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Quantitative Analysis for RBS and PIXE Spectra of Thin Cu_2ZnSnS_4 (CZTS) Films

Metin USTA*[1]

[1]*Hatay Mustafa Kemal Üniversitesi, Fen Edebiyat Fakültesi, Fizik Bölümü, 31060, Hatay, Türkiye*

**corresponding author e-mail: musta@mku.edu.tr*

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Abstract: The objective of this work is to introduce a different technique to existing studies that determine the stoichiometric ratios of thin CZTS structures. To this end, the CZTS targets were propagated by sol-gel process and later RBS and PIXE spectra were achieved by irradiating these samples with protons of 3.034 MeV energy into microbeam chamber. RBS spectrum was taken with RBS detector and PIXE spectra were collected with IGe and SDD detectors. As energy calibration was performed to these spectra and the RBS spectrum was fixed with the SIMNRA simulation program and the PIXE spectra adjusted with the Gaussian function. In the RBS spectrum, quantitative analysis measurements could not be performed due to the presence of Mo peak, which supplies electrical conductivity, while PIXE spectra results close to expected values. For this, least squares regression method were carried out PIXE spectra for the reference material, and the analytical elemental amount ratios for CZTS were specified with the calibration coefficients found. It was observed that the results acquired with the SDD detector were convenient with the required values, except sulfur content. This technique is a fast and simple method that can be employed analytically to help improve the accuracy of the existing methods in the literature that used to determine the constituent quantities and the depth analysis of thin films. However, this method should be compared with inverse least squares model or eigenvector quantitative analysis methods.

***Key words**:* RBS, PIXE, CZTS thin film, Proton

İnce Cu_2ZnSnS_4 (CZTS) Filmlerin RBS ve PIXE Spektrumları için Nicel Analiz

Özet: Bu çalışmanın amacı, ince CZTS yapılarının stokiyometrik oranlarını belirleyen mevcut çalışmalara farklı bir teknik sunmaktır. Bu amaçla, CZTS hedefleri sol-jel yöntemi ile üretilmiş ve daha sonra bu numuneleri 3.034 MeV enerjili protonlarla mikro ışın odasında ışınlayarak RBS ve PIXE spektrumları elde edilmiştir. RBS spektrumu RBS detektörü ile ve PIXE spektrumları ise IGe ve SDD detektörleri ile alınmıştır. Bu spektrumlara enerji kalibrasyonu yapılarak, RBS spektrumu SIMNRA simülasyon programı ile ve PIXE spektrumları Gauss fonksiyonu ile fit edildi. PIXE spektrum sonuçları beklenen değerlere yakın çıkarken RBS spektrumunda elektriksel iletkenliği sağlayan Mo pikinin varlığından dolayı kantitatif analiz ölçümleri yapılamadı. Bunun için PIXE spektrumlarına en küçük kareler regresyon yöntemi referans malzeme için uygulanmış ve bulunan kalibrasyon katsayıları ile CZTS için analitik temel miktar oranları belirlenmiştir. SDD dedektörü ile elde edilen sonuçların kükürt içeriği dışında istenen değerlere uygun olduğu görülmüştür. Bu teknik, ince filmlerin bileşen miktarlarını ve derinlik analizini belirlemek için kullanılan literatürdeki mevcut yöntemlerin doğruluğunu iyileştirmeye yardımcı olmak için analitik olarak kullanılabilen hızlı ve basit bir yöntemdir. Ancak bu yöntem, ters en küçük kareler modeli veya özvektör nicel analiz yöntemleriyle karşılaştırılmalıdır.

Metin USTA, musta@mku.edu.tr, ORCID: https://orcid.org/0000-0002-7896-397X

Anahtar kelimeler: RBS, PIXE, CZTS ince film, Proton

1. Introduction

Today, it is extremely important to use and develop alternative energy sources against existing fossil fuel consumption in order to prevent global warming and environmental pollution in energy production. Having an important place among these alternative energy sources, solar energy is the best alternative, renewable and environmentally friendly solar energy that can meet the energy needs of modern society. Solar cells, which operate on the photovoltaic principle and convert solar energy into electrical energy, need to be cost-effective, clean and have high energy efficiency in order to expand the usage area [1, 2].

Because the phase formation of CZTS thin films is complex, it is difficult to control with the large number of possible binary and triple phases generated during magnification. So, it is not easy to control the stoichiometric ratios of these films because of the high vapor pressure and low cohesion coefficients of the sulfur, zinc and tin elements, which form CZTS thin films. Although an efficiency close to 10% has been achieved with CZTS-based solar cells so far, the increase in the number of elements that make up this structure can lead to some lattice defects that are difficult to control in this complex compound. These defects have significant effects on the conduction and valence band of the semiconductor. Therefore, non-stoichiometric composition control is of great importance in CZTS structures. In addition, when used as a solar cell, fast, simple, and convenient methods are needed that will contribute to methods that accurately calculate these ratios in order to improve the performance and achieve to high efficiency of these films. Although there have been some studies on the elemental concentration of CZTS thin films to date [3-7], the quantitative analysis methods used to determine the stoichiometric ratios of these films are not at sufficient level.

The goal of this work is to offer a present technique to available studies that defines the stoichiometric ratios of thin CZTS films. So, CZTS films were firstly fabricated by sol-gel procedure and afterwards RBS and PIXE spectra were acquired by irradiating these samples with proton beams in microbeam chamber. RBS spectrum was obtained with RBS detector and PIXE spectra with IGe and SDD detectors. The energy calibration was implemented to these spectra, and the RBS spectrum was adjusted with the SIMNRA program and the PIXE spectra fixed with the Gaussian function. 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 constituent quantities and depth analysis of thin films.

2. Material and Method

2.1 Fabrication of CZTS structures and irradiation process

The CZTS structures were generated with sol-gel spin coating procedure. CZTS solutions were prepared by dissolving copper (II) acetate monohydrate (0.3M, 98%+), zinc (II) acetate dihydrate (0.3M, 99.99%), tin (II) chloride (0.3M, 98%+ from Sigma Aldrich) and thiourea (1.2M, 99.0%+ from Sigma Aldrich) to 2-methoxyethanol (20 ml, 99.8% from Sigma Aldrich). The final solutions were mixed for 1 hour at 45 °C, 850 rpm to completely dissolve the metal compounds. During mixing, 2 ml diethanolamine (DEA) was gradually introduced into each solution as stabilizer. Quartz-glass slides were used from substrates individually ultrasonically wiped with detergent, nitric acid (1:4), acetone and ethanol for 10 minutes. To manufacture CZTS films, the prepared solutions were spin coated onto quartz and n-type silicon substrates for 30 seconds at 3000 rpm while solvent drying at 175 °C for 10 minutes on a hot plate. Finally, the samples were tempered for 2 hours at 500 °C in a quartz tube containing 10 g of elemental sulfur. See [8] for details.

Table 1. Mass fraction and coverage factor values for SRM 1107 Naval Brass B

Elements	Mass Fraction (%)	Coverage Factor (k)
Copper (Cu)	61.18300	1.98
Zinc (Zn)	37.39600	1.96
Lead (Pb)	0.18500	1.97
Iron (Fe)	0.00389	1.99
Tin (Sn)	1.06600	1.98
Nickel (Ni)	0.09460	1.99
Aluminum (Al)	0.08300	2.00

Irradiation experiments were conducted at the Jožef Stefan Institute Tandetron accelerator facility. For energy calibration, CZTS and NIST 1107 naval brass targets irradiated with protons with 3.034 MeV energy. Because naval brass includes most of the elements constituent CZTS film, the NIST 1107 naval brass example, which Table 1 indicates its composition, was employed [9] as reference material. Simultaneously, two X-ray spectra were taken with a SDD and IGe detectors, a RBS signal from the chopper and RBS spectrum was acquired. The diameter of the incident proton beam is 30 micrometers and it was scanned over area of 500x500 micrometers. To obtain the number of input protons, the chopper signal was taken into account and the calibration constant was determined from the measurements of NIST 1107. See [8] for details.

2.2 Energy calibration

In RBS analysis, the energy of the particles scattered from known surface elements can be calculated with the necessary correlation. Hence, one can use a standard sample for energy calibration, which comprises at least two elements on its surface. From the position of the surface peaks or steps and the corresponding energy values, the calibration coefficients are evaluated through linear regression. In order to get a reasonable energy calibration, we measured a reference sample with known compositions and then performed an energy calibration by using the high-energy edges of several elements as reference points. Naval brass 1107 contains a single disk approximately 3.2 cm diameter and 1.9 cm thick and analyzed depth in RBS method for protons is about 20.

Table 2. The number of channels corresponding to the energy of the scattered protons

Elements	Energy of the detected particle (keV)	Channel
Cu	2874.07	797.50
Zn	2878.48	800.00
Pb	2984.03	858.50
Fe	2852.69	787.00
Sn	2947.32	837.00
Ni	2861.23	793.00
Al	2640.56	669.00

So, the energy of the particles scattered from the elements forming the naval brass sample can be calculated by the following:

$$E = E_0 \left[\frac{\sqrt{M_2^2 - M_1^2 \sin^2\theta} + M_1 \cos\theta}{M_1 + M_2} \right]^2 \tag{1}$$

Where M_1 is the mass of the incident protons, M_2 is the mass of the target nuclei, E_0 is the initial energy of incoming protons and θ is the scattering angle. The calculated values are shown in Table 2. Then, as shown in RBS spectrum of naval brass in Figure 1, for each element, the number of channels corresponding to the energy of the scattered protons were determined.

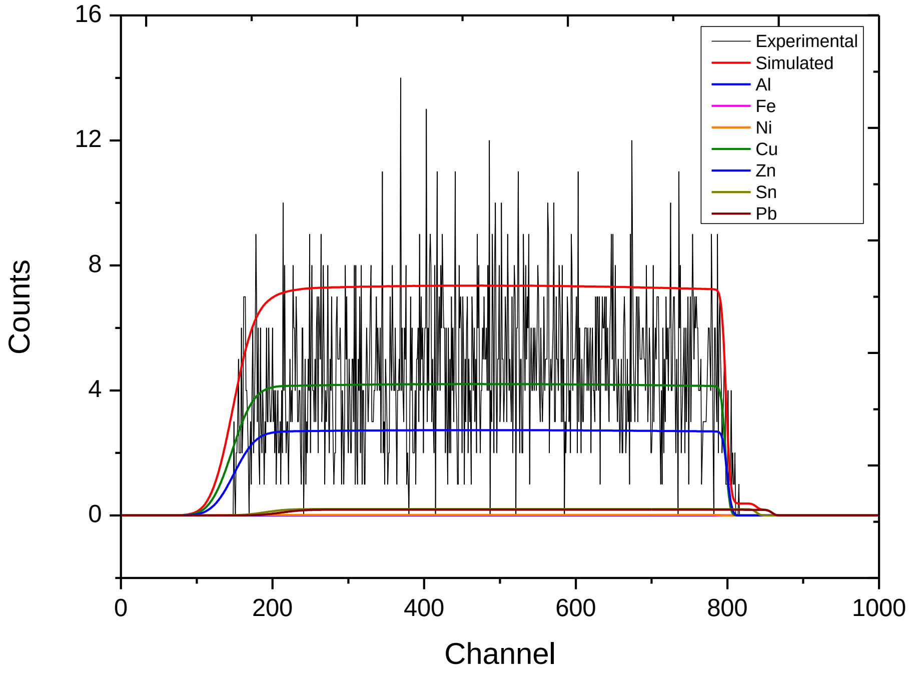


Figure 1. RBS spectrum of the thick naval brass

From the position of the surface peaks and the corresponding energy values in Table 2, the calibration coefficients were calculated with the linear regression relation in Equation 2:

$$E = m.ch + n \tag{2}$$

Here ch is the channel number, m is the energy per channel (keV/ch) and n is the calibration offset (keV). Linear regression curve is displayed in Figure 2. Above parameters are required for the evaluation of the spectrum or for fitting a theoretical spectrum to the experimental one. Thus, from Equation 2, for m and n, 1.8177 and 1423.52 values were obtained, respectively.

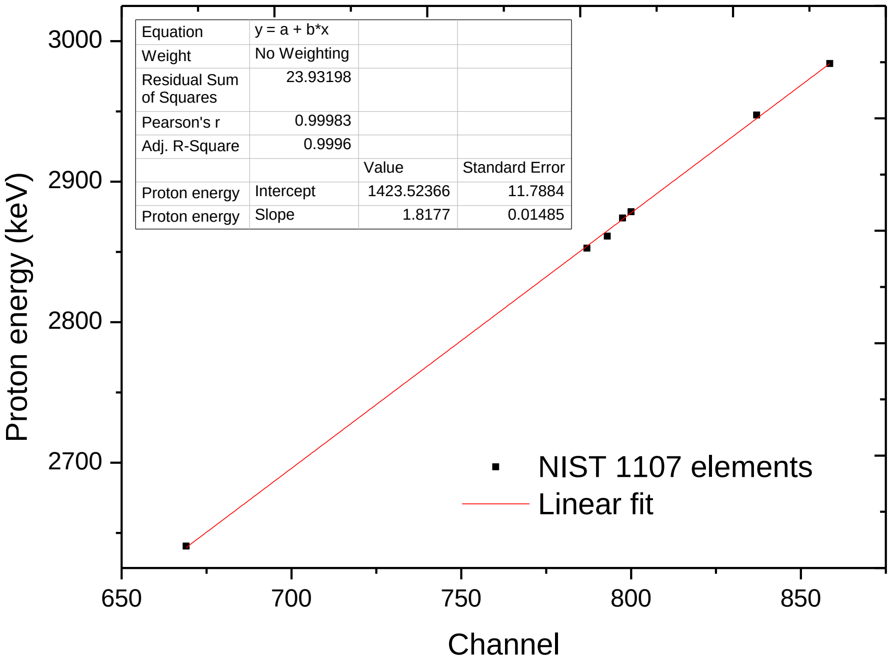


Figure 2. Linear regression curve for NIST 1107 elements

The area under the main peak in RBS spectrum just surveys the dose quantitative measurements because the abnormally high yield of backscattering from each element in sample stems from an elastic nuclear resonance. Since no collected charge measurements were made with the Faraday cup, the beam intensity of RBS signal from a gold foil, which has about 442 nm, was assigned with the help of a chopper intersecting beams before the microbeam chamber. Then, the proportional constant between the RBS areas and the charge according to the measurements on standards were calculated. So, the area under the peak of thin gold foil was defined with the peak analysis method. First of all, the peak of gold foil was fitted with Gaussian peak function for naval brass. The total number of detected particles can be written as follows [10]:

$$A = \Omega Q N_t \frac{\sigma\left(E_0,\theta\right)}{\cos\alpha} \tag{3}$$

Where Ω is the solid angle of detector, Q is the total number of the incident protons, N_t is the number of target atoms per unit area, $\sigma\left(E_0,\theta\right)$ scattering cross section, α is the angle of the incoming protons. Later, form peak analysis processes, value of A was calculated from the integrated counts in the region of interests in Figure 3 (a).

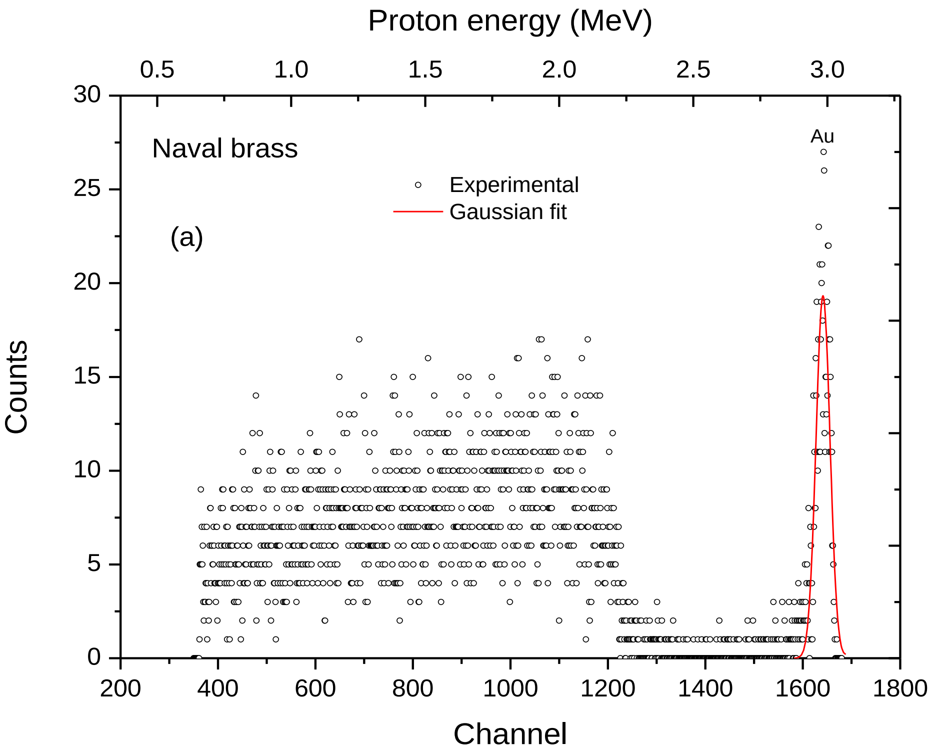


Figure 3 (a). The beam intensity of thin gold foil from quantitative measurements for naval brass sample

Thus situated, the background correction is nearly negligible. Accordingly the A value was found as 696.7 units. Also, $\sigma\left(E_0,\theta\right)$ can be determined from Rutherford scattering cross section. From this relation, σ was obtained 1.199 b value. Since N_t is 2.6082e18 for thin gold foil and the solid angle of detector, Ω, is 4.59e-3, total number of incident particles, Q, was calculated as 4.854e10 protons. According to Figure 3 (b), for CZTS thin films, From Equation 3, the A value was discovered as 6083.47 units. As N_t and Ω are given above, the number of incident protons, Q, was estimated as 4.238e11.

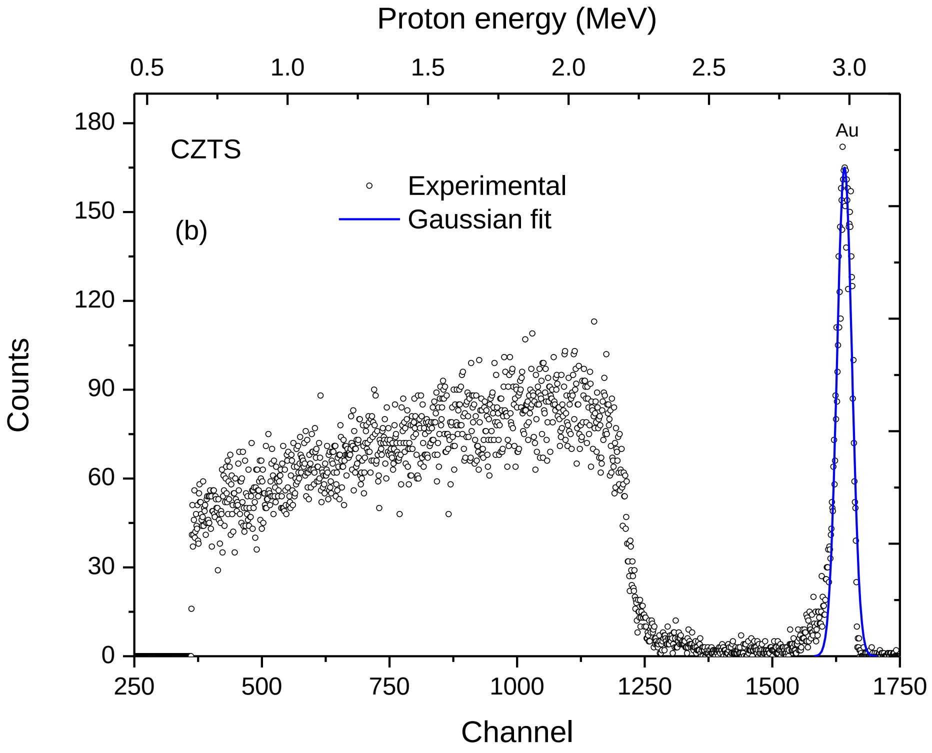


Figure 3 (b). The beam intensity of thin gold foil from quantitative measurements for CZTS sample

3. Results

3.1 RBS spectrum

The RBS spectrum simulated with SIMNRA [11] is shown in Figure 4 [8]. The RBS spectrum was obtained by entering the previously calculated calibration values and the necessary initial parameters into the SIMNRA simulation program. The stoichiometric ratios of O and Si elements containing Cu, Zn, Sn and S elements forming CZTS thin film, Mo element providing conductivity and the base materials were added to this program. Correction factors for the roughness and stopping power of the substrate were not taken into account. Instead, the Chi2 channel evaluation option was chosen as the fit parameter for the roughness of each layer, and the fit values were calculated with a maximum of 50 iterations and an accuracy of 0.01. Rutherford cross sections were used to backscatter the bullets in the internal file of the SIMNRA program.

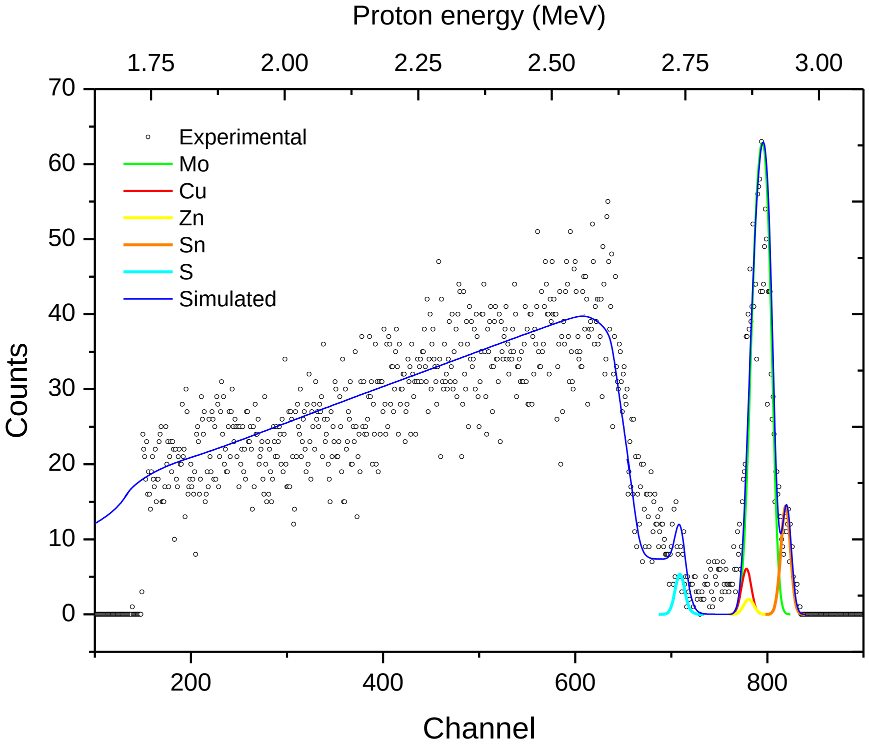


Figure 4. The RBS spectrum of the CZTS thin film

In Figure 4, 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 varied depending on the concentration in the film and 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 the thickness, and the elements including the CZTS were not clearly visible. Especially, the peaks of the Cu and Zn elements overlapped because of their atomic numbers were very close together, but still remained dimmed alongside the Mo peak. On the contrary, the Sn peak appears a little more pronounced since the RBS analysis is very sensitive to heavy elements.

The RBS method is a technique widely used for the analysis of the elemental composition and depth profile of individual elements in layers near the surface of the solids without any calibration process. In this method, the area under each peak is directly proportional to the concentration of the elements. When the RBS spectrum of the CZTS sample was investigated, the Mo and Cu, Zn, Sn peaks were overlapped due to the position of the Mo peak, and the distinctive peaks of the elements concerning the film have not been revealed. Therefore, this method does not allow to determine the depth profile and elemental concentration of the CZTS thin film. RBS is very sensitive to heavy elements, but its mass resolution decreases with it. In order to carry out the quantitative analysis by the RBS method on the CSTZ sample, the elements with lower atomic number should be preferred instead of Mo which used to provide electrical conductivity between the layers in the film.

3.2 PIXE spectra

Figures 5-6 demonstrate that the PIXE spectra of the CZTS thin film and the naval brass thick sample were fitted with the Gaussian peak function. Because, in an ideal X-ray analysis, a monoenergetic X-ray produces a pure Gaussian line shape in the spectrum. In peak analysis, user defined baseline mode is handled, which included Adjacent-

Averaging smoothing method with a window size of 1 and a threshold of 0.05 and no weight function was made use of during this process. It can be said that the fitting is provided in a very harmonious manner with the peaks related to the atomic transitions. When compared with the experimental data, the error rates of peak functions vary between 5-10% for amplitude and 0.1-0.9% for other parameters. Since the PIXE method is not sensitive to O, no O peak is observed in all PIXE spectra.

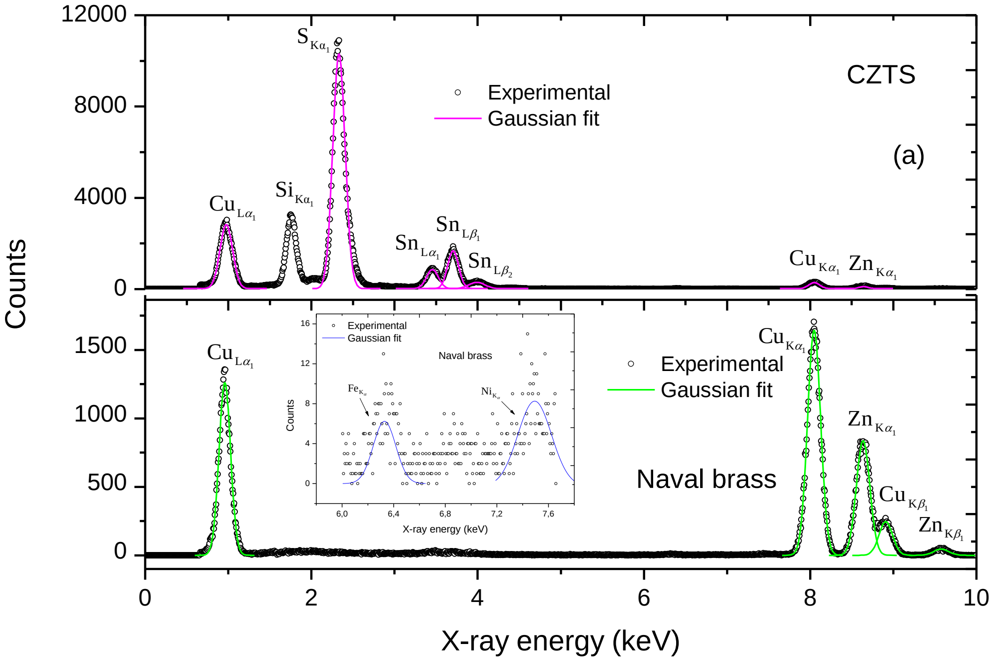


Figure 5 (a). PIXE spectrum taken from IGe detector

Figure 5 (a) displays the PIXE spectrum taken with the IGe detector. K and L X-ray lines of Cu and Zn, which are common elements of CZTS and naval brass targets, have emerged. As can be seen, the X-ray line intensities of these elements are distributed according to their stoichiometric ratios. In particular, the K X-ray lines of S are significantly increased. However, the Kα and Kβ line intensities of Cu and Zn were lower in the CZTS target than the naval brass. It is also noteworthy that the L X-ray line intensities of Sn are considerably augmented with respect to Cu and Zn. This feature is related to the cross section as mentioned above. Because the substrate material is made of quartz material containing O and Si, only X-ray lines of Si have appeared about this.

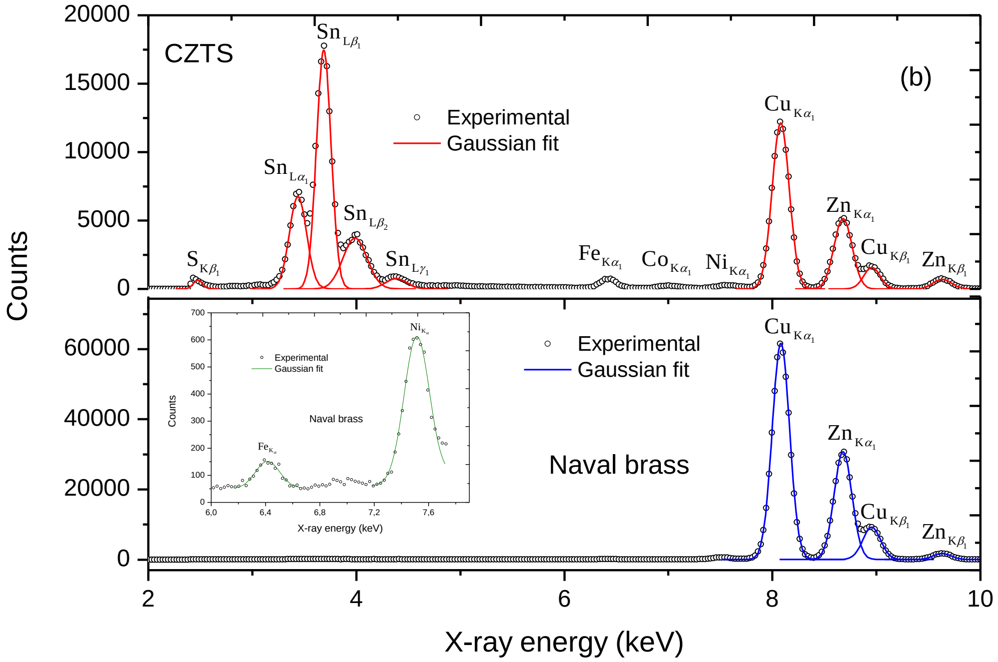


Figure 5 (b). PIXE spectrum taken from SDD detector

Figures 5 (b) and 6 show the PIXE spectrum received with the SDD detector. In the spectrum, X-ray lines of all the elements belonging to CZTS appeared, and the lines of the Sn element were taken over (even Lγ). Particularly, the intensities of Kα and Kβ lines concerning to Cu and Zn have come quite clearly out, in contrast to the spectrum obtained with IGe. Furthermore, X-ray lines of Fe, Co and Ni elements were observed due to the surface contamination of the substrate material or the impurities in the solutions used. The line intensities of these elements are quite small and do not affect the stoichiometric ratio of the CZTS thin film. The spectrum also indicates K X-ray lines of the Mo element used for electrical conductivity between the substrate material and the thin film. Although the Mo layer is between the substrate and the CZTS, the X-ray line intensities of Mo are higher than the Sn. Thus, it is demonstrating that there is more Mo in the produced sample according to the thin film.

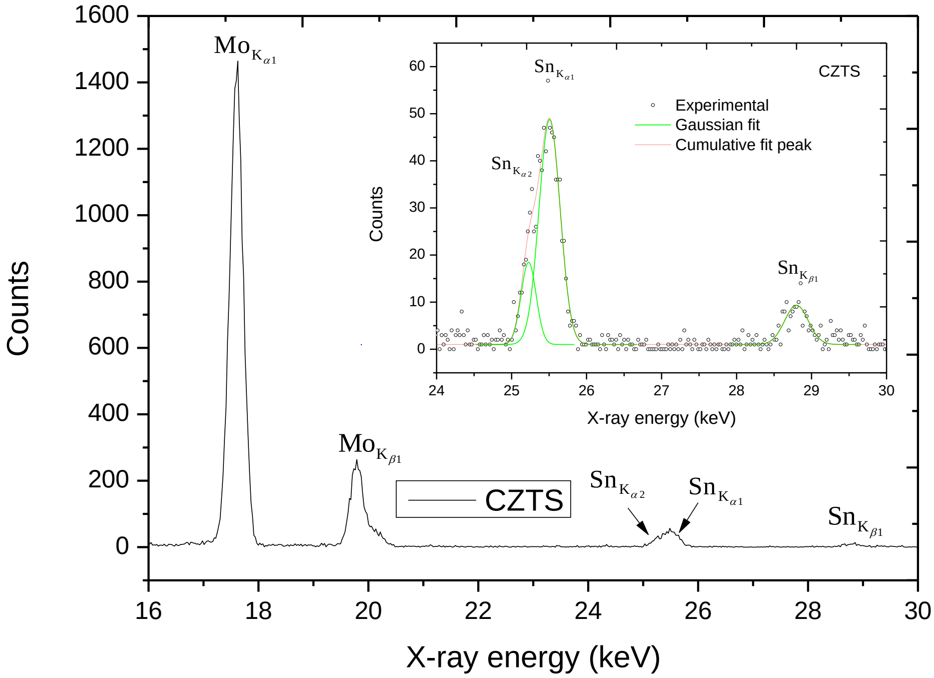
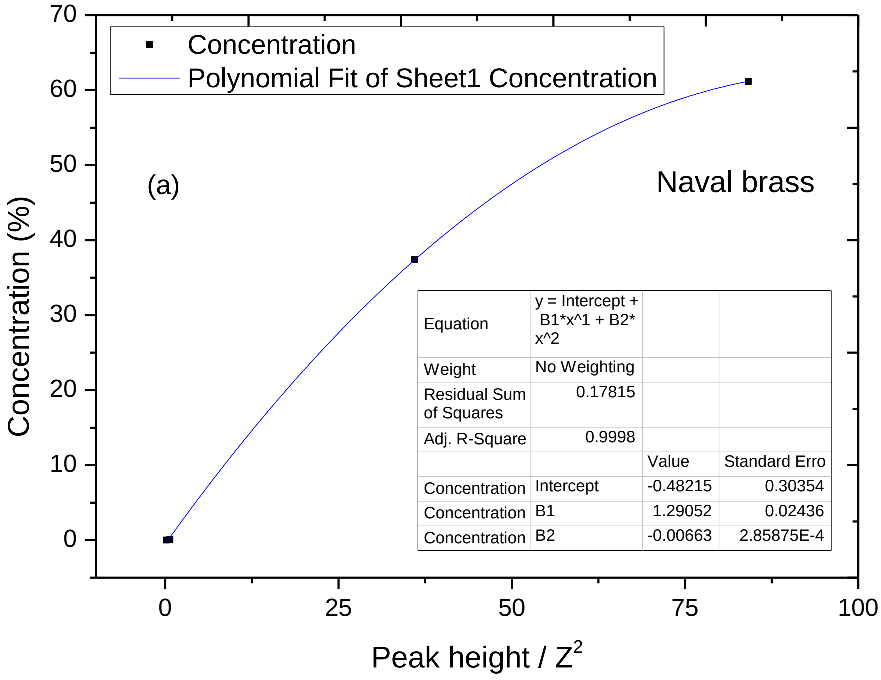


Figure 6. PIXE spectrum of molybdenum and tin elements taken from SDD detector

In this study, we tried to find the concentrations of elements in content of the CZTS film from the quantitative analysis of the obtained PIXE spectra. As is known, in the quantitative analysis of the PIXE spectra, an attempt is made to establish a correlation between the dependent variable (concentration) and the independent variables (peak height, field, etc.) including the calibration equations. To this end, the least squares regression method was used in that the height of the selected peaks in the PIXE spectrum of the naval brass was assumed to be proportional to the constituent quantities with a second-order polynomial. For the work of the model, the peaks of each element should not be overlapped on the sample. According to this model, the equation corresponding to the selected variables can be written as:

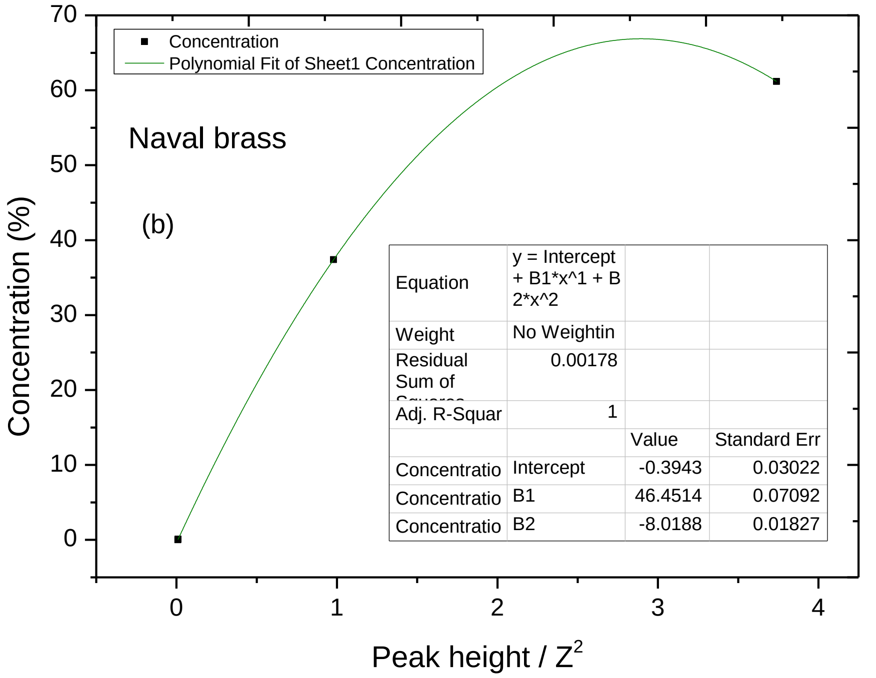
$$C = B_2(Height)^2 + B_1(Height) + B_0 \tag{4}$$

Where C is the elemental concentration, and B's are the calibration coefficients. Figures 7 (a) and (b) show the peak height/Z^2 curve against concentration of naval brass sample for SDD and IGe detectors. For the height values in the equation, the maximum height data of the Gaussian fit values including the K and L X-ray lines of each element in these Figures were used. When the calibration equation was applied for CZTS, the elemental concentrations in the film for SDD detector were found to be 20.63%, 7.88, 14.34, and 2.75 for Cu, Zn, Sn, and S, respectively. These values should be partly close to the constituent quantities, which should be of 25, 12.5, 12.5 and 50, except S value. However, these rates for the IGe detector were quite high for other elements, except for the consistent value of 10.5% for Zn.



Equation	y = Intercept + B1*x^1 + B2*x^2		
Weight	No Weighting		
Residual Sum of Squares	0.17815		
Adj. R-Square	0.9998		
		Value	Standard Erro
Concentration	Intercept	-0.48215	0.30354
Concentration	B1	1.29052	0.02436
Concentration	B2	-0.00663	2.85875E-4

Figure 7 (a). Peak height/Z^2 curve against concentration of naval brass sample for SDD detector



Equation	y = Intercept + B1*x^1 + B 2*x^2		
Weight	No Weightin		
Residual Sum of	0.00178		
Adj. R-Squar	1		
		Value	Standard Err
Concentratio	Intercept	-0.3943	0.03022
Concentratio	B1	46.4514	0.07092
Concentratio	B2	-8.0188	0.01827

Figure 7 (b). Peak height/Z^2 curve against concentration of naval brass sample for IGe detector

In order to validate the calibration equation in the least squares regression model, it is necessary to identify isolated peaks with respect to the constituent elements and not to overlap these peaks. This model is used for simple samples, pure compounds and binary mixtures, although it is easy to understand and its calculations are very fast. However, this method cannot be employed for complex samples where the spectral bands of individual constituent overlap. It may also contain selected polynomial error rates because the spectroscopic system can be solved with simple straight lines that are faulty. When the obtained PIXE peaks are analyzed, it is seen that the peaks of Cu_{K_α} and Zn_{K_β} for both samples and the peaks of Sn for CZTS overlap. Significant differences in elemental concentration are due to the overlapping of spectral bands, the impurities in CZTS and uncertainties in the calculation of Gaussian fit function. In a more realistic quantitative analysis of the PIXE spectrum, it is possible to obtain more reasonable results with computer codes such as Gupix [12], Geopixe [13], etc., which use the intensity-concentration relationship considering to the atomic sensitivity factor. The results obtained by the presented method compared with the data received with these codes.

4. Conclusion and Comment

In this study, thin CZTS samples were generated via sol-gel procedure and later RBS and PIXE spectra were obtained by irradiating these targets with protons into microbeam chamber. To concentration analysis on this film, it is possible with PIXE spectra instead of RBS spectrum. Thus, the least squares regression method was applied to the PIXE spectra and the results close to the required values were acquired. Analytical method used in this study, will help to improve the accuracy of the existing techniques which used to calculate the constituent quantities of thin films and to perform depth profile. Although the method is analytically fast, simple and useful, it needs to be improved. For this reason, this method should be checked against inverse least squares model or eigenvector quantitative analysis methods.

Author Statement

Metin Usta: Methodology, Software, Formal Analysis, Investigation, Resource/Material Supply, Original Draft Writing, Review and Editing.

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Conflict of Interest

As the authors of this study, we declare that we do not have any conflict of interest statement.

Ethics Committee Approval and Informed Consent

As the authors of this study, we declare that we do not have any ethics committee approval and/or informed consent statement.

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