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Experimental and Theoretical Investigation of the Elastic Properties of Zinc oxide

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Abstract-The main aim of this study is to review and compile the elastic properties of zinc oxide and investigate which density functional method either the LDA or the GGA method have excellent agreement with the experimental data. The LDA values and the GGA values of elastic stiffness constant Cij(GPa) and poisson's ratio of zno are analyzed statistically and compared with the surface ultrasonic , brillouin zone and acoustic technique experimental values. Similarly, the LDA and GGA values of Bulk modulus and Young's modulus (GPa) are statistically analyzed and compared with the experimental values. Moreover, it was found that that the LDA values of stiffness constant exhibited maximum deviation 17.8%,15.84%,14.2% from the ultrasonic, brillouin and acoustic values, whereas, the GGA indicated 27.6%,29.67%,2.7% maximum deviation from the ultrasonic, brillouin and acoustic experimental values respectively. The Poisson's ratio LDA values are exhibited deviation 32.7%,16.1%,2.1% while the GGA values exhibited 51.3%,28%,0.24% from the ultrasonic, brillouin zone and acoustic experimental values separately. The bulk modulus and young modulus LDA values exhibited deviation 2.6% and 10% while GGA values exhibited 6.4% and 33% from the experimental values. As a result, it is revealed that the LDA method has good agreement than the GGA.

Keywords: ZnO, Local Density Approximation, Generalized Gradient Approximation, Elastic properties, wurtzite

1. INTRODUCTION

Zinc oxide is an organic compound with the formula ZnO. ZnO is a white powder that is insoluble in water. It is II-VI compound semiconductor whose iconicity resides at the borderline between the covalent and ionic semiconductor. [1] Zinc Oxide is among the most popular that have received considerable attention because of its applications in various technological important areas such as solar cells, gas sensors, flat panel display, antireflection coating and also used as an additive in numerous materials and products including cosmetic glass, cement, lubricants paints ointment, adhesive sealants, pigments, food batteries, ferrites, fire retardants and especially in the rubber industry as a hardening tool.[2]-[4] Zinc oxide mostly available in hard crystalline form in two varieties hexagonal wurtzite and cubic zinc blend. The wurtzite is most stable structure in normal condition, and zinc blend grows in crystal lattice structure [5]-[6] in both of these forms Zinc Oxide present as central molecule and stayed in tetrahedral form. Hexagonal and zinc blend polymorphous have no inversion symmetry (reflection of a crystal relative to any given point does not transform into itself).This type of crystal lattice symmetry is actually responsible for various important elastic properties of ZnO such as high tensile, Young's modulus and elasticity.[7] Zinc Oxide is a compound widely used in a rubber industry due to excellent property as a vulcanization in rubber[8]. Vulcanization is a chemical process by which the physical properties of natural or synthetic rubber are improved, zinc oxide hardened the rubber finished rubber has higher tensile strength and resistance to swelling and abrasion and is elastic over a greater range of temperatures. Zinc Oxide acts as vulcanizing agent as name liquipress in the rubber tires [9]-[10]. Zinc Oxide has vast applications in rubber as curing to harden the rubber. Hardening properties of zinc oxide depends upon the factors namely elastic stiffness, plasticity, strain, toughness and viscousity. In short, the demand of Zinc Oxide as an elastomer is increasing day by day in rubber industry [11]-[12]. We can say that Zinc Oxide has tremendous applications in rubber industry.

Currently, a lot of research has been done on theoretical and experimental basis to study fundamental properties of existing materials and new materials research. Theoretical studies based on analytical method or computer simulations. The density functional theory (DFT) is one of the most accurate and effective theories in computational materials science, which precisely describes the ground state properties of the electronic system using LDA-PW91 or GGA-PBE as the exchange-correlation energy functional [13]-[15]. Calculations in these local (semi) approximations are sufficiently are sufficiently accurate and are helpful for interpretation of experimental data regarding ground state properties. Although, DFT calculations with GGA-PBE do not properly reproduce the excited-state properties, which results in underestimation of the band gap and overestimation of the electron delocalization, especially for system with localized d and f electrons. Since in ZnO: Zn has full-filled d state and O belonged to p block so that mechanical properties of zinc oxide might be effect [16]-[22].

In this research, we will investigate and analyze the elastic properties of zinc oxide theoretical data based on local density approximation and generalized gradient approximation and compared with the experimental data and will determine which theoretical DFT method exhibit excellent agreement with experimental data.

2. COMPUTATIONAL METHOD AND DETAILS

Under ambient conditions, ZnO crystallizes in a hexagonal (P63mc) wurtzite shape with the space group having lattice constant a=b, c and lattice angles α=β=90°, Ý=120° [23]. The Zinc Blend ZnO can be described as cubic shape with a=b=c and α=β=Ý=90°, having the space group (P63mc) [23]. The two structures of ZnO crystals are shown in Figure1. In this study, first principle calculation based on DFT calculations were performed using the Viena ab initio (VASP) simulation package [24-25]. The elastic properties of zinc oxide were calculated in account of DFT technique as applied in (CASTEP) Cambridge series total energy package uses a plan wave basis set and psuedpotential method within the framework of Kohn-Sham DFT [26]. In Kohn-Sham equation the exchange- correlation potential and is acknowledged and a challenging term in DFT. To approximate this potential, LDA [27], GGA [28] functionals are adopted. Moreover, the valence electronic configuration of Zn ($4s^2$) and that of O ($2p^4$), introducing the Hubbard correlation U term improves the approximation. The K-point sampling of the brillouin zone was constructed using Monkhorst and pack mesh scheme [29].

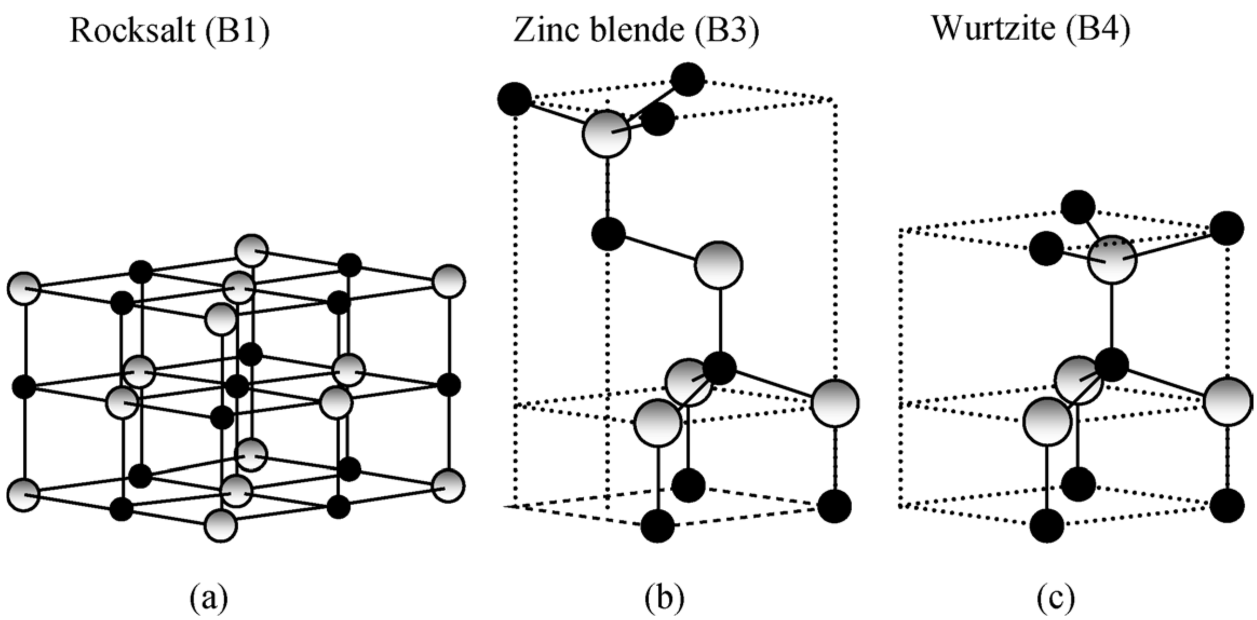


Figure1: Cubic rock salt (B1) cubic zinc blend (B2) Hexagonal wurtzite

3. DISCUSSION

Since the Zinc Oxide has a solid phase wurtzite at ambient conditions. The calculated LDA ,GGA and experimental values of mechanical properties of zinc oxide namely elastic stiffness constants, Poisson's ratio, Bulk modulus and young's modulus reported from (Ozgur et al) for further overview and investigation in Table 1, Table 2 and Table 3. There were three types of experimental values found surface ultrasonic approach, brillouin zone and acoustic investigation technique in literature. Furthermore, we used statistical analysis to investigate the theoretical and experimental data.

Thus, statistical data showed that calculated LDA values of zinc oxide for elastic stiffness constants in GPa C11, C12, C13, C33, C44 and C66 are underestimated and have excellent agreement with the ultrasonic experimental values and exhibited relative deviation from the experimental stiffness values 0.16%, 17.81%, 5.04%, 12.28%, 4% and 4.3% respectively [shown in fig.2a] whereas the analysis of GGA values of elastic stiffness constants are showed overestimated from the ultrasonic experimental values and GGA stiffness values indicated relative deviation from the ultrasonic experimental values 4.6%, 19.2%, 24.3%, 7.8%, 27.6% and 8.1% respectively and do not show top agreement with the experimental value[shown in fig2b] and given in the table 1. Similarly, the LDA values of ZnO stiffness constants C11, C12, C13, C33, C44, C66 showed deviation from the brillouin zone experimental data 0.72%, 15.84%, 10.79%, 12.26%, 1.88% and 4.6% respectively [shown in fig.2c] while GGA calculated values showed deviation from experimental date 5.5%, 17.5%, 29.67%, 7.86%, 12.80% and 8.5% separately [shown in fig.2d] and given in table 2. The LDA values exhibited most deviation 15.84% and GGA values exhibited most deviation 29.67% from the brillouin zone experimental values which shows up that LDA values has excellent agreement with the experiment. Likewise, statistical analysis tells us that the LDA values showed deviation from acoustic experimental values 14.2%, 2.2%, 6.7%, 12.9%, 9.52% and 8.84% for stiffness tensors separately [shown in fig2e] although the GGA stiffness tensors exhibited deviation from the acoustic approach 18.8%, 4.0%, 13%, 8.57%, 32.7%, 5.02% respectively [shown in fig.2f] and given in table 3 . The acoustic approach displayed maximum deviation 14.2% from the LDA and showed 32.7% from the GGA which uncovered LDA have top agreement with experimental data.

TABLE 1

Mechanical values	**LDA Values**	Experimental values	Relative Deviation %	GGA values	Experimental Values	Relative Deviation%
Stiffness constants(GPa) C11	209[f]	209.7[a]	0.167	230[g]	209.7[a]	4.6
C12	85[f]	121.1[a]	17.811	82[g]	121.1[a]	19.2
C13	95[f]	105.1[a]	5.04	64[g]	105.1[a]	24.3
C33	270[f]	210.9[a]	12.28	247[g]	210.9[a]	7.8
C44	46[f]	42.47[a]	4	75[g]	42.47[a]	27.6
C66	40.6[f]	44.29[a]	4.3	37.6[g]	44.29[a]	8.1
Poisson’s Ratio	0.3231[f]	0.6375[a]	32.7	0.2051[g]	0.6375[a]	51.3
Bulk Modulus	135.088[f]	142.4[j]	2.6	125.22[g]	142.4[j]	6.4
Young’s Modulus	136.987[f]	111.2±47[q]	10	221.56[g]	111.2±47[q]	33

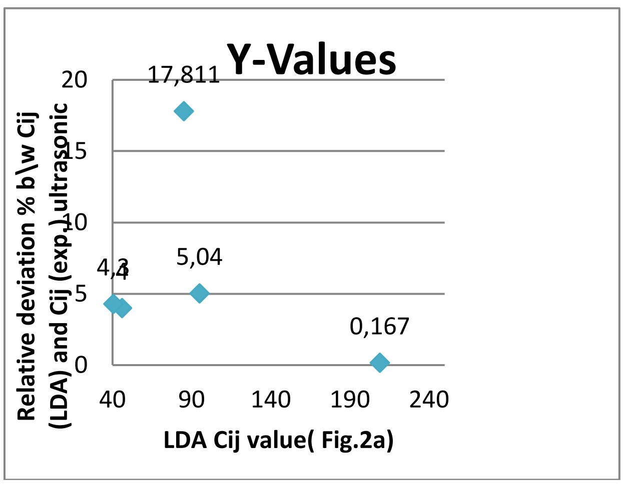
TABLE 2

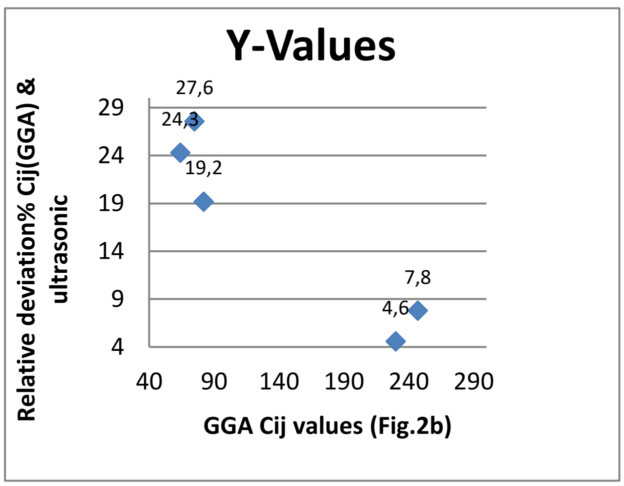
Mechanical values	LDA values	Experimental Values	Relative Deviation %	GGA values	Experimental Values	Relative Deviation%
Stiffness constants(GPa) C11	209[f]	206[b]	0.722	230[g]	206[b]	5.5
C12	85[f]	117[b]	15.84	82[g]	117[b]	17.5
C13	95[f]	118[b]	10.79	64[g]	118[b]	29.67
C33	270[f]	211[b]	12.26	247[g]	211[b]	7.86
C44	46[f]	44.3[b]	1.88	75[g]	44.3[b]	12.8
C66	40.6[f]	44.6[b]	4.6	37.6[g]	44.6[b]	8.5
Poisson’s Ratio	0.3231[f]	0.3653[b]	6.1	0.2051[g]	0.3653[b]	28

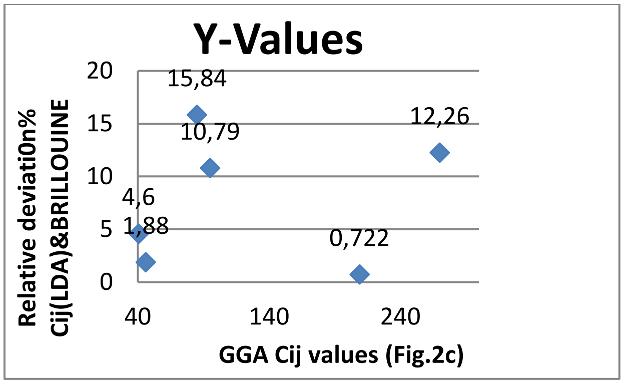
TABLE 3

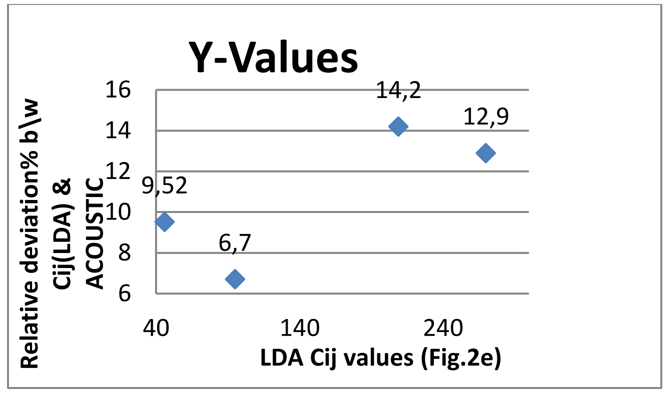
Mechanical values	LDA Values	Experimental Values	Relative Deviation%	GGA values	Experimental Values	Relative Deviation %
Stiffness Constants(GPa) C11	209[f]	157[c]	14.20	230[g]	157[c]	18.8
C12	85[f]	89[c]	2.2	82[g]	89[c]	4.0
C13	95[f]	83[c]	6.7	64[g]	83[c]	13
C33	270[f]	208[c]	12.9	247[g]	208[c]	8.57
C44	46[f]	38[c]	9.52	75[g]	38[c]	32.7
C66	40.6[f]	34[c]	8.84	37.6[g]	34[c]	5.02
Poisson's Ratio	0.3231[f]	0.3373[c]	2.1	0.2051[g]	0.3373[c]	0.24

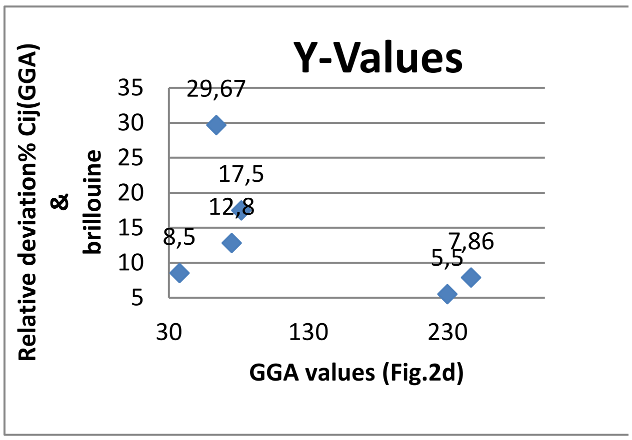
Here in tabels
[a] ultrasonic measurement on single-crystal ZnO grown by chemical reaction in vapour [30]
[b] Surface Brillouin scattering on polycrystalline ZnO film deposited by r.f sputtering on (100) Si substrate [31]
[c] Acoustic investigation technique on ZnO film deposited by r.f magnetron sputtering on sapphire substrate [32]
[j] X-ray diffraction using synchrotron radiation on polycrystalline ZnO (99.99% purity) [33]
[q] Spherical nano-identation on bulk ZnO [34]
[f] Calculated by using LDA [35]
[g] Calculated by using GGA [35]

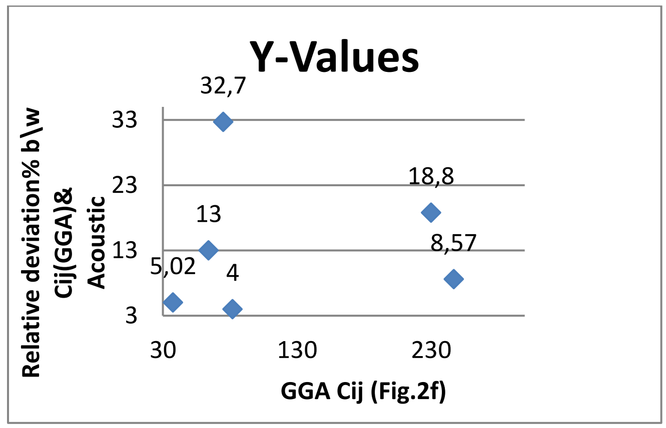






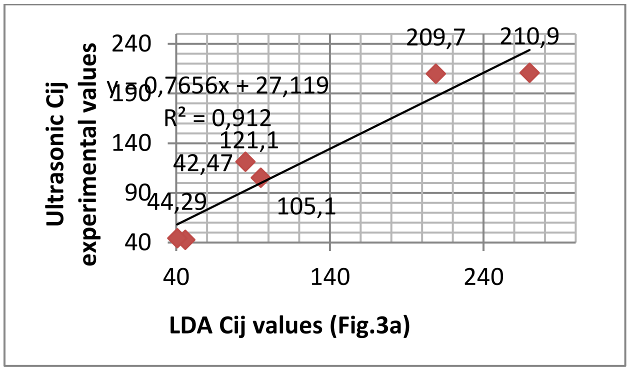


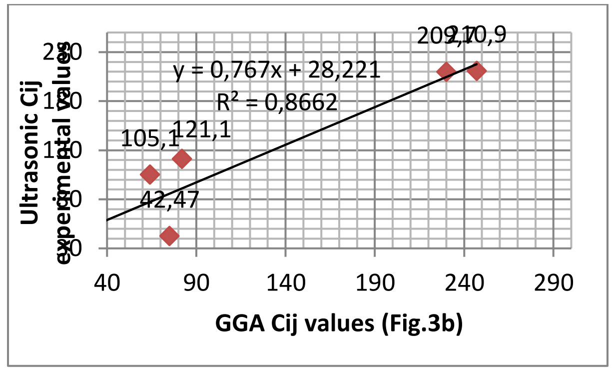


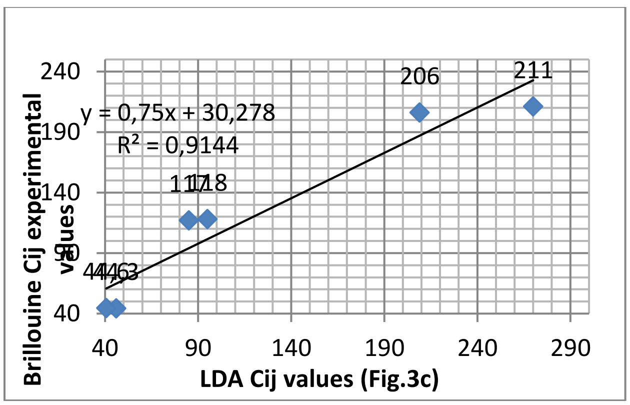


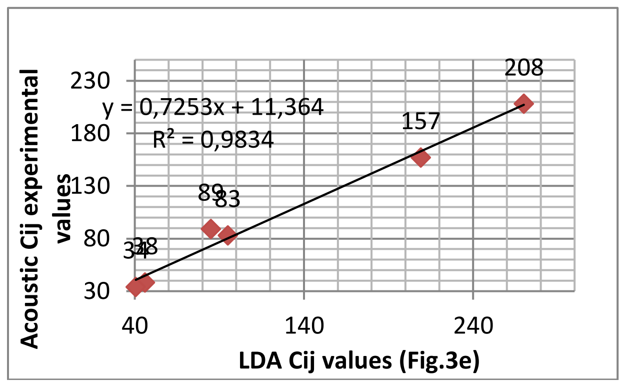
We used Benchmark research to research distinction among DFT and experimental statistically. The maximum not unusualplace traits investigated are the suggest mistakess. In order to decide the scatter of experimental values from the theoretical values we used line regression for Cij among LDA, GGA and experimental data. The linear regression is accomplished by using a least rectangular fit, from which we received the slope in addition to the scatter with appreciate to the regression line [36].The version therefore presume that best correlation among test X and Theory T exists, distorted via way of a random mistakess έ targeted across the zero suggest: X=BT+έ. If the precise exchange-correlation practical have been known, it'd about result in έ=0 and β=1.Figure 3a and Figure 3b is the graph among Cij ultrasonic values on y-axis and Cij LDA, GGA values on x-axis separately. The equation of linear regression line has proven at the every graph. It represented β=0.766 and mistakess of estimation έ=0.119 for LDA whilst GGA displayed β=0.767 and έ=0.151 which is bigger than the LDA. In the equal way, Fig.3c and Fig.3d is the linear regression graph among Brillouin region Cij values alongside y-axis and LDA and GGA values alongside x-axis respectively. The equation line has proven on every of graph. It represented that β=0.75, mistakess of estimation έ=0.115 for LDA simply as β=0.741 and έ=0.159 for GGA which is bigger than LDA. Furthermore, Fig 2e and Fig 2f is the graph between acoustic experimental Cij values along y-axis and LDA, GGA values on x-axis respectively. It may be discovered that β=0.725, έ=0.047 but for the GGA it's miles discovered that β=0.711 and έ=0.122 which is bigger than LDA. Poisson's ratio extensively implemented to assess the steadiness of the crystal beneathneath shear deformation. The poisson's ratio suggests that LDA values exhibited 32.7% deviation from the ultrasonic experimental values while GGA value exhibited 51.3% deviation. Similarly, Poisson's LDA value and brillouin zone experimental displayed 6.1% deviation despite the fact that GGA value represented 28% deviation from the brillouin zone technique. Likewise, Poisson's ratio LDA values and acoustic technique confirmed deviation 2.1% and GGA value confirmed 0.24% from acoustic technique. As a result, it's miles discovered that the LDA poissin's ratio confirmed big settlement with the GGA value.

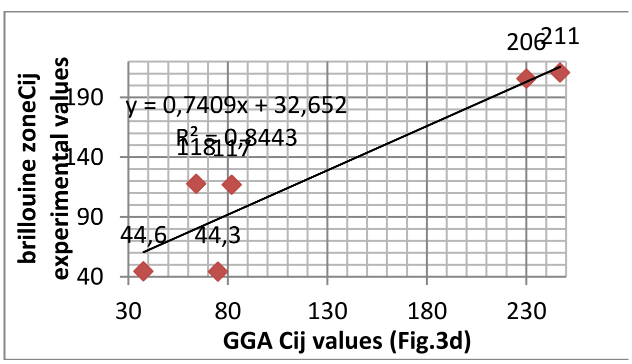
Even the statistical evaluation of the bulk modulus of the LDA value for ZnO and experimental value confirmed that
LDA value for bulk modulus exhibited 2.6% deviation from the experimental value whilst the GGA value confirmed 6.4% deviation. Also, for the Young's modulus statistical examine confirmed that LDA value have deviation 10% and GGA from the experimental value which showed that bulk modulus and Young's modulus exhibited significant agreement with the experimental value.

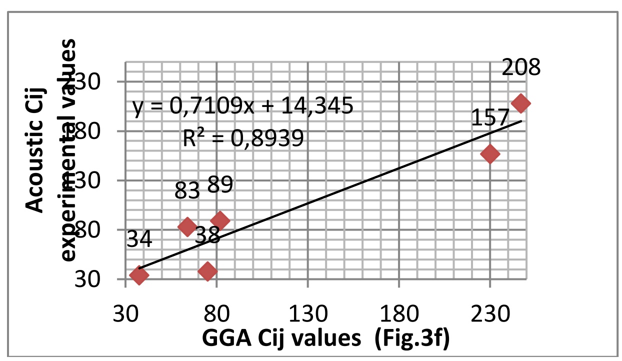












The study suggested that the DFT-LDA yield the most accurate estimate of elastic stiffness constants, Poisson's ratio, Bulk modulus and Young's modulus. Nevertheless, it still needs to improve the reliability of exchange-correlation function in the DFT-GGA method because of the overestimation of the values from the experimental of zinc oxide.

4. CONCLUSION

The elastic properties of wurtzite ZnO were investigated by theoretical DFT-LDA, DFT-GGA methods to determine which DFT method both of either LDA or GGA would have excellent agreement with the experimental values. We analyzed data statistically, it was found that elastic stiffness tensors of ZnO have shown maximum deviation 17.811% and GGA has shown maximum deviation 27.6% from the ultrasonic experimental values. Similarly, elastic stiffness constants of ZnO LDA values showed maximum deviation 15.84% and GGA values showed 29.67% from the brillouin zone experimental values. Furthermore, LDA value of Cij exhibited maximum deviation 14.2% and GGA 32.7% from the acoustic experimental values. Likewise, the poisson's ratio LDA values are found deviation 32.7% and GGA showed 51.3% from the ultrasonic experimental values. On the other hand, Poisson's ratio exhibited deviation 6.1%, 28% from the LDA and GGA

whereas acoustic investigation experimental values exhibited relative deviation from LDA 2.1% and from GGA 0.24%. Moreover, LDA and GGA values of Bulk Modulus were compared with the experimental values and it was found that LDA showed deviation 2.1% and GGA exhibited 0.24%.The LDA and GGA values of Young's Modulus also compared and found 2.6% and 6.4% deviation respectively. Overall, the LDA values found to be excellent agreement with experimental data than GGA values for elastic stiffness constants, poisson's ratio, bulk modulus, Young's modulus. The excellent agreement between the LDA and experimental data, presented in this work, may encourage additional studies of mechanical properties of ZnO than GGA.

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