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RESEARCH ARTICLE

L.Jithendar *et al*, The *Experiment*, *2014., Vol. 18(3), 1284-1291*

Thermal properties of X-ray study of Bi metal Nanopowders Prepared by Mechanical Milling

ABSTRACT

Bismuth metal nanopowders have been prepared by a Retsch Planetary PM 100-ball mill. The time of milling has been extended up to 32 hours. After every spell of 4 hours of milling, XRD patterns have been recorded for Bi sample. The particle size has been estimated using Hall-Williamson method. The Debye temperatures, Debye-waller factors and amplitudes of vibration of Bi metal nanopowders have been obtained from integrated X-ray intensities. The intensities have been measured with an upgraded JEOL JDX 8P powder diffractometer fitted with a scintillation counter using filtered CuKα radiation at room temperature and have been corrected for TDS effect. The values of Debye temperature obtained for Bi metal nanoparticles have been compared with the values obtained from other methods. The X-ray Debye temperatures obtained in the present work have been used to estimate the E_f values for Bi metal nanoparticles. The Debye temperature of metal nanopowders of bismuth decreases from 122 K to 75 K with decreasing particle size from 96 nm to 15 nm.

Keywords: Mechanical milling, Debye temperature and Debye-Waller factor.
PACS: No.65

1. INTRODUCTION

In the last few decades, the synthesis of nanoparticles is having considerable attention due to its interesting properties like electrical, optical, chemical, and magnetic etc. and which could not be achieved by their bulk nanoparticles [1]. The mechanical milling process has been successfully employed in the synthesis of wide range of materials [2,3]. There are considerable works on the determination of mean square amplitudes of vibration and Debye temperatures of hexagonal close packed (hcp) metals from our laboratory. Debye temperatures and mean square amplitudes of vibration of hcp rare earth metals were reported by Gopi Krishna et al. [4]. Recently, Arnaud et al. [5] have computed the effective electron-phonon coupling constant governing the electron cooling in photoexcited bismuth. The synthesis of Bi nanotubes in the conditions of microwave heating as a lower–cost and simple technique in comparison with traditional methods reported by Kharissova et al. [6]. The effect of particle size on the thermal properties of Bi, W, Ag, Al, Au, Zn, and Co nano materials has been studied using model calculations [7]. The studies on the size dependence of cohesive energy of W, Ag and Co nanoparticles have been carried out [8-11].

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The purpose of this communication is report the results of an X-ray investigation to determine Debye temperature (θ_M), Debye-Waller factor (B) and amplitudes of vibration $<u^2>$ of Bi metal nanoparticles for different milling hours.

2. EXPERIMENTAL DETAILS

In the present work Bi nanopowders were prepared from spectroscopically pure materials by high-energy ball milling. High-energy ball milling is an effective way of producing nano-crystalline, amorphous, solid solution and other non- equilibrium structured powders mainly through a solid-state reaction [12-14]. The technique of ball milling has been successfully employed in the synthesis of a wide range of nanomaterials [15,16]. Bi elemental powder with particle size less than 100 m was ballmilled in a Retsch Planetary PM 100 ballmill with a speed of 300 rpm using tungsten carbide vial and balls 5 mm diameter. The ball to powder ratio is 5:1. The milling time has been extended up to 32 hours. In order to prevent excessive rise in temperature of vial, ballmilling was performed 1 hour followed by 10 minutes interval of time. After each spell of 4 hours of milling, X-ray diffractograms have been recorded with an upgraded JEOL JDX-8P powder diffractometer using copper radiation and a scintillation counter at a goniometer speed of ½ ^{o} per minute. The X-ray tube was operated at 40 kV and 25 mA. All the measurements were made at room temperature. The X-ray diffraction patterns of Bi metal nanopowders for different milling hours are given in Fig.1 (A)-(I). The integrated intensities of these reflections

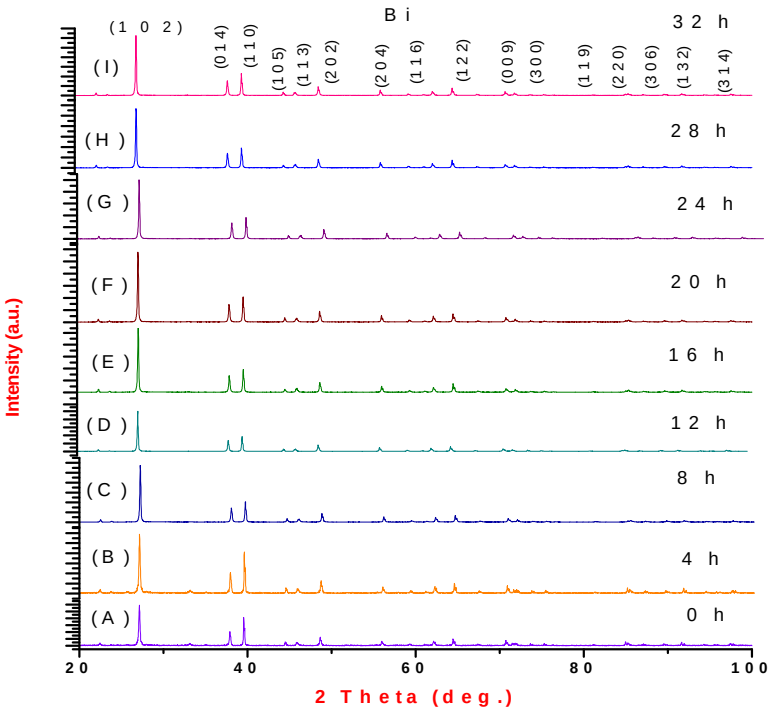

FIGURE 1 (A)-(I) : The X-ray diffraction patterns of Bi metal nanoparticles.

have been corrected for thermal diffuse scattering (TDS) using the method of Chipman and Paskin [17].

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3. ANALYSIS OF DATA

Bismuth metal has a rhombohedral structure. Rhombohedral crystals can be described in terms of a hexagonal cell (hcp) [18]. The integrated intensity of Bragg reflection from a hexagonal cell may be written as follows [19-21]

$$Io = CIc \exp\{-(4\pi\sin\theta/\square\square\square^{\square\square}\square(\langle u_{\eta}^2\rangle \cos^2\Psi + \langle u_{\perp}^2\rangle \sin^2\Psi)]\} \quad (1)$$

Where c is a constant, I_c is the calculated intensity. $\langle u_{\eta}^2\rangle$ 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 and the hexagonal axis and $\square$ the wavelength. The calculated intensity I_c is given by

$$I_c = L_p J F^2 \quad (2)$$

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

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

Where z = 0.237 for Bi [22] and f is the atomic scattering factor. The structure factors are calculated from the atomic scattering factors given by Cromer and Waber [23]. These are corrected for anomalous dispersion [24]. $\langle u_{\eta}^2\rangle$ and $\langle u_{\perp}^2\rangle$ are obtained from a least square analysis of the logarithmic form of Eq.(1). From these, the directional Debye-Waller factors $B_{\perp}$ and B_{η} are obtained from the equations.

$$B_{\perp} = 8\pi^2\langle u_{\perp}^2\rangle, \; B_{\eta} = 8\pi^2\langle u_{\eta}^2\rangle \quad (4)$$

The mean Debye-Waller factor B is given by

$$B = (2B_{\perp} + B_{\eta})/3 \quad (5)$$

The directional Debye temperatures $\theta_{\perp}$, θ_{η} and mean Debye temperature θ_M are obtained from $B_{\perp}$, B_{η} and B respectively using the Debye-Waller theory [21] relation

$$B = (6h^2/M k_B \theta_M)W(x), \; B_{\perp} = (6h^2/M k_B \theta_{\perp})W(x), \; B_{\eta} = (6h^2/M k_B \theta_{\eta})W(x) \quad (6)$$

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

$$W(X) = [\phi(X)/X + (1/4)] \quad (7)$$

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[25].

4. RESULTS AND DISCUSSION

The particle size for various milling hours has been estimated by using Hall-Williamson method [26]. The particle size has been determined by measuring the integrated width of the diffraction peaks rather than half widths. After eliminating the instrumental broadening effects, the particle size (t) and lattice strain (ε) have been determined using the equation

$$B_r\text{Cos}\theta = k\square/t + \varepsilon\,\text{Sin}\theta \quad (8)$$

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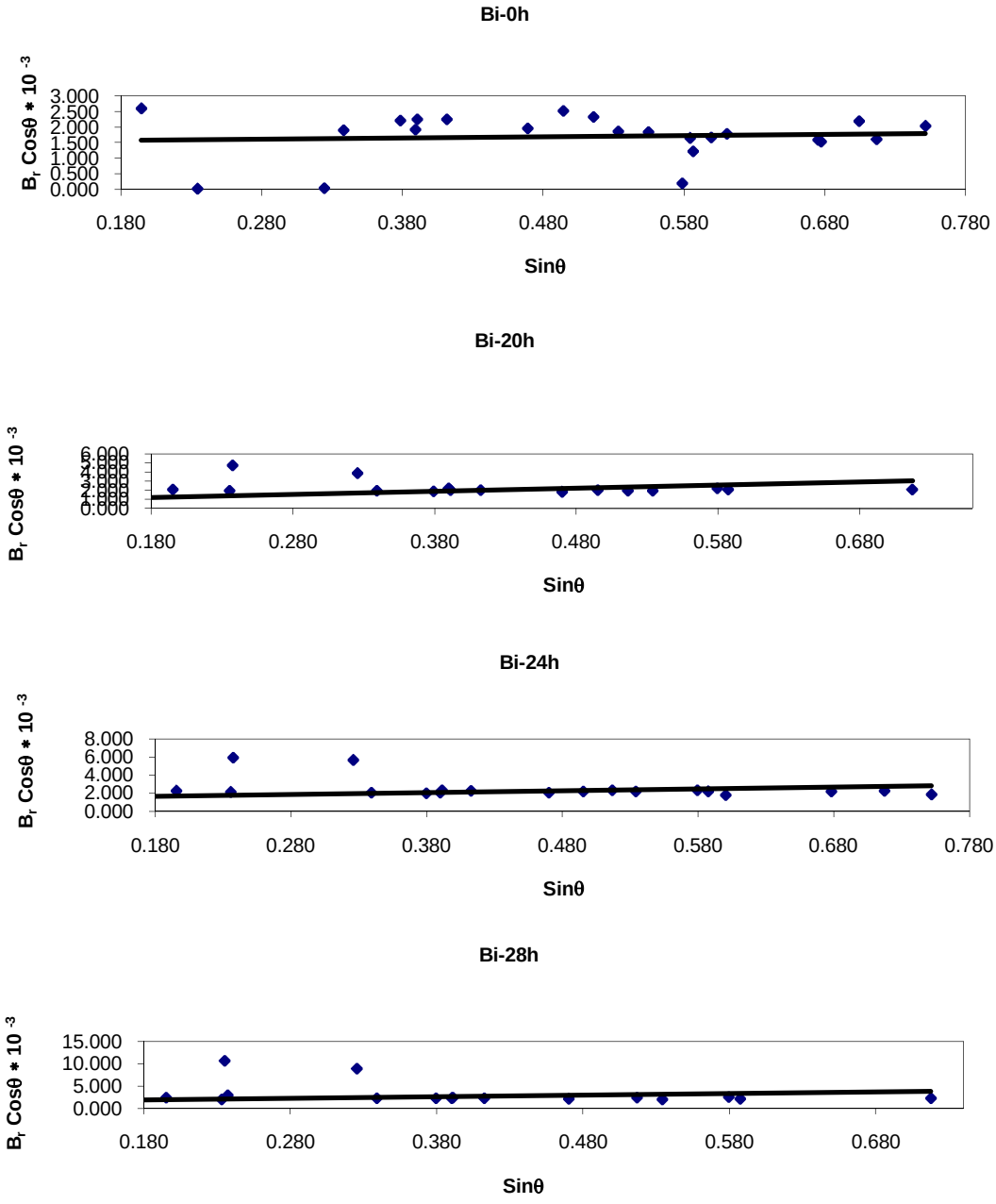
Where B_r is the peak broadening due to crystallite size and ε the lattice strain, k the shape factor usually taken as 1.0 and t the particle size in nanometer, θ and □□ are the Bragg angle and the wavelength of incident X-ray beam in nm. The typical Hall-Williamson plots for Bi nanopowders milled for 4, 20 and 28 hours have been shown in Fig. 2.

The results of Bi metal nanoparticles for different milling hours as mean square amplitudes of vibration $<u^2>$, the Debye-waller factor (B) and the Debye temperature (θ) and particle size (t), obtained in the present work are given in Table 1.



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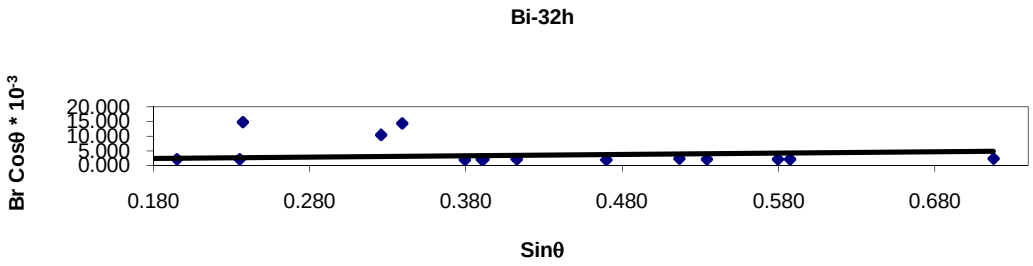

FIGURE 2 : ***The typical Hall-Williamson plots for Bi nanopowders for different milling hours.***

TABLE 1 : ***The values of particle size (t), mean square amplitudes of vibration <u^2>, Debye temperature (θ), Debye-waller factor (B) and vacancy formation energy<E$_f$> for the Bi nanoparticles with different milling hours.***

Milling Time (h)	(t) (nm)	$\langle u_{\perp}^2 \rangle$ (Å^2)	$\langle u_{\parallel}^2 \rangle$ (Å^2)	$B_{\perp}$ (Å^2)	$B_{\parallel}$ (Å^2)	$\theta_{\perp}$ (K)	$\theta_{\parallel}$ (K)	B (Å^2)	θ_M (K)	θ_D (K)	θ_E (K)	E_f (eV)
0	96	0.0143(4)	0.0148(2)	1.13(3)	1.16(2)	120(10)	119(8)	1.15(2)	119(9)			0.60
								1.14[28]		**116[27]**	**113[27]**	
								1.10[29]				
4	81	0.0147(2)	0.0152(2)	1.23(2)	1.26(1)	116(9)	115(7)	1.24(1)	115(10)			0.56
8	75	0.0161(1)	0.0165(2)	1.33(1)	1.37(2)	112(7)	110(5)	1.35(2)	111(8)			0.52
12	68	0.0172(2)	0.0177(1)	1.41(1)	1.44(1)	108(9)	107(9)	1.42(1)	107(10)			0.48
16	59	0.0183(2)	0.0186(2)	1.50(1)	1.54(2)	105(8)	103(7)	1.52(1)	104(8)			0.45
20	47	0.0213(3)	0.0218(3)	1.73(2)	1.74(1)	98(14)	96(13)	1.73(2)	97(14)			0.39
24	39	0.0221(3)	0.0226(3)	1.80(2)	1.83(2)	95(13)	94(12)	1.81(2)	94(13)			0.37
28	26	0.0291(2)	0.0294(1)	2.44(2)	2.47(2)	82(9)	80(9)	2.45(2)	81(10)			0.27
32	15	0.0362(3)	0.0357(3)	2.94(3)	2.96(2)	75(9)	74(7)	2.95(3)	74(9)			0.23

It can be observed from Table 1 that the particle size progressively decreases with increasing milling time. In the present work, Bi metal nano particles have been produced by high-energy ball milling, the plastic deformation produced by milling gives rice to changes in the particle size of nano powders. The variation of particle size on milling time has been shown in Fig. 3.

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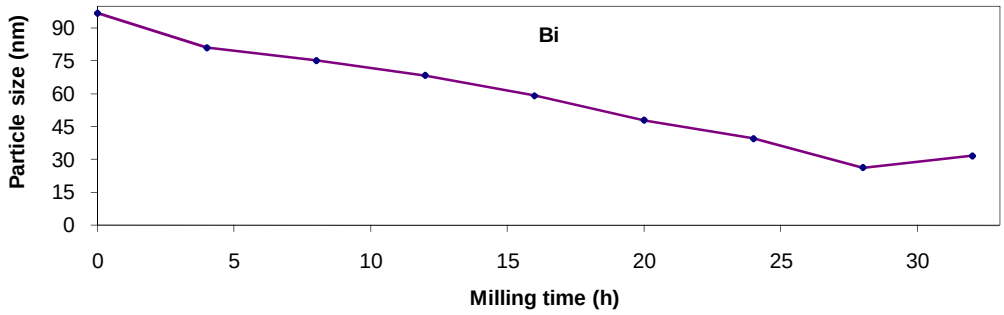

FIGURE 3 : Variation of particle size with milling time.

It is observed from Table 1 that the Debye temperature decreases with decreasing of particle size. It could be due to the softening of the thermal vibrations of the atoms at the free surface. The values of Debye temperature and Debye-Waller factor obtained in the present work for bulk Bi have been compared with the values obtained from specific heat data, elastic constant data and other workers [27-29] and the agreement is good.

The X-ray Debye temperatures obtained in the present work have been used to estimate vacancy formation energies for Bi metal nanoparticles using Glyde relation [30] and the values are also included in Table 1. The values of E_f as a function of particle size 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 1.17×10^{-2}, M the molecular weight and h and k are the plank's and the Boltzmann's constants, respectively. Glyde [30] recommended the use of X-ray based values for use in Eq.(9). The validity of Eq.(9) was verified for a number of fcc, bcc and hcp metals [31].

A model proposed by Raghuvesh kumar and Munish kumar [7] to study the size dependence of Debye temperature for nanoparticles by considering the spherical shape for the particles. The results obtained for □$_p$ in the present work have been shown in Fig.3 along with the values computed from the equation proposed by Raghuvesh kumar and Munish kumar for comparison. The equation given by them is

□ □$_{Dn}$ □□□□$_{Db}$ [1- 2d/D]$^{1/2}$ □□□ □□□□□□□□□□□□□□□□

where □$_{Dn}$ is the Debye temperature of nanomaterial, □$_{Db}$ the Debye temperature of corresponding bulk material, d is the diameter of the atom and D the diameter of nanosolid.

High energy ball milling is an established technique for producing nanocrystalline metal powders. During the process of milling, due to the plastic deformation of the powder particles, large lattice strains are also introduced into the powder particles [32]. These lattice strains in nanopowders cause static displacement of atoms in the lattice-giving rise to static component of the Debye-Waller factor. The static component of the Debye-Waller factor increases with milling time. Consequently, the measured values of Debye-Waller factors of

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particles prepared by ball milling increase faster than the corresponding strainfree particles as the particle size decreases. The increase in the value of Debye-Waller factor causes a decrease in the value of Debye temperature and hence, in the present work the reduction in the values of Debye temperature as shown in Fig.4. started at slightly larger particle size than the values predicted by the Eq. (10) proposed by Raghuvesh kumar and Munish kumar [7].

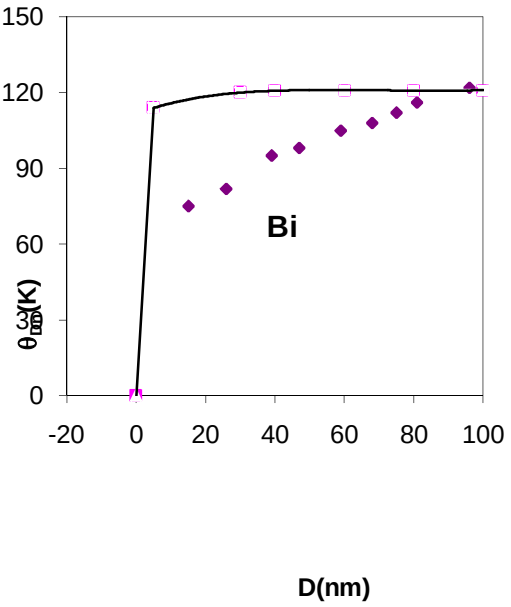

FIGURE 4 : The size dependence of Debye temperature of Bi nanopowders.

5. CONCLUSION

The results on the X-ray determination of Debye temperature, amplitudes of vibration and Debye-Waller factor of bismuth metal nanopowders for different milling hours have been reported. The mechanical milling is a technique has been used to prepare the Bi nanopowders. The values of vacancy formation energy (E_f) are estimated for Bi nanopowders.

The θ_M Debye temperatures of Bi nanoparticles for different milling hours have been obtained for the first time. The average particle size varies from 96nm to 15nm for different milling hours of Bi nanopowders.

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