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The Effect of Addition of ZnO to Granite Body on Sintering and Mechanical Properties

Savaş Elmas[1*]

[1]Ceramic and Glass Department, Fine Arts Faculty, Çanakkale Onsekiz Mart University, Çanakkale, Turkey
[*]savaselmas@comu.edu.tr
*Orcid: 0000-0003-2913-0303

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Abstract

In granite body, 1-3-5 wt% ZnO was replaced instead of feldspar and fired in an industrial continuous production kiln. Physical properties of the tiles were determined including dried strength, fired strength, water absorption, fired loss, and colorimeter values. X-Ray Diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-Ray (EDX) measurements for distinctive microstructural changes and phases formed were done. The fired strength values of the standard and 3% ZnO added body are 400 kg/cm^2, 511 kg /cm^2, respectively. Water absorption and firing shrinkage values are close to each other. In the analysis of the sample with 3% added ZnO with XRD, it was observed that the solubility of quartz was increased, mullite formation was prevented; besides 27.4 wt.% spinel phase and 13.8 wt.% albite formation was observed.

Keywords: Ceramics, characteristics, microstructure, porcelain stoneware (granite tile), sintering, ZnO

1. Introduction

In the competitive conditions increasing with globalization, efficiency and exceeding customer expectations force companies to obtain products with superior features. In ceramic production, granite tile has been in demand in recent years with its superior properties. Turkey's share in the world total in 2018 was 2.6 % with 335 million m^2[1].

Many studies have been done in the literature on the production of porcelain stoneware [2-5]. Ceramic bodies consist of 3 basic raw materials. Clay gives properties such as workability, green strength, body color, rheology. Feldspars affect the solubility, the amount of the glassy phase, the viscosity and the formation temperature of the glassy phase. Quartz, with its inert structure, prevents the body from cracking during drying and deformation during firing [6-7]. The microstructure, which determines the properties of the material, includes the amount, shape and distribution of phases and pores. At the same time, the composition of the glassy phase formed, its homogeneity and the structural stress between different phases affects the properties [8]. Body undergoes some changes with its body firing. The removal of residual moisture below 200 °C, the removal of organics at 200-650 °C, conversion of kaolin into metakaolin at 450-600 °C, 500-600 °C quartz transformation, the initiation of reactions between 900-1000 °C silica and alumina, > 1000 °C eutectic formation and partial melting begins [9-11]. Liquid content increases after 1200 °C as a result of the increase in quartz solubility. Small mullite (primary) and γ-alumina crystals are formed between the degraded clay particles, while secondary mullite crystals are formed between the clay and feldspar [12].
Some oxides have been studied in the literature in the form of dopant to the vitrified body. In a study conducted by Bhattacharyya and Snehesh [13] on the subject, it was observed that the addition of Cr_2O_3 to the porcelain body in the range of 0-4 wt.%, negatively affected the structural properties. In the same study, it was observed that the addition of 1-5 wt.% NiO, improved physical and mechanical properties at 1200 °C. Beside the mullite, nickel aluminate spinel phase was formed. It was observed that the addition of NiO also affected mullite morphology. With the addition of 5 wt.% NiO, maximum shrinkage, minimum porosity, high bulk density and maximum fired strength were observed at 1200 °C. In another study conducted by Bhattacharyya and Snehesh [14] on the subject, it was observed that 1-5 wt% CoO was added and gave positive results in physical and mechanical properties as

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a result of firing at 1100-1200 °C. Feldspar's solubility and mullitization were increased with the addition of CoO. The addition of 1 wt.% CoO has given the body optimum fired properties at low temperatures. In a study by Bhattacharya, Das and Mıtra [15], TiO_2 was added to the porcelain body in the range of 3-6-9 wt.% and fired at 1200-1250-1300-1350-1400 °C. It was observed that excess liquid phase was formed at temperatures above 1300 °C and as a result, swelling occurred in the product. At 1300 °C, negligible porosity and maximum strength value of 45 MPa were observed. It was determined that with increasing TiO_2 amount, quartz amount decreased, mullite and liquid phase amount increased. After the 6 wt.% TiO_2 increase, no significant property change appears. In a study about the addition of ZnO to porcelain body (Chaudri 1974; transmited Bhattacharyya,Das and Mitra, 2005) it was observed that with the addition of 4% ZnO to the porcelain body, a minimum of mullite was formed[16]. In a study conducted by Iya, Noh, Razak, Sharip and Kutty [17], it was observed that the addition of 5 wt.% Fe_2O_3 at 1150 °C increased mullitization and the amount of liquid phase. Maximum strength value, bulk density and hardness values were reached to 138.94 MPa, 2.515 g / cm^3, 829 HV, respectively. It has been observed that the maturing temperature is 100-120 °C lower than the standard body. The addition of Fe_2O_3 inside the porcelain body instead of quartz, the chemical analyzes of standard and Fe_2O_3 added bodies are respectively, 46.5% quartz, 35.4% aluminosilicate, 5.1% calcium, 13.1% sulfuric acid and 42% quartz, 32% mullite, 21% anorthite, 5% iron. The peaks are more precise with the addition of Fe_2O_3. By the help of the presence and interaction of anorthite and mullite crystals, bulk density and strength increased. This effect is evident especially with the addition of 5% Fe_2O_3. In a study by Tulyaganov, Agathopoulos, Fernandes and Ferreria [18] Li_2CO_3 was added to the porcelain structure at increasing rates of 1-7 wt.%. Positive results were achieved when Li_2O does not exceed 1.5 wt.%. In a study by Chaudhuri and Sarkar [19], mullite formation increased in the porcelain body where V_2O_5 and Nb_2O_5 additions were 3% and 2%, respectively; It has been found that they are effective nucleators for crystal formation. At the same time, while the amount of cristobalite was almost 0 % among other samples, it was found to be as high as 24.8% in only 2% Nb_2O_5 added body. In another study [20], $FeO_{1.5}$, CoO and NiO were added and the order of reducing viscosity was seen as $FeO_{1.5}$> CoO> NiO.

In this study, the addition of ZnO to the granite body was made as 1-3-5 wt.% and firing shrinkage, water absorption, fired strength, dried strength, fired losses were determined. In addition, crystalline phases after firing were detected by X-ray analysis (XRD); surface morphology, microstructure, phase and elemental analysis were investigated using energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM).

2. Materials and Methods

The addition of ZnO instead of sodium feldspar in the prepared industrial body was made as 1-3-5 wt. %. The materials were prepared in the proportions specified in the recipe and at a density of 1650gr / lt, >63 microns residue with 3.6 %. After being kept in the dryer for 8-10 hours at 110 °C, water was added to the powder with a spray to obtain granules with a moisture value of 5-6%, then these granules were pressed to 300 kg / cm^2.Firing was carried out in an industrial continuous kiln at 1180-1185 °C in 63 minutes. Dwelling timey at the maximum temperature is 3 minutes. Chemical analysis of the raw materials used are shown in Table 1, and the prescriptions prepared are shown in Table 2. The strength measurement was made in a 3-point gabrielli brand strength device according to equation (Eq. 2.1).

$$S= \frac{30 \cdot P}{L \cdot h^2} \qquad \textbf{(2.1)}$$

formula is used for strength (kg / cm^2).
S: the breaking strength (kg/cm^2)
P: the load breaking the tile (kg / cm^2)
L: the width of the tile (cm) and
h : the thickness of the tile (cm)

In the water absorption process is used equation (Eq. 2.2) below:

$$\text{water absorbtion (\%)} = \frac{(w_2 - w_1)}{w_1} \cdot 100 \qquad \textbf{(2.2)}$$

W_1 : dry weight
W_2: water absorbed weight (sample was kept in boiling water for 2 hours to cool, then it was wiped with a damp cloth then weighed).
XRD measurements were made by XRD Pan Analytic Empeyron Series 45kV, K alpha. Microstructure photos were measured by SEM-JEOL- JSM -7100 F. EDX measurements were made in Oxford Instruments x-max quorum 1mbar / Pa, 10mA, Au / Pa (80/20%) coating.
Color measurement was made on the Minolta CR 300 instrument. Color difference measurement is made with equation (Eq. 2.3).

$$\Delta E=\sqrt{(L2 - L1)^2 + (a2 - a1)^2 + (b2 - b1)^2} \qquad \textbf{(2.3)}$$

ΔE: criterion for detecting color difference
L: lightness value
a: redness value
b: yellowness value

ZnO from Tekkim Kimya extra pure grade is used.

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Table 1. Chemical analysis of used raw materials.

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	ZnO	F.L.
Kaolin	52	34.05	0.80	0.30	0.15	0.30	0.15	1.30	-	12
Albite	69	19.6	0.017	0.04	0.95	0.11	10.30	0.23	-	0.12
Quartz sand	91	7	0.8	0.3	0.02	0.02		0.76	-	0.1
Clay	54	31.05	0.67	1.17	0.3	0.45	0.13	2.3	-	10.05
ZnO	-	-	-	-	-	-	-	-	99.6	0.1

F.L: Fired loss

Table 2. Used recipes.

Recipes	**1**	**2**	**3**	**4**
Kaolin	25	25	25	25
Albite	30	29	27	25
Quartz sand	5	5	5	5
Clay	40	40	40	40
ZnO	-	1	3	5

3. Results and Discussion

3.1. Physical Measurements

The firing shrinkage increased up to 3 % ZnO addition, then decreased. In a study on the subject, it was found that the sintering degree increased with early sintering and consequently firing shrinkage and strength increased [21]. There is an increase up to 3 % ZnO addition in parallel with the increased sintering and firing shrinkage in the fired loss value. While the maximum value of the fired strength value was 400 kg/cm^2 in the standard body, it increased to 511 kg / cm^2 in the body with added 3 % ZnO. The water absorption value also showed a value close to the standard (0.05%) as 0.06% in the addition of 3% ZnO.

Table 3. Pysical characteristics of bodies.

Recipes	**1**	**2**	**3**	**4**
Fired Shrinkage (%)	6.45	7.75	8.45	7.80
Fired Lost (%)	3.9	4.9	5	4.1
Dried Strength (kg/cm^2)	16.0	14.2	14.9	16.7
Fired Strength (kg/cm^2)	400	498	511	471
Water Absorpsition %)	0.05	0.13	0.06	0.05

Table 4. Aritmetic mean, variance and standard deviation of measurements

	μ	**σ^2**	**σ**
Viscosity (sn)	57	191.3	13.83
Fired Shrinkage (%)	7.61	0.70	0.83
Fired Lost (%)	4.47	0.31	0.55
Dry Strength (kg/cm^2)	15.45	1.24	1.11
Fired Strength (kg/cm^2)	470	2455	49
Water Absorbtion (%)	0.07	0.001	0.04

μ= aritmetic mean,σ2=variance, σ = standard deviation

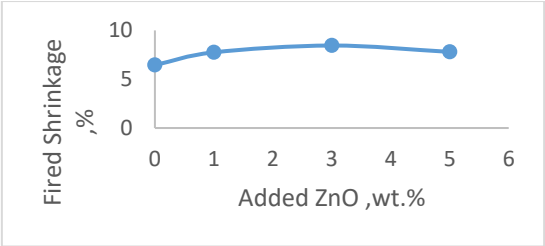

Figure 1. F. shrinkage % - added ZnO wt.% graphic.

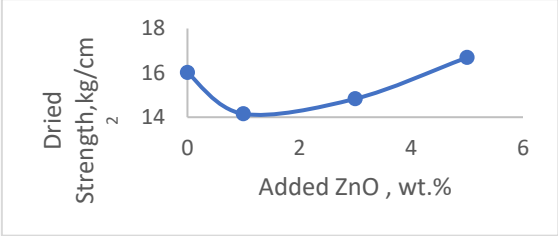

Figure 2. Dried strength- added ZnO wt.% graphic.

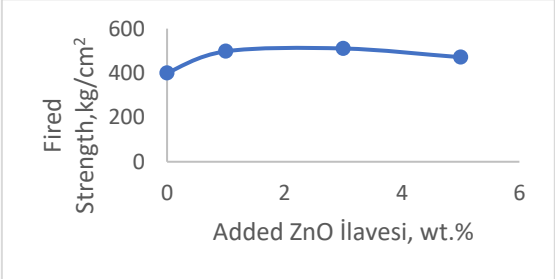

Figure 3. Fired strength - added ZnO wt.% graphic.

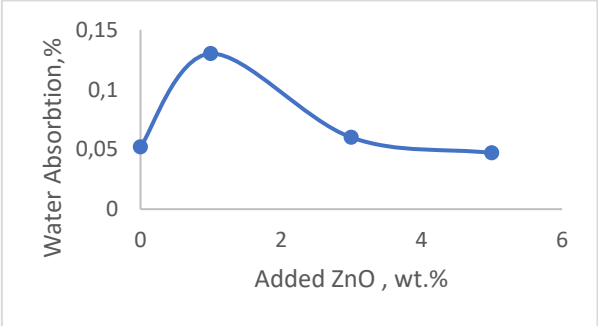

Figure 4. Water absorbtion % - added ZnO wt.% graphic

Physical characteristics of bodies are shown in Table 3. All trials meet the requirement of maximum 0.5% according to ISO 10545-3 water absorption standard and minimum 350 kg / cm^2 according to ISO 10543-5 bending strength requirement. The increase in firing shrinkage and fired strength and the decrease in water absorption by using ZnO up to 3% is an indication that it has a positive effect on sintering. It has been determined that the addition of ZnO increases the viscosity of the slurry, that is, it impairs the relogical properties.

3.2. Microstructural Analyses

The SEM images of the standard and 3wt.% ZnO added samples are shown in Figure 5.1.a.b.c and Figure 5.2.a.b.c.

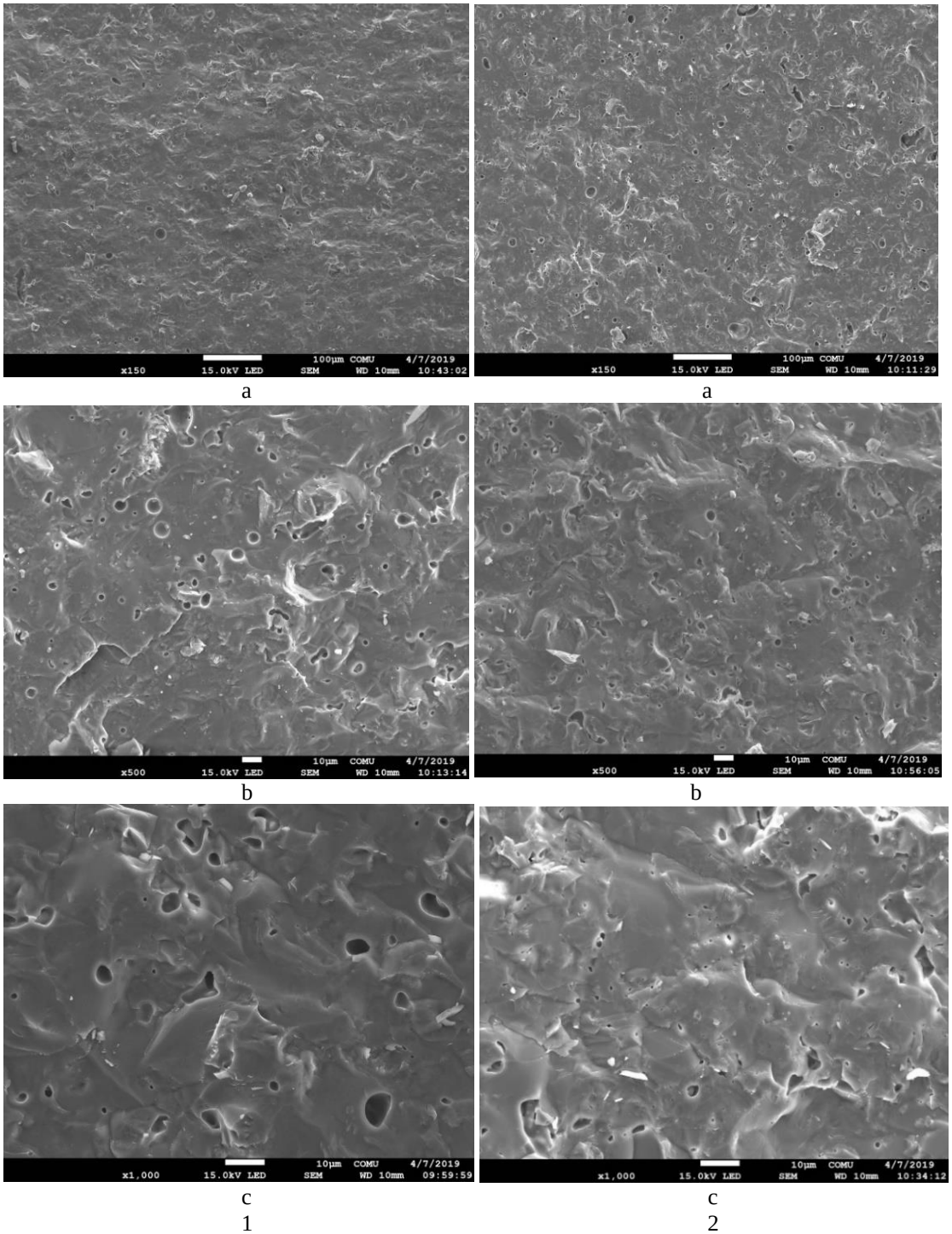

Figure 5.1.a.b.c SEM images of standard sample
Figure 5.2.a.b.c Added 3 wt. ZnO sample's SEM images.

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There is a decrease in the size of the pores on the fractured surface that shows close pores in the recipe 3 as seen at 500x and 1000x magnification. Pore sizes decrease according to feret diameter measurements. The lower the temperature of the liquid phase formation with eutectic reactions (Na_2O-K_2O-ZnO-Al_2O_3 -SiO_2), the more positively it contributes to rapid firing[22]. The viscosity of the glassy phase should also be at an optimal level, which is high enough not to cause pyroplatic deformation, but low enough to respond easily and quickly to gas release. High level of glass phase formation is observed in both body types. Another reason for the increase in strength is that the closed pore volume decreases due to the positive effect of ZnO on sintering. As seen Figure 6 and Figure 7 for EDX analyses, both standard and doped samples have high vitrification. Alkali metals and zinc were detected in the quartz base amorph matrix in the analysis performed on the sample added ZnO that is no.3. Zinc has diffused into the glassy matrix by showing its melting property. One reason for the increase in strength is thought to be the change in glassy matrix composition. The presence of carbon element in EDX analysis indicates short firing time that cannot provide enough time for organics to escape. In a study performed on stoneware tiles, C element was not found in EDX analysis of the standard sample [23].

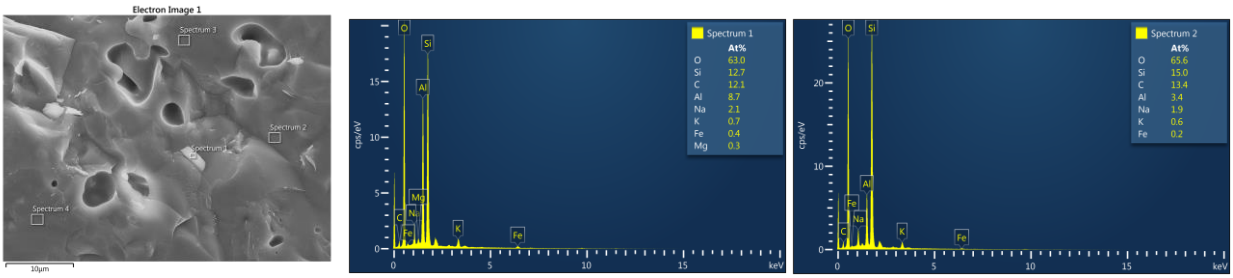

Figure 6. Standard (1 no) sample's EDX images.

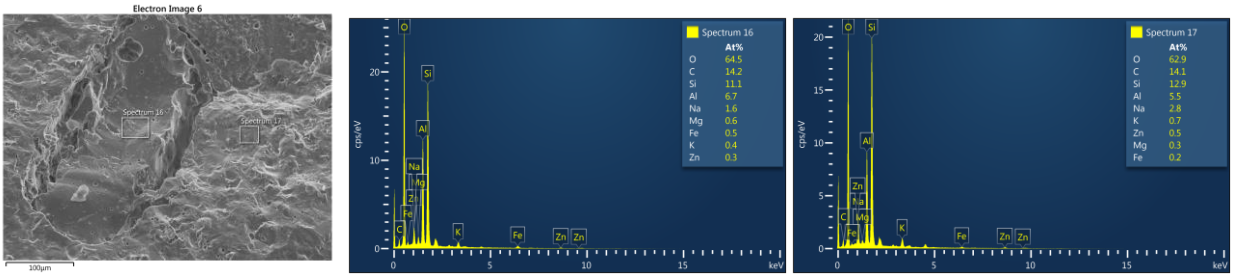

Figure 7. 3 wt. % added ZnO (no 3) sample's EDX images.

3.3. Crystalline Phase Analyses

The XRD graphics of the standard and 3wt. % added ZnO samples are shown in Figure 8. Rietveld method was used for quantatative analyzes. The presence of ZnO in the ceramic body decreased the viscosity of the liquid phase and increased the solubility of quartz by increasing its chemical activity; spinel phase was occured, mullitization was prevented and albite formation was triggered. While quartz in the standard body was 77.2%, mullite 22.8%, in body no.3, quartz was 56.4%, cristobalite 2.5%, spinel 27.4% and albite 13.8%. It has been observed that the addition of NiO also creates a spinel phase [13]. In the study conducted by Chaudhuri, it was observed that with the addition of 4 wt.% ZnO to the porcelain body, a minimum of mullite was formed[16] .With increasing quartz solubility, increased the amount of quartz in the glassy phase and thus cristobalite formation was observed in XRD [8]. In a study, it was determined that the addition of ZnO to the household porcelain body creates cristobalite and increases with the amount of ZnO added. In the same study, it was observed that the amount of quartz decreased [21].

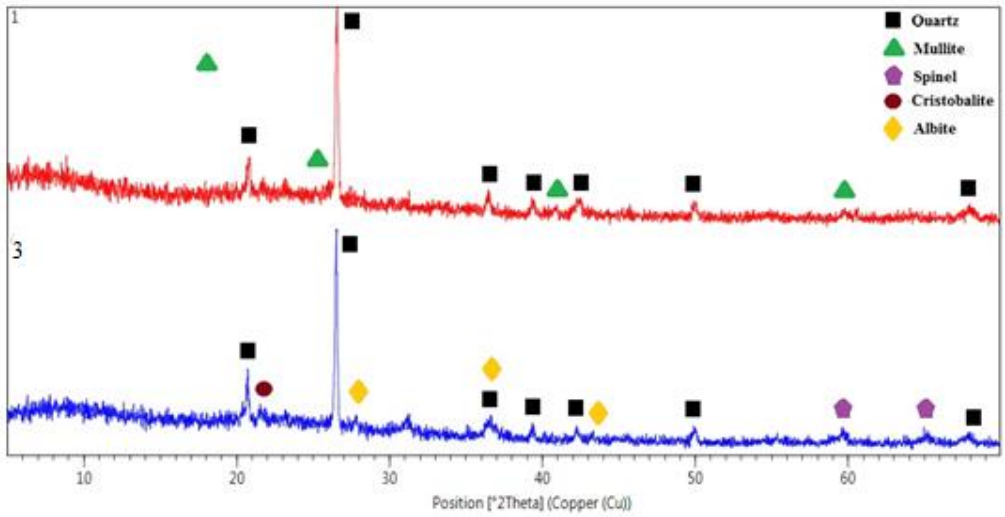

Figure 8. Standard (1) and 3 wt.% ZnO added sample (3).

3.4. Colour Analyses of the Samples

Colorimeter values of bodies are shown in Table 5. As a result of colorimeter measurements, it was determined that the L (lightness) value increased, a (redness) and b (yellowness) values decreased and -a value (green) increased with increasing ZnO. Especially in the 5% ZnO sample, the value of a decreases from 3.91 to 0.30 compared to the standard. L (lightness) value increases with increasing ZnO. With increased ZnO, the (yellowness) value of b decreased by 1% and reached the smallest value with 5% added value. When ΔE <1, the human eye cannot detect color difference. According to this, the color change that occurs in all doped samples can be detected by the human eye. Fired samples are shown in Figure 9.

Table 5. Colorimeter degrees of bodies.

Sample	L	a	b	ΔE
1	47.75	3.91	15.31	Std.
2	48.61	3.99	11.68	3.73
3	50.41	2.53	12.31	4.24
4	54.68	0.30	10.60	9.1

Std:Standard

Figure 9. Images of fired bodies.

3. Conclusion

According to study,
1. It has been determined that the added of 3 wt.% ZnO, increased the strength increase from 400 kg/cm^2 to 511 kg / cm^2, respectively, as standard and added samples.
2. While there was quartz 77.2% and 22.8% mullite in the standard body, 56.4% quartz, 2.5% cristobalite, 27.4% spinel and 13.8% albite were detected in 3% ZnO added body. With the addition of 3% ZnO, the liquid phase viscosity decreased and the amount of quartz in the body decreased, and the formation of cristobalite was triggered by the increasing amount of quartz in the liquid phase. Mullite formation was prevented and spinel phase formed.

3. It was determined that the L (openness value) value of the standard sample and the 5% ZnO added sample increased from 47.75 to 54.68. The values where a (redness) and b (yellowness) value are the smallest and the values that falls according to the standard are a: 0.3 and b: 10.70 in the 5% added ZnO.

In the production of wall tiles and sanitaryware, studies can be carried out on the use of ZnO in recipes to determine the effect of different compositions and firing times. The benefit / cost parameter can be revealed in a detailed work.

Author's Contributions

Savaş Elmas: Drafted and wrote the manuscript, performed the experiment and result analysis.

Ethics

There are no ethical issues after the publication of this manuscript.

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