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Effect of Fe^{3+} Doping Concentration in Cu_2ZnSnS_4 Thin Film: Structural and Optical Analysis

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Abstract: CZTS (copper zinc tin sulfide), Cu_2ZnSnS_4, is a potential demanding candidate that is used as absorber layer in solar cell. The CZTS, Fe^{3+} doped CZTS and CFTS (replacing Zn be Fe^{3+}) thin films were deposited on a glass substrate using spin coating technique. The structural andoptical properties of all the thin films were studied to investigate the effect of iron doping in CZTS. The XRD (X-ray diffraction) results show that all the thin films grow tetragonal crystal system. The crystallite size of the doped CZTS was higher than the pristine CZTS although it was lowest for CFTS. The optical band gaps varied from 1.45 eV and 1.83 eV which are suitable for absorbing sunlight.

Key words: CZTS, CFTS, solar cell, absorption coefficient, band gap.

1. Introduction

Solar energy is a renewable energy that is used to produce electricity to minimize the dependency on the conventional energy sources such as oil, gas, coal, etc. using the photovoltaic technology. Photovoltaic cell is mainly based on P-type and N-type semiconducting materials in which electron-hole pair is generated by the absorption of sunlight in the depletion region of the P-N junction. Researchers are trying to improve the photovoltaic conversion efficiency by using different materials like silicon [1, 2], CdTe (cadmium telluride) [3, 4], perovskite materials [5, 6], CIGS (copper indium gallium selenide) [7, 8], CZTS (copper zinc tin sulfide) [9, 10], etc. used as absorber layer in solar cell for sunlight absorption. Among these CZTS is a promising candidate because of the earth-abundancy, ecofriendliness, and non-toxicity [11]. CZTS is a demanding compound having direct band gap of about 1.4 to 1.5 eV and optical absorption coefficients of about 10^4 cm^{-1} in the visible portion of the sunlight spectrum [12]. CZTS thin films have been prepared or synthesized using different synthesis techniques, for example spin coating, dip coating, spray pyrolysis, SILAR method, sol-gel method, chemical bath deposition method, sputtering, thermal evaporation etc. by different researchers [13]. Researchers are trying to improve CZTS film also to improve the efficiency of CZTS solar cell in different ways. Unveroglu and Zangari [14] in 2019 reported an increase in crystallinity, grain size and finally a better photo-response in Bismuth doped Cu_2ZnSnS_4 as compared to pure Cu_2ZnSnS_4. Besides, Rawat and Shishodia [15] in 2016, Hussein and Yazdani [16] in 2019 also studied on Bismuth doping effect in CZTS film and reported better crystallinity and photo-response. In 2020, Liu et al. [17] showed the effect of sodium (Na) doping on CZTS thin film and on CZTS:CdS solar cell. They there proved that due to Na doping, the grain size of CZTS increased with increase of carrier concentration and also increase of conductivity. They also claimed a noticeable amount of power conversion efficiency by Na-doped CZTS [17]. Many other researchers [18-20] have also studied over Na doping effect in CZTS thin film. The efficiency of CZTS, however, can be improved by rational manipulation of crystal, morphology, and doping [14]. In this study, we have prepared iron doped CZTS films via spin coating method. We have

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studied the effect of variation of molar concentration of iron in CZTS.

2. Experimental Details

2.1 Synthesis of CZTS, Fe^{3+} Doped CZTS and CFTS Films

Firstly, the soda lime glass substrates and beakers were cleaned by distilled water, then ethanol and then acetone. After that the substrates and beakers were dried in oven at 60 °C for 5 min. Cu_2ZnSnS_4 thin film was synthesized by spin coating technique starting with a solution containing copper (II) chloride ($CuCl_2$) (2.1 M), zinc (II) chloride ($ZnCl_2$) (1.4 M), tin (IV) chloride ($SnCl_4$) (1 M), and thiourea ($CS(NH_2)_2$) (9.4 M) into a mixture of 2-methoxy ethanol and few drops of mono-ethanolamine (MEA) as a stabilizer. By mixing the solutes in the solvent, a clear yellow solution was observed and then was stirred for half an hour at 40 °C to ensure that all metal salts have been dissolved completely. To prepare thin film, this solution was spin-coated onto soda lime glass substrate at 2,500 rpm for 30 s followed by drying at 110 °C for 10 min on a hot plate. The spin-coating and drying processes were repeated 3 times to have a suitable thickness of the film. Finally, the annealing temperature was elevated to 300 °C during 20 min in a furnace for growing crystalline CZTS thin film. Similarly, using 1 M $ZnCl_2$ and 0.4 M Fe_2O_3, 0.4 M Fe^{3+} doped CZTS, using 0.7 M $ZnCl_2$ and 0.7 M Fe_2O_3, 0.7 M Fe^{3+} doped CZTS, using 0.4 M $ZnCl_2$ and 1 M Fe_2O_3, 1 M Fe^{3+} doped CZTS and eventually by 1.4 M Fe_2O_3 as a replacement of $ZnCl_2$, CFTS films were prepared.

2.2 Characterization of the Thin Films

The structural property was measured using PW3040 XPert PRO X-ray diffractometer which was facilitated by the Materials Science Division, Atomic Energy Center, Bangladesh Atomic Energy Commission, Dhaka. The optical property was determined by using UV-Vis spectrometer of Specord 205 at Wazed Mia Science Research Center, Jahangirnagar University, Savar, Dhaka.

3. Results and Discussions

3.1 Structural Characterization

The thickness of the films was 0.90 µm for CZTS, 0.92 µm for 0.4 M Fe^{3+} doped CZTS, 0.96 µm for 0.7 M Fe^{3+} doped CZTS, 1 µm for 1 M Fe^{3+} doped CZTS and 0.9 µm for CFTS measured by a dial gauge.

The XRD (X-ray diffraction) patterns of the synthesized undoped and doped CZTS also CFTS thin films are shown below in Fig. 1.

The highest intensity peak for all the doped samples is at about 2θ of 33° corresponding to (112) plane whereas the CZTS thin film shows two peaks of almost equal intensity at 2θ values of 27.3662° and 28.7370° corresponding to the planes of (112) and (200) respectively. The diffraction peaks corresponding to 2θ values of all the samples confirm that both the doped and undoped CZTS have tetragonal polycrystalline structure of Kesterite phase. These data are in good agreement with the results obtained by other research groups [21, 22].

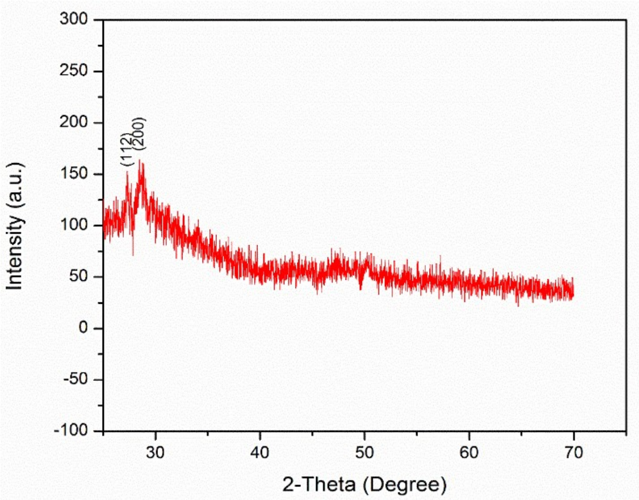
The average crystallite sizes D of the thin films were determined using Scherer's formula [23].

$$D = \frac{K\lambda}{\delta_W \cos\theta}$$

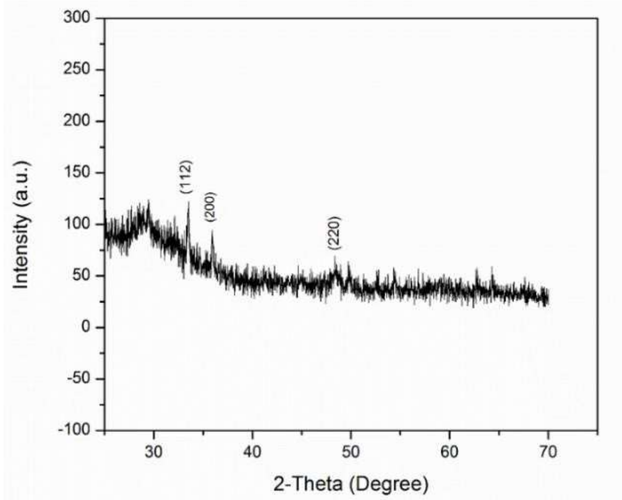
where, K is a constant of value 0.9, λ is the wavelength of X-ray employed which is numerically equal to 1.54 Å, δ_w is the full width at half maximum, θ is the Bragg's angle.

The calculated average crystallite sizes for all the thin films are shown in Table 1. The different sizes may have an effect on the properties of the thin films.

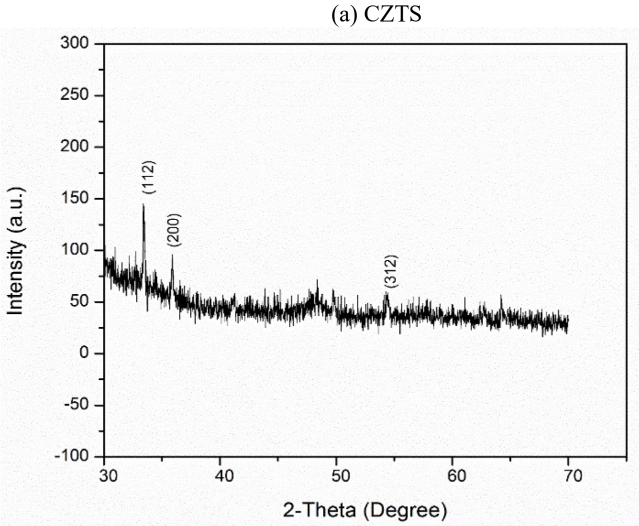
It is seen that the crystallite size increases with the increase of iron concentration in CZTS which confirms the better crystallinity but CFTS film shows low crystallite size.



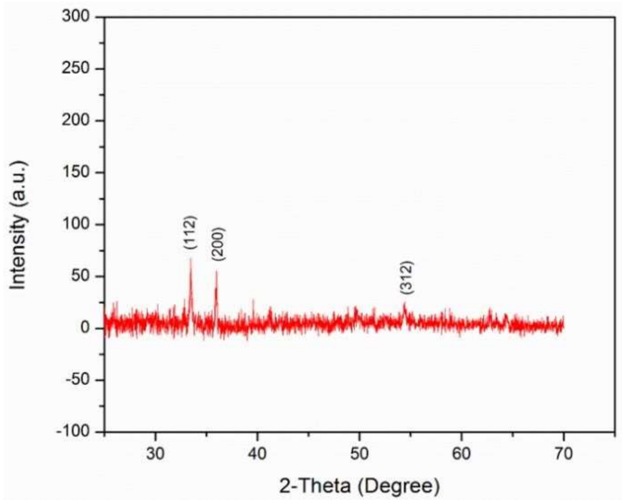
(a) CZTS



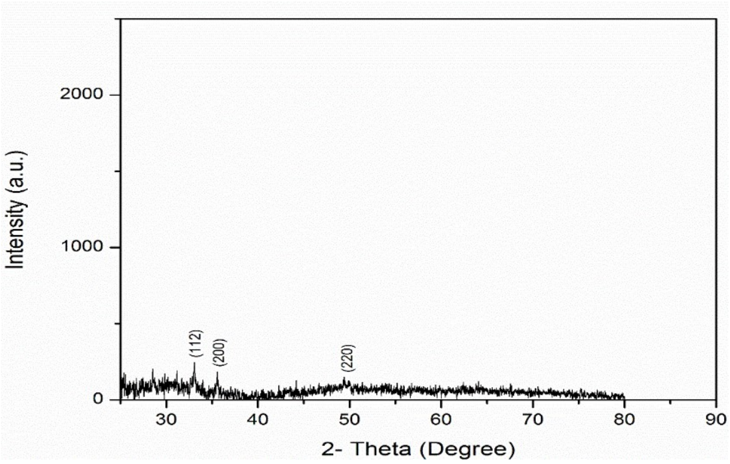
(b) 0.4 M Fe^{3+} doped CZTS



(c) 0.7 M Fe^{3+} doped CZTS



(d) 1 M Fe^{3+} doped CZTS



(e) CFTS

Fig. 1 XRD patterns of CZTS, doped CZTS and CFTS thin films.

Table 1 Crystallite sizes of the synthesized CZTS, doped CZTS and CFTS thin films.

Films	Average crystallite Size (Å)
CZTS	2.65
0.4 M Fe^{3+} doped CZTS	4.54
0.7 M Fe^{3+} doped CZTS	6.02
1 M Fe^{3+} doped CZTS	8.84
CFTS	0.18

3.2 Optical Characterization

The optical absorption and transmission spectra were obtained for various wavelengths (400-1,100 nm) using UV-Vis spectrometer. The absorbance and transmittance at different wavelengths of the thin film samples are exhibited in the following.

Considering three optical phenomena, absorption, transmission and reflection, as dominant into the CZTS, CFZTS (Fe doped CZTS) and CFTS thin film samples, the reflectance was found from the relation $R + A + T = 1$, where, R = reflectance, A = absorbance and T = transmittance.

It is pellucid from Fig. 2 that the absorbance decreases with increasing wavelength from 400 nm to 1,100 nm and it happens for all the samples. Similar decreasing trend of transmittance is observed, shown in Fig. 3, for all the samples. On the other hand, Fig. 4 shows that the reflectance increases with increasing wavelength. If we go for absorbance, then it is seen that the absorbance is maximum for 1 M Fe^{3+} doped CZTS while it is lowest for undoped CZTS thin film. Two absorption peaks, one in the visible region and another in the infrared region, for all the films except CZTS are observed.

The absorption coefficient describes how much light of a given wavelength is absorbed by a material of a given thickness. The absorption coefficient will be higher when more light is absorbed. The absorption coefficient depends on the material and also on the wavelength of light which is being absorbed. The absorption coefficient can be calculated by using the formula [24].

$$\alpha=(1/d)\ln[(1-R)^2/T]$$

where, R is the reflectance, T is the transmittance and d is the film's thickness.

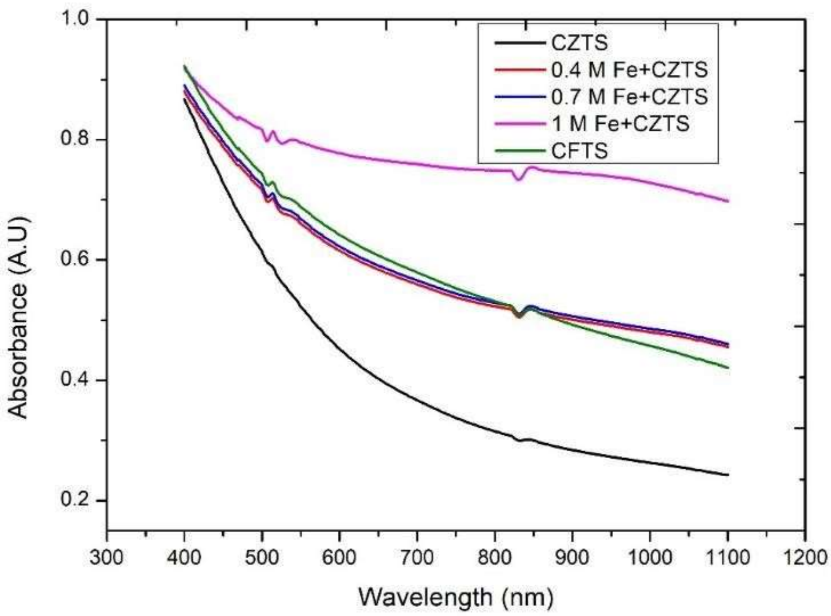


Fig. 2 Absorbance spectra of CZTS, doped CZTS and CFTS thin films.

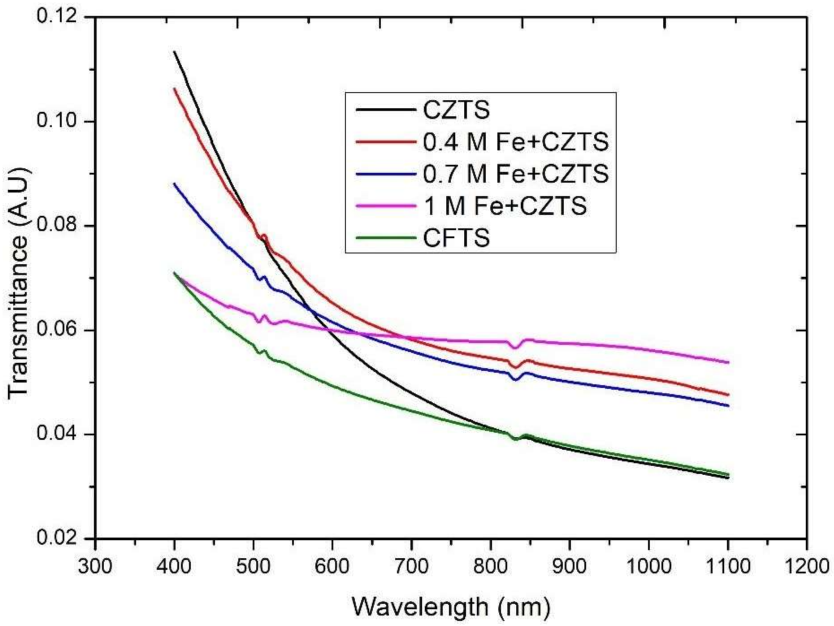


Fig. 3 Transmittance spectra of CZTS, doped CZTS and CFTS thin films.

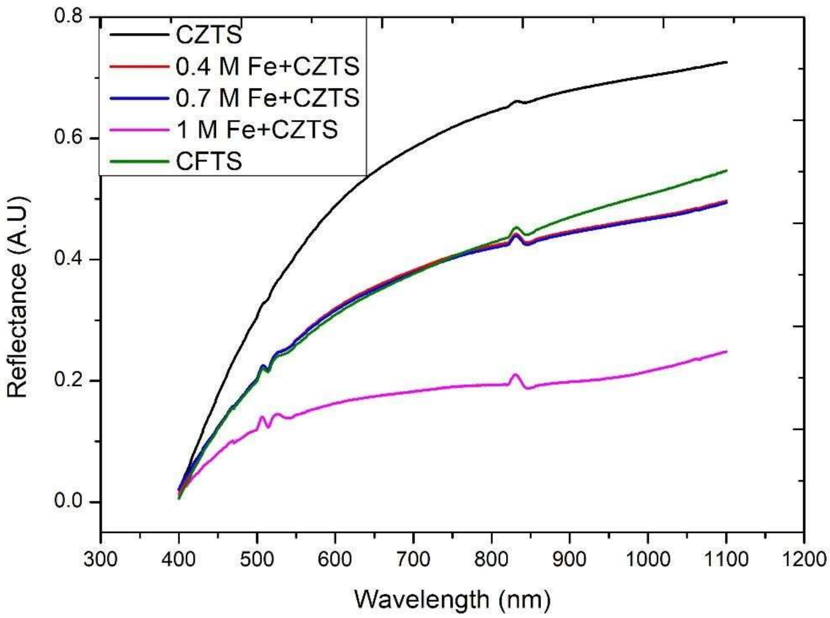


Fig. 4 Reflectance spectra of CZTS, doped CZTS and CFTS thin films.

It is observed from Fig. 5 that the absorption coefficient of CFTS thin film is highest in the wavelength region of 400-650 nm while it is highest for 1 M Fe^{3+} doped CZTS in rest of the region of spectrum than all other thin films, and the values of absorption coefficient are high for all the samples that is of the order of 10^4 cm^{-1}. The absorption coefficient of all the samples follows the same decreasing trend with wavelength.

The band gap energy is very significant for a thin film to be applied as an absorber layer in solar cell. The band gap is basically the energy difference between the valence band and conduction band. The band gap indicates how amount and which portion of energy of sunlight will be absorbed in the layer. Only that light of energies compatible with the band gap will be absorbed. The optical band gap was calculated by a well-known relation [24, 25]:

$$\alpha h\upsilon = k(h\upsilon - Eg)^n$$

where, $n = 1/2$ for direct allowed transition, 2 for indirect allowed transition.

Therefore, the direct optical band gap can be estimated using Tauc's model as plotting $(\alpha h\upsilon)^2$ against photon energy ($h\upsilon$) and then the extrapolation of the linear portion of the curve, Fig. 6, will give the band gap energy [26].

The band gaps obtained by extrapolating the linear portion of the curve for all the thin films are shown in Table 2. It is seen that after introducing iron, the band gap of the thin film changes. The band gap of pristine CZTS is maximum while with iron doping it decreases. The bad gap among the iron doped CZTS thin films is high for CFTS thin film when zinc is replaced by iron.

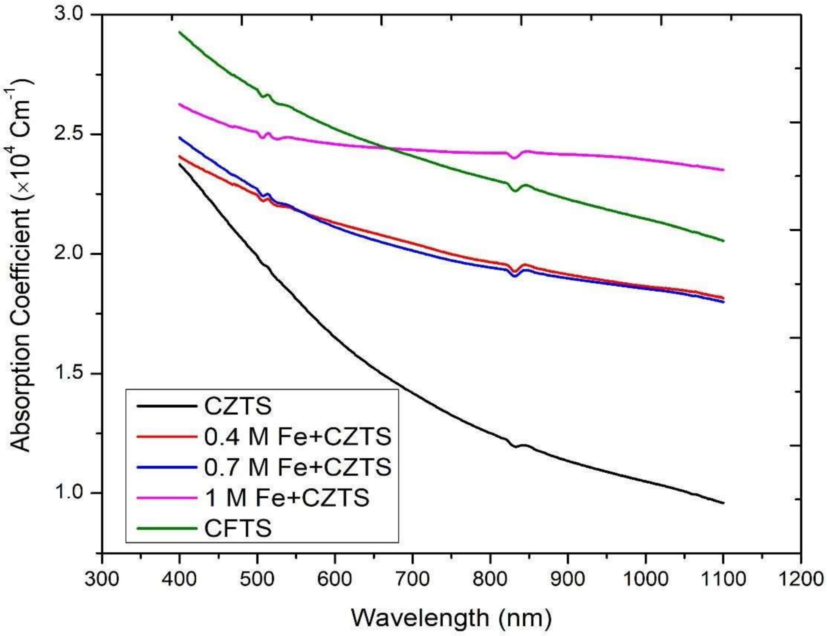


Fig. 5 Absorption coefficient versus wavelength plot of the thin films.

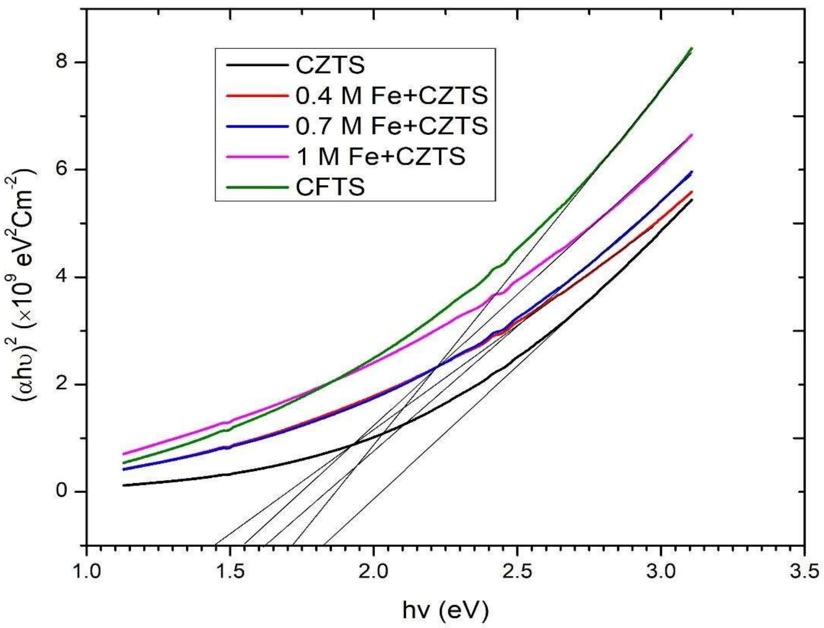


Fig. 6 $(\alpha h\upsilon)^2$ versus $h\upsilon$ plot of the thin films.

Table 2 Optical band gap of the thin films.

Samples	Band gap in eV
CZTS	1.83
0.4 M Fe^{3+} doped CZTS	1.45
0.7 M Fe^{3+} doped CZTS	1.63
1 M Fe^{3+} doped CZTS	1.55
CFTS	1.73

Refractive index of a medium indicates the propagation of light through that medium. Some part of light is attenuated during passing through a medium, which is taken into account by introducing an imaginary part of refractive index as [27],

$$n_{total} = n - ik$$

where, the real part n is called the refractive index indicating the phase velocity while the imaginary part k is called the extinction coefficient.

The extinction coefficient, imaginary part of refractive index, k was calculated from absorption coefficient α using the following relation, and is plotted in Fig. 7 [24, 28].

$$k = \alpha\lambda/4\pi$$

where, α is the absorption coefficient and λ is the wavelength of light.

The extinction coefficient for 1 M Fe^{3+} doped CZTS is highest above 650 nm of the spectrum, that is also observed from the absorption coefficient spectra.

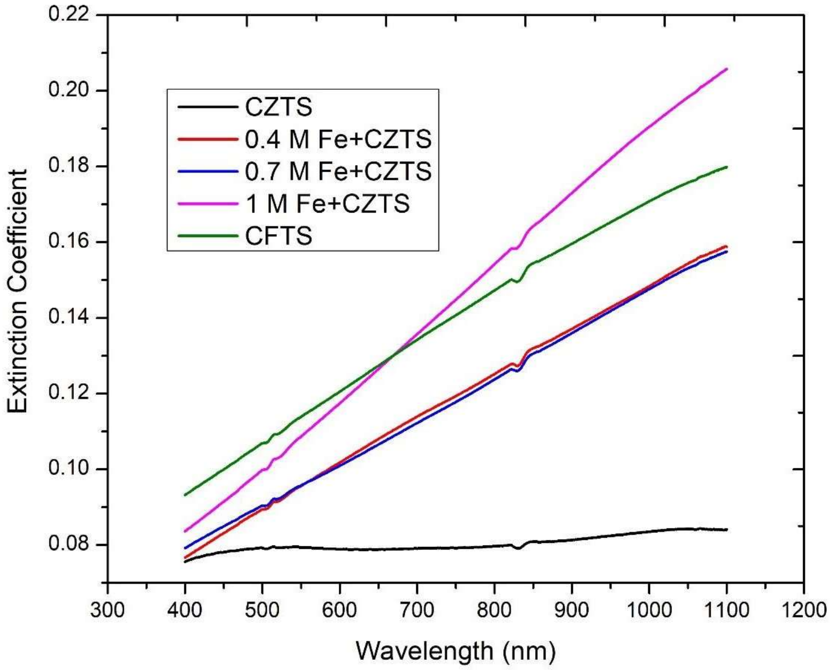


Fig. 7 Extinction coefficient versus wavelength plot of the samples.

In the low wavelength region up to 650 nm from 400 nm, CFTS thin film shows the maximum extinction coefficient. It is seen that iron doping increases the extinction coefficient value that indicates light is strongly absorbed there. The extinction coefficient unlike absorption coefficient follows increasing trend with wavelength for all the thin films.

The refractive index can be determined from reflectance using the relation [24].

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1-R)^2} - k^2}$$

The values of the refractive indices against wavelength are plotted in Fig. 8. The refractive indices of all the samples are low in the small wavelength region and high in the long wavelength region. The refractive index of CZTS is highest which means that it is most dense film than others [24]. The film which has high

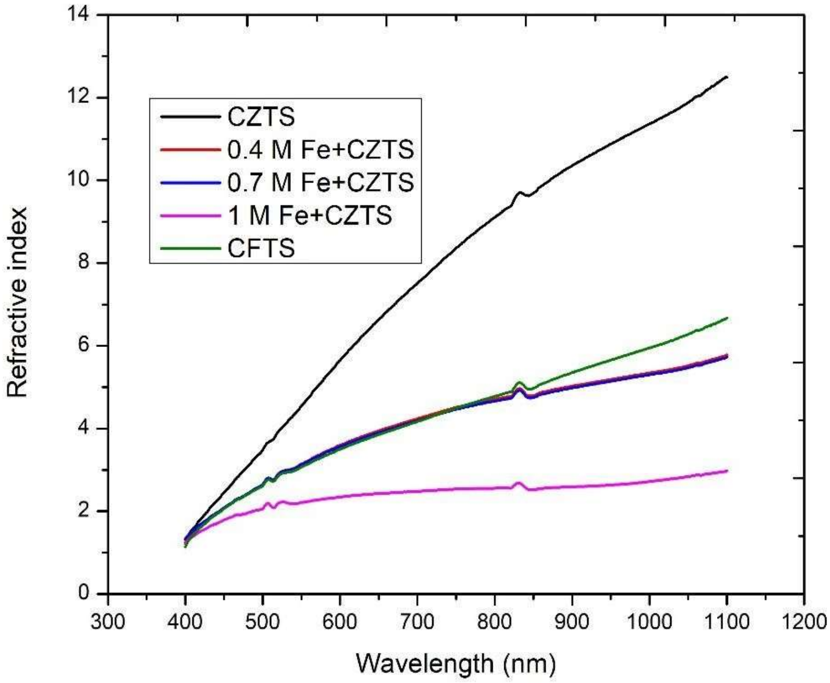


Fig. 8 Refractive index versus wavelength plot of the samples.

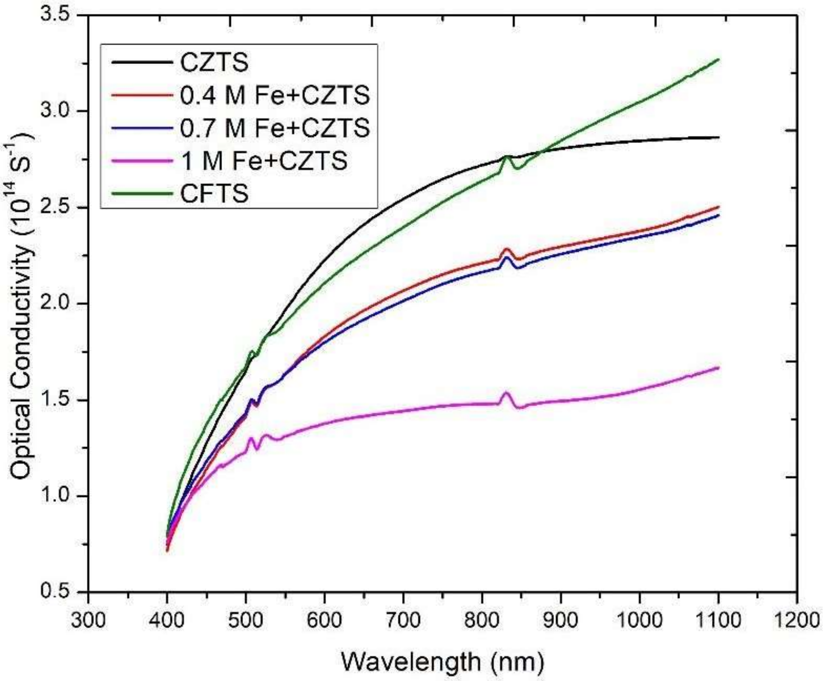


Fig. 9 Optical conductivity versus wavelength plot of the samples.

refractive index would have high reflectivity meaning more energy loss would happen in solar cell that would have poor power conversionefficiency.

The optical conductivity was determined using the below relation [24].

$$\sigma = \alpha nc/4\pi$$

where, c is the velocity of light.

The dependency of optical conductivity with the wavelength of light is shown below.

The optical conductivity refers to the conductivity due to the absorption of light. The optical conductivity of all the samples is high of the order of 10^{14} S^{-1}. Among all the samples, CZTS films show high values of optical conductivity in the 500 nm to 900 nm wavelength region while CFTS films show maximum optical conductivity before 500 nm and above 900 nm region with two separate peaks in different regions.

4. Conclusions

In conclusion, Cu_2ZnSnS_4 thin films were synthesized using spin coating technique and the Fe^{3+} doping effect was investigated in this work. The XRD pattern of the thin films confirms the formation of tetragonal kesterite phase while because of doping, the crystallite size changed that represents the change of crystalline quality. The optical absorption coefficient for iron doped CZTS is higher than the pristine CZTS, and its value for all the thin films is of the order of 10^{14} cm^{-1} over the whole region of the spectrum. The optical band gap changes from 1.45 eV to 1.73 eV while the band gap for pristine CZTS obtained is 1.83 eV. All these samples are suitable to use as an absorber layer in solar cell.

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