# Synthesis of zinc aluminate ($ZnAl_2O_4$) by mechanochemical processing with different molar ratios of ZnS:Al

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## ABSTRACT

Zinc aluminate spinel structure ($ZnAl_2O_4$) was synthesized from mixtures of zinc sulfide (with sphalerite structure) and aluminum. The starting materials with different molar ratios were milled for 3 hours. The as-milled powders were heated isothermally at 800 ºC under an air atmosphere for one hour. The heated samples finally were washed out with diluted sulfuric acid and the remained residuals were dried at 110 ℃ for two hours. The results showed that aluminium content and the molar ratios of ZnS:Al in the starting materials have significant effect on the formation of $ZnAl_2O_4$.The as-milled results showed that although the reduction of ZnS by aluminum occurred during milling, the reaction was not completed with increasing the Al content in the starting materials. Except the molar ratio of 1:2, no signs of un-reacted Al were observed in other mixtures of ZnS-Al after milling for three hours. The XRD patterns and FT-IR spectra of the acid treated sample revealed that zinc aluminate could be synthesized from mixtures of ZnS-Al and the ZnS-Al mixture with molar ratio of 4:2 was the best among all mixtures.

## 1-Introduction

Due to high chemical and thermal stability, high mechanical resistance, high fluorescence efficiency, high photocatalytic activity and low surface acidity, spinel type Zinc aluminate ($ZnAl_2O_4$) is suitable for a wide range of applications [1,2]. Additionally, Zinc aluminate with a wide band gap energy ($E_g$) is a semiconductor material [2,3]. There are various methods to synthesize $ZnAl_2O_4$ spinel; Namely, solid-state reaction [4,5], co-precipitation [6], combustion [7], sol-gel [8,9], and hydrothermal process [10]. Wang et al. [2] studied the fluorescence behavior of zinc aluminate and showed that the particle size of $ZnAl_2O_4$ has a large effect on its optical and fluorescence properties. The large particle size of the product is the main disadvantage of spinel-type zinc aluminate composition synthesized by traditional routes, such as co-precipitation approach, solid-state reaction method and others [2].

Recently, synthesis of ceramic materials, nanocomposites and advanced compounds with high-energy milling or mechanochemical processes has been successfully used [11-15]. Meanwhile, there are few published papers on mechanochemical synthesis of zinc aluminate ($ZnAl_2O_4$) in the literature [16-19]. Zdujic et al. [18] reported the synthesis of spinel-type $ZnAl_2O_4$ by mechanochemical reaction between ZnO and $Al_2O_3$ induced by ball milling. In another study, Wu [19] synthesized fine

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$ZnAl_2O_4$ powders using displacement solid-state reaction induced by milling of aluminum and zinc oxide. XRD patterns indicated the presence of $ZnAl_2O_4$ spinel structure after annealing the 22-hour-milled ZnO-Al mixtures at 900℃ for 2 hours [19].

Previous studies on the metallothermic reduction of zinc sulfide induced by ball milling confirmed that in the stoichiometric mixture of ZnS-Al the reduction reaction was slow [20]. However, the effect of different molar ratios in the ZnS-Al mixtures was not studied in the previous work [20]. In the present work, the mechanochemical reaction of ZnS-Al system and the formation of $ZnAl_2O_4$ spinel structure from zinc sulfide (with sphalerite structure) and aluminum as starting materials is studied. The starting raw materials were mixed with different molar ratios and milling was done in a high energy ball mill for 3 hours. The effects of different molar ratios of raw materials (ZnS and Al) on the reduction reaction of zinc sulfide induced by ball milling and the possibility of zinc aluminate formation ($ZnAl_2O_4$) from as-milled powders were also discussed in the present work.

## 2- Experimental Procedure

The starting materials were zinc sulfide (Merck grade, 1.08898) with sphalerite structure (JCPDS file No. 05-0566) and pure aluminum powder (Merck grade, 1.01056). Based on the thermodynamic calculations, the reduction reaction of zinc sulphide (ZnS) with aluminium (reactions 1 and 2) is exothermic at room temperature [21]. Mixtures of zinc sulphide and aluminium with different molar ratios of 3:2 and 4:2 of ZnS:Al (abbreviated as ZnAl32 and ZnAl42 respectively) were prepared on the basis of reactions 1 and 2. Another mixture of ZnS-Al with molar ratio of 1:2 was also prepared (abbreviated as ZnAl12).

$$\mathrm{ZnS} + \frac{1}{2}\mathrm{Al} \rightarrow \frac{1}{4}\mathrm{ZnAl_2S_4} + \frac{3}{4}\mathrm{Zn} \qquad (1)$$

$$\mathrm{ZnS} + \frac{2}{3}\mathrm{Al} \rightarrow \frac{1}{3}\mathrm{Al_2S_3} + \mathrm{Zn} \qquad (2)$$

The ZnS-Al mixtures were mechanically milled in a closed chamber using a planetary ball mill (Farapazhouhesh, FP2 model) for 3 hours. The milling conditions were similar to previous work [20]. All 3 h-milled samples were heated isothermally at 800℃ for one hour in a tube furnace (Lenton, LFT, 16-180), then cooled to room temperature under the flow of air. The heated samples were acid-washed with diluted sulphuric acid in order to remove any undesirable acid soluble phases. Preliminary works showed that unlike zinc aluminate ($ZnAl_2O_4$), zinc oxide is soluble in the diluted sulphuric acid. The acid washed residues were dried in an oven at 110 ℃ for two hours. The phase composition of samples was analysed using X-ray diffraction (XRD, Phillips Analytical, 40 kV, 40 mA, X'Pert APD) using CoKα radiation,) over a 2θ range of 25-85º. The microstructure of heated samples was studied using a scanning electron microscope (TESCAN-VEGA3). Fourier transform infrared (FTIR) spectra were recorded in the range of 400-4000 $cm^{-1}$ using a JASCO Ft-IR460 spectrometer. Dielectric studies of synthesized zinc aluminate were carried out in the frequency range of 1 kHz to 110 MHz using an impedance analyzer (HP-4294).

## 3- Results and discussion

Thermodynamic assessment on the ZnS-Al system was undertaken using HSC Chemistry software [21] based on reactions (1) and (2) at 298K. According to previous results, although $ZnAl_2S_4$ phase could be thermodynamically stable as an intermediate phase in the ZnS-Al system at 298K, no sign of $ZnAl_2S_4$ phase was observed in the XRD patterns of as-milled samples [20]. The amounts of $\Delta H^{\circ}_{298K}$ in Table (1) show that both reactions 1 and 2 are exothermic at room temperature, however the $\frac{-\Delta H^{0}_{298K}}{\sum C_{p(298K)}}$ ratios for both reactions are much less than 2000K. As a result, the initiation of a mechanically induced self-sustaining reaction (MSR reaction) during milling is not possible for ZnS-Al system, as was reported in the literature [20, 22-24].

**Table 1.** Thermodynamics assessments and lattice parameters for ZnS-Al mixtures with different molar ratios. Lattice parameters were determined for acid washed samples.

| reaction | $-\Delta H^{0}_{298K}\,(kJ)$ | $-\Delta G^{0}_{298K}\,(kJ)$ | $\frac{-\Delta H^{0}_{298K}}{\sum C_{p(298K)}}$ | Lattice parameter |
|---|---|---|---|---|
| Reaction 1. (***ZnS:Al = 4:2***) | 39.08 | 37.86 | 755.5K | 8.0721 |
| Reaction 2. (***ZnS:Al = 3:2***) | 39.66 | 40.85 | 723.88K | 8.0516 |

Figure 1 shows the XRD patterns of ZnS-Al samples with different molar ratios milled for 3 hours. For ZnS-Al mixture with molar ratios of 4:2 and 3:2, the relative intensity of main peaks at $2\theta \approx 50.6°$(JCPDS No. 04-0831) is much higher than the ZnS-Al mixture with molar ratio of 1:2. For ZnS-Al mixture with molar ratio of 1:2, the main peak of ZnS with sphalerite structure is present at ~33.3°, however according to the main peak of Al (JCPDS No. 04-0787) at ~45° only a small amount of reduction reaction occurs after 3 hours of milling. According to Fig. 1, in ZnS-Al mixtures with molar ratios of 4:2 and 3:2, the majority of the zinc sulfide was reduced by Al after milling for 3 hours. However, the signs of zinc sulfide phase (sphalerite structure) are also observed in those mixtures. Based on reactions (1) and (2) and the related thermodynamic calculations, metallic zinc should be formed at 298K in the ZnS-Al system [21]. The previous results showed that the reduction reaction of ZnS by aluminum progresses gradually during milling and no signs of other aluminum products (either aluminum sulfide or $ZnAl_2S_4$) were observed in the XRD patterns of as-milled mixtures [20].

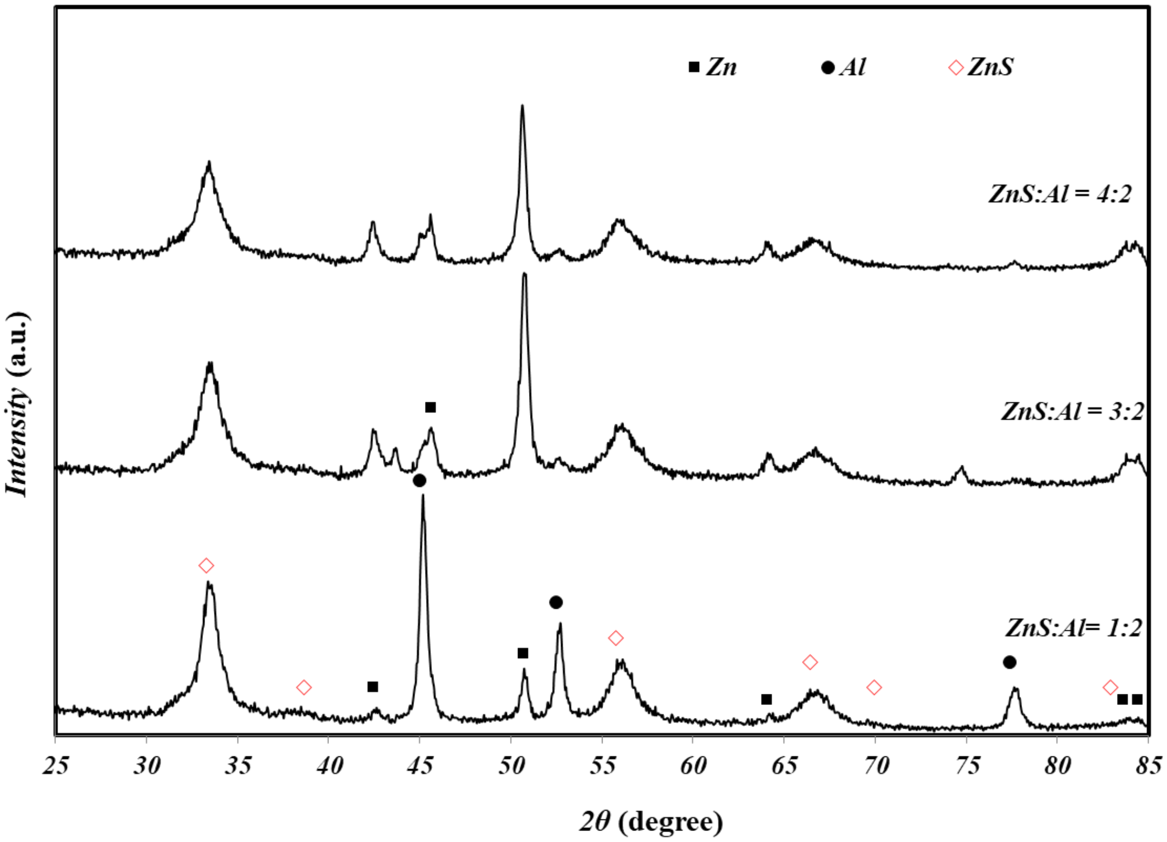


**Fig.1.** XRD patterns of 3 hours milled mixtures of ZnS-Al with different molar ratios.

After annealing at 800 °C under air atmosphere, the peaks of ZnO (JCPDS No.36-1451) and $ZnAl_2O_4$ (JCPDS No. 71-0968) phases were clearly observed in the isothermally heated samples with different molar ratios (Fig.2). The relative intensity of zinc oxide peaks at 2θ~37°, 40.2° and 42.3° are increased somewhat in the 4:2 ratio sample compared to other molar ratios of ZnS:Al samples. The XRD results of Fig.2 show that the traces of $Al_2O_3$ peaks (JCPDS No. 42-1468) are only present in the ZnS:Al mixture with 1:2 molar ratio, and no signs of $Al_2O_3$ is observed in other mixtures. Accordingly, the un-reacted aluminum in the as-milled mixture of ZnS-Al with molar ratio of 1:2 can be easily oxidized due to isothermal heating under air atmosphere.

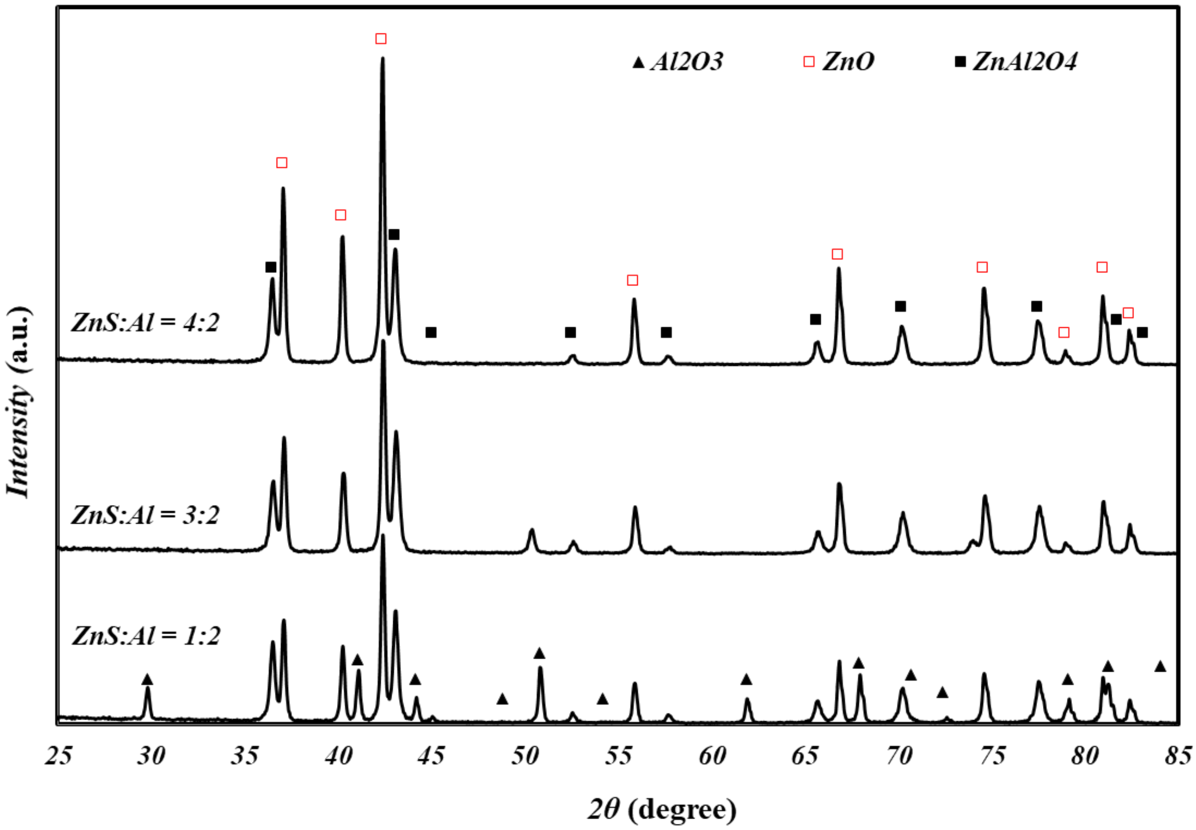


**Fig.2.** XRD patterns of 3 hours milled mixtures of ZnS:Al with different molar after isothermal heating at temperature of 800°C under an air atmosphere.

Figure 3 indicates the XRD patterns of acid-washed samples after drying in an oven. The main peaks of $ZnAl_2O_4$ at 2θ~36.4°and 43° are clearly observed in the ZnS:Al mixtures with molar ratios of 4:2, 3:2 and 1:2 (ZnAl42, ZnAl32 and ZnAl12 samples). By comparing Fig.3 to Fig.2, it is clear that all zinc oxide (ZnO) peaks disappeared in the acid-washed samples. However, the traces of alumina peaks are only observed in the ZnS-Al mixture with molar ratio of 1:2. Therefore, the results of Fig.3 show that $ZnAl_2O_4$ is the final product after acid washing only for ZnS-Al mixtures with molar ratios of 3:2 and 4:2 (ZnAl32, and ZnAl42 samples).

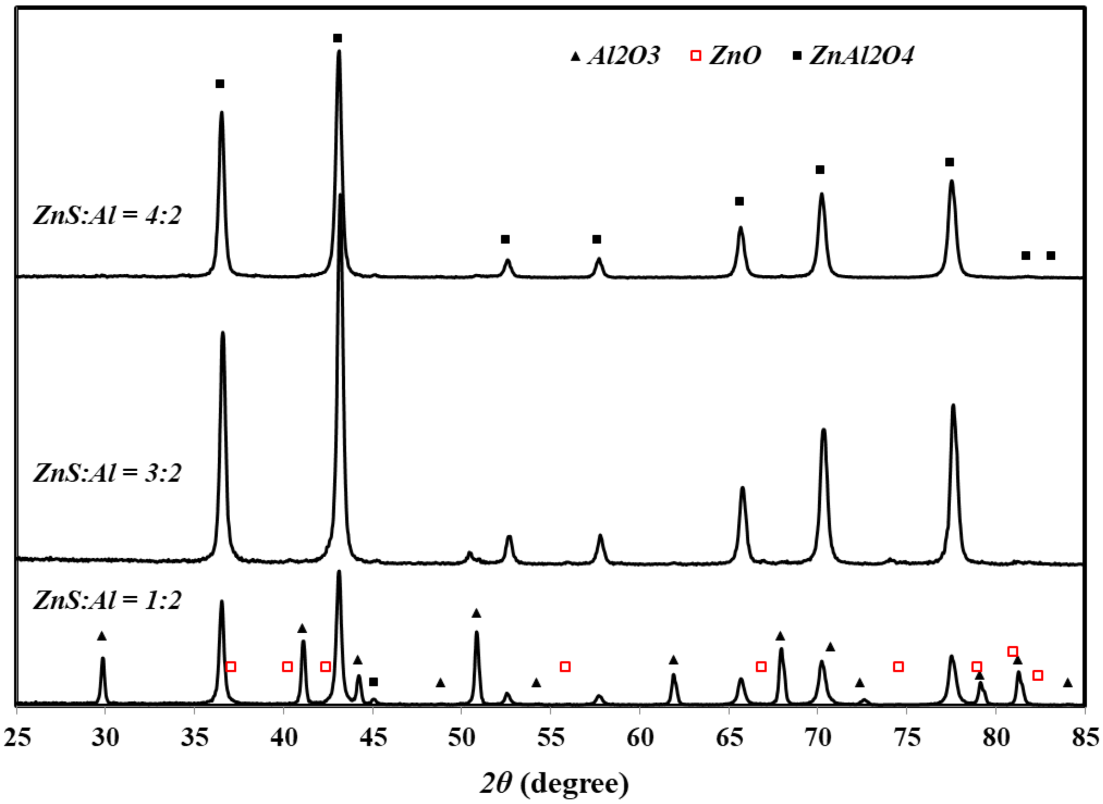


**Fig.3.** XRD patterns of dried solid residuals after acid washing with diluted sulfuric acid.

Assuming that no reduction reaction occurs during ball milling process, the reactions (3) to (5) are anticipated to occur for samples during isothermal heating at 800 ℃ under an air atmosphere for all molar ratios (ZnAl42, ZnAl32 and ZnAl12 samples).

$$4ZnS + 2Al + {}^{15}\!/_{2}\,O_2 \rightarrow ZnAl_2O_4 + 3ZnO + 4SO_2 \quad (3)$$

$$3ZnS + 2Al + 6O_2 \rightarrow ZnAl_2O_4 + 2ZnO + 3SO_2 \quad (4)$$

$$ZnS + 2Al + 3O_2 \rightarrow {}^{1}\!/_{2}\,ZnO + {}^{1}\!/_{2}\,Al_2O_3 + {}^{1}\!/_{2}\,ZnAl_2O_4 + SO_2 \quad (5)$$

After dissolution of zinc oxide phase in diluted sulfuric acid, the theoretical mass losses for reactions (3) to (5) were about 57%, 47% and 22% respectively. The mass losses of all molar ratios of the raw materials (ZnAl42, ZnAl32 and ZnAl12 samples) were determined after each acid washing process. The determined value for ZnS:Al with molar ratio of 3:2 was about 50%, however the corresponding value for molar ratio of 4:2 was ~57%. Those values of mass losses for both molar ratios indicate that the reactions (3) and (4) can occur for ZnAl32 and ZnAl42 mixtures during isothermal heat treatment at 800 ℃ under an air atmosphere.

The heated mixture of ZnS-Al with molar ratio of 1:2 was also washed with diluted sulfuric acid and the amount of mass loss was about 38%. The repeated acid washing treatment on the ZnS-Al mixture with molar ratio of 1:2 showed that the mass loss is about 37%. These values of mass losses are much greater than the theoretical value which was computed from reaction (5) assuming that ZnO dissolves completely in diluted sulfuric acid. For ZnS-Al mixture with molar ratio of 1:2, the traces of $Al_2O_3$ and $ZnAl_2O_4$ phases were observed in the XRD results of Fig.3, confirming that these phases cannot dissolve in the diluted sulfuric acid. The results of Fig.2 show that the relative intensities of ZnO phase are much higher than $ZnAl_2O_4$ in the all molar ratios of the ZnS-Al mixtures. Therefore, for molar ratio of 1:2 the amount of ZnO will be greater than the theoretical value which was determined by reaction (5). The XRD patterns of Figs. 2 and 3 and the determined mass losses after acid washing process reveal that the occurrence of reactions (3) and (4) in the isothermal heat treatment at 800 ℃ are likely reasonable for ZnAl42 and ZnAl32 samples.

According to the results of Figs. 2 and 3, the molar ratios in the ZnS-Al mixture and the amount of aluminum in the starting materials have significant role in the formation of $ZnAl_2O_4$. Increasing the amount of aluminum in the starting mixtures results in reduction of zinc sulfide during milling operation and this scenario is clearly observed in Fig.1 for ZnS-Al mixtures with molar ratios of 3:2 and 4:2, The weak traces of aluminum peaks comparing to high relative intensity of zinc peaks in those molar ratios (Fig.1), reveals the significant role of aluminum in the 3 hours-milled samples. The previous results, however, indicated that reduction reaction of zinc sulfide by aluminum is not completed after 10 hours of milling in the ZnS-Al mixtures with molar ratios of 4:2 [20].

The lattice parameter of zinc aluminate ($ZnAl_2O_4$) with cubic structure is 8.088 [JCPDS No. 71-0968]. The corresponding values of $ZnAl_2O_4$ for ZnS-Al mixtures with molar ratios of 3:2 and 4:2 after acid washing were determined using XRD results of Fig.3. The results of Table 1 show that although the computed lattice parameters for these molar ratios are close to each other, the calculated lattice parameter for ZnAl42 sample (molar ratio of 4:2) is very close to the value of zinc aluminate ($ZnAl_2O_4$) spinel structure.

Figure 4 shows the Fourier transform infrared (FTIR) spectra of the final product after acid washing of the isothermally heated mixtures. The Fourier transform infrared (FTIR) spectra (Fig.4) show a series of adsorption peaks in the range of 400-4000 $cm^{-1}$.

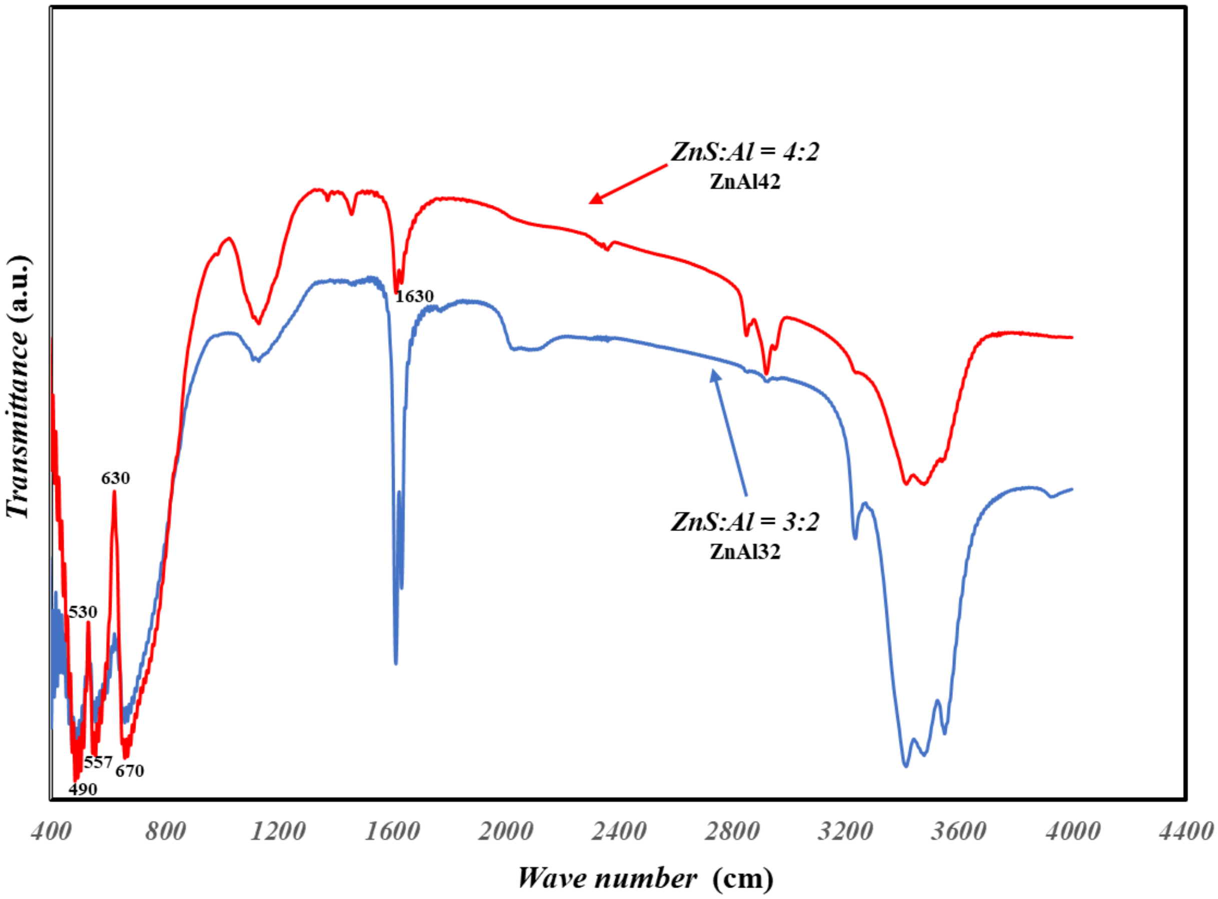
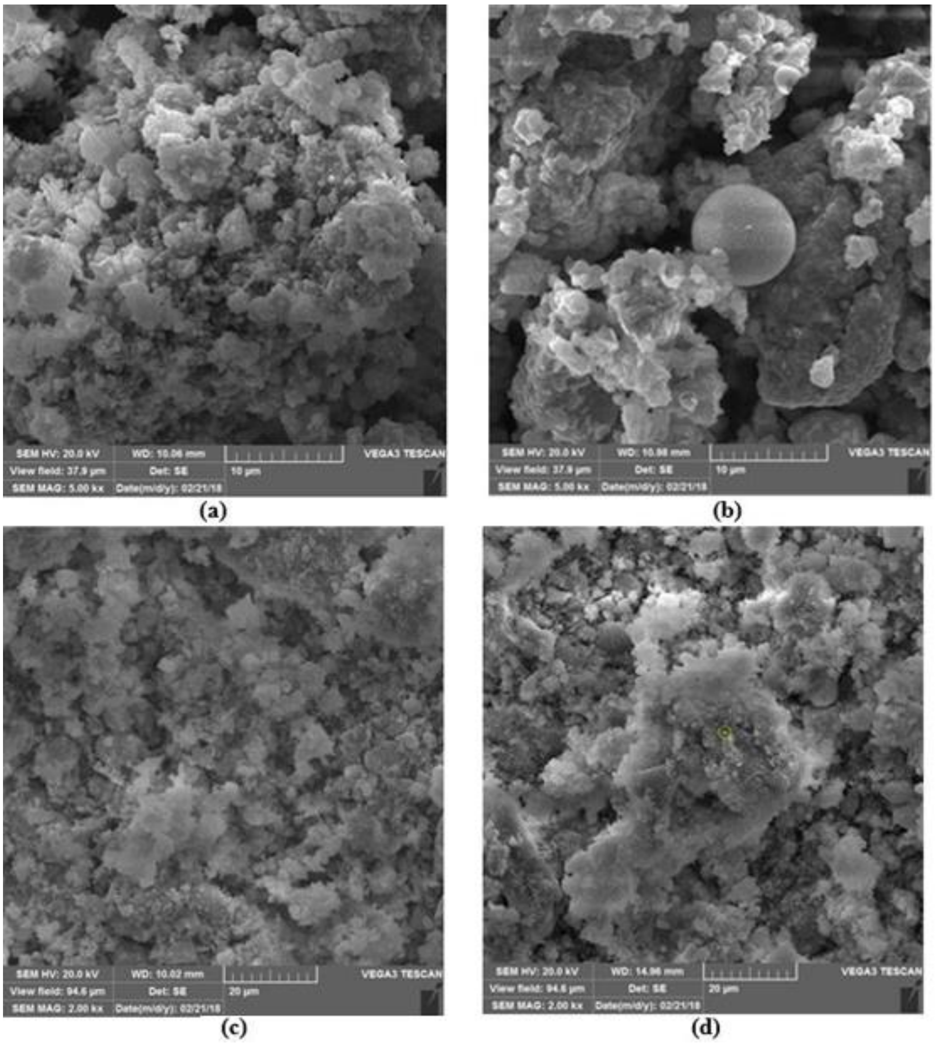


**Fig.4.** Fourier transform infrared (FTIR) spectra of dried solid residuals after acid washing the isothermal heated mixtures.

According to the specific frequencies of the absorption peaks and the FTIR spectra of Fig.4, the peaks appear at ~490, 630 and 1630 $cm^{-1}$ for all samples. The previous results indicated that in zinc aluminate spinel powder, metal–oxygen stretching frequencies appear in the range of 500–900 $cm^{-1}$, which is associated with the vibrations of Zn–O, Al–O, and Zn–O–Al bands [2,8]. The previous results also indicated that the metal–oxygen stretching frequencies in the range of 400–1000 cm$^{-1}$ are related to the zinc aluminate nanomaterial [25]. The bands at low energy (400–1000 cm$^{-1}$) are related to the stretching mode (peaks at 669 and 560 cm$^{-1}$) and to the bending mode (peak at 500 cm$^{-1}$) of Al–O in octahedral coordination state ($AlO_6$ octahedral units) [26]. These bands are characteristics for zinc aluminate spinel structure and these adsorption peaks are also observed in the FTIR spectra of the present work. The adsorption peaks are observed at 1630 and around 3440 cm$^{-1}$ in both spectra of Fig. 4 (ZnAl42 and ZnAl32 samples). These bands can be assigned to the vibration mode of chemically bonded hydroxyl groups [26].

Figure 5 shows the SEM micrographs of the ZnS-Al samples (ZnAl32 and ZnAl42 samples) before and after acid washing treatment. SEM micrographs of powders (Fig.5-a and 5-b) show that the physical appearance and morphology of the isothermal heated samples of ZnS-Al mixtures with molar ratios of 3:2 and 4:2 are quite different before acid washing. Acid washing treatment results in different morphologies in the ZnS-Al mixtures with these two molar ratios (Fig.5). Unlike the different particle sizes, the morphology and physical appearance of both molar ratios after acid washing treatment (Fig. 5-c and 5-d) are somewhat similar. EDAX analyses of the SEM morphology in Fig.5-d (not shown here) confirmed the presence of Zn, Al and oxygen in the samples. It is clear that XRD analysis is the best technique for indicating the exact composition of a phase, however, SEM photographs are useful to study the variation in the morphology during different processes.



(a) (b) (c) (d)

**Fig.5.** SEM micrographs of the isothermal heated samples of ZnS-Al before and after acid washing treatment, (a) ZnAl32 sample before acid washing, (b) ZnAl42 sample before acid washing. (c) ZnAl32 sample after acid washing, (d) ZnAl42 sample after acid washing.

The variations in dielectric constant ($\varepsilon_r$) and dielectric loss (tanδ) of ZnAl32 and ZnAl42 samples (ZnS:Al mixtures with moral ratios of 3:2 and 4:2) with frequency are shown in Fig. 6 (a-b). As it is seen, with increasing the applied frequency, $\varepsilon_r$ and tanδ decreased steadily up to frequency of 100 KHz, but after that a sharp breakage is observed in the curves. The amounts of dielectric constant and loss at the frequency of 110 MHz were $\varepsilon_r$=4.3, tanδ=0.0060 and $\varepsilon_r$=5.6, tanδ=0.0057 for ZnAl32 and ZnAl42, respectively. This is consistent with the XRD results and the better dielectric properties of ZnAl42 sample (ZnS:Al with molar ratio of 4:2) can be attributed to the better synthesis of this composition compared to ZnAl32. Abduljamal et al., [27] synthesized zinc aluminate nanoparticles via sol-gel combustion method. They also reported a steady decrease in dielectric properties obeying Debye equations [27]. However, the value of dielectric constant of this study at the frequency of 8 MHz ($\varepsilon_r$ =5.4) was approximately twice the value that they reported in their paper ($\varepsilon_r$ =2.45) and the dielectric loss (tanδ=0.018) was much lower than what they reported for ZnAl$_2$O$_4$ nano particles (tanδ=0.15).

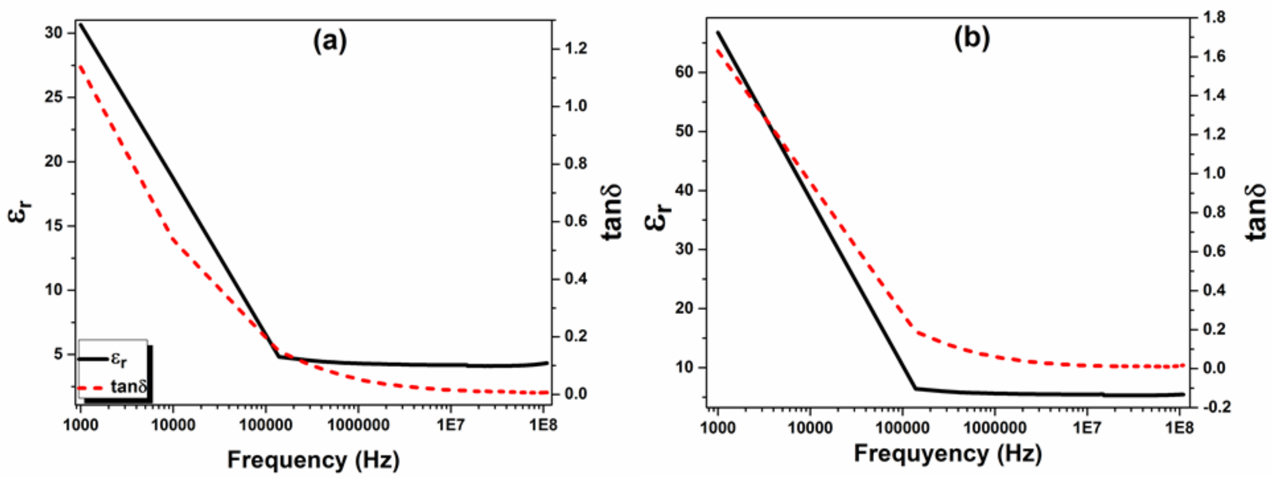


**Fig.6.** The variations in dielectric constant ($\varepsilon_r$) and dielectric loss (tanδ) with frequency for (a) ZnAl32 and (b) ZnAl42 samples.

## 4- Conclusions

In this work zinc aluminate ($ZnAl_2O_4$) was successfully synthesized from ZnS-Al mixtures using mechanochemical process. The molar ratio of raw materials (ZnS:Al) in the mixtures had a significant role in the ball milling process and the final products of isothermal heated samples. Reduction reaction of zinc sulfide took place in the as-milled mixtures of ZnS-Al with molar ratios of 3:2 and 4:2, however, the reduction reaction of these samples was not completed after milling for 3 hours. Additionally, acid washing was useful to remove the undesirable phases (such as zinc oxide) from the heated samples. The computed lattice parameter of dried solid residuals after acid washing treatment indicated that these values in ZnS-Al mixture with molar ratio of 4:2 and 3:2 are nearly close to the value of zinc aluminate ($ZnAl_2O_4$) spinel structure. Due to better synthesis, the dielectric properties of ZnAl42 with the amounts of $\varepsilon_r$=5.6 and $\tan\delta$=0.0057 were better than those of ZnAl32 sample (ZnS:Al molar ratio of 3:2). The low cost raw materials and the simple equipment are the major advantages of our proposed procedure to synthesize $ZnAl_2O_4$ particles in the present work.

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