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X-ray Study of ZnAlO, ZnAlOMn and ZnAlODy Powders

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Abstract

Sol gel and X-ray study method have been adopted to prepare the ZnAlO, ZnAlOMn and ZnAlODy powders and to determine the values of Debye temperature (θ_M), Debye-Waller factor (B) and amplitude of vibrations $<u^2>$ respectively in the present investigation. X-ray diffractograms (XRD) have been recorded for ZnAlO, ZnAlOMn and ZnAlODy powders. The Debye temperature, Debye-Waller factor and amplitude of vibrations have been obtained from integrated intensities of X-rays. The intensities have been measured with an upgraded JEOL JDX-8P powder diffractometer. The Powder X-ray diffractometer fitted with a NaI (Tl) scintillation counter using filtered CuKα radiation at room temperature and have been corrected for thermal diffuse scattering (TDS) effect. Filtered copper radiation was employed at a goniometer speed of 1/2° per minute. The X-ray tube was operated at 40 kV and 30 mA power. The XRD patterns correspond to those of the standard patterns of ZnO polycrystalline and to hexagonal wurtzite structure (JCPDS No 75-0576).

Keywords: Debye temperature, Debye-Waller factor, X-ray diffraction and Sol-gel technique.

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1. Introduction

Sol-gel process is a wet-chemical technique (also known as chemical solution deposition) widely used recently in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (*sol*, short for solution) which acts as the precursor for an integrated network (or *gel*) of either discrete particles or network ploymers [1]. Formation of a metal oxide involves connecting the metal centres with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. Thus, the sol evolves towards the formation of a gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks [2]. The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth metals, can be introduced in the sol and end up uniformly dispersed in the final product. It can be used in ceramics processing and manufacturing as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio) sensors, medicine (e.g. controlled drug release) and separation (e.g. chromatography) technology [3,4]. The synthesis of nanoparticles of magnetic metals oxides have been reported in recent times by using different chemical methods viz. sonochemical, sol-vothermal, micro emulsion etc. [5]. There are considerable theoretical and experimental works on the determination of mean square amplitudes of vibration and Debye temperatures of hexagonal close packed (hcp) metals and nanoparticles. Mean square amplitudes of vibration and directional Debye temperatures of hcp rare earth metals were reported by Gopi Krishna et al. [6,7]. Sirdeshmukh et al. [8] discussed the anisotropy in Debye-waller factors of seventeen hcp metals. Gopi Krishna and Sirdeshmukh [9] compiled directional Debye-Waller factors of several hcp elements. Shankar Narayana et al. [10] reported Debye-waller factors for some hcp metals. Sing and Varshini [11] made theoretical calculation of directional X-ray Debye temperatures of several hcp metals. They made a comparison of their calculated results with experimental results.

Recently, Yang Zeng et al. [12] have investigated the influence of rapid thermal annealing on structural, luminescent, and electrical properties of Al-doped ZnO film grown by atomic layer deposition. Xiaofei Zhao et al. [13] have studied the Novel $ZnO/ZnAl_2O_4$ nanocomposites with $ZnAl_2O_4$ nanoparticles homogeneously dispersed inside a network of ZnO are fabricated by thermal treatment of a single-source precursor of ZnAl-layered double hydroxides (ZnAl-LDHs) at 800°C. The effects of the Zn/Al molar ratio of the LDH precursors on the structure, composition, morphology, textural as well as UV-absorbing properties and photocatalytic activities of the nanocomposites are investigated in detail. The results show that the $ZnO/ZnAl_2O_4$ nanocomposites derived from the ZnAl-LDHs precursors have superior photocatalytic performances to either single phase ZnO or similar $ZnO/ZnAl_2O_4$ samples fabricated by chemical co precipitation or physical mixing method. Magnesium-doped ZnAlO thin films were grown on quartz substrate by ablating the sintered target with a KrF excimer laser and the effect of growth temperature from 30 °C to 700 °C on structural, optical, and electrical properties has been studied by R.K.Guptha [14]. Elastic moduli (E, G, K, m) of calcium aluminosilicate glasses with <10 mol% of SiO_2 doped with Er_2O_3 and Yb_2O_3, melted in air and under vacuum conditions, have been measured using the pulse echo ultrasonic technique by J.A. Sampaio [15]. J. C. Lashley et al. [16] reported a comparison of the specific-heat measurements on isoelectronic Cu-Zn-Al shape-memory alloys in the parent cubic phase ($L2_1$) and in the close-packed martensitic phase (18R). Measurements were made by thermal-relaxation calorimetry over the temperature range $1.9 \le T \le 300$ K. For the close-packed martensitic phase we find that the specific heat behaves similarly to that of pure copper which is also close packed. However, they observe deviations from Debye behavior for the cubic phase at low temperatures. This deviation is accounted for by the addition of ~5% of Einstein localized modes to the Debye modes.

The reports mentioned above, no attempt was made to calculate the X-ray Debye temperature that is a parameter of considerable interest. By also motivating the inexpensive synthesis, we have undertaken a systematic X-ray determination of amplitudes of vibration $<u^2>$, Debye-Waller factor (B) and Debye temperature (θ_M) of ZnAlO, ZnAlOMn and ZnAlODy Powders. The values of are being reported for the first time for ZnAlO, ZnAlOMn and ZnAlODy Powders, and the purpose of this communication is to report the results of an X-ray investigation to determine Debye temperatures and the associated mean square amplitudes of vibration of ZnAlO, ZnAlOMn and ZnAlODy Powders.

2. Experimental Details

Sol gel synthesis technique has been adopted to prepare the ZnAlO, ZnAlOMn and ZnAlODy powders in the present investigation. ZnAlO, Mn (Manganese) doped ZnAlO, Dy (Dysprosium) doped ZnAlO compounds have been prepared by using zinc acetate, aluminium acetate, manganese acetate and dysprosium acetate respectively. The zinc acetate (1M), aluminium acetate (1M) was dissolved in 2M methoxy ethanol. The acidic acid and Ethylene glycol were added 1:1 ratio to the precursor solution. The ammonium hydroxide added in the resulting solution to adjust the $P.^H$ value. The solution will keep under constant stirring at 80^0C temperature using magnetic stirrer. The resultant sol gel was dried at 80^0C. The final product was annealed at 900^0C for 2 hours. The Mn and Dy were also doped with ZnAl2O4 also synthesized and synthesized in the same procedure. X-ray diffractograms (XRD) have been recorded for ZnAlO, ZnAlOMn and ZnAlODy powders. The XRD patterns correspond to those of the standard patterns of ZnO polycrystalline and to hexagonal wurtzite structure (JCPDS No 75-0576). The Debye temperature, Debye-Waller factor and amplitude of vibrations have been obtained from integrated intensities of X-rays. The intensities have been measured with an upgraded JEOL JDX-8P powder diffractometer. The Powder X-ray diffractometer fitted with a NaI (Tl) scintillation counter using filtered CuKα radiation at room temperature and have been corrected for thermal diffuse scattering (TDS) effect by using the method Chipman and Paskin

[17]. Filtered copper radiation was employed at a goniometer speed of 1/2° per minute. The X-ray tube was operated at 40 kV and 30 mA power. The XRD patterns of ZnAlO, ZnAlOMn and ZnAlODy powder particles have been shown in figure 1.

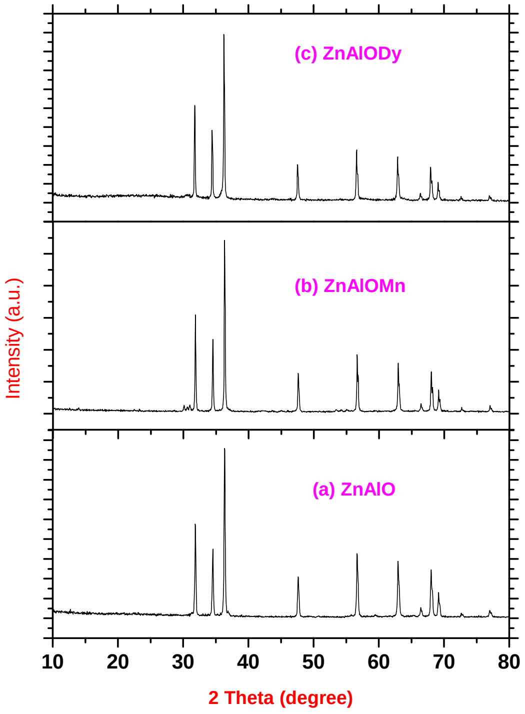

Figure 1. XRD patterns of (a) ZnAlO, (b) ZnAlOMn and (c) ZnAlODy powders.

3. Analysis of data

ZnAlO, ZnAlOMn and ZnAlODy powders have hexagonal structure (hcp) (JCPDS No 75-0576). The integrated intensity of Bragg reflection from a hexagonal cell may be written as follows [18-20]

$$Io = CIc \exp \{-(4\pi \sin\theta/\lambda)^2 [(\langle u_{\parallel}^2\rangle \cos^2\Psi + \langle u_{\perp}^2\rangle \sin^2\Psi)]\} \qquad (1)$$

where C is a constant, Ic is the calculated intensity. $\langle u_{\parallel}^2\rangle$ and $\langle u_{\perp}^2\rangle$ refer to the components of the average vibrational amplitude projected onto the hexagonal axis and basal plane respectively. Ψ is the angle between the diffraction vector to the hexagonal axis and λ the wavelength. The calculated intensity Ic is given by

$$Ic = L_pJF^2 \qquad (2)$$

where L_p is the Lorentz polarization factor, J the multiplicity factor and F the structure factor. The structure factor is given by

$$F^2_{hkl}=36f^2 \cos^2 2\pi \quad \text{for} \quad -h+k+l = 3n \tag{3}$$

The structure factors are calculated from the atomic scattering factors given by Cromer and Waber [21]. These are corrected for anomalous dispersion [22]. $<u_{II}^2>$ and $<u_\perp^2>$ are obtained from a least square analysis of the logarithmic form of Equation (1).

From these, the directional Debye-Waller factors $B_\perp$ and B_{II} are obtained from the equations.

$$B_\perp=8\pi^2<u_\perp^2>, \qquad B_{II}=8\pi^2<u_{II}^2> \tag{4}$$

The mean Debye-Waller factor B is given by

$$B = (2B_\perp + B_{II})/3 \tag{5}$$

The directional Debye temperatures $\theta_\perp$, θ_{II} and mean Debye temperature θ_M are obtained from $B_\perp$, B_{II} and B respectively using the Debye-Waller theory [23] relation

$$B = (6h^2/M\, k_B\, \theta_M)W(x),\ \ B_\perp= (\ 6h^2/Mk_B\theta_\perp)W(x),\ \ B_{II} = (6h^2/M\, k_B\theta_{II})W(x) \tag{6}$$

where h is the Plank's constant, k_B the Boltzmann constant, M the atomic weight and θ_M the Debye temperature. The function W(x) is given by

$$W(X) = [\phi(X)/X + (1/4)] \tag{7}$$

where $X= \theta_M/T$, T is the temperature of the crystal and $\phi(X)$ is the Debye function. The values of W(X) for a wide range of X can be obtained from standard tables [24].

4. Results and Discussion

In the present work, the values of Debye temperature (θ_M), Debye-Waller factor (B) and amplitude of vibrations $<u^2>$ for the sample ZnAlO, ZnAlOMn and ZnAlODy powders have been determined by X-ray method [25-27] for the first time. These values have been given in Table.1

Table 1. Values of Debye temperature (θ_M), Mean square amplitude of vibrations $<u^2>$, Debye-Waller factor (B) and vacancy formation energy (E_f) of ZnAlO, ZnAlOMn and ZnAlODy powders.

Parameter (Powder Compound)	Particle size(t) (nm)	$<u^2>$ (Å^2)	B (Å^2)	θ_M (K)	(E_f) (eV)
ZnAlO	99.80	0.00272(5)	0.21(4)	393(7)	2.51
ZnAlOMn	35.50	0.00194(5)	0.15(2)	468(4)	3.50
ZnAlODy	49.39	0.00227(4)	0.17(2)	432(5)	2.98

The particle size (t) has been determined by measuring the (FWHM) full width at half maximum of the diffraction peaks rather than half widths. The particle size (t) has been estimated by using the Hall-Williamson method [28] and the equation is

$$B_r \cos\theta = k\lambda/t + \varepsilon \sin\theta \tag{8}$$

where B_r is the peak broadening due to crystallite size and ε the lattice strain, k the shape factor usually taken as 1.0 and t the crystallite size in nanometers, θ and λ are the Bragg angle and the wavelength of incident X-ray beam in nm. Typical Hall-Williamson plot has been shown in Figure 2.

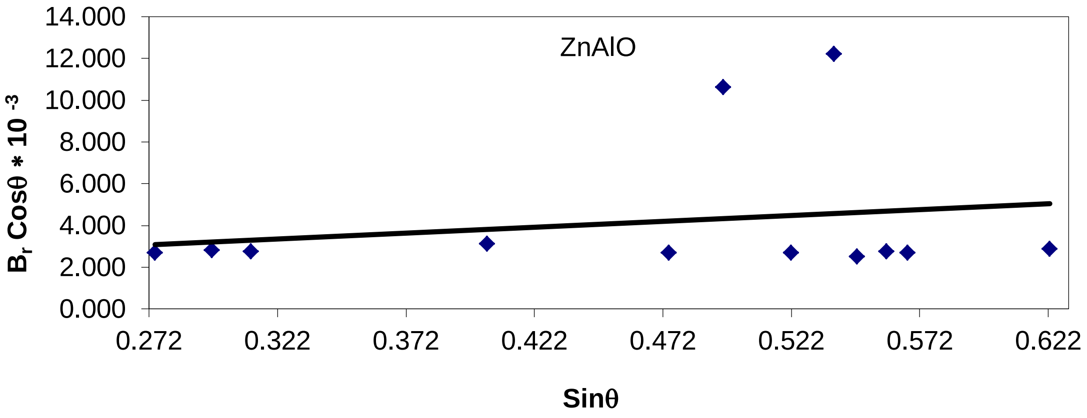

Figure 2. Typical Hall-Williamson plot for the sample ZnAlO powder.

The Debye temperatures obtained in the present work have been used to estimate vacancy formation energies for ZnAlO, ZnAlOMn and ZnAlODy powders using Glyde relation [29] and the values are also included in Table 1. The values of E_f are not available for comparison.

$$E_f = A(k/\hbar)^2 M\theta^2 a^2 \qquad (9)$$

where a is the inter-atomic spacing, A a constant shown to be equal to 1.17 x 10^{-2}, M the molecular weight and h and k are the plank’s and the Boltzmann’s constants, respectively.

5. Conclusions

The values of solid state parameters like Debye temperature (θ_M), Debye-Waller factor (B), amplitude of vibrations $<u^2>$ and vacancy formation energy (E_f) for ZnAlO, ZnAlOMn and ZnAlODy powders have been determined for the first time. ZnAlO, Mn (Manganese) doped ZnAlO, Dy (Dysprosium) doped ZnAlO compounds have been prepared and studied by sol-gel synthesis technique and X-ray method respectively.

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