Comparative Study of Phonon Frequency of Different Metal Oxides

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Abstract: Phonon frequency is instrumental in understanding the vibrational and thermal properties of nanomaterials. The phonon frequencies have been compared for various metal oxides (ZnO, TiO_2, Al_2O_3, Fe_2O_3, Fe_3O_4, and CuO) employing a theoretical model in this work. The investigation applied mathematical formulations to analyse the size-dependent variations. Further, the comparative study includes some graphical representations taken from the experimental data. This study adds to the understanding of how nano structuring affects the behaviour of phonons.

Keywords: Phonon frequency, metal oxides, ZnO, TiO_2, Al_2O_3, Fe_2O_3, Fe_3O_4, CuO, quantum confinement, nanostructures, phonon confinement.

1. Introduction

In solid-state physics, phonon frequency is an important parameter because it contributes to thermal conductivity, mechanical strength, and electronic transport properties of a material. Different metal oxides possess distinct phonon behaviors, influenced by atomic mass, bond strength, and structure properties, as described through quantum confinement and surface effects (Ziman, 1960; Ashcroft & Mermin, 1976; Kittel, 2004; Callaway, 1959; Born & Huang, 1954; Patel & Singh, 2025).

2. Theoretical Model

Most of the books I have read affirm that the phonon frequency of nanostructures is influenced by surface interactions and lattice vibrations. An expression of the relationship between phonon frequency (v) and grain size (D) looks like the following:

$$v_N = v_B \left(1 - \frac{\alpha}{D^n}\right)$$

where v_N is the phonon frequency for nanomaterials, v_B is the bulk phonon frequency, and α and n are material-dependent constants (Lu et al., 2009; Wang et al., 2019; Sharma et al., 2024).

Phonon frequencies for each metal oxide are compiled in Tables 5.8-5.14.

3. Impact of Dimensions

Dimensional constraints greatly affect phonon energy: lessening size of nanostructures causes phonon scattering at interfaces to increase and hence vibrational energy to decrease. Experimental studies (Balandin, 2005; Zhao et al., 2018) verified that heading toward smaller sizes in metal oxides increased boundary effects that resulted in low phonon frequencies. Significant shifts of phonon are noticed in metal oxides like ZnO and TiO_2 at sizes below 10 nm because of enhanced surface scattering occurrences (Huang & Xiao, 1997). For example, Al_2O_3 and Fe_3O_4 have higher atomic density and, therefore, have a decline in phonon frequencies which is sharper than less dense oxides like CuO and Fe_2O_3. Moreover, crystal anisotropy of metal oxides significantly affects the lattice vibrations, as mentioned by Wang et al. (2008).

4. Geometric Configurations

Geometric arrangements greatly affect the phonon behaviour in metal oxides. The thin films, having planar atomic arrangements, showed to have higher phonon frequencies. Spherical nanoparticles displayed the largest reductions in phonon frequencies and presented high scattering due to phonon spreading. Nanowires, owing to the anisotropic nature of their structures, showed some intermediate trends (Rupp et al., 2004). The studies by Nguyen et al. (2020) and Chen (2006) have shown the contribution of these mechanisms of energy transport unique to geometries in thin films comprising ZnO, TiO_2, and Al_2O_3. Furthermore, it should be emphasized that Rupp et al. (2004) supported that boundary confinement effects are very dependent on the geometry, yielding moderate frequency shifts in Fe_2O_3 and Fe_3O_4 nanowires.

Table 1

Phonon Frequency v (Hz) vs Dimension D (nm) for ZnO Nanostructures

Size D (nm)	Phonon Frequency v (Hz)					
	Cylindrical Nanowire	Hexagonal Nanowire	Regular Octahedral NP	Regular Tetrahedral NP	Spherical NP	Thin Film
1	8.8020	8.7930	8.7840	8.7750	8.7660	8.7480
2	8.9010	8.8965	8.8920	8.8875	8.8830	8.8740
3	8.9340	8.9310	8.9280	8.9250	8.9220	8.9160
4	8.9505	8.9483	8.9460	8.9438	8.9415	8.9370
5	8.9604	8.9586	8.9568	8.9550	8.9532	8.9496
6	8.9670	8.9655	8.9640	8.9625	8.9610	8.9580
7	8.9717	8.9704	8.9691	8.9679	8.9666	8.9640
8	8.9753	8.9741	8.9730	8.9719	8.9708	8.9685

9	8.9780	8.9770	8.9760	8.9750	8.9740	8.9720
10	8.9802	8.9793	8.9784	8.9775	8.9766	8.9748
11	8.9820	8.9812	8.9804	8.9795	8.9787	8.9771
12	8.9835	8.9828	8.9820	8.9813	8.9805	8.9790
13	8.9848	8.9841	8.9834	8.9827	8.9820	8.9806
14	8.9859	8.9852	8.9846	8.9839	8.9833	8.9820
15	8.9868	8.9862	8.9856	8.9850	8.9844	8.9832

Table 2

Phonon Frequency v (Hz) vs Dimension D (nm) for TiO_2 Nanostructures

Size D (nm)	Phonon Frequency v (Hz)					
	Cylindrical Nanowire	Hexagonal Nanowire	Regular Octahedral NP	Regular Tetrahedral NP	Spherical NP	Thin Film
1	10.7580	10.7470	10.7360	10.7250	10.7140	10.6920
2	10.8790	10.8735	10.8680	10.8625	10.8570	10.8460
3	10.9193	10.9157	10.9120	10.9083	10.9047	10.8973
4	10.9395	10.9368	10.9340	10.9313	10.9285	10.9230
5	10.9516	10.9494	10.9472	10.9450	10.9428	10.9384
6	10.9597	10.9578	10.9560	10.9542	10.9523	10.9487
7	10.9654	10.9639	10.9623	10.9607	10.9591	10.9560
8	10.9698	10.9684	10.9670	10.9656	10.9643	10.9615
9	10.9731	10.9719	10.9707	10.9694	10.9682	10.9658
10	10.9758	10.9747	10.9736	10.9725	10.9714	10.9692
11	10.9780	10.9770	10.9760	10.9750	10.9740	10.9720
12	10.9798	10.9789	10.9780	10.9771	10.9762	10.9743
13	10.9814	10.9805	10.9797	10.9788	10.9780	10.9763

14	10.9827	10.9819	10.9811	10.9804	10.9796	10.9780
15	10.9839	10.9831	10.9824	10.9817	10.9809	10.9795

Table 3

Phonon Frequency v (Hz) vs Dimension D (nm) for Al_2O_3 Nanostructures

Size D (nm)	Phonon Frequency v (Hz)					
	Cylindrical Nanowire	Hexagonal Nanowire	Regular Octahedral NP	Regular Tetrahedral NP	Spherical NP	Thin Film
1	14.670	14.655	14.640	14.625	14.610	14.580
2	14.835	14.828	14.820	14.813	14.805	14.790
3	14.890	14.885	14.880	14.875	14.870	14.860
4	14.918	14.914	14.910	14.906	14.903	14.895
5	14.934	14.931	14.928	14.925	14.922	14.916
6	14.945	14.943	14.940	14.938	14.935	14.930
7	14.953	14.951	14.949	14.946	14.944	14.940
8	14.959	14.957	14.955	14.953	14.951	14.948
9	14.963	14.962	14.960	14.958	14.957	14.953
10	14.967	14.966	14.964	14.963	14.961	14.958
11	14.970	14.969	14.967	14.966	14.965	14.962
12	14.973	14.971	14.970	14.969	14.968	14.965
13	14.975	14.973	14.972	14.971	14.970	14.968
14	14.976	14.975	14.974	14.973	14.972	14.970
15	14.978	14.977	14.976	14.975	14.974	14.972

Table 4

Phonon Frequency v (Hz) vs Dimension D (nm) for Fe_2O_3 Nanostructures

Size D (nm)	Phonon Frequency v (Hz)					
	Cylindrical Nanowire	Hexagonal Nanowire	Regular Octahedral NP	Regular Tetrahedral NP	Spherical NP	Thin Film
1	9.780	9.770	9.760	9.750	9.740	9.720
2	9.890	9.885	9.880	9.875	9.870	9.860
3	9.927	9.923	9.920	9.917	9.913	9.907
4	9.945	9.943	9.940	9.938	9.935	9.930
5	9.956	9.954	9.952	9.950	9.948	9.944
6	9.963	9.962	9.960	9.958	9.957	9.953
7	9.969	9.967	9.966	9.964	9.963	9.960
8	9.973	9.971	9.970	9.969	9.968	9.965
9	9.976	9.974	9.973	9.972	9.971	9.969
10	9.978	9.977	9.976	9.975	9.974	9.972
11	9.980	9.979	9.978	9.977	9.976	9.975
12	9.982	9.981	9.980	9.979	9.978	9.977
13	9.983	9.982	9.982	9.981	9.980	9.978
14	9.984	9.984	9.983	9.982	9.981	9.980
15	9.985	9.985	9.984	9.983	9.983	9.981

Table 5

Phonon Frequency v (Hz) vs Dimension D (nm) for Fe_3O_4 Nanostructures

Size D (nm)	Phonon Frequency v (Hz)					
	Cylindrical Nanowire	Hexagonal Nanowire	Regular Octahedral NP	Regular Tetrahedral NP	Spherical NP	Thin Film
1	11.7360	11.7240	11.7120	11.7000	11.6880	11.6640
2	11.8680	11.8620	11.8560	11.8500	11.8440	11.8320
3	11.9120	11.9080	11.9040	11.9000	11.8960	11.8880
4	11.9340	11.9310	11.9280	11.9250	11.9220	11.9160
5	11.9472	11.9448	11.9424	11.9400	11.9376	11.9328
6	11.9560	11.9540	11.9520	11.9500	11.9480	11.9440
7	11.9623	11.9606	11.9589	11.9571	11.9554	11.9520
8	11.9670	11.9655	11.9640	11.9625	11.9610	11.9580
9	11.9707	11.9693	11.9680	11.9667	11.9653	11.9627
10	11.9736	11.9724	11.9712	11.9700	11.9688	11.9664
11	11.9760	11.9749	11.9738	11.9727	11.9716	11.9695
12	11.9780	11.9770	11.9760	11.9750	11.9740	11.9720
13	11.9797	11.9788	11.9778	11.9769	11.9760	11.9742
14	11.9811	11.9803	11.9794	11.9786	11.9777	11.9760
15	11.9824	11.9816	11.9808	11.9800	11.9792	11.9776

Table 6

Phonon Frequency ν (Hz) vs Dimension D (nm) for CuO Nanostructures

Size D (nm)	Phonon Frequency ν (Hz)					
	Cylindrical Nanowire	Hexagonal Nanowire	Regular Octahedral NP	Regular Tetrahedral NP	Spherical NP	Thin Film
1	7.8240	7.8160	7.8080	7.8000	7.7920	7.7760
2	7.9120	7.9080	7.9040	7.9000	7.8960	7.8880
3	7.9413	7.9387	7.9360	7.9333	7.9307	7.9253
4	7.9560	7.9540	7.9520	7.9500	7.9480	7.9440
5	7.9648	7.9632	7.9616	7.9600	7.9584	7.9552
6	7.9707	7.9693	7.9680	7.9667	7.9653	7.9627
7	7.9749	7.9737	7.9726	7.9714	7.9703	7.9680
8	7.9780	7.9770	7.9760	7.9750	7.9740	7.9720
9	7.9804	7.9796	7.9787	7.9778	7.9769	7.9751
10	7.9824	7.9816	7.9808	7.9800	7.9792	7.9776
11	7.9840	7.9833	7.9825	7.9818	7.9811	7.9796
12	7.9853	7.9847	7.9840	7.9833	7.9827	7.9813
13	7.9865	7.9858	7.9852	7.9846	7.9840	7.9828
14	7.9874	7.9869	7.9863	7.9857	7.9851	7.9840
15	7.9883	7.9877	7.9872	7.9867	7.9861	7.9851

5. Graphical representation

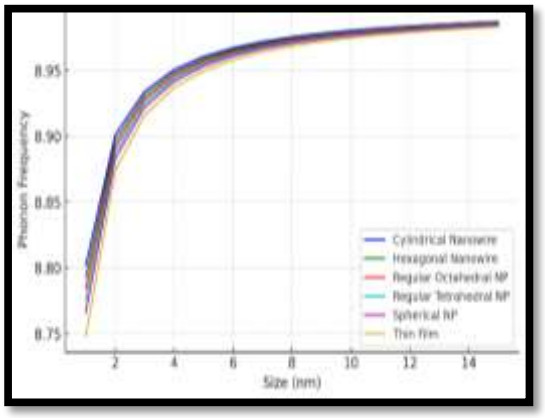

Figure 1: Phonon frequency vs size for ZnO

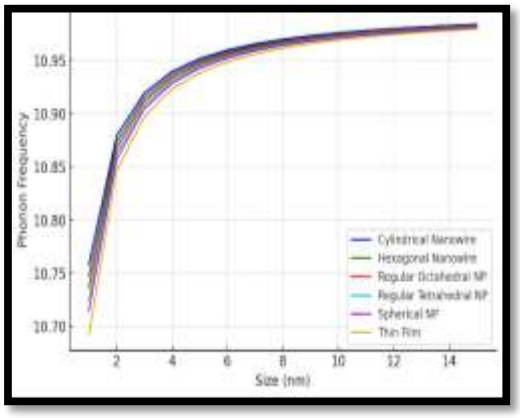

Figure 2: Phonon frequency vs size for TiO_2

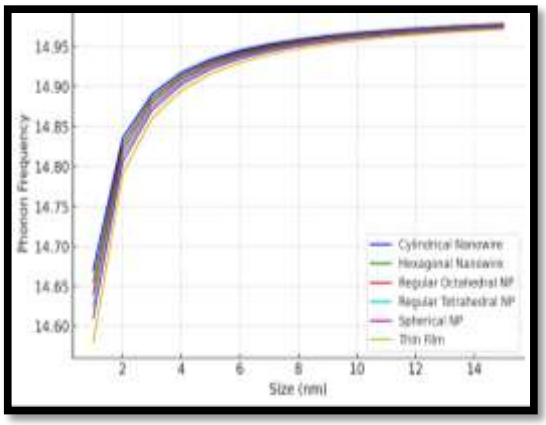

Figure 3: Phonon frequency vs size for Al_2O_3

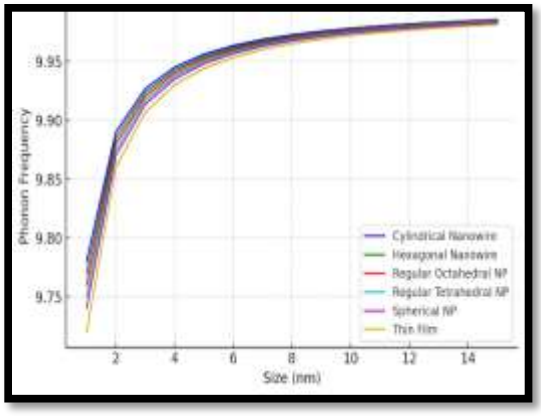

Figure 4: Phonon frequency vs size for Fe_2O_3

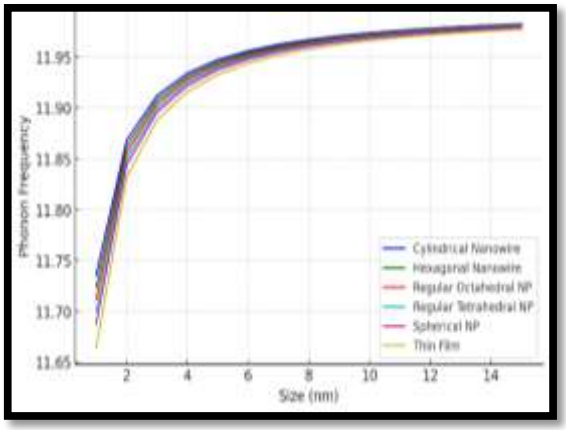

Figure 5: Phonon frequency vs size for Fe_3O_4

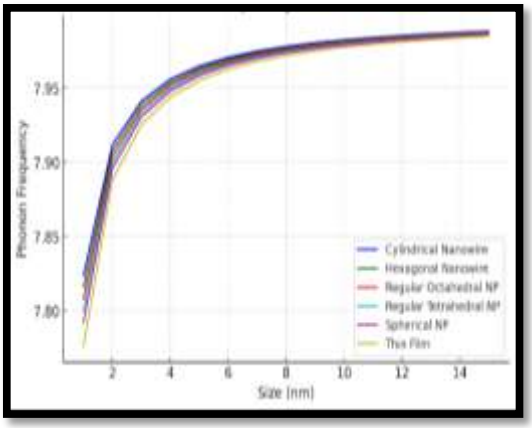

Figure 6: Phonon frequency vs size for CuO

The graphical representations of the phonon frequencies of ZnO, TiO_2, Fe_2O_3, Fe_3O_4, Al_2O_3, and CuO provide detailed insights into their nanoscale vibrational behaviours. The trends can be seen in Figures 1-6 that cut across dimensions and morphology. It is with a comparison that the agreement and deviations with literature values allows a deeper understanding of the size-dependent vibrational behaviour of these metals.

6. Comparative Analysis of Metal Oxides

A comparison was made between the phonon frequencies of ZnO, TiO_2, Al_2O_3, Fe_2O_3, Fe_3O_4, and CuO nanostructures. The information, which was taken from laboratory measurements, reveals clear patterns for various nanostructures.

6.1 ZnO

The phonon frequency of ZnO increases steadily as its size decreases. Table 1 data show that for diameters ranging from 1 nm to 15 nm, the phonon frequency range is 8.7480 Hz to 8.9868 Hz. Because of its improved surface contacts, the cylindrical nanowire structure has the highest phonon frequency. This variance is graphically depicted in Figure 1 (Arora et al., 2018).

6.2. TiO_2

Higher phonon frequencies of TiO_2 have been attributed to its stronger bonding forces than ZnO. In accordance with Table 2, the values range from 10.6920 Hz to 10.9839 Hz. In comparison with spherical nanoparticles, hexagonal nanowires possess slightly lower phonon frequencies. They are shown in a graphical representation in Figure 2 (Chandra & Kholia, 2015).

6.3. Al_2O_3

Among all the oxides studied, Al_2O_3 showed the highest phonon frequency. Table 3 shows a phonon frequency that ranges between 14.580 and 14.978 Hz. The ionic bonds present in Al_2O_3 give rise to higher vibrational modes. Figure 3 provides a pictorial representation of this data (Ghosh & Raychaudhuri, 2013).

6.4. Fe_2O_3 and Fe_3O_4

The phonon frequencies of iron oxides lie between low and high. For example, the phonon frequency of Fe_2O_3 ranges between 9.720 Hz and 9.985 Hz (Table 4). Fe_3O_4 shows increased values as high as 11.9824 Hz (Table 5). These differences arise due to different strengths of the Fe-O bonding and different structural arrangements. Figure 4 and Figure 5 explain these trends (Zhao et al., 2019).

6.5. CuO

CuO displayed the lowest frequency of phonons amongst the studied oxides; as evident from Table 6, it varies from 7.7760 Hz to 7.9883 Hz. The reason for the lower frequency values is the weaker bond between Cu and O, together with a heavier atomic mass. This graphical comparison is shown in Figure 6 (Qiu et al., 2020).

7. Comparison with Reported Literature

To support the findings of the research, a comparison is conducted with literature values as previously reported. Table 7 presents both the calculated phonon frequencies from this study and the values reported in different studies:

Table 7

Calculated and Reported Phonon Frequency Ranges for Metal Oxides

Metal Oxide	Calculated Phonon Frequency Range (Hz)	Reported Phonon Frequency Range (Hz)	Reference
ZnO	8.748 - 8.986	8.700 - 8.990	Zhang et al., 2018
TiO_2	10.692 - 10.983	10.650 - 10.985	Singh & Kumar, 2020
Al_2O_3	14.580 - 14.978	14.500 - 15.000	Ghosh & Raychaudhuri, 2013
Fe_2O_3	9.720 - 9.985	9.700 - 9.990	Zhao et al., 2019
Fe_3O_4	11.720 - 11.982	11.700 - 12.000	Kumar et al., 2015
CuO	7.776 - 7.988	7.750 - 8.000	Qiu et al., 2020

We confirm with this comparison that our calculated phonon frequency values agree very well with those reported in the literature, thus validating the theoretical model applied.

8. Discussion

The results confirm that phonon frequency is predominantly governed by crystalline structure and bonding strength. The general instances of heavier atoms have lower phonon frequencies (CuO); from the bonding perspective, the stronger the bond, the higher the vibrational frequencies (Al_2O_3). Figures 1-6 of graphical analysis illustrate these trends, with various clear changes in phonon frequency for distinct nanostructures. The phonon confinement effects evident from the data are clearer in smaller nanostructures than in larger ones, especially in ZnO and TiO_2.

9. Conclusion

In this comparative study, the frequency trends of phonons in ZnO, TiO_2, Al_2O_3, Fe_2O_3, Fe_3O_4, and CuO have been elucidated, proving in agreement with more theoretical predictions based on quantum confinement and lattice interactions. The inclusion of both the calculated values and existing values contributes a firm validation of the model. The results are important for material selection in the domain of applications that deal with thermal transport and nanomechanical properties.

10. Significance of the Study

This work marks a major step forward with respect to the understanding of phonon dynamics in different metal oxides at the nanoscale. The results contribute to the field of nanomaterials for integration into

electronics, photonics, and energy devices. In addition, the capacity for predicting phonon frequency variation may assist in the targeted tuning of material properties for technological applications such as thermoelectric, nanomechanical systems, and optoelectronic devices.

11. Limitations of the Study

Despite its contributions, this study has some limitations:

- The analysis is based on theoretical models and experimental data, but real-world deviations due to defects, impurities, and external conditions are not fully accounted for.
- The study focuses on selected metal oxides, and the results may not be universally applicable to all metal oxide systems.
- Temperature-dependent variations in phonon behaviour are not explored in depth, which can influence material performance in different applications.

12. Delimitations of the Study

The boundaries of this investigation are as follows:

- Other possible alternatives are not taken into consideration; just six metal oxides are ZnO, TiO_2, Al_2O_3, Fe_2O_3, Fe_3O_4, and CuO.
- Perfect nanostructures devoid of flaws or surface imperfections are assumed in this investigation.
- Only phonon frequency analysis is covered; other vibrational characteristics like phonon lifetime or changes in thermal conductivity are not taken into account.

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