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X-ray Debye temperature of mechanically milled $Ni_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite

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Abstract : The X-ray Debye temperatures, θ_M, of spinel ferrite composition $Ni_{0.5}Zn_{0.5}Fe_2O_4$, mechanically milled upto 9 hrs, were determined from integrated intensities of selected Bragg reflections. The θ_M was found to increase with milling time. The results are explained in the light of milling induced grain orientation and surface effect. The values of θ_M were found to be lower as compared to the Debye temperatures obtained from infrared spectral data analysis. The difference can be explained on the basis of increase in an excess free volume in the form of vacancies and vacancy clusters associated with grain boundaries.

Keywords : Magnetic oxide, X-ray diffraction, nanomaterials, Debye temperature.

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1. Introduction

Micro-structural characterization of nanocrystalline materials is necessary to understand the origin of novel and/or improved properties in comparison with the conventional coarse-grained counterpart. In nanocrystalline materials, a large fraction of atoms are located on the grain boundaries and their vicinities and hence the atomic relaxations in these regions are the main micro-structural elements that play an important role in the determination of the properties of nanocrystalline materials

The Debye temperature is an important parameter in solid state and materials science problems involving lattice vibrations. Various physical parameters such as the mean square displacements, the elastic constants, sound velocities, lattice instabilities *etc.* are known to depend upon the Debye temperature of a solid. It has been shown that Debye temperatures obtained from different experimental methods (*e.g.* measurements of elastic constant, specific heat and infrared spectroscopy) will not, in general, be

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equal [1]. To the best of our knowledge, very scant attention has been paid to X-ray Debye temperatures for ferrite materials in general, except on Ni-Li-Fe-O and Zn-substituted $CuFeCrO_4$ systems [2,3], and mechanically milled ferrite materials in nano regime in particular.

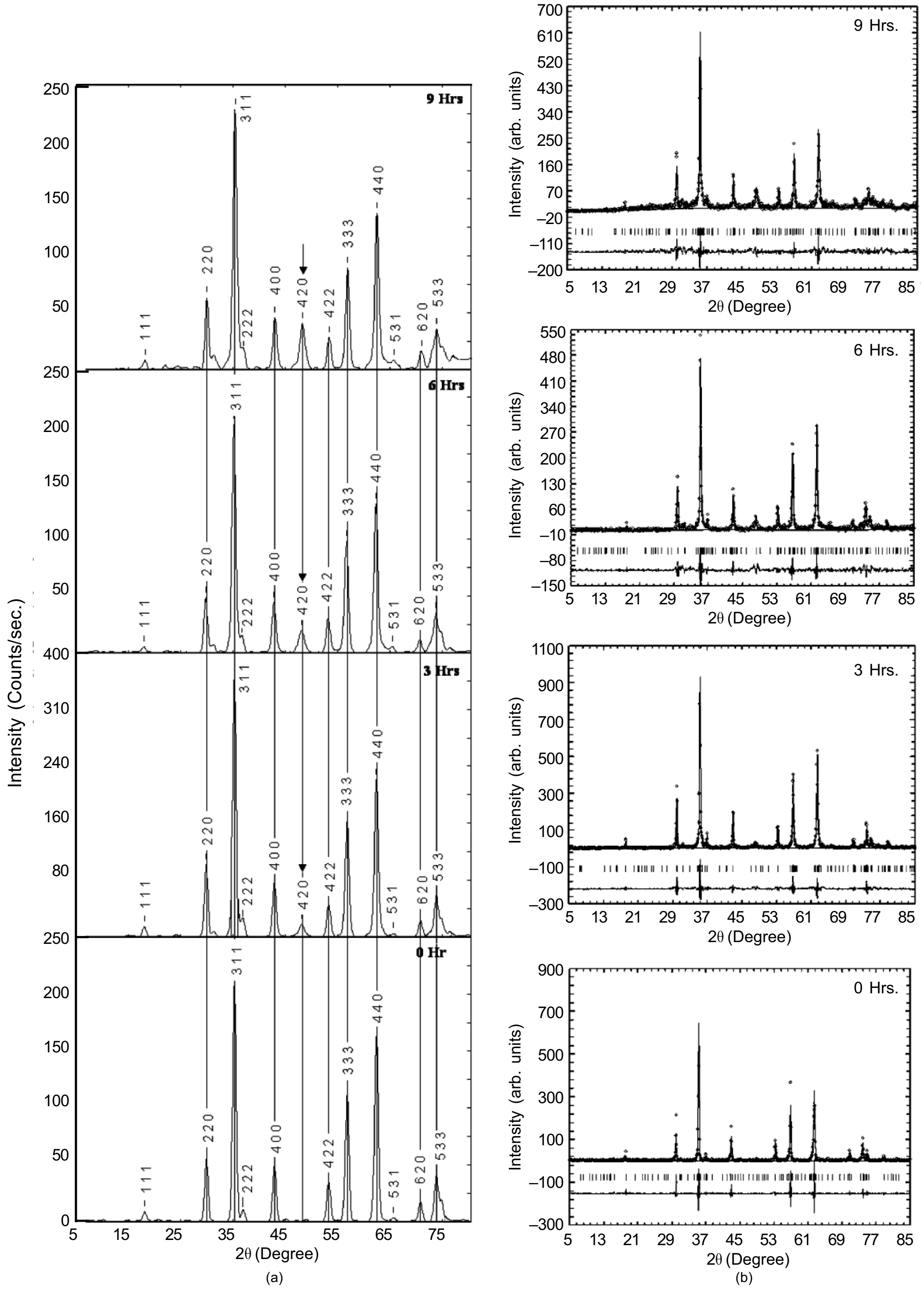
The present paper reports the X-ray Debye temperature, θ_M, for un-milled and milled samples of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite determined from the room temperature X-ray diffraction intensities. The θ_M, so obtained is compared with the Debye temperature obtained from infrared spectral analysis.

2. Experimental details

Bulk quantity (about 20 grams) of spinel ferrite material with composition $Ni_{0.5}Zn_{0.5}Fe_2O_4$ was prepared by the conventional ceramic route. The 99.5% pure powders of Fe_2O_3, ZnO and NiO all supplied by Sigma Aldrich were thoroughly mixed in appropriate stoichiometry, wet ground and calcined at 900°C for 24 hours. Two more cycles of grinding and heating were used to ensure complete reaction. In pre-sintering process, the powder was kept at 950°C for 18 hours and, slowly cooled to room temperature and in the final sintering process, the powder was once again kept at 950°C for 12 hours and cooled to room temperature at the rate of 2°C/min. The as-prepared sample was milled up to 9 hours using high energy planetary ball mill (Fritsch, Pulverisette 6) with tungsten carbide vials and balls. The milling intensity was 600 rotations per minute, and ball to powder ratio of 8 : 1 was chosen. To improve particle mobility during milling water was added to the container. The milling process was interrupted after selected times (3 hours, 6 hours and 9 hours) to take out small amount of powder, which were heated in air at 50°C until completely dry. The stoichiometry of the powder sample was checked by energy dispersive analysis of X-rays (EDAX). The samples were characterized for single phase formation and the determination of structural parameters by X-ray powder diffractometry using CuK_α radiation at 300 K.

3. Results and discussion

The room temperature (300 K) X-ray diffraction patterns of the samples were obtained by X-ray powder diffractometry. Indexing and Rietveld refinement using general scattering analysis software (GSAS) [4] of X-ray diffraction patterns of un-milled and milled samples revealed that these are single phase compounds, crystallizing in a face centered cubic (*fcc*) structure (Space group O_h^7 ($F3dm$)). Figure 1(a) shows X-ray powder diffraction patterns for the un-milled (0 Hr) and the ball milled samples for various milling times (3 hrs, 6 hrs, 9 hrs). Figure 1(b) displays Rietveld fitted X-ray diffractograms for the same samples. One of the most important Rietveld error indices or discrepancy values is that of "Chi-squared" or χ^2 [5]. It is found that χ^2 for different samples lie in the range 1.2–1.4. The χ^2 values obtained in the present analysis suggest good refinements of the data.



(a) (b)

Figure 1. (a) X-Ray powder diffraction patterns and (b) Rietveld fitted X-ray powder diffraction patterns of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ spinel samples at 300 K.

The average grain size (*D*) for ball milled samples is calculated from the broadening of the respective high intensity (311) peak using the Debye Scherrer formula :

$$D = \frac{K\lambda}{B\cos\theta} \,. \tag{1}$$

Here, λ is the wave length of the CuK$_\alpha$ radiation. The constant *K* (= 0.9) is related both to the crystallite shape and the way in which *B* and *D* are defined. *B* is the contribution to the XRD peak width due to the small size of crystallites in radians. The contribution must be separated out from the measured line width B_m, which includes the instrumental broadening *b* remaining present irrespective of the particle size. For this, the XRD pattern of a well crystallized, bulk, standard material such as silicon powder under identical geometrical conditions is recorded and the peak width *b* is measured. The broadening parameter *B* is obtained from the relation :

$$B = (B_m^2 - b^2)^{1/2}. \tag{2}$$

The average grain size reduces from 70 nm for 3 hrs milled sample to 45 nm for 9 hrs milled sample (Table 1). The grain size decreases as the milling time increases because the kinetic energy due to the series of collisions among balls is transferred to the system. The grain sizes calculated at different θ values were at variance, indicating the effect of strain. The detailed work on mechanical milling induced structural property modifications in $Ni_{0.5}Zn_{0.5}Fe_2O_4$ has been presented elsewhere [6].

3.1. X-ray Debye temperature of $Ni_{0.5}Zn_{0.5}Fe_2O_4$:

A method which depends on the principle of measuring the integrated intensities of a large number of Bragg reflections at a fixed temperature was first outlined by Buerger [7] and later described in detail by Walford *et al* [8], for the determination of X-ray Debye temperature. Recently, we have used this method to obtain θ_M for $Li_{0.5(1-x)}Ni_xFe_{2.5-0.5x}O_4$ and $Zn_xCu_{1-x}FeCrO_4$ spinel ferrite systems [2,3]. The details of the method can be found from Refs. [6,7], however, we briefly present here.

The average vibrational amplitudes are related to the Bragg intensities, within the quasi harmonic approximation, through the Debye-Waller theory. The integrated intensity, I_{hkl}, from a cubic structured material can be expressed as follows :

$$I_{hkl} = L_p P_m \left|F_{hkl}\right|^2 \tag{3}$$

where F_{hkl} is the modulus of the structure factor, P_m the multiplicity factor and L_p is the Lorentz polarization factor = $(1 + \cos^2 2\theta/\sin^2\theta \cos\theta)$.

The structure factor for present composition can be written as :

$$F_{hkl} = 0.5 f_{Ni} F_{Ni} e^{-M\mathrm{Ni}} + 0.5 f_{Zn} F_{Zn} e^{-M\mathrm{Zn}} + 2 f_{Fe} F_{Fe} e^{-M\mathrm{Fe}} + 4 f_{O} F_{O} e^{-M\mathrm{O}}. \tag{4}$$

The exponential terms in eq. (4) represent the temperature factor in terms of Debye-Waller factors for the four constituent atoms of nickel, zinc, iron and oxygen,

Table 1. Grain size (D), plane (hkl), Bragg angle (θ), integrated intensity (I), Lorentz polarization factor (L_p), multiplicity factor (P_m), slope (B_M), Debye temperature (θ) and structure factor (F) for $Ni_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite.

Plane (hkl)	θ (degree)	I_{hkl}* (%)	I* (%)	L_p	P_m	$\sin^2\theta/\lambda^2$	B_M	θ_M (K)	θ_D (K)	Structure factor (F)
0 hr milled sample $(Zn^{+2}_{0.2}Fe^{+3}_{0.8})^A\ [Zn^{+2}_{0.3}Ni^{+2}_{0.5}Fe^{+3}_{1.2}]^B\ O^{-2}_4$										$D = 1\ \mu m$**
220	14.9975	37.85	28.37	27.056	12	0.0281				$-8\ f_a$
400	21.4735	23.08	20.75	12.315	6	0.0564				$-8(f_a + 2f_b + 4f_0)$
422	26.6545	13.01	12.16	7.545	24	0.0847	1.6217	262	467	$-8\ f_a$
440	31.2170	52.43	37.34	5.285	12	0.1131				$-8(f_a + 2f_b + 4f_0)$
3 hr milled sample $(Zn^{+2}_{0.2}Fe^{+3}_{0.8})^A\ [Zn^{+2}_{0.3}Ni^{+2}_{0.5}Fe^{+3}_{1.2}]^B\ O^{-2}_4$										$D = 70$ nm
220	14.9540	38.09	31.25	27.224	12	0.0280				$-8\ f_a$
400	21.4545	23.11	17.90	12.340	6	0.0563				$-8(f_a + 2f_b + 4f_0)$
422	26.8550	13.00	10.45	7.417	24	0.0859	1.2577	298	466	$-8\ f_a$
440	31.1895	52.50	47.13	5.296	12	0.1128				$-8(f_a + 2f_b + 4f_0)$
6 hr milled sample $(Zn^{+2}_{0.25}Fe^{+3}_{0.75})^A\ [Zn^{+2}_{0.25}Ni^{+2}_{0.5}Fe^{+3}_{1.25}]^B\ O^{-2}_4$										$D = 55$ nm
220	14.8970	34.15	25.85	27.448	12	0.0278				$-8\ f_a$
400	21.3970	26.79	21.07	12.414	6	0.0559				$-8(f_a + 2f_b + 4f_0)$
422	26.5830	11.62	10.86	7.591	24	0.0843	1.0699	323	472	$-8\ f_a$
440	31.1525	53.20	49.27	5.309	12	0.1127				$-8(f_a+2f_b+4f_0)$
9 hr milled sample $(Zn^{+2}_{0.2}Fe^{+3}_{0.8})^A\ [Zn^{+2}_{0.3}Ni^{+2}_{0.5}Fe^{+3}_{1.2}]^B\ O^{-2}_4$										$D = 45$ nm
220	15.016	37.98	28.07	26.984	12	0.0282				$-8\ f_a$
400	21.503	23.12	17.11	12.277	6	0.0566				$-8(f_a + 2f_b + 4f_0)$
422	26.679	13.06	8.47	7.529	24	0.0849	1.0460	327	475	$-8\ f_a$
440	31.243	52.64	45.15	5.276	12	0.1133				$-8(f_a + 2f_b + 4f_0)$

* Relative intensity with respect to 100% intensity of (311) plane.

** Determined from SEM analysis.

'f' and 'F' are their respective atomic scattering factor and structure factor, which are sine and cosine functions of the hkl values.

The Debye-Waller factor is defined as [9] :

$$M(T) = \frac{6h^2T}{mk\theta_M^2}\left\{\varphi(x) + \frac{x}{4}\right\}\frac{\sin^2\theta}{\lambda^2}$$

or

$$M(T) = B_M\,\frac{\sin^2\theta}{\lambda^2},\quad \text{where } B_M = \frac{6h^2T}{mk\theta_M^2}\left\{\varphi(x) + \frac{x}{4}\right\}. \tag{5}$$

Here m is the mass of the vibrating atom given by A/N_A, where A is the atomic weight taken as the mean atomic weight (molecular weight of $Ni_{0.5}Zn_{0.5}Fe_2O_4$/number of atoms in formula unit *i.e.* 7), N_A is the Avogadro's number, h is the Planck's constant, k is the Boltzmann's constant, θ_M is the X-ray Debye temperature, T is the temperature (300 K), θ is the Bragg angle, λ is the wavelength of the X-rays (for CuK_α radiation λ = 1.5405 Å), $x = \theta_M/T$, and function $(\Phi(x) + x/4)$ is calculated by the procedure described by James *et al* [9].

As the atomic masses of nickel, zinc and iron are nearly equal, the respective Debye-Waller factors (M_{Ni}, M_{Zn} and M_{Fe}) will also be approximately equal in $Ni_{0.5}Zn_{0.5}Fe_2O_4$. To the first approximation; let M_{Ni}, M_{Zn}, M_{Fe}, and M_O be equal to each other eq. (4), therefore becomes :

$$F_{hkl} = \sum f \cdot e^{-M}$$

where, $\sum f = (0.5 f_{Ni} F_{Ni} + 0.5 f_{Zn} F_{Zn} + 2 f_{Fe} F_{Fe} + 4 f_o F_o)$. (6)

Eq. (3) may be written using eqs. (4) and (5) as :

$$I_{hkl} = L_p . P_m . \left|\sum f\right|^2 e^{\frac{-2B_M \sin^2\theta}{\lambda^2}} . \tag{7}$$

The experimental structure factor, F_{exp}, may be obtained from eq. (7) using experimentally measured integrated intensity I as :

$$\left|F_{exp}\right|^2 = \frac{I}{L_p P_m} = \left|\sum f\right|^2 e^{\frac{-2B_M \sin^2\theta}{\lambda^2}} . \tag{8}$$

The measured intensities were corrected for thermal diffuse scattering (TDS) using the correction for cubic structure powders [10]. In addition to the TDS correction, intensities were also corrected for Lorentz polarization and absorption. The plots of $\ln\left(\left|F_{exp}\right|^2 / \left|\sum f\right|^2\right)$ against $2\sin^2\theta/\lambda^2$ for un-milled (0 hr.), 3 hrs, and 6 hrs milled samples of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ at 300 K are shown in Figure 2. The even-even ($h + k = 2n$, $l + k = 2n$), even-odd ($h + k = 2n$, $l + k = 2n + 1$), odd-even ($h + k = 2n + 1$, $l + k = 2n$), odd-odd ($h + k = 2n + 1$, $l + k = 2n + 1$), reflections lie on the same straight line indicates that $M_{Ni} \sim M_{Zn} \sim M_{Fe} \sim M_{O.}$ Thus the experiment has not distinguished between the individual Debye temperatures or mean square atomic displacements appropriate to the atoms of nickel, zinc, iron and oxygen in the system. The solid lines in Figure 2 are least squares fit to the experimental data points. This validates the approximation made for θ_M determination. It follows from eq. (8) that the slope of $\ln\left(\left|F_{exp}\right|^2 / \left|\sum f\right|^2\right)$ against $2\sin^2\theta/\lambda^2$ plot yields the Debye-Waller parameter (B_M) and hence θ_M can be obtained from eq. (5) by substituting the value of various parameters. The equation for θ_M in its simplified form is given by :

$$\theta_M = (11.165 \times 10^4/B_M)^{1/2}. \tag{9}$$

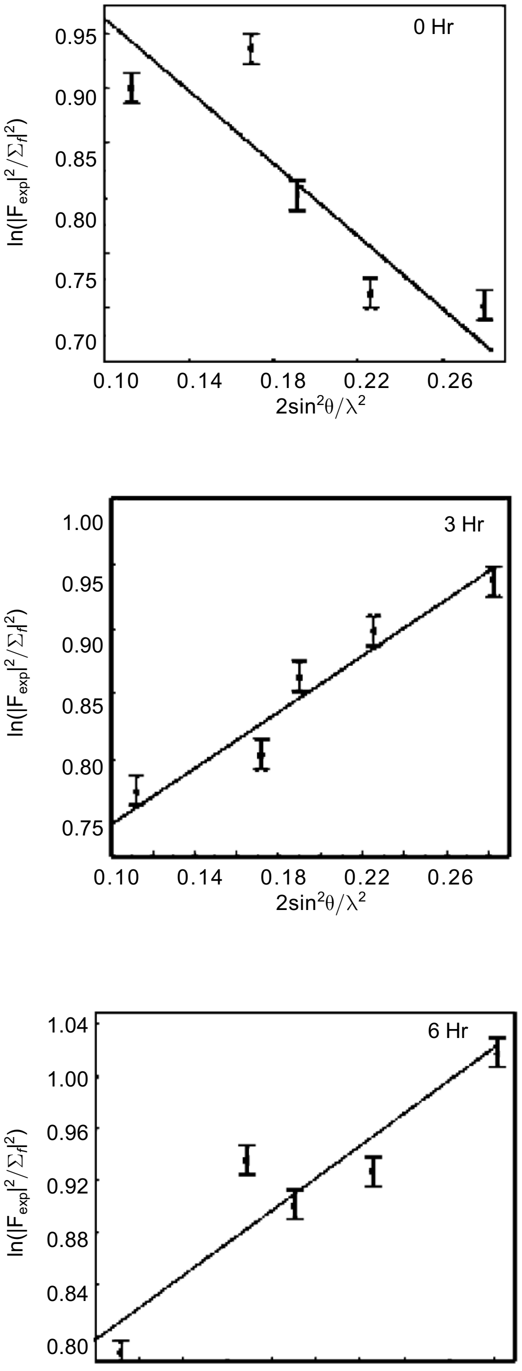


Figure 2. Plots of $\ln\left(\left|F_{exp}\right|^2/\left|\sum f\right|^2\right)$ against 2 $\sin^2\theta/\lambda^2$ at 300K for $Ni_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite composition.

The experimental values of Bragg angle (θ), integrated intensity of diffraction line (I), calculated integrated intensity of diffraction line (I_{hkl}), Debye-Waller parameter (B_M) (*i.e.* slope of the $\ln\left(\left|F_{exp}\right|^2/\left|\sum f\right|^2\right)$ *vs.* 2 $\sin^2\theta/\lambda^2$ plot) and the Debye temperature (θ_M) along with other structural parameters used in the calculation for selected planes, (220), (400), (422) and (440) for different samples are summarized in Table 1. The I_{hkl} has been obtained from the cation distribution determined from X-ray diffraction line intensity calculations [6]. The final cation distribution thus determined is also included in the Table 1 as a ready reference.

The Debye temperature, θ_M obtained at 300 K from X-ray data analysis lies in the range between 260–330 K; in contrast the Debye temperature, θ_D, obtained from infrared spectral analysis is ranging from 465 K to 475 K [11] for 0 hr to 9 hrs milled samples. This is in accordance with the assertion of Salter *et al* [1]. The discrepancy between the two approaches may be explained on the basis of the existence of peaks in the vibrational spectra at low frequencies [12,13]. Such low frequency active modes involve oscillations of the metal ions in the isotropic force fields of their octahedral or tetrahedral environments. It is interesting to note that there is significant difference in the Debye temperature obtained from the X-ray and infrared data and need to be clarified. This difference can be explained on the basis of the following arguments. In the case of nanomaterials, there is a stress field induced by the defects in grain boundaries which affects the volume and there is an excess free volume in the form of vacancies and vacancy clusters [14,15]. The excess free volume associated with grain boundaries is a function of grain size and dependent on preparation method. The excess free volume ($\varDelta V_g$) is defined as : ($\varDelta V_g$) = $(V_g - V_0)/V_0$, where V_g and V_0 are the molar volumes of grain boundary and a perfect crystallite respectively. For the nanomaterials prepared by other technique, this $\varDelta V_g$ decreases with decreasing the size [14]; while it increases with decreasing grain size for the ball milled samples. It seems that the X-ray data obtained for the ball milled materials are able to take consideration of defects and clusters, while for infrared radiation the nanocrystallite sample is a simple elastic sphere and oscillates as a whole.

Finally, an attempt has been made to calculate the ΔV_g of the atoms at the grain boundaries as a function of the grain size (D) using the expression :

$$\varDelta V_g = \left[\left(D + \varDelta/2\right)^2 - D^2\right] \Big/ D^2 = \frac{V_g - V_0}{V_0}\,. \tag{10}$$

Here, $\varDelta$(~1 nm) is the thickness of the grain boundary plane assumed to be independent of D [15]. The $\varDelta V_g$ is found to increase with the milling time : 0.4×10^{-3} for 0 hr milled sample, 14.3×10^{-3} for 3 hrs milled sample, 18.26×10^{-3} for 6 hrs milled sample and 22.35×10^{-3} for 9 hrs milled sample with decreasing grain size as discussed earlier.

The Debye temperature is the temperature at which maximum lattice vibrations take place. The observed increase in θ_M with milling time suggested that the lattice vibrations are hindered due to mechanical milling. This is consistent with our earlier result on variation of elastic moduli with milling time or reducing grain size [11]. The increase in Debye temperature can be attributed to the reduction in grain size with milling time. A fine grained material has a greater total grain boundary area and surface to volume ratio as compared to coarse grained counterpart. Total grain boundary area and surface to volume ratio increase with reducing grain size. The influence of the surface on the vibrational properties becomes relevant for smaller particles. We feel that milling induced grain orientation [6] increase the grain-grain contact area and as a result lattice vibrations get restricted, which in turn increase the Debye temperature.

The mean square displacement of the atom can be estimated from the Debye-Waller parameter B_M, using the relation [16] : $\overline{u^2} = \left(B_M/8\pi^2\right)$, assuming isotropic displacement of the atoms from their ideal lattice positions. Though this condition may not be true for the atoms in the distorted layer near the grain boundaries, the resulting errors are expected to be small [17]. In the present case, it is not possible to distinguish between the distribution of the atomic displacement inside the grain and in the distorted layers near grain boundaries of the milled samples. Earlier, we have observed that the intensity of the background scattering in the XRD patterns increases with milling time [6] and it is attributed to the displacement of atoms from their mean positions. On the other hand, calculated values of $\overline{u^2}$ were found to decrease with milling time. This suggests that the atomic displacements increase inside the grain but, within the grain boundary region, which is probably of several atomic distances wide, some kind of alignment due to grain orientation have taken place. In other words, low-angle grain boundary formation takes place. Consequently, grain boundary energy (analogous to surface energy due to atomic mismatch in a transition from the crystalline orientation of one grain to that of an adjacent one) reduces and lattice energy (measure of strength of bond) in that compound increases with milling time. Taking in to account these facts one can assume that the main reason for increasing the Debye temperature with milling time is its increased value of ordered near boundary regions and surface effect.

4. Conclusions

We report the X-ray Debye temperature from measurements of X-ray powder diffraction intensities at room temperature. The observed enhancement in Debye temperature value with milling time is due to increase in grain-grain contact area as a result of milling induced grain-orientation that restricts the lattice vibrations and the formation of low-angle grain boundary because of reduction in the mean square atomic displacement that reduces grain boundary energy and increases lattice energy. The lower values of Debye temperature (X-ray data) as compared to those determined from infrared spectral analysis is due to the increase in excess free volume in the form of vacancies and vacancy clusters associated with grain boundaries.

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References

[1] L S Salter *Adv. Phys.* **14 (53)** 1(1965)

[2] S S Bhatu, V K Lakhani, A R Tanna, N H Vasoya, J U Buch, P U Sharma, U N Trivedi, H H Joshi and K B Modi *Indian J. Pure Appl. Phys.* **45** 596 (2007)

[3] K B Modi *J. Mat. Sci*. **39** 2887 (2004)

[4] H M Reitveld *J. Appl. Cryst.* **2** 65 (1969)

[5] N H Vasoya, L H Vanpariya, P N Sakariya, M D Timbadiya, T K Pathak, V K Lakhani and K B Modi *Ceram. Int.* **36** 947 (2010)

[6] B H Toby *Powder Diff.* **21** 67 (2006)

[7] M J Buerger *Crystal Structure Analysis* (New York : Wiley) 231 (1960)

[8] L K Walford and J A Schooffel *Philos. Mag.* **21** 375 (1970)

[9] R W James *The Optical Principles of the Diffraction of X-Rays* (London : Bell) 216 (1967)

[10] D R Chipman and A Paskin *J. Appl. Phys.* **30** 1998 (1959)

[11] K B Modi *Infrared spectroscopic study on mechanically milled $Ni_{0.5}Zn_{0.5}Fe_2O_4$ spinel ferrite* (un- published work)

[12] R G Kulkarni and G K Bichile *J. Appl. Phys.* **48** 1844 (1977)

[13] R G Kulkarni and G K Bichile *J. Mater. Sci.* **15** 2927 (1980)

[14] K Lu, R Luck and B Predel *Mat. Sci. Eng*. **A179** 536 (1994)

[15] P P Chattopadhyay, P M G Nambissan, S K Pabi and I Manna *Phys. Rev*. **B63** 054107 (2001)

[16] B D Culity Elements of X-Ray Diffraction (Reading, New York : Addison-Wesley Pub. Co.) (1978)

[17] J A Eastman, M R Fitzsimmons and L J Thompson *Philos. Mag.* **B66** 667 (1992)