STUDY ON STRUCTURAL, MICROSTRUCTURAL AND VIBRATIONAL CHARACTERISTICS OF NANOSIZED COBALT-ZINC ALUMINATES

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Abstract

Nanosized Cobalt-Zinc Aluminates with the formula $Co_{1-x}Zn_xAl_2O_4$ (where x = 0.00, 0.25, 0.50, 0.75 and 1.00) were prepared by solid state reaction method by using Analytical Reagent (AR) grade CoO, ZnO and Al_2O_3. Structural, microstructural and vibrational characteristics of the samples were studied by XRD, SEM and FTIR spectroscopy. XRD patterns showed all characteristic peaks of the spinel structure and confirmed the phase formation indicating the absence the others impurity phases. The observed peaks perfectly matched with the crystalline phase of cubic spinel structure with the identification of satndard JCPDS. The crystallite sizes were estimated by using Debye-Scherrer's formula to examine the nanosized aluminates materials. SEM micrographs showed that the samples were cauliflower shapes and composed of agglomerated particles with poor grain boundary. FTIR spectra indicated that the stretching vibrations of divalent cations (ν_1-mode) and trivalent cations (ν_2-mode) of the samples. These two modes indicated that the vibrational characteristics of $Co_{1-x}Zn_xAl_2O_4$.

Keywords: $Co_{1-x}Zn_xAl_2O_4$, XRD, SEM, FTIR, cubic spinel.

Introduction

Numerous researches have shown that a characteristic of solid-state gas sensors is the reversible interaction of the gas with the surface of a solid-state material [Akbar, (2006)]. In addition to the conductivity change of gas-sensing material, the detection of this reaction can be performed by measuring the change of capacitance, work function, mass, optical characteristics or reaction energy released by the gas/solid interaction [Buchholt, (2011)].

Aluminates are chemical compounds consisting of ceramic materials based upon Aluminium Oxide as principal component. The materials based on the aluminates are potential candidates for modern technological applications due to their unique potential application in high density magnetic recording, microwave devices, magnetic fluids, heterogeneous catalysis and absorbent materials [Deraz, (2013)]. Spinel structure oxides constitute one of the most interesting classes of advanced ceramic materials due their intrinsic physical and chemical properties [Deraz, & Fouda, (2013)]. Among the spinel oxides, Cobalt Aluminate ($CoAl_2O_4$) and Zinc aluminates ($ZnAl_2O_4$) possess interesting properties for technological application [Ummartyotin, (2009)]. Specifically, Cobalt Aluminate ($CoAl_2O_4$) possesses important applications in various fields such as humidity sensor, gases sensor, catalyst in the oxidation reaction of benzyl alcohol, thermoelectric properties, photocatalyst for degradating the pollutants in aqueous solution, solar absorber, oxygen carrier in chemical-looping combustion and optical and dielectric properties [Abaide, (2015)].

$ZnAl_2O_4$ is a spinel type oxide, which have high chemical and thermal stability, high mechanical resistance and low surface acidity, being suitable for a wide range of applications, such as optical coating or host matrix, high temperature ceramic material, catalyst and catalyst

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support [Battiston, (2014)]. The aim of this work was to prepare **C**obalt-Zinc Aluminates, $Co_{1-x}Zn_xAl_2O_4$ by solid state reaction method and their structural, microstructural and vibrational characteristics were reported by using XRD, SEM and FTIR spectroscopy.

Experimental Details

Preparation of Cobalt-Zinc Aluminates

Cobalt-Zinc Aluminates, $Co_{1-x}Zn_xAl_2O_4$ (where x = 0.00, 0.25, 0.50, 0.75 and 1.00) were prepared by solid state reaction method. Analytical Reagent (AR) grade Cobalt Oxide (CoO), Zinc Oxide (ZnO) and Aluminium Oxide (Al_2O_3) were used as the raw materials. The starting materials were weighed with desired stoichiometric compositions and mixed. The mixed powders were pre-heated at 950°C for 5 h and followed heated at 1100°C for 5 h in JLab Tech Electric Oven. Flow diagram of the sample preparation procedure is shown in Figure 1.

XRD, SEM and FTIR Measurements

X-ray diffraction (XRD) patterns of the samples were observed by PC-controlled RIGAKU MULTIFLEX X-ray Diffractometer [Universities' Research Centre (URC), University of Yangon] in the diffraction angle range of 10° – 70° using CuK_α radiation with Ni filter at 40 kV and 40 mA.

Microstructural characteristics of the samples were investigated by using JCM-6000Plus SEM [Department of Physics, West Yangon University] with the accelerating voltage of 15 kV and 5000 – 6000 times of photo magnifications.

FTIR transmission spectra of the samples with Potassium Bromide, KBr pellet were observed by PC-controlled SHIMADZU FTIR-8400 Spectrophotometer [Universities' Research Centre (URC), University of Yangon] at room temperature.

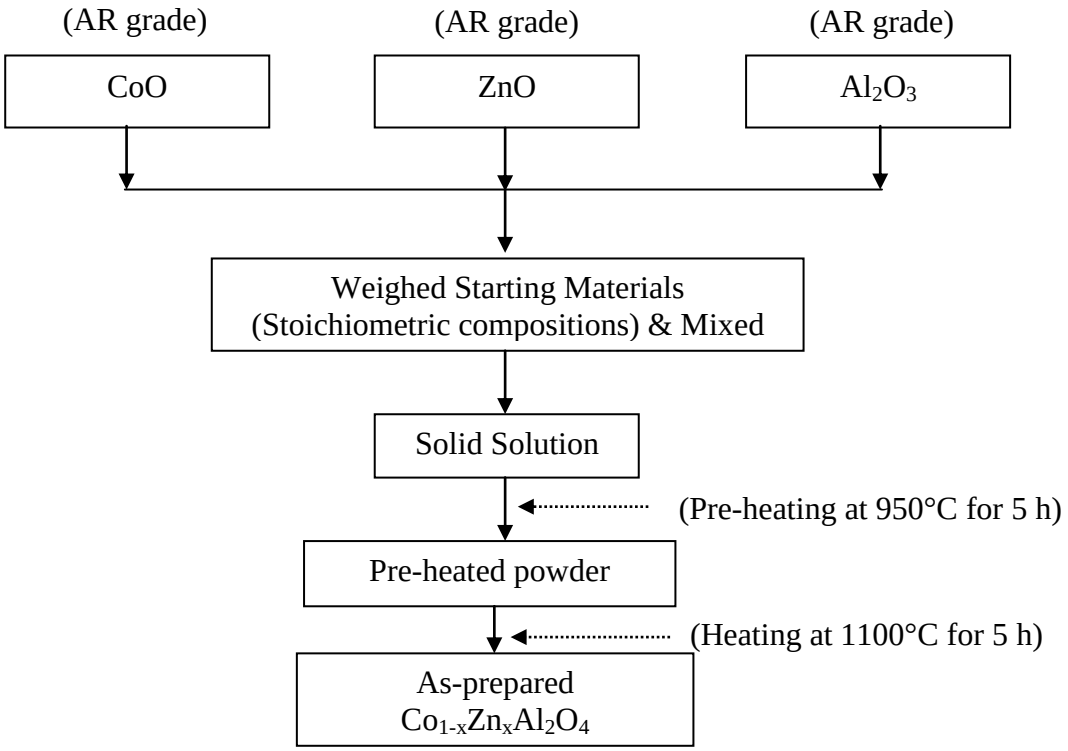

Figure 1 Preparation procedure of $Co_{1-x}Zn_xAl_2O_4$

Results and Discussion

Structural Analysis

Powder X-ray diffraction patterns of the samples are shown in Figure 2. The observed XRD lines were identified by using standard JCPDS (Joint Committee on Powder Diffraction Standards) data library files of Cat. No. 82-2252> Spinel – $CoAl_2O_4$ and Cat. No. 74-1138> Gahnite magnesian – $ZnAl_2O_4$. The patterns show all characteristic peaks of spinel structure and confirms the phase formation indicating the absence the others impurity phases. The observed peaks perfectly match with the crystalline phase of cubic spinel structure of spinel (JCPDS data library files: Cat. No. 82-2252 and Cat. No. 74-1138). As shown in the observed XRD patterns, the observed XRD lines are found to be agreed with standard JCPDS. It indicates that the appearance of the diffraction peaks demonstrate the single-phase spinel type cubic crystalline $Co_{1-x}Zn_xAl_2O_4$. The diffraction line of (331) plane (*) indicates the diffraction line of $ZnAl_2O_4$ and it appears at the Zn contents x = 0.50, 0.75 and 1.00.

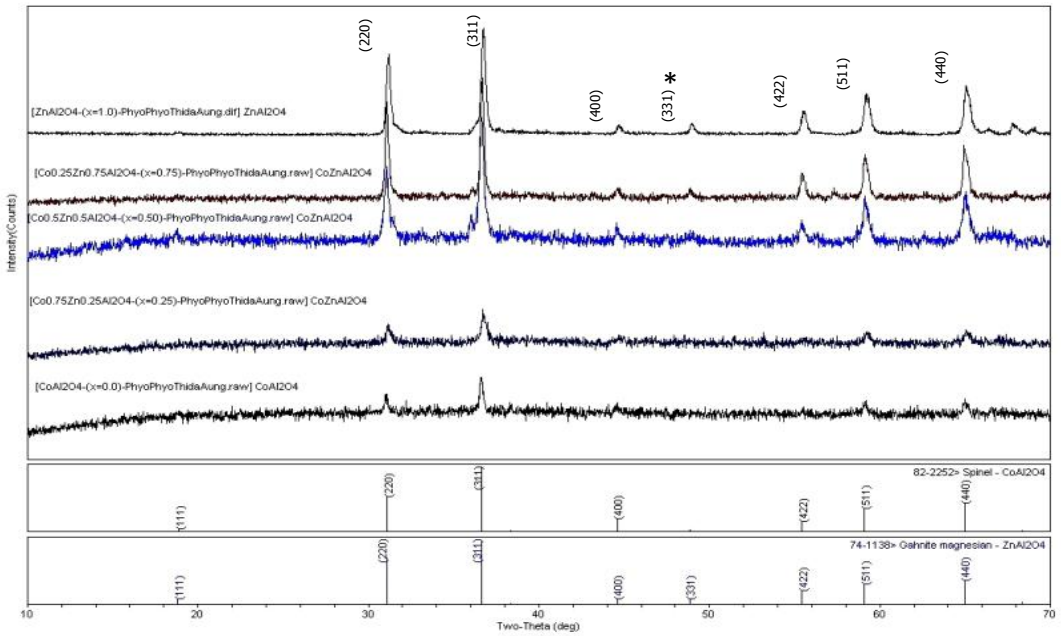

Figure 2 XRD patterns of $Co_{1-x}Zn_xAl_2O_4$

The lattice parameters are evaluated by using crystal utility of the equation $\frac{\sin^2\theta}{(h^2+k^2+l^2)}=\frac{\lambda^2}{4a^2}$, where "(hkl)" is the Miller indices, "λ' is the wavelength of incident X-ray (Å), "θ" is the diffraction angle of the peak (°) and "*a*" is the lattice parameter (Å).

The crystallite sizes of each of the samples were estimated by using Debye-Scherrer's formula, $D=\frac{0.9\lambda}{B\cos\theta}$, where "*D*" is the crystallite size (nm), "λ' is the wavelength of incident X-ray (Å), "θ" is the diffraction angle of the peak under consideration at FWHM (°) and "B" is the observed FWHM (radians). The experimental results of the calculated average lattice parameters, the observed lattice parameters and the crystallite sizes are tabulated in Table 1. It is seen that the crystallite sizes of the samples are nanosized crystalline materials.

Table 1 The lattice parameters and crystallite sizes of $Co_{1-x}Zn_xAl_2O_4$ samples

Sample (Contents x of Zn)	Obs. *a=b=c* (Å)	Cal. *a=b=c* (Å)	*D* (nm)
0.00	8.1404	8.1453	54.20
0.25	8.0879	8.0893	58.35
0.50	8.1122	8.1121	52.09
0.75	8.0880	8.0915	29.15
1.00	8.1064	8.1012	33.74

Microstructural Analysis

SEM micrographs of the samples are shown in Figure 3. Except the x = 1.00 sample, the observed SEM images of the samples generally reveal that the spherical shapes with poor grain boundary. As shown in SEM images of $Co_{1-x}Zn_xAl_2O_4$ (where x = 0.00, 0.25, 0.50, 0.75 and 1.00) samples, a large grain composed of many small grains of nearly spherical. The images show that the powder samples are composed of agglomerated particles. In each of the image, some pores formed due to the heat-treatment of the starting materials in the sample preparation process. The grain sizes of the samples are evaluated by the use of (equal bar code) same scale in length of corresponding representative bar of 5 μm. In this work, the obtained grain sizes are tabulated in Table 2. In these images of mixed aluminates samples, some pores were also found and they are larger area than pure aluminates samples. The pores serve as adsorption sites due to the heat-treatment of starting materials in the preparation of desired materials. Furthermore, it was found that the shape of the samples varied from the cauliflower to poly-face with the concentration of Zn^{2+} on $Co_{1-x}Zn_xAl_2O_4$ sample.

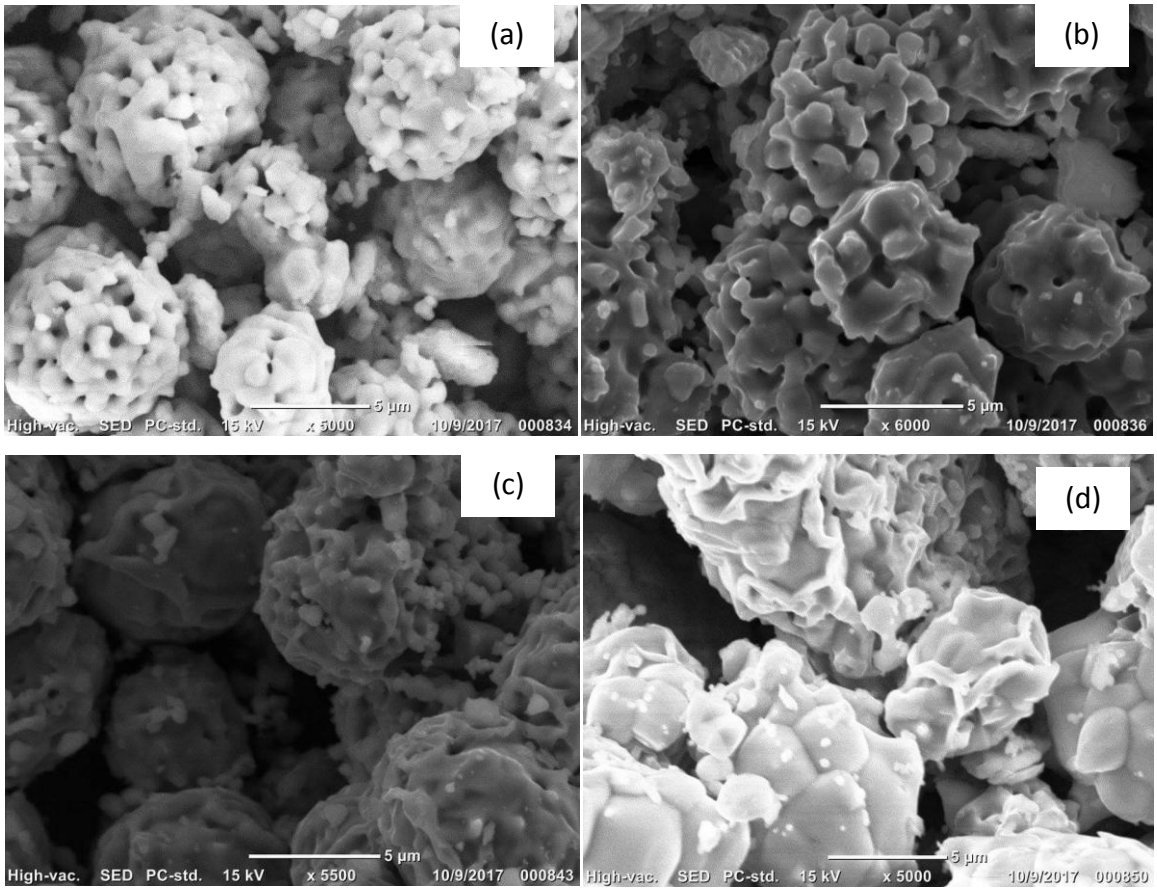

Figure 3 SEM micrographs of $Co_{1-x}Zn_xAl_2O_4$ where (a) x = 0.00, (b) x = 0.25, (c) x = 0.50 and (d) x = 0.75

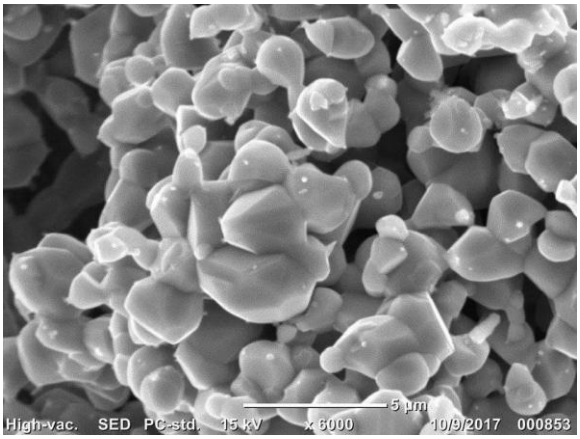

Figure 3(e) SEM micrograph of $Co_{1-x}Zn_xAl_2O_4$ where x = 1.00

Table 2 The grain sizes of $Co_{1-x}Zn_xAl_2O_4$ samples

Sample (Contents x of Zn)	Grain size (µm)
0.00	0.42 – 1.00
0.25	0.25 – 1.20
0.50	0.22 – 1.50
0.75	0.45 – 3.10
1.00	0.50 – 2.50

Vibrational Analysis

Spinels are generally formulated as AB_2X_4 that formally consider the structure as consisting of isolated ion of B and isolated AX_4 molecules. The spinel structure is cubic with eight molecules in the unit cell (Z = 8), and has the B atoms on octahedral sites D_{3d} symmetry, and the A atoms on tetrahedral sites of T_d symmetry. The oxygen atoms occupy C_{3v} sites. The coordination polyhedron around B is a regular octahedron. The vibrational frequencies of a molecule may be varied with the crystalline environments. Sometime the vibrational frequencies of octahedral site (B-atoms) and tetrahedral site (A-atoms) molecules are assigned as υ_2-mode and υ_1-mode respectively. These two modes are stretching vibrations of spinel type samples.

The standard vibrational frequencies (wavenumbers) of $CoAl_2O_4$ are mainly 658 cm^{-1} for A atoms on tetrahedral sites (assigned as υ_1-mode) and 494 cm^{-1} and 574 cm^{-1} for B atoms on octahedral sites (assigned as υ_2-mode). Vibrational frequencies of $ZnAl_2O_4$ are mainly appeared at 667 cm^{-1} for A atoms on tetrahedral sites (assigned as υ_1-mode) and 562 cm^{-1} and 510 cm^{-1} for B atoms on octahedral sites (assigned as υ_2-mode). In this work, FTIR transmission spectra of the samples are shown in Figure 4. In this Figure, the shifting of wavenumbers indicates with ellipses. These bands are clearly indicated that the increasing concentrations of $ZnAl_2O_4$ on $CoAl_2O_4$.

The observed absorption lines and corresponding vibrational characteristics of constituent molecules are identified by using standard wavenumbers of $CoAl_2O_4$ and $ZnAl_2O_4$. The detail assignments of observed wavenumbers and corresponding molecular vibrations are tabulated in Table 3. Furthermore, the observed spectral lines in the observed FTIR spectra corresponding to the optical properties of wavelength, frequency, oscillation time and energy of are also listed in Table 3.

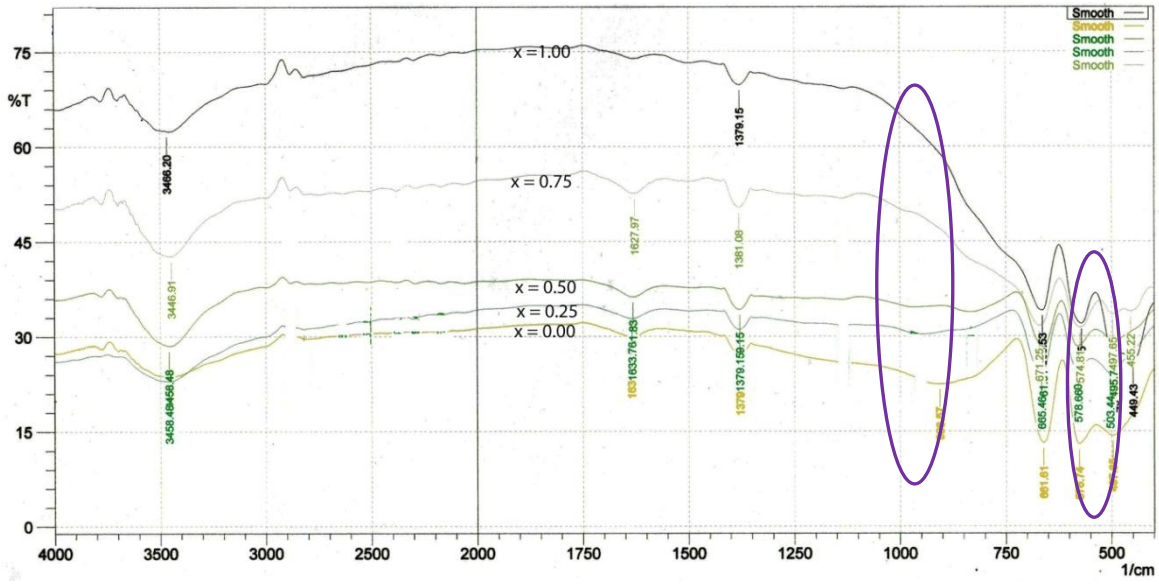

Figure 4 FTIR transmission spectra of $Co_{1-x}Zn_xAl_2O_4$

Table 3 (a)Vibrational properties of wavelength, frequency, oscillation time and energy of the $Co_{1-x}Zn_xAl_2O_4$ (where x = 0.00)

Wavenumber $\bar{\nu}$ (cm^{-1})	Wavelength λ (nm)	Frequency υ (Hz)	Oscillation time τ (s)	Energy E (eV)
498 (υ_2-mode)	20080	1.493E+13	6.698E-14	0.0618
577 (υ_2-mode)	17331	1.730E+13	5.781E-14	0.0716
662 (υ_1-mode)	15106	1.985E+13	5.039E-14	0.0822
907 (Com:)	11025	2.719E+13	3.678E-14	0.1126
1379 (Com:)	7252	4.134E+13	2.419E-14	0.1712

Table 3(b) Vibrational properties of wavelength, frequency, oscillation time and energy of the $Co_{1-x}Zn_xAl_2O_4$ (where x = 0.25)

Wavenumber $\bar{\nu}$ (cm^{-1})	Wavelength λ (nm)	Frequency υ (Hz)	Oscillation time τ (s)	Energy E (eV)
496 (υ_2-mode)	20161	1.487E+13	6.725E-14	0.0616
581 (υ_2-mode)	17212	1.742E+13	5.741E-14	0.0721
662 (υ_1-mode)	15106	1.985E+13	5.039E-14	0.0822
833 (Com:)	12005	2.497E+13	4.004E-14	0.1034
1379 (Com:)	7252	4.134E+13	2.419E-14	0.1712

Table 3(c) Vibrational properties of wavelength, frequency, oscillation time and energy of the $Co_{1-x}Zn_xAl_2O_4$ (where x = 0.50)

Wavenumber $\bar{\nu}$ (cm^{-1})	Wavelength λ (nm)	Frequency υ (Hz)	Oscillation time τ (s)	Energy E (eV)
503 (υ_2-mode)	19881	1.508E+13	6.632E-14	0.0624
579 (υ_2-mode)	17271	1.736E+13	5.761E-14	0.0719
665 (υ_1-mode)	15038	1.994E+13	5.016E-14	0.0825
1379 (Com:)	7252	4.134E+13	2.419E-14	0.1712

Table 3(d) Vibrational properties of wavelength, frequency, oscillation time and energy of the $Co_{1-x}Zn_xAl_2O_4$ (where x = 0.75)

Wavenumber $\bar{\nu}$ (cm^{-1})	Wavelength λ (nm)	Frequency υ (Hz)	Oscillation time τ (s)	Energy E (eV)
455 (υ_2-mode)	21978	1.364E+13	7.331E-14	0.0565
498 (υ_2-mode)	20080	1.493E+13	6.698E-14	0.0618
575 (υ_1-mode)	17391	1.724E+13	5.801E-14	0.0714
671 (υ_1-mode)	14903	2.012E+13	4.971E-14	0.0833
1381 (Com:)	7241	4.140E+13	2.415E-14	0.1714

Table 3(e) Vibrational properties of wavelength, frequency, oscillation time and energy of the $Co_{1-x}Zn_xAl_2O_4$ (where x = 1.00)

Wavenumber $\bar{\nu}$ (cm^{-1})	Wavelength λ (nm)	Frequency υ (Hz)	Oscillation time τ (s)	Energy E (eV)
449 (υ_2-mode)	22272	1.346E+13	7.429E-14	0.0557
492 (υ_2-mode)	20325	1.475E+13	6.780E-14	0.0611
571 (υ_1-mode)	17513	1.712E+13	5.842E-14	0.0709
664 (υ_1-mode)	15060	1.991E+13	5.024E-14	0.0824
1379 (Com:)	7252	4.134E+13	2.419E-14	0.1712

As shown in FTIR spectra, except the $ZnAl_2O_4$ or x = 1.00 sample, the band observed in the wavenumber range of about 1628 cm^{-1} – 1636 cm^{-1} indicates the bending vibration of H_2O molecules. Also the band observed in the wavenumber range of about 3447 cm^{-1} – 1466 cm^{-1} indicates the anti-symmetric stretching vibration of H_2O molecules. These bands are often appeared in the FTIR transmission spectra of KBr pellet method due to the distribution of humidity around the FTIR spectrophotometer.

Conclusion

Cobalt-Zinc Aluminates, $Co_{1-x}Zn_xAl_2O_4$ (where x = 0.00, 0.25, 0.50, 0.75 and 1.00) samples were successfully prepared by solid state reaction method. Structural, microstructural and vibrational characteristics were studied by XRD, SEM and FTIR spectroscopy. XRD patterns showed all characteristic peaks of the spinel structure and confirmed the phase formation indicating the absence the others impurity phases. The observed peaks perfectly matched with the crystalline phase of cubic spinel structure with the identification of satndard JCPDS. From the SEM micrographs, except the x = 1.00 sample, the grains shapes of others samples were spherical in shape and some particles were found as agglomerated with poor grain boundary. The pores serve as adsorption sites due to the heat-treatment of starting materials in the preparation of desired materials. The grain sizes were varied with the concentration of Zn. It can be said that the lattice substitution of Zn^{2+} on Co^{2+} in the samples. The grains were found to be gray colour and similar shapes (spherical and poly-face blocks). It indicates that the candidate materials are taken as the single phase and the results well confirmed from the XRD results. FTIR spectra showed that the vibrational characteristics of stretching vibrations of tetrahedral sites (A atoms, assigned as υ_1-mode) and octahedral sites (B atoms, assigned as υ_2-mode) of the AB_2X_4 [$Co_{1-x}Zn_xAl_2O_4$ sample] and their combination bands. It indicates that the candidate materials are taken as the single phase and the results well confirmed with structural phase identification of XRD results.

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