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Study of Nanocrystalline $ZnAl_2O_4$ and $ZnFe_2O_4$ with SiO_2on Structural and Optical Properties Synthesized by Sol-Gel Method

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ABSTRACT

Zinc aluminate ($ZnAl_2O_4$) and zinc ferrite ($ZnFe_2O_4$) nanocrystalline structures dispersed into SiO_2 matrix were prepared by sol-gel method. Phase formation of $ZnAl_2O_4$ and $ZnFe_2O_4$ was confirmed by X-ray diffraction (XRD) analysis. The crystallite sizes was determine using Scherer's equation from the broadening of dominant peak at (311) plane. It was found the crystallite size of both compound decreased due to the decrement compositions of Zn^{2+} ion and Al^{3+} / Fe^{3+} ions. The crystallite sizes for $ZnAl_2O_4$ and $ZnFe_2O_4$ was calculated to be around ~ 14.16 – 11.27 nm and ~ 11.27 – 4.72 nm, respectively. FTIR analysis was done to determine the formation of spinel structures. FTIR results analysis confirmed that the formation of spinel structure where it has been observed that the bands around 800 cm^{-1} was associated to the vibrations of aluminum-oxygen and metal-oxygen-aluminum bonds. This characteristic was identified to the formation of zinc aluminate spinel structure. The optical properties have been done to determine the energy bandgap of $ZnAl_2O_4$and $ZnFe_2O_4$ samples. The Uv-Visible absorption spectra have been done within wavelength 300 – 800 nm and the graph was plotted into the Tauc plot. This new dielectric material was purposed to improve the value of dielectric permittivity with addition of SiO_2 where it can be applied as microwave dielectric material without changing the original spinel structures.

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INTRODUCTION

Spinel structure is well known with compound structure AB_2O_4 where A sites can be represented with divalent ions (e.g., A = Zn, Ba, Co or Ni) and B sites can be represented with trivalent ions (e.g., B = Al, Fe or Ga) while O indicates the oxygen anion site. This spinel structures produced face centered cubic (fcc) which belong to group of fd3m. The cubic cell contained of closed packed array of 32 oxygen atoms with divalent ions that were occupied in the tetrahedral siteswhiletrivalent ions were occupied in the octahedral sites (Simeone, *et al*., 2002, Surendran, *et al*., 2004).Spinel structures normally have unique properties that qualified to be used as microwave dielectric material. This can be applied as microwave dielectric material where the produced material must have high quality factor, low dielectric constant (ε_r< 15) and near zero temperature coefficient (Tsunooka, *et al*., 2003).Silica matrix was used to prepare aluminate-dielectric and ferrite dielectric properties. This is because SiO_2well known as dielectric material in semiconductor industry. By mixing the metal oxide ions with dielectric material will produced new dielectric material (Jiang, *et al*., 2005) that can be used as microwave absorbing material that can be applied at high frequency range.

There are many methods that can be used to synthesize $ZnAl_2O_4$ and $ZnFe_2O_4$ such as solid state reaction (Liu, *et al*., 2005), hydrothermal method (Yamauchi, *et al*., 2009, Zhen, *et al*., 2008), precipitation route (Tang, *et al*., 2006) and sol-gel process are common techniques that have been used to synthesize ferrite and aluminate material. However, there are some problem that might be occurs during the synthesize using one of this technique. For example, solid state reaction have limitations to its inherent disadvantages which are chemical inhomogeneity, high cost needed for raw materials and impurities that will introduced during the ball milling mixing (Liu, Fu, Xiao and Huang, 2005).In this study, sol-gel method was used due to

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the advantages that have been compared with other researcher findings which can produce nanocrystalline structures. Sol-gel method was used to synthesize these materials where this method make possible to apply with various concentrations with different components in a matrix with molecular homogeneity and will produced crystalline structures in nanoscale range.Nanocrystalline structures can be obtained using appropriate method during the synthesize process. Other than that, nanocrystalline structures also can be produced depend on chemical composition, annealing or sintering time, particle size, temperature process and also doped material (Zhang, *et al*., 2006, da Silva and Mohallem, 2001).

The aim of this study is to analyze the structural and optical properties of $ZnAl_2O_4$ and $ZnFe_2O_4$ dispersed in 15% silica matrix. The produced samples of dielectric material can be applied as microwave absorbing material. This can be applied as microwave dielectric material as patch antenna for wireless communication system was within frequency range of 1 – 5 GHz.

Methodology:

The zinc aluminate and zinc ferrite samples was prepared by referring the compositional formula of $(1\text{-}x)ZnB_2O_4 - xSiO_2$ where [B represents = Al and Fe] with compositions of x = 0.00 and 0.15 synthesized by sol-gel method. The preparations of $ZnAl_2O_4$ and $ZnFe_2O_4$using zinc nitrate hexahydrate, aluminum nitrate hexahydrate, iron nitrate hexahydrate and silicon dioxide as a starting materials. The procedure was illustrated in Figure 1. In this experimental, the metal ions was dispersed into silica matrix withcomposition of x = 0.15 where distilled water was used as a solvent and citric acid was added as chelating agent. The produced solutions were heated at 85 °C for 1h while stirred using magnetic stirrer to produce homogeneous solutions. The produced gel solution was heated at 180 °C for several hours to complete the chemical reaction and produced loose powder. The obtained powder was annealed at 450 °C for 1h with heating and cooling rate of 1 °C/min. The X-ray diffraction (XRD) analysis was carried out with CuKα radiation λ = 1.5418 Å). Fourier transform infrared (FTIR) analysis was analyzed within range of 400 – 4000 cm^{-1}. Ultraviolet visible (Uv-Vis) analysis was carried to determine the energy band gap (E_g) of $ZnAl_2O_4$ and $ZnFe_2O_4$ with SiO_2.

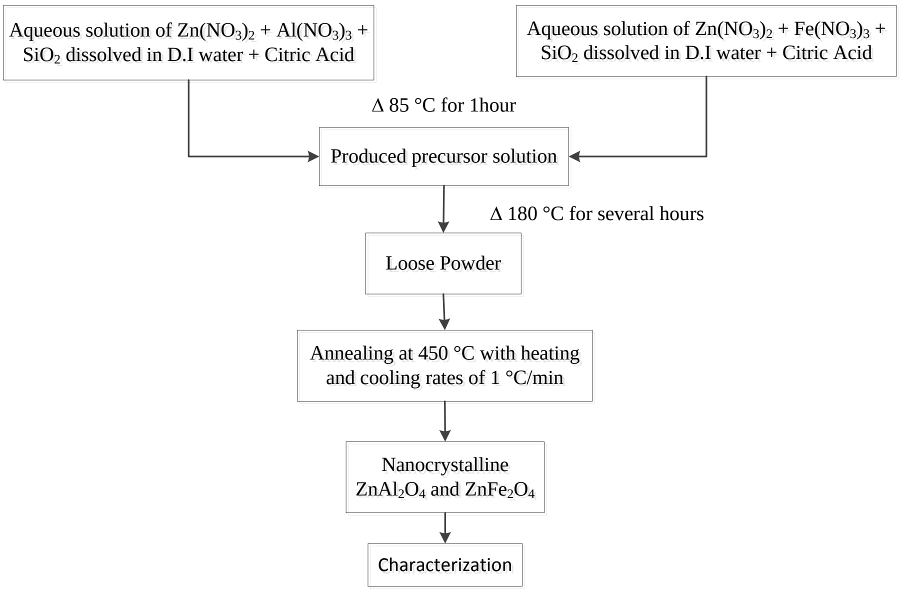

Fig. 1: Flowchart for the preparation of nanocrystalline structure of $ZnAl_2O_4$ and $ZnFe_2O_4$ with SiO_2 by sol-gel method

RESULTS AND DISCUSSION

XRD Analysis:

Figure 2 displays the XRD graph pattern for $ZnAl_2O_4$ and $ZnFe_2O_4$ with SiO_2 samples. XRD analysis was done to extend the crystallization of the samples(Zhang, 2004).The diffraction pattern indicates single phase crystalline formation and peak positions which are match with the standard data of zinc aluminate (JCPDS card No. 077-0732) and zinc ferrite (JCPDS card No. 00-022-1012). Both $ZnAl_2O_4$ and $ZnFe_2O_4$ formed face centered cubic (fcc) structures which belong to the Fd3m group. For $ZnAl_2O_4$ and $(0.85)ZnAl_2O_4 - 0.15SiO_2$ samples, there were 4 major diffraction peaks have been observed. The peaks have been observed at 2θ = 31.60 °, 36.08 °, 47.29 ° and 65.90 ° which represent for indices miller (220), (311), (331) and (422), respectively. For samples $ZnFe_2O_4$ and $(0.85)ZnFe_2O_4 – 0.15SiO_2$, there have been observed more major diffraction peak at 2θ = 29.44 °, 31.36 °, 35.08 °, 42.44 ° and 56.60 °. These peaks represent the indices miller plane for (220), (100), (311), (400) and (511), respectively. However, SiO_2 phase has been found to be amorphous phase for all samples (Jiang, Liu, Yu, Gao, Liu and Nan, 2005). It has been reported that by increasing the annealing temperature will help to produce the SiO_2 phase formation. However, Plocek *et al*. (2003) has been reported that the SiO_2 still remained amorphous phase formation where the sample was annealed at 800 °C. (Plocek, *et al*., 2003).

The average crystallite sizes, *D* of the produced samples can be calculated using Scherrer's equation(Jenkins and Snyder, 2012) by referring to the broadening peak of (311) planes. It was found that the crystallite sizes for $ZnAl_2O_4$ and $ZnFe_2O_4$ decreased when SiO_2 was introduced into the compound. The crystallite size for $ZnAl_2O_4$ was 14.16 nm while for $ZnFe_2O_4$ was 11.27 nm. The crystallite size was decreased when the composition of Zn^{2+} and Al^{3+}/Fe^{3+} ion was reduced with x = 0.15 where SiO_2 was introduced into the parent compound. The crystallite size for $ZnAl_2O_4$ with SiO_2 was 11.27 nm and $ZnFe_2O_4$ with SiO_2 was 4.72 nm.

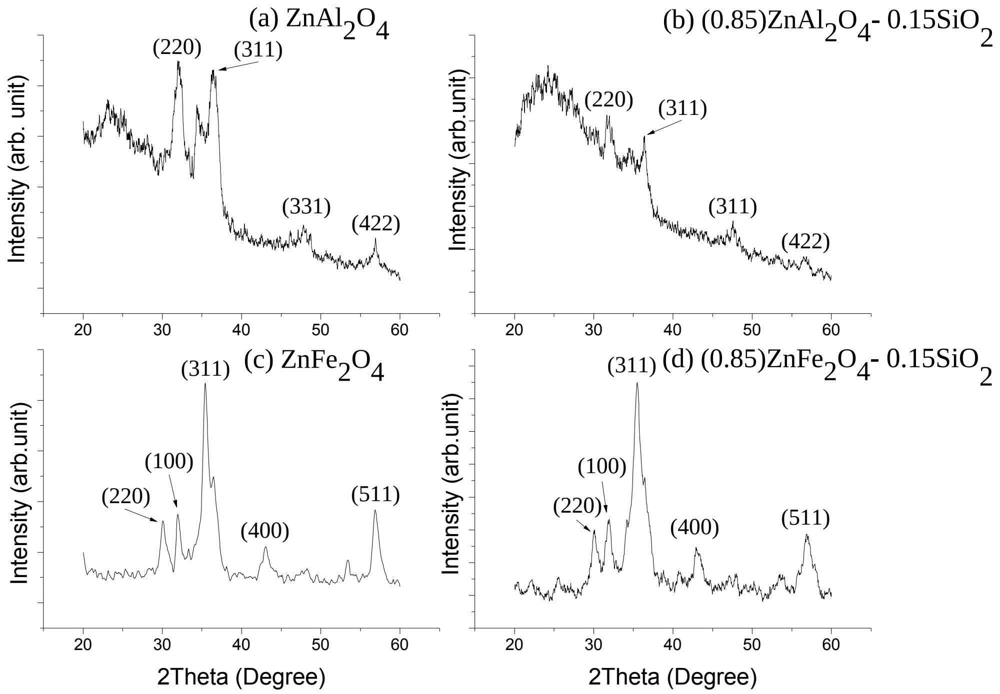

Fig. 2: XRD graph pattern for $ZnAl_2O_4$ and $ZnFe_2O_4$samples with 15% dissolved in silica matrix annealed at 450 °C for 1h.

FTIR Analysis:

The FTIR spectra analysis for samples $ZnAl_2O_4$ and $ZnFe_2O_4$ with SiO_2 were shown in Figure 3. FTIR analysis was used to determine the vibrational stretch frequency of metal-oxygen bonds (Zhang, 2004). All spectra exhibit a common broad band near 3400 cm^{-1} and 1600 cm^{-1} which are due to the -OH stretching vibrations and deformative vibration of water molecules (Kumar, *et al*., 2012).A band has been observed near 2350 cm^{-1} was attributed to the vibrations of carbon impurity atoms which correspond to the stretching of Si-C bonding (Shokri, *et al*.) For samples $ZnAl_2O_4$ and $ZnAl_2O_4$ with 15%. silica it have been observed the bands around 800 cm^{-1} was associated to the vibrations of aluminum-oxygen and metal-oxygen-aluminum bonds. This characteristic was identified to the formation of zinc aluminate spinel structure (Ragupathi, *et al*., 2014, He, 2006). For samples $ZnFe_2O_4$ and $ZnFe_2O_4$ with 15%. silica, bands was observed around 422 and 546 cm^{-1} was attributed to the stretching vibration of Fe^{3+} - O^{2-} in the octahedral and tetrahedral sites, respectively (Slatineanu, *et al*., 2011).

Uv-Vis Analysis:

Uv-Vis diffuse by absorption spectra of the samples have been done within wavelength region 300 – 800 nm. The result from UV-Vis absorption was plotted using Tauc plot to determine the energy bandgap of the produced samples as shown in Figure 4. For a direct energy bandgap has been obtained can be rearranged using absorption coefficient near the band edge where the equation can be written in the form:

$$(\alpha h v)^2 = A^2\ (h v\ -\ E_g) \qquad (1)$$

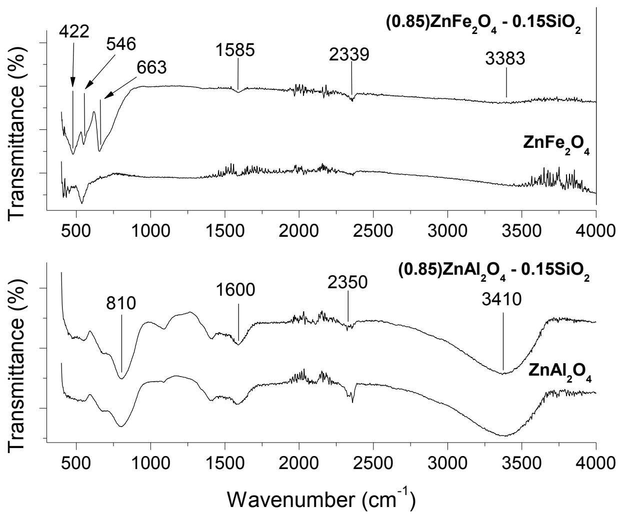

Fig. 3: FTIR spectra analysis for $ZnAl_2O_4$ and $ZnFe_2O_4$ samples with 15% dissolved in silica matrix annealed at 450 °C for 1h.

where α is the absorption coefficient, A is a constant depending on the type of transition, hv the photon energy and E_g the energy bandgap (Jamal, *et al.*, 2011). The energy bandgap for $ZnAl_2O_4$ was found to be around 3.97 eV while for $ZnAl_2O_4$ with SiO_2 the energy bandgap tend to decrease due to the dielectric properties of SiO_2. This energy bandgap was found to be a little bit higher than the other reported journal where the E_g for $ZnAl_2O_4$ around 3.80 eV (Davar and Salavati-Niasari, 2011). A new energy bandgap for samples $ZnAl_2O_4$ that was dispersed into 15% silica matrix was found to be around 3.34 eV. This has been reported that when the metal oxide ion mixed with other material that has high energy bandgap will produced a new energy bandgap that will located between that semiconductor materials (Cheng, *et al.*, 2004). However, the E_g for $ZnFe_2O_4$ a bit higher as reported where the E_g that was found to be around 3.90 eV and similar findings have been reported (Joshi, *et al.*, 2001). $ZnFe_2O_4$ was known as n-type semiconductor and has smaller energy bandgap which are (1.90 eV). The energy bandgap for samples $ZnFe_2O_4$ with SiO_2produced higher energy bandgap due to the dielectric properties of the SiO_2 where Eg was found to be around 4.10 eV.

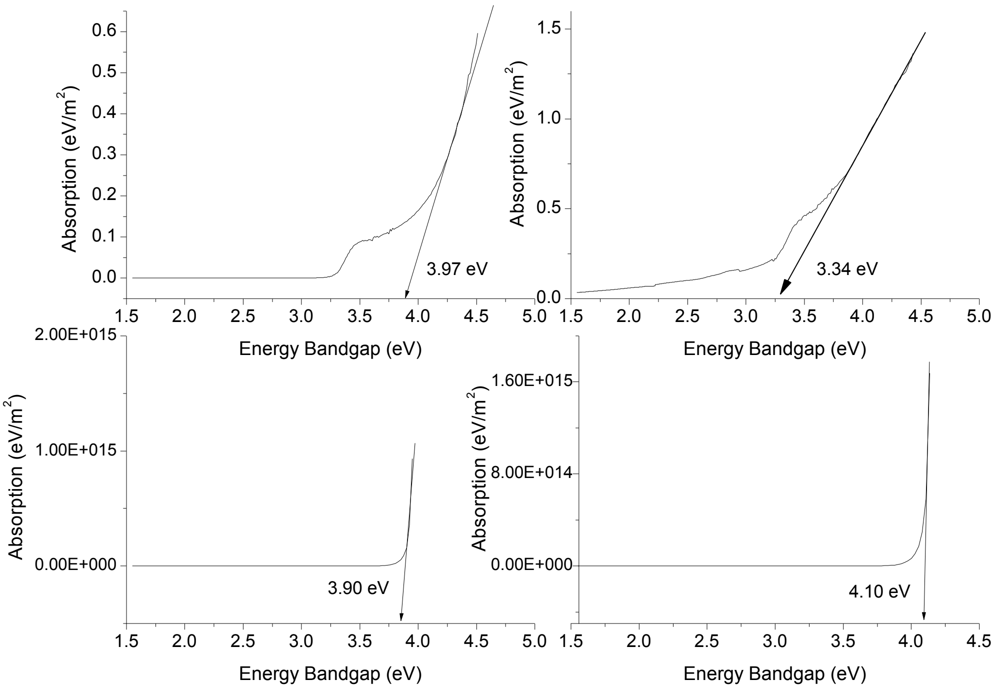

Fig. 4: Tauc plot to determine the optical energy bandgap for samples $ZnAl_2O_4$ and $ZnFe_2O_4$ with 15% silica.

Conclusion:

As conclusion, samples of $ZnAl_2O_4$ and $ZnFe_2O_4$ dispersed into 15%. Silica network was successful synthesized by sol-gel method. It was found that the addition of SiO_2 into $ZnAl_2O_4$ and $ZnFe_2O_4$ did not change the spinel structures. The crystallite size tend to decrease due to the decrement of Zn^{2+} and Al^{3+} / Fe^{3+} ion compositions. The main aims were by dispersed $ZnAl_2O_4$ and $ZnFe_2O_4$ into silica network to produce nanoparticle structures. Other than that, SiO_2 was introduced to enhance the dielectric properties of $ZnAl_2O_4$ and $ZnFe_2O_4$. This is because these materials can applied as microwave dielectric material as absorbing material for certain frequency range for example wireless communication system. In the future, further experimental will be done to investigate the response of $ZnAl_2O_4$ and $ZnFe_2O_4$ as microwave absorbing material within frequency range 1 – 4 GHz.

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