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Energy loss analysis from RBS spectrum of thin Cu_2ZnSnS_4 (CZTS) film

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Abstract
The goal of this work is to offer an alternative method to the available literature on determining the energy loss of CZTS thin films. For this purpose, thin CZTS film structures were first produced by sol-gel method and then the RBS spectrum was received with RBS detector irradiating this structure with 3.034 MeV proton beams in a microbeam chamber. The energy calibration was implemented to this spectrum, where the it was fitted with SIMNRA program. In the RBS spectrum of the thin film generated, a method for the calculation of energy loss was used for the position and energy width analysis of the corresponding peaks and a polynomial fit was obtained from the stopping power of the CZTS thin film by making certain approaches. Also, the effective charge approach that we used in our previous studies for the stopping power was employed with atomic natural orbitals and it was founded that the results were close to each other at certain error rates. The data obtained from this study will inspire the future studies on the interaction of radiation with matter.

Keywords: Energy loss, CZTS, RBS.

İnce Cu_2ZnSnS_4 (CZTS) filmin RBS spektrumundan enerji kaybı analizi

Öz
Bu çalışmanın amacı, CZTS ince filmlerinin enerji kaybını belirlemek için mevcut literatüre alternatif bir yöntem sunmaktır. Bu amaçla, ince CZTS film yapıları ilkönce sol-gel yöntemiyle üretildi ve daha sonra bu yapı bir mikroışın çemberinde 3.034 MeV protonlarla ışınlanarak RBS detektörüyle RBS spektrumu alındı. SIMNRA programıyla fit edilen bu spektruma enerji kalibrasyonu uygulandı. Üretilen ince filmlerin RBS spektrumunda, ilgili piklerin konum ve enerji genişliği analizinden enerji kaybı hesaplaması için bir yöntem kullanıldı ve belirli yaklaşımlar yaparak CZTS ince filmin durdurma gücünden bir polinom fit elde edildi. Ayrıca, durdurma gücü için önceki çalışmalarda kullandığımız etkin yük yaklaşımı atomik doğal orbitaller ile kullanıldı ve sonuçların belirli hata oranlarında birbirine yakın oldukları bulundu. Bu çalışmadan elde edilen veriler maddeyle radyasyonun etkileşmesi üzerine yapılacak çalışmalara ilham verecektir.

Anahtar kelimeler: Enerji kaybı, CZTS, RBS.

1. Introduction

As well as cosmic rays, slow and fast particles penetrate into the interior and the exterior. Significant representatives of our outer solar system are solar rays consisting of solar wind, proton, electron and helium ions. These particles interact with the planets' atmosphere. Sunburn is probably the best-known radiation effect that these particles cause. Analyzes of meteors and moon samples offer evidence of exposure of materials to high radiation doses and consent modeling of solar wind and intergalactic radiation. The exposure of spacecraft to local radiation fields upsets the material properties of the spacecraft, the functioning of computerized instruments, and the health of astronauts. Particularly the interaction of radiation with spacecraft and solar batteries placed on satellite wings changes the function and energy efficiency of these materials. Therefore, it is very important to examine the interaction of charged particles with solar batteries and therefore to determine the energy loss [1].

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The development of clean energy resources as an alternative to fossil fuels has become one of the most important requirements of the 21st Century. Among the renewable energy sources, the best alternative to meet the energy needs of modern society is solar energy. In order to make photovoltaic devices widespread, cheap, high efficiency and environmentally friendly solar cells are needed. In particular, the Cu_2ZnSnS_4 (CZTS) compound is a good candidate for the absorbent layer in solar cell applications [2, 3].

Despite being a film with great potential as absorbent material, studies on CZTS solar cells are still in its infancy. The examination of the interaction of CZTS solar cells with radiation, or rather the determination of the stopping power for charged particles, has a great proposition in terms of efficiency. To the best of our knowledge, there is no scientific study of the energy loss of CZTS thin films. In the light of the information thus far, it is necessary to study the theoretical and experimental stopping power of CZTS films. The aim of this work is to present an alternative method to available works on determining the energy loss of CZTS thin films. Therefore, thin CZTS film structures were first produced by sol-gel method and then the RBS spectrum was obtained by irradiating this structure with proton beams in microbeam chamber. The RBS spectrum was taken with RBS detector and the energy calibration was then applied to this spectrum, where the RBS spectrum was fitted with SIMNRA [4] program. Then, in the RBS spectrum of the CZTS thin film, the individual peaks of each element constituent the film were generated. These peaks produced were matched to Gaussian type function by chi2 method. The values obtained by the peak analysis were used instead of the energy loss statements derived from the linear approach and the stopping power data of these elements were calculated by iterations. At least squares method was applied to these obtained values and the stopping power of CZTS thin film was determined by Bragg additivity rule. The results were compared with the theoretical effective charge approach presented in this study and the available reference data in the literature. This technique is a fast and simple method that can be used analytically to help improve the accuracy of the existing methods in the literature used to determine the energy loss of thin films.

2. Material and Method

2.1. Experimental procedure

2.1.1. Production of CZTS thin films

The CZTS films were produced by using sol-gel spin coating method. The CZTS precursor solutions were arranged by melting copper (II) acetate monohydrate (0.3M, 98+%), zinc (II) acetate dihydrate (0.3M, 99.99%), tin (II) cloride (0.3M, 98%) from Sigma Aldrich and thiourea (1.2M, 99.0+% from Sigma Aldrich) into 2-methoxyethanol (20 ml, 99.8% from Sigma Aldrich). The last solutions were commingled at 45^{o}C, 850 rpm for 1 h to liquefy the metal compounds entirely. Throughout mixing, 2 ml of diethanolamine (DEA) was put stepwise inside each solution as a stabilizer. The quartz-glass slides were use as substrates which were ultrasonically wiped out one by one with detergent, nitric acid (1:4), acetone and ethanol for 10 min. To fabricate the CZTS films, the already made solutions were spin-coated onto quartz and n-type silicon substrates at 3000 rpm for 30 s in the course of solvent-drying at 175^{o}C for 10 min on a hot plate. To provide electrical conductivity, molybdenum layer was sandwiched between quartz-glass substrate and CZTS thin film layer. Lastly, the samples were subjugated to an annealing procedure for 2 h at 500^{o}C in a quartz tube including 10 g of elemental sulfur. The thickness of the produced films was determined from the SEM cross section images. The completed sample is shown in Figure 1 below.

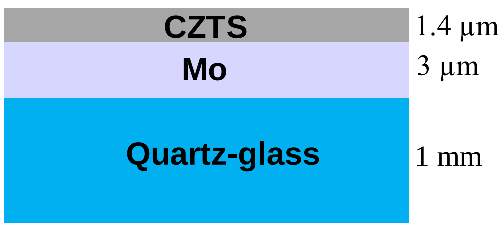

Figure 1. Fabricated CZTS thin film and its thickness

2.1.2. Set up and detection procedure

The experimental set up and procedure were carried out at the Jožef Stefan Institute Tandetron accelerator facility. Test measurements were made for both CZTS samples and NIST 1107 naval brass sample for energy calibration using protons of 3.034 MeV. Since the NIST 1107 naval brass contains most of the elements in the produced CZTS film, it was used [5] as reference material. For convenience, the microbeam chamber was employed with the RBS detector at 135 degrees scattering angle. The solid angle of the RBS detector is 4.59e-3, the resolution is 18 keV, the diameter of the detector aperture with circular shape is 4 mm, the sample-detector aperture is 52.3 mm, and the thickness of the aluminum foil material in front of the detector is 800 nm. RBS signal from the chopper and RBS spectrum was obtained. The incoming proton beam had a diameter of 30 micrometers but was scanned over an area of 500x500 micrometers. To get the number of input particles, the chopper signal was considered and the calibration constant was found from the measurements of NIST 1107. Experimental set up is displayed in Figure 2.

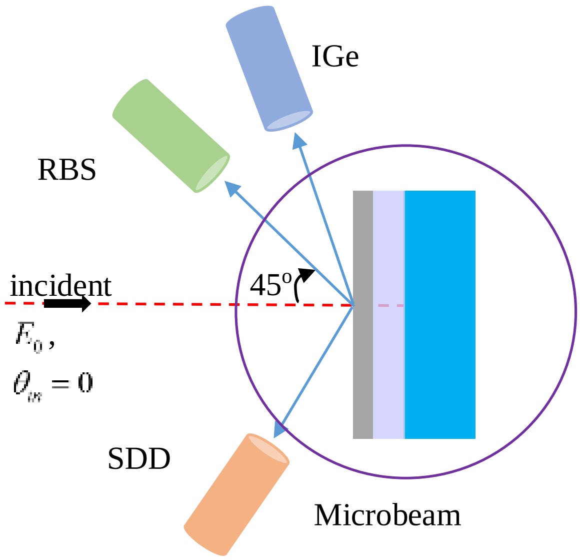

Figure 2. Experimental set up

2.1.3. Determination of energy loss

The RBS spectrum shown in Figure 3 was simulated by means of SIMNRA. Previous calibration values and necessary initial parameters were entered into the program and the spectrum was obtained. The target material consists of three different layers. Cu, Zn, Sn and S elements containing CZTS thin film as the first layer, Mo element as the second layer and O and Si elements with the inclusion of the quartz substrate as the last layer were selected and the conjectural concentration values of these elements were inserted into this program. The roughness for the layer and the substrate materials and the correction factors for stopping power of these layers were not considered. Instead, the Chi2 channel evaluation option was used as the fit parameter for the roughness of each layer, and the fit values were obtained with a maximum iteration of 50 and an accuracy of 0.01. As reaction kinematics, Rutherford cross-sections were employed for backscattering of projectiles present in the program's internal file.

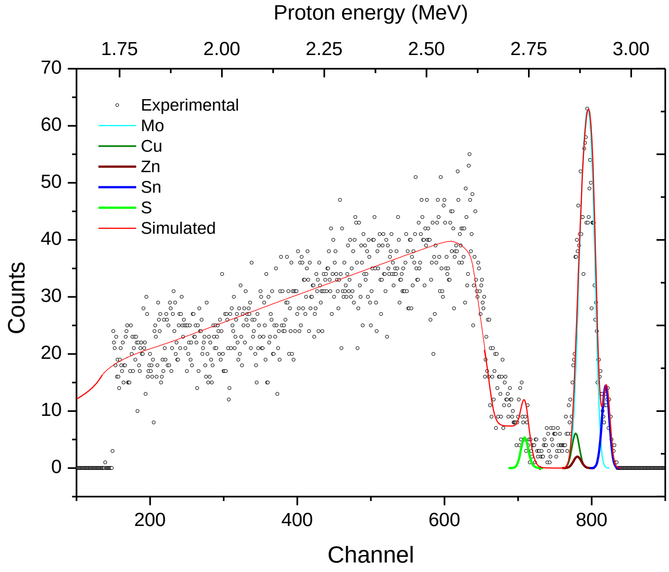

Figure 3. The RBS spectrum of the CZTS thin film

Backscattering technique is one of the methods used to determine the energy loss, the ingredients with the depth scale and the stopping cross section of the samples can be assigned from the RBS analysis. However, due to the peak of the Mo layer used to provide conductivity between the substrate and film, the peaks of elements constituting the CZTS thin film in the RBS spectrum of Figure 3 are not clearly visible. Hence, the RBS spectrum of the film was simulated with SIMNRA and the peaks of the elements forming the sample were generated.

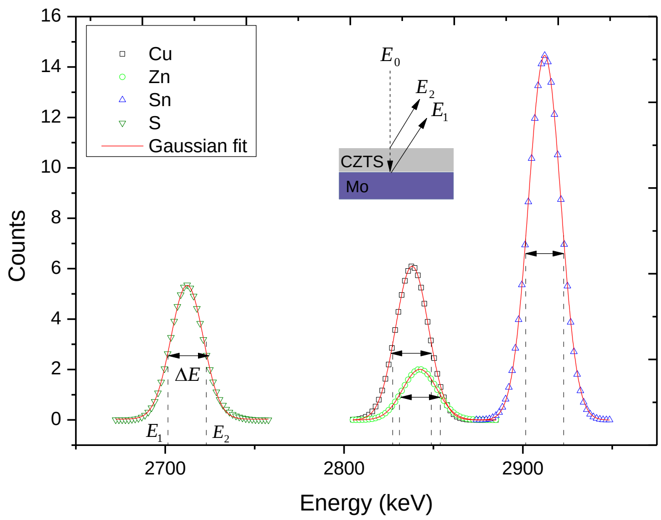

Figure 4. The Gaussian fit functions for these values with the fit values of experimental data SIMNRA program for Cu, Zn, Sn and S

As can be seen from Figures 3 and 4, a procedure was used to calculate the stopping power, that is, the energy loss from the signal height and energy width values of the respective elements in the RBS spectrum. Thus, energy loss along the paths of the incoming and outgoing protons on target was considered (Figure 4). To obtain the spectrum peaks of the individual elements, the positions of E_2, E_1 energy particles and ΔE widths equal to the full widths at half maximum (FWHM) scattered from the front and rear surfaces of the CZTS thin film, which are simulated with SIMNRA software and containing peaks of these elements, were obtained from the peak analysis. The simulated spectrum was fitted with the Gaussian function by five times iterations with chi-square method (χ^2). Then, considering the linear approach, the stopping power of each element was calculated according to the following expressions:

$$S_i\left(\overline{E_i}\right)=\frac{\Delta E}{N_t\Delta x\left\{k\left|\sec\theta_i\right|+\frac{S_i\left(\overline{E_0}\right)}{S_i\left(\overline{E_i}\right)}\left|\sec\left(\theta_i-\theta_0\right)\right|\right\}} \quad (1)$$

$$S_0\left(\overline{E_0}\right)=\frac{\Delta E}{N_t\Delta x\left\{k\frac{S_0\left(\overline{E_i}\right)}{S_0\left(\overline{E_0}\right)}\left|\sec\theta_i\right|+\left|\sec\left(\theta_i-\theta_0\right)\right|\right\}} \quad (2)$$

Here, θ_0 and θ_i are the angles between the surface normal of the incoming and the scattered ions respectively. For details can be examined Ref. [6].

Before and after the scattering, followed by the assumption that the path of the projectile is straight and assuming the initial value of stopping power ratio is 1 ($S_i\left(\overline{E_0}\right)/S_i\left(\overline{E_i}\right)=S_0\left(\overline{E_i}\right)/S_0\left(\overline{E_0}\right)=1$), stopping power was expanded to the power series of the energy using the least squares method with iteration [7]:

$$S(E)=(a_1E^{-0.5}+a_2E^{-0.25}+a_3E^{0.25}+a_4E^{0.5}+a_5E^{0.75})/\Delta x \quad (3)$$

Where a's are the coefficients and unit of energy is eV. Finally, the stopping power values of the CZTS thin film were calculated with the Bragg's additivity rule [8].

2.1. Theoretical procedure

The stopping power of a material is defined as the average energy loss per unit path length and the total stopping power (S) is the sum of collision (S_{coll}) and nuclear (S_{nuc}) constituents:

$$S(E)=S_{coll}(E)+S_{nuc}(E) \quad (4)$$

For protons, the highest addition to the total stopping power is supplied by the collision stopping power which based on inelastic collisions with target's electrons. Inversely, the least contribute to the total stopping power comes from nuclear stopping power which stem from elastic Coulomb collisions with target's nucleons and since it is only considerable at very low energies, it was not considered in this study.

The collision stopping power is specified by allowance the number of velocity-dependent effective charge and effective mean excitation energies of the target material. Taking into account the interaction potential between the protons with target in Ref [9], the collision stopping power for protons is given by

$$S_{coll}(E)=\frac{4\pi e^4}{m_e c^2\beta^2}Z^*\ln\left(\frac{q_{\max}}{q_{\min}}\right) \quad (5)$$

where e is charge of electron, $\beta=\upsilon/c$ is the proton's velocity in light velocity units, m_e is mass of electron, Z^* is the effective charge of target, $q_{\max}$ and $q_{\min}$ are maximum and minimum momentum transfer to the target from projectile, respectively.

In this present study, the electronic charge densities required for the effective charge and effective mean excitation energy of the target were calculated using atomic natural orbitals (ANO-RCC) from Gaussian type orbitals [10].

3. Results and Discussion

In Figure 3, it is seen that the simulation with SIMNRA is quite compatible with the experimental values. In the simulation, separate spectra were generated for constituents forming the CZTS thin film and for the Mo element. As expected, the fit distributions of the elements vary depending on the concentration in the film and the increased the cross-section with increasing atomic number. However, the peak of the Mo element appeared in the foreground plane due to its atomic number and thickness, and because the elements including the CZTS were not clearly visible. Especially, the peaks of the Cu and Zn elements were overlapped because of their atomic numbers were very close together, but still remained dimmed alongside the Mo peak. On the contrary, the Sn peak appeared a little more pronounced since the RBS analysis is very sensitive to heavy elements.

Table 1. Fit function coefficients for stopping power values of elements forming CZTS thin film

Elements	Coefficients				
	a_1	a_2	a_3	a_4	a_5
Cu	-4.59E+02	2.51E+02	-1.15E+00	-7.22E-01	7.09E-02
Zn	-7.06E+02	3.94E+02	-1.21E+01	1.21E+00	-2.77E-02
Sn	-1.80E+03	1.05E+03	-6.21E+01	1.04E+01	-5.17E-01
S	-8.74E+02	5.89E+02	-3.73E+01	6.17E+00	-2.98E-01

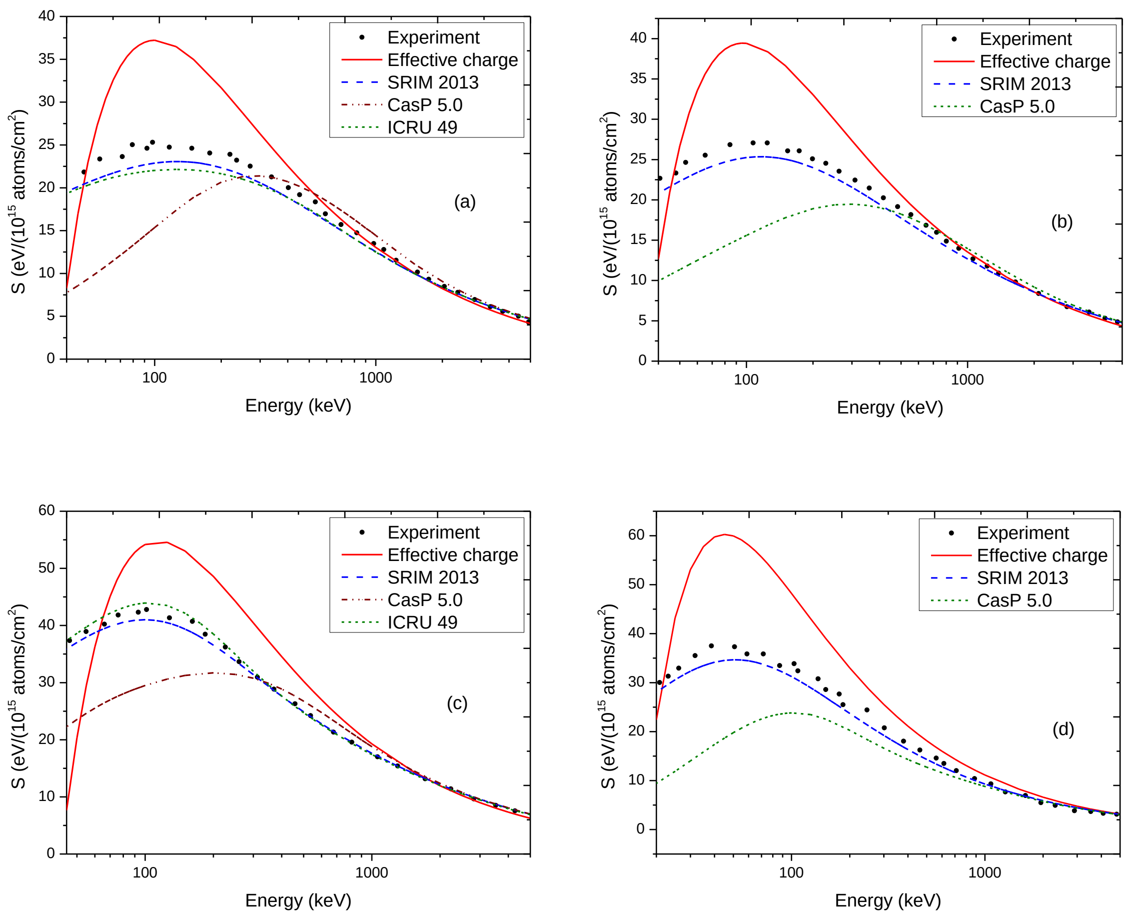

Figure 5. The stopping power values of (a) Cu (b) Zn (c) Sn (d) S

The coefficients related to the fit functions obtained by using Equation (3) are shown in Table 1 and Figures 5 (a)-(d) indicate the stopping power values of Cu, Zn, Sn and S acquired by these fit functions in the 45 keV-5 MeV energy range. Although the data are compatible with the energies of 1 MeV and above, there are differences in the low energies as expected. The peak point values in the stopping power curves of the experimental data seem to be closer to the ICRU [11] and SRIM [12] values than the effective charge approach we used in this study. There are significant variances in the positions of the peaks for CasP [13] data. While the peak values of the curve in Cu, Zn and Sn are approximately 100 keV, this value is localized at approximately 300 keV for CasP. For S, these values are about 100 keV for CasP and 55-60 keV for the others. However, lower values than the peak points of the effective charge approach decrease very quickly compared to other reference data. Figure 6 represents the stopping power data of the CZTS thin film calculated according to the Bragg's sum rule with the fit function composed by matching the experimental data. The reference data included here are also the data of Andersen-Ziegler [14] and Ziegler-Biersack [15] currently available in the SIMNRA program. The values are generally compatible with each other, but an important point here is that there is little change between the fit function and the SRIM values in energies greater than 1 MeV. It is also noteworthy that the fit function and the energy values of the maximum of the effective charge approach overlap. The compliance rate with fit function was founded as 6.40% for SRIM, 7.49% for Ziegler-Biersack, 10.28% for Andersen-Ziegler, 16.45% for effective charge and 16.93 for CasP.

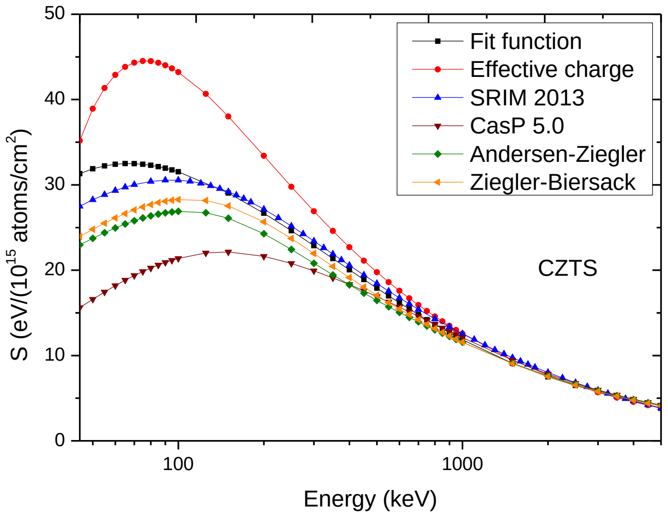

Figure 6. The stopping power of CZTS thin film

In this work, energy loss calculations of CZTS thin films were made by RBS technique. Accordingly, it is the SRIM data that is most compatible with the fit function. The effective charge approach handled under the Bethe-Bloch theory is actually valid for energies of 1 MeV and above, since it includes the first Born approximation. In this approach, no correction term was needed as the target's atomic numbers and mean excitation energies were taken as effective values. Based on the stopping power curve at the energies less than 1 MeV, it is very important that this method used gives reasonable results. The scattering peaks of these elements were obtained by corresponding the entire spectrum with the SIMNRA program since the scattering peaks of the elements constituting CZTS film were not visible. Therefore, it is worth noting that the method used is actually quasi-experimental rather than experimental. Even if the results are calculated by iteration, they have certain margins of error because they have been obtained directly by simulation instead of experimental. However, the results obtained may be applied to the conditions affecting the efficiency of the thin films used as solar cells as a result of exposure to radiation. In order to expand the study, CZTS thin film should be produced directly on the substrate and the corresponding peaks should be observed directly then the calculations should be done on this process. Also, the channeling effects were neglected in this study because the angle between the surface normal of target and the incoming beam was zero degrees. Therefore, to avoid these channeling effects, the incident beam should make a certain angle with the normal of the surface. In addition, to review the results with the dielectric theory and to use different orbital wave functions for the electronic charge density will carry the study to a different dimension.

4. Conclusion

In this paper, CZTS thin film structures used as solar cell were fabricated by means of sol-gel method and then RBS spectrum was gained by irradiating these films with protons in microbeam chamber. In the RBS spectrum of the thin film produced, a method for the calculation of energy loss was used for the position and energy width analysis of the respective peaks and a polynomial fit was determined for the stopping power of the CZTS thin film by making specific approaches. In addition, the effective charge approach that we used in our preceding studies for the stopping power was first discussed with atomic natural orbitals and it was perceived that the results were close to each other at certain error rates. The data obtained from this study will inspire the future studies on the interaction of radiation with matter.

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