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Study of Thermoacoustic Properties of Boron Nitride Methanol based Nanosuspension

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ABSTRACT

Boron nitride nanoparticles (BN) were synthesized by high chemical route method and its characterization has been carried out by X ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), SEM, TEM, etc. Methanol based BN Nanosuspension were synthesized by two step method. Average particle size of BN nanoparticle has been estimated by using Debye-Scherrer formula. It was found to be 70 nm. As thermoacoustic properties of nanomaterials related to the surface of nanoparticles and nanoparticle surfactant interactions, these properties of BN nanosuspension was studied by non-destructive technique.

Keywords : BN, XRD, Debye-Scherrer Formula, Nanosuspension, Thermoacoustic Properties.

I. INTRODUCTION

Nanoparticle of metals, metal oxide and semiconductor exhibited significantly distinct physical, chemical, optical, magnetic and biological properties from their matter because of their high surface to volume ratio. When a small number of nanoparticles dispersed in host fluids, can provide dramatic improvements in the thermal properties of the fluids. More recently there has been an increasing interest in the thermoacoustic properties of nanosuspensions in base fluids. Characterization of nanoparticle is important to understand and to control nanoparticle synthesis for various applications [1-3].

Boron nitride nanoparticles possess high thermal conductivity, and are a good conductor of heat. They are also a good electrical insulator, and have high-temperature lubricity features. Boron nitride nanoparticles are graded as an irritant and could possibly causes serious eye irritation, and allergy or asthma symptoms or breathing difficulties if inhaled. Boron nitride nanoparticles should be sealed in vacuum and stored in cool and dry room so as to avoid damp reunion as it would affect its dispersion performance and other usage effects.

Synthesis of Boron nitride Nanoparticles:

Boron Nitride is synthesized by using 6.18g boric acid (H_3BO_3, Merck) dissolved in 200 ml distilled water. The solution is kept at 100^{0}C. The 6.30g melamine $C_3H_6N_6$ Merck is now added to the solution. The material prepared is placed up to 48 hours in room temperature. $B_4N_3O_2H$ is obtained after filtering and drying the solution. This is the precursor of BN. Then it is heated at 500^{0}C temperature for three hours without any gas flow. After that, material heated under nitrogen gas flow. Nitrogen gas flow is allowed for one hour with 800^{0}C. The sample so obtained was grinded to get it in powdered form [4-6].

XRD Pattern of Boron nitride Nanoparticles:

Many techniques are used to identify the various properties of nanomaterials. Some of the most important techniques are discussed below. X-ray diffraction [7-9] is a versatile, non-destructive technique that reveals details information about the chemical composition and crystallographic structure of natural and manufactured materials. In a crystalline solid, the constituent particles are arranged in regular periodic manner. An interaction of a particular crystalline solid with X-ray helps in investigation of its actual structure. Crystal is found to act as diffraction grating for X-ray and this indicates that the constituent particles in the crystal are arranged in planes at close distance in repeating patterns. The 2θ a value corresponding to peak in the X- ray diffraction is an important tool to understand the properties of characterizes materials. In nanomaterials number of atoms is very small. Nanoparticles cannot be considered as an infinite arrangement at of atoms. In case of amorphous nanoparticles broad diffraction peaks are expected to occur similar to amorphous bulk solid materials. However, in case of nanoparticles atoms do not have ordered lattices, some changes in diffraction are to be expected as compared to single crystal. Nanoparticles do not have grain boundaries. It has been found that diffraction peaks in nanocrystalline particles are broadened compared to a single or polycrystalline solid of same materials. From WRD pattern, Debye Scherrer gives an equation to determine nanoparticles size as,

$$D = \frac{0.9\lambda}{\beta Cos\theta} \quad \text{--} \quad (3.1)$$

In above equation β is the broadening caused by nanoparticles size, θ is the Bragg's angle and λ is the wavelength of X-ray beam.

Figure 1 shows the XRD pattern of Boron nitride (BN) nanoparticles. The XRD measurement carried out by using "PAN analytical" X-ray diffractometer keeping the parameter constant at start position [°2Th.]: 10.0154 End Position [°2Th.]: 89.9834, Step Size [°2Th.]: 0.0170, Scan Step Time [s]: 5.7150, Scan Type: Continuous, Measurement Temperature [°C]: 25.00 Anode Material: Cu, K-Alpha1 [Å]: 1.54060. It is seen that the materials is well crystalline in nature and well agreed with standard JCPDS file number 034-0421. The estimate size of BN nanoparticles using Debye Scherrer formula is found about 70 nm.

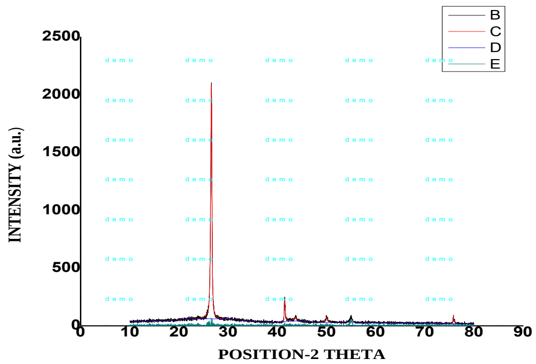

Fig. 3.1 X- ray diffraction pattern of Boron nitride nanoparticles

Results and Discussion:

The experimentally measured values of ultrasonic velocity, density and viscosity are used to derive thermo acoustical parameters such as viscosity, adiabatic compressibility, Acoustic impedance, free length, free Volume, internal Pressure, isothermal compressibility, isothermal bulk modulus, molar compressibility, molar sound velocity, molar volume, Poisson ratio, relaxation time, Van der Wall's Constant, volume expansivity, effective mass and thermal conductivity. These parameters are represented are given in tables 1 (A) and 1 (B). In BN Methanol based nanosuspension there might be nanoparticle fluid interaction favors in increase in ultrasonic velocity [10]. Rise in ultrasonic velocity may concluded as the strong interaction between nanoparticles of Boron Nitride (BN) and microsize molecules of methanol hence there is agglomerisation of BN nanoparticles due to polar nature of methanol base fluid. Therefore sound will travel faster through the more compact structure by means of longotudinal waves [11-13].

Ultrasonic velocity gets increases with increasing the molar concentration of the BN nanoparticles in methanol this shows that the physical parameters of the sample changes by increasing the molar concentration. Nanoparticles suspensions do not settle which provides a long self- life which imparts ultrasonic velocity to them. For BN nanoparticle the velocity of the nanofluid is higher than methanol and also by increasing the molar concentration of the BN nanoparticle the velocity gets increases up to 0.6 and then decreases. This represents strong aggregation of BN nano suspension in methanol-based fluid at molar concentration 0.6. The cause behind this increase of ultrasonic velocity with increase in molar concentration (x) is due to strong interaction between nanosized particle and micro sized fluid molecule and also due to increase in density of nanofluid with increase of molar concentration. Ultrasonic velocity can be interpreted as the nanosized BN particles have more surfaces to volume ratio and which can absorb more methanol molecules on its surface, which enhances the ultrasonic velocity. The decrease of ultrasonic velocity with increase in concentration is due weakening of interaction between BN nano sized particles and micro sized fluid molecules of methanol. Nonlinear variation of ultrasonic velocity may due to the Brownian motion of BN nanoparticles. Brownian motion is the erratic and constant motion of suspended nanoparticles in fluid. Motion of the particle becomes more rapid with increase in temperature of the medium which enhances ultrasonic velocity of the nanofluid. Aggegation of BN nanoparticles in nanofluids may occurs due to the interstitial accommodation of BN nanoparticles in nanofluids or due to lack of perfect symmetry and decrease in available space between the components of the nanosuspension.

Densities of the nanosuspension were calculated by measuring the weight of the nanosuspension using 25 ml of specific gravity bottle and also by using the standard value of density of water. Nanosuspension BN has more density than methanol. Increase in density indicates the close packing between the BN nanoparticles in methanol-based fluids. Nonlinear variation of density may be due to Brownian motion of BN nanoparticles in methanol.

When BN nanoparticles suspended in methanol fluid, motion of particle becomes more rapid, lighter the particles, faster the motion and denser the particles slower the motion. Also suspended nanoparticles do not settle and they have long self-life. Hence, they can be easily suspended despite high solid density.

The densities of BN nanoparticles in methanol based nanosuspension shows that the density steeply increases with increase in concentration. This increase in density decreases the volume indicating association of BN nanoparticles in nanosuspension. It may be increase due to structural reorganization. The viscosity slightly increases with increase in molar concentration of BN nanoparticles in methanol base nanosuspension. As the motion of nanoparticles becomes more rapid when the temperature of the medium was raised which lowers the viscosity of the medium as the size of the particles was reduced. Hence viscosity of nanosuspension decreases with increase in temperature.

The viscosity of BN nanoparticle strongly depends on structure of BN nanoparticles and consequently interactions between the BN nanoparticles and molecules of the fluid. Thus, the viscosity depends on interactions between components of nanosuspension as well as on the size and shape of the BN nanoparticles. Measurements of viscosity of nanosuspension yield some reliable information in the study of nano cluster. The viscosity gives the strength of interaction between the interacting BN nanoparticles and molecules of methanol. The interactions between BN nanoparticles and molecules of methanol increase the viscosity of nanosuspension.

The adiabatic compressibility (β_a) decreases with increase in molar concentration indicating strong interaction between BN nanoparticles and molecules of methanol showing agreegation of nanoparticles. The surface area of the material is increased by the reduction in particle size. Due to this higher percentage of the BN Nanoparticles can interact with surrounding fluids. It may due to decrease in interspacing of BN nanoparticles in nanosuspension with increase in molar concentration. It is a measure of association or dissociation or repulsion. It also determines the orientation of the nanoparticles in nanosuspension. Kiyohara and Benson [14] suggest that adiabatic compressibility is the result of several opposing effects like strong interactions between nanoparticles and molecules of the fluids also interstitial accommodation leads to a more compact structure and decreases adiabatic compressibility. The magnitudes of the various contributions depend mainly on the relative size of the BN nanoparticles. Isothermal compressibility (β_i) and adiabatic compressibility (β_a) exhibits similar trend and both decreases with increase in molar concentration of BN nanoparticles in nanosuspension.

The relaxation time slightly decreases with increase in molar concentration of BN nanoparticles indicating less stability of BN nanoparticles in nanosuspension. It has high value at molar concentrations 0.2, 0.8 and 0.9. For the nanoparticles in nanosuspension, the gravitational pull is not stronger than the random thermal motion of the particles hence nanoparticles do not settle which provides long self life at these molar concentrations which increases the relaxation time. Stability of BN nanoparticles in nanosuspension is totally depends on its surface energy. Less surface energy more stable will be the BN nanoparticles. The relaxation is caused by the energy transfer between translational and vibrational degrees of freedom and all these degrees take part in the process observed [15].

Free length is the distance between the surfaces of the neighboring BN nanoparticles. The free length slightly decreases with increase in molar concentration up to 0.7 and then increases. The free length (L_f) of a nanosuspension is a measure of attraction between BN nanoparticles and molecules of the methanol in nanosuspension. Decrease in free length is a result of increase in surface to volume ratio of BN nanoparticles with methanol molecules, association through interactions between nanoparticles and molecules of the constituents of the nanosuspension.

The internal pressure (π_i) and free volume (V_f) versus molar concentration of BN nanoparticles in nanosuspension represented that the internal pressure as well as free volume in nanosuspension is a measure of attraction between their constituents. In this nanosuspension, free volume decreases and internal pressure increases. Further, the increase in free volume and decrease in internal pressure with rise in concentration clearly show the increasing magnitude of interactions [16]. Such behavior of internal pressure and free volume generally indicates the association through interactions between BN nanoparticles and molecules of methanol.

Acoustic impedance is found reciprocal to that of adiabatic compressibility [17-20]. It is in good agreement with the theoretical requirements. In this case, acoustic impedance increases with increase in the molar concentration of BN nanoparticles in nanosuspension up to 0.7 molar concentration and then decreases. As the size of the material decreases, the percentage of surface atoms increases, hence large amount of substance comes in contact with surrounding materials. This results in increase in acoustic impedance. The increase in acoustic impedance (Z) with molar concentration can be explained on the basis of the interactions between components of the nanosuspension, which decreases the distance of their components.

The molar volume (Vm) of BN nanoparticles depends on the structural arrangement and interactions between the components of the nanosuspension medium. The structural arrangement may be decided by the interaction forces in the nanosuspension medium. It is decreases with increase in molar concentration because the molecular weight is directly proportional to the molar volume. The molar volume is found to have similar type of trend as that of molar compressibiliry [21-30]. The Vander Waal's constant increases with increase in molar concentration and decreases beyond 0.7. This is because of the association of the interacting molecules inside the fluid medium. The change in Vander Waal's constant (b) would be due to a change in geometry of the BN nanoparticles.

The sound velocity (R) increases with increase in molar concentration up to 0.7 then decreases. It may due to increase in surface to volume ratio. It shows similar treands as that of ultrasonic velocity as it depends on it. The molar compressibility (W) decreases with increase in molar concentration of BN nanoparticles in methanol based nanosuspension due to aggration of BN nanoparticles in the medium. As it is function of adiabatic compressibility, its variation is similar as that of adiabatic compressibility. The isothermal Bulk modulus (B_i) increases with increase in molar concentration, it exhibits similar trends as that of ultrasonic velocity and inverse trend as that of isothermal compressibility. The volume expansivity decreases with increase in molar concentration due to aggration of BN nanoparticles in nanosuspension. As it is depends on internal pressure and isothermal compressibility it shows their resultant effects.

The effective thermal conductivity of nanosuspension increases with temperature. It has substantially higher value at molar concentration 0.7 and then decreases. The thermal conductivity enhancements are highly dependent on specific surface area of nanoparticle, with an optimal surface area for the highest thermal conductivity. There is strong relationship between Brownian motion and temperature of nanoparticles. Furthermore, the effect of temperature on thermal conductivity is not very well understood and documented. It is reported that it shows the similar behavior as that of ultrasonic velocity.

Poission's ratio σ depends upon adiabatic compressibility and isothermal Compressibility. It is ratio of lateral strain to longitudinal strain and its limiting values are in between 1 and 0.5. Its value 0.286 is constant for BN Methanol based nanosuspension, and same for all temperatures.

Tabular representation of BN Methanol Based Nanosuspension

Table- 1 (A) Experimental values of thermoacoustic Parameters at 5 MHz.

X	U (m/s)	P (Kg/m³)	$\eta*10^{-3}$ (NS/m²)	$\beta a*10^{-9}$ (m²/N)	$\beta i*10^{-10}$ (ms²/kg)	$\tau*10^{-12}$ (s)	L_f*10^{-11} (m)	π_i*10^{6} (N/m²)	V_f*10^{-8} (m³/mol)
T=293K									
0.1	1462	773.83	0.5393	6.0459	7.26	4.35	4.79	9.2799	8.83
0.2	1510	777.28	0.6071	5.6424	6.77	4.57	4.63	9.9849	7.51
0.3	1615	780.76	0.6155	4.9106	5.89	4.03	4.32	10.0259	7.84
0.4	1700	783.03	0.5932	4.4191	5.31	3.51	4.11	9.8903	8.62
0.5	1710	787.43	0.6412	4.3431	5.21	3.71	4.06	10.5965	7.46
0.6	1735	790.56	0.6579	4.2021	5.04	3.69	4.01	11.0097	7.05
0.7	1726	793.13	0.6578	4.2323	5.08	3.71	4.01	11.4075	6.73
0.8	1540	797.55	0.6922	5.2869	6.34	4.88	4.48	12.8342	5.04
0.9	1515	801.32	0.6771	5.4371	6.52	4.91	4.55	13.2624	4.88
T=298 K									
0.1	1472	770.62	0.5221	5.99	7.19	4.17	4.81	9.0744	9.37
0.2	1521	774.34	0.5899	5.58	6.69	4.39	4.65	9.7821	7.91
0.3	1625	777.47	0.5984	4.87	5.84	3.89	4.34	9.8276	8.25

0.4	1712	780.07	0.5757	4.37	5.24	3.35	4.11	9.6847	9.12
0.5	1720	784.85	0.6236	4.31	5.17	3.58	4.08	10.3968	7.84
0.6	1745	787.82	0.6403	4.17	5.01	3.56	4.02	10.8052	7.41
0.7	1736	790.49	0.6402	4.21	5.04	3.59	4.03	11.1965	7.07
0.8	1552	794.35	0.6746	5.23	6.28	4.71	4.51	12.5871	5.31
0.9	1525	798.23	0.6702	5.39	6.47	4.82	4.57	13.1175	5.01
T=303K									
0.1	1481	767.59	0.5049	5.94	7.13	4.01	4.84	9.1760	9.94
0.2	1530	771.29	0.5726	5.54	6.65	4.23	4.67	9.9111	8.35
0.3	1635	773.61	0.5807	4.84	5.81	3.75	4.37	9.9478	8.71
0.4	1722	776.81	0.5583	4.34	5.21	3.23	4.13	9.8066	9.63
0.5	1730	781.29	0.6063	4.28	5.14	3.46	4.10	10.5388	8.25
0.6	1754	784.58	0.6228	4.14	4.97	3.44	4.04	10.9618	7.78
0.7	1746	787.26	0.6227	4.17	5.01	3.46	4.05	11.3554	7.43
0.8	1561	790.66	0.6571	5.19	6.23	4.55	4.52	12.7701	5.57
0.9	1535	795.16	0.6596	5.34	6.41	4.71	4.58	13.3494	5.18
T=308K									
0.1	1490	764.44	0.4877	5.89	7.07	3.83	4.86	9.1144	1.06
0.2	1540	768.96	0.5552	5.48	6.58	4.06	4.69	9.8682	8.83
0.3	1644	770.81	0.5633	4.81	5.76	3.61	4.38	9.9081	9.19
0.4	1731	774.01	0.5421	4.31	5.17	3.12	4.15	9.7736	1.01
0.5	1739	778.25	0.5891	4.25	5.11	3.34	4.13	10.5051	8.68
0.6	1765	781.88	0.6055	4.11	4.93	3.32	4.06	10.9274	8.21
0.7	1755	783.95	0.6053	4.14	4.97	3.34	4.07	11.3194	7.82
0.8	1571	787.44	0.6398	5.15	6.18	4.39	4.54	12.7331	5.85
0.9	1544	792.32	0.6423	5.29	6.35	4.53	4.61	13.3494	5.43
T=313K									
0.1	1497	761.62	0.4705	5.86	7.03	3.68	4.89	9.0541	11.23
0.2	1547	765.81	0.5378	5.46	6.55	3.91	4.72	9.8207	9.32
0.3	1651	767.93	0.5459	4.77	5.73	3.48	4.41	9.8664	9.69
0.4	1738	770.67	0.5238	4.29	5.16	3.01	4.19	9.7154	10.74
0.5	1746	775.11	0.5719	4.23	5.08	3.23	4.16	10.4692	9.13
0.6	1772	777.93	0.5883	4.09	4.91	3.21	4.09	10.8875	8.61
0.7	1763	780.39	0.5881	4.12	4.95	3.23	4.11	11.2785	8.21
0.8	1578	783.86	0.6226	5.12	6.15	4.25	4.57	12.6978	6.13
0.9	1551	788.68	0.6251	5.27	6.32	4.39	4.64	13.3142	5.69

Table- 1(B) Experimental values of thermoacoustic Parameters at 5 MHz

X	$Z*10^6$ (kg/m^2s)	$Vm*10^{-2}$ (m^3/mol)	$b*10^{-5}$ (m^3/mol)	$R*10^{-4}$(m3/mol) $(m/s)^{1/3}$	$W*10^{-4}$ ($m^{19/7}/S^1$)	$Bi*10^9$ (N/m^2)	$\alpha*10^{-5}$ (1/K)	$T*10^{-3}$ (W/mK)	Meff (mol
293 K									
0.1	1.1313	4.0471	1.9931	501.95	8.40	1.38	2.30	3.66	31.32
0.2	1.1736	3.9363	1.9931	513.66	8.25	1.48	2.31	3.85	30.59
0.3	1.2609	3.8263	1.9935	544.21	8.18	1.71	2.02	4.20	29.87
0.4	1.3311	3.7231	1.9937	567.65	8.08	1.89	1.79	4.50	29.15
0.5	1.3465	3.6105	1.9937	565.18	7.85	1.92	1.88	4.62	28.43
0.6	1.3716	3.5049	1.9937	567.79	7.66	1.98	1.89	4.78	27.71
0.7	1.3689	3.4025	1.9936	559.29	7.43	1.97	1.98	4.85	26.99
0.8	1.2282	3.2931	1.9927	493.62	6.96	1.58	2.78	4.43	26.26

0.9	1.2141	3.1875	1.9925	480.36	6.71	1.53	2.95	4.45	25.54
298 K									
0.1	1.1343	4.0641	1.9931	380.18	8.44	1.39	2.19	3.68	31.32
0.2	1.1777	3.9512	1.9931	506.09	8.29	1.49	2.20	3.87	30.59
0.3	1.2633	3.8425	1.9935	518.06	8.22	1.71	1.93	4.21	29.87
0.4	1.3354	3.7371	1.9937	548.35	8.12	1.91	1.70	4.52	29.15
0.5	1.3499	3.6223	1.9937	572.38	7.89	1.93	1.80	4.64	28.43
0.6	1.3747	3.5171	1.9937	569.11	7.69	2.01	1.81	4.80	27.71
0.7	1.3723	3.4138	1.9936	571.72	7.46	1.98	1.89	4.87	26.99
0.8	1.2328	3.3064	1.9927	563.16	7.00	1.59	2.65	4.45	26.26
0.9	1.2173	3.1998	1.9925	498.13	6.75	1.55	2.85	4.47	25.54
303 K									
0.1	1136801	4.0801	1.9931	509.85	8.49	1.41	2.16	3.69	31.32
0.2	1180074	3.9669	1.9931	521.81	8.33	1.51	2.18	3.88	30.59
0.3	1264852	3.8616	1.9935	552.64	8.27	1.72	1.91	4.23	29.87
0.4	1337667	3.7528	1.9937	576.53	8.16	1.92	1.69	4.54	29.15
0.5	1351632	3.6389	1.9937	573.28	7.93	1.95	1.79	4.65	28.43
0.6	1376153	3.5316	1.9937	575.47	7.73	2.01	1.80	4.81	27.71
0.7	1374556	3.4278	1.9936	567.17	7.50	2.01	1.87	4.89	26.99
0.8	1234220	3.3218	1.9927	501.79	7.04	1.61	2.63	4.46	26.26
0.9	1220571	3.2122	1.9925	487.95	6.78	1.56	2.83	4.49	25.54
308 K									
0.1	1.1390	4.0969	1.9929	513.65	8.53	1.41	2.13	3.70	31.32
0.2	1.1841	3.9789	1.9931	525.74	8.37	1.52	2.14	3.90	30.59
0.3	1.2672	3.8757	1.9934	556.36	8.31	1.74	1.88	4.24	29.87
0.4	1.3398	3.7664	1.9937	580.24	8.20	1.93	1.67	4.55	29.15
0.5	1.3533	3.6531	1.9936	577.01	7.97	1.96	1.77	4.66	28.43
0.6	1.3800	3.5438	1.9937	579.74	7.77	2.03	1.78	4.83	27.71
0.7	1.3758	3.4423	1.9935	570.91	7.54	2.01	1.86	4.90	26.99
0.8	1.2370	3.3354	1.9927	505.69	7.08	1.62	2.61	4.48	26.26
0.9	1.2233	3.2237	1.9925	491.39	6.82	1.57	2.81	4.50	25.54
313 K									
0.1	1.1401	4.1121	1.9929	516.71	8.57	1.42	2.03	3.71	31.32
0.2	1.1847	3.9952	1.9931	528.85	8.41	1.53	2.06	3.91	30.59
0.3	1.2678	3.8902	1.9934	559.42	8.35	1.75	1.81	4.25	29.87
0.4	1.3394	3.7827	1.9937	583.42	8.24	1.94	1.61	4.55	29.15
0.5	1.3533	3.6679	1.9936	580.12	8.01	1.97	1.71	4.67	28.43
0.6	1.3784	3.5618	1.9936	583.02	7.81	2.04	1.71	4.83	27.71
0.7	1.3758	3.4581	1.9935	574.37	7.58	2.02	1.78	4.91	26.99
0.8	1.2369	3.3506	1.9927	508.72	7.12	1.63	2.49	4.48	26.26
0.9	1.2235	3.2378	1.9924	494.34	6.85	1.58	2.69	4.51	25.54

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