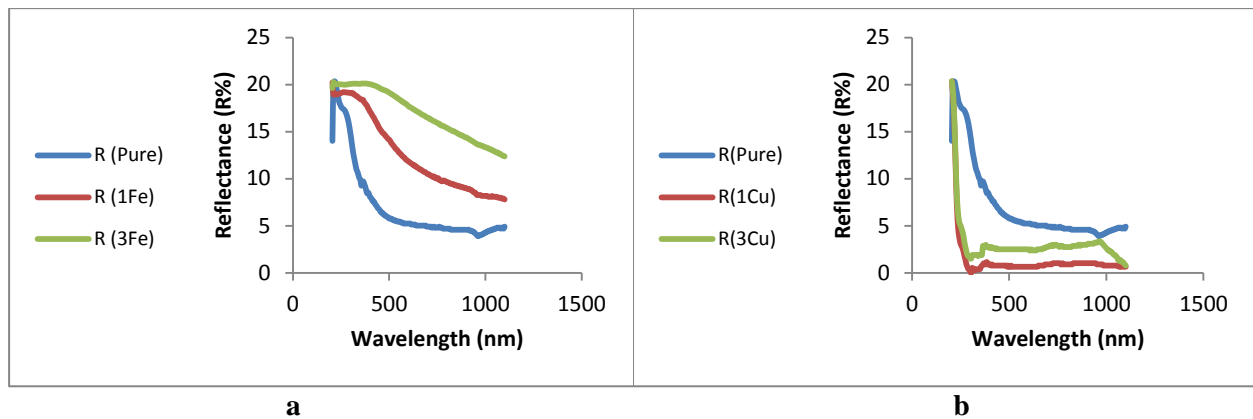


**Figure 7-** UV/Visible absorption spectrum as a function of wavelength  
(a) for pure and doped with iron ions (b) for pure and doped with copper ions



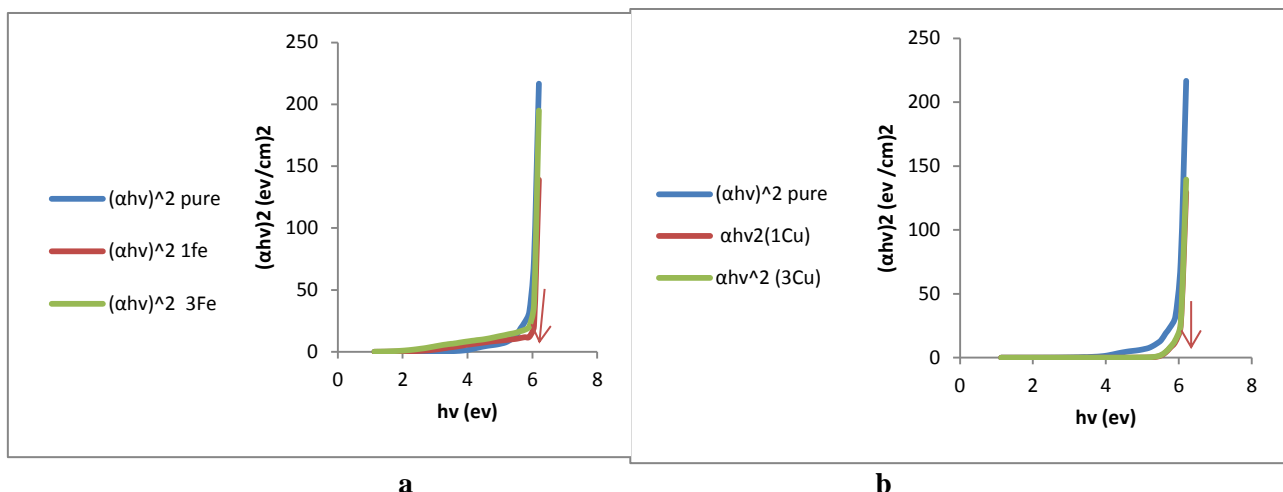
**Figure 8-** Optical transmittance spectra as a function of wavelength  
(a) for pure  $K_2SO_4$  and doped with iron ions (b) for pure  $K_2SO_4$  and doped with Copper ions





**Figure 9-** Optical reflection spectra as a function of wavelength  
 (a) for pure  $K_2SO_4$  and doped with iron ions (b) for pure  $K_2SO_4$  and doped with copper ions

The value of  $\alpha$  is used to determine the optical energy band gap from Tauc's relation [14]. By plotting graph of  $(\alpha h\nu)^2$  versus  $h\nu$  as shown in Figures-10a, -10b, it is possible to determine the direct band gap, for the sample. It is obtained by extrapolating the linear part of the curve to the zero of the ordinate, the obtained optical energy gap is 5.9eV and 6.048 for pure and doped samples respectively which are refer to insulator nature.



**Figure 10-**  $(\alpha h\nu)$  versus  $(h\nu)$  (a) for pure  $K_2SO_4$  and doped by iron ions  
 (b) for  $K_2SO_4$  pure and doped by copper ions

## Conclusion

The dielectric constant and its loss of  $K_2SO_4$  and doped samples decreases with frequency increases, while its UV-visible spectra confirmed that the doped sample filter blocks the unwanted transmission in the range 400-600 nm and 1000-800 nm ranges, and hence act as efficient filter. Energy gap ( $E_g$ ) of pure  $K_2SO_4$  and doped with copper and iron ions were found to be 5.9eV and 6.048 eV respectively, which is reasonable for typical dielectric materials. The absence of absorption bands in the visible region and the wide band gap of the sample attest to the suitability of the sample.

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