1.1 Classification of nanocrystalline materials by size of their structural elements: 0D (zero-dimensional: clusters, quantum dots); 1D (one-dimensional: nanotubes, fibres, and rods); 2D (two-dimensional: films and coats); 3D (three-dimensional: polycrystals). ........................................... 2

1.2 For palladium clusters the percentage of the surface atoms varies with cluster diameter size. Adapted from reference [2]. ........................................... 6

1.3 Schematic illustration of the changes of the density of quantum states (DOS) with changes in the number of atoms in materials (MO: molecular orbital; AO: atomic orbital). Adapted from reference [21]. .................. 7

1.4 Predicted Curie temperatures as a function of lattice constant for a variety of semiconductors. The materials predicted to have high TC values have large p-d hybridization and small spin-orbit interaction. Adapted from reference [55]. ........................................... 15

1.5 Mass spectrum of aluminum oxide (a) cations Al_xO_y^+ (adapted from reference [123]), and (b) anions Al_xO_y^- (adapted from reference [124]) produced by laser vaporization. The spectrum is congested by the many possible oxidation states of aluminum. The most intense peaks are identified as (x,y). Mass Spectrum (c) for gas phase AlO.(Al_2O_3)_n clusters (adapted from reference [125]), and (d) AlO.(Al_2O_3)_n clusters cations produced by IR-REMPI (adapted from reference [126]), the index numbers represents the number n. ........................................... 24

2.1 Schematic representation of pseudopotentials and their corresponding wavefunctions. The solid line represent the true, all-electron part while the pseudoelectron part is depicted by the dotted line. At the cutoff radii r_c, the true and pseudopotentials match [175]. ........................................... 37

2.2 Schematic representation of the boundary for a cluster, in a real-space method. ........................................... 41

3.1 The lowest energy and some of the low-lying isomers of (Al_2O_3)_n, (n = 1–4) clusters with their point group symmetry. The energy of an isomer is given with respect to the energy (taken to be zero) of the lowest energy isomer for a given size. White (larger) spheres represent Al atoms and red (smaller) spheres represent O atoms. ........................................... 57

3.2 The calculated IR and Raman spectra of the lowest energy neutral isomers (1a, 2a, and 3a) of n = 1–3 as in Figure 3.1 and obtained from the Gaussian program. The calculated spectra have been convoluted with Gaussian functions (full width at half maximum (FWHM) ≈ 23 cm^{-1}) .............. 61
3.3 The experimental IR-multiple photon dissociation spectrum of a [(Al$_2$O$_3$)$_4$]$^+$ cation cluster taken from reference [215], along with the calculated IR spectra of cation and neutral isomers (4a), (4b), (4c), (4d), and (4e) in Figure 3.1 for $n = 4$. For a comparison, the calculated spectra in (4a-4e) have been convoluted with Gaussian functions (FWHM $\approx$ 23 cm$^{-1}$). Note that, the x-scale on the experimental and calculated spectra is different.

3.4 The calculated Raman spectra of (Al$_2$O$_3$)$_4$ cation and neutral isomers (4a), (4b), (4c), (4d), and (4e) in Figure 3.1. The calculated spectra have been convoluted with Gaussian functions (FWHM $\approx$ 23 cm$^{-1}$).

3.5 The lowest energy and some of the low-lying isomers of (Al$_2$O$_3$)$_n$, ($n = 5$ – 10) clusters with their point group symmetry. Other details are same as in Figure 3.1.

3.6 The BE (eV/atom) for (a) the lowest energy isomers of (Al$_2$O$_3$)$_n$ clusters with $n = 1$ – 10, along with the average coordination number (CN) for aluminum and oxygen atoms (inset). The BE and the average CN for Al and O atoms in $\alpha$- and $\gamma$-Al$_2$O$_3$ phases are also shown. The BE for (b) the lowest energy neutral and ionic (Ga$_2$O$_3$)$_n$ clusters with $n = 1$ – 10, along with the average CN for gallium and oxygen atoms (inset). The BE and the average CN for Ga and O atoms in $\alpha$- and $\beta$-Ga$_2$O$_3$ phases are also shown.

3.7 The total DOS for the lowest energy configurations for (Al$_2$O$_3$)$_n$, ($n = 1$ – 10) clusters. The total DOS for the bulk $\alpha$- and $\gamma$-Al$_2$O$_3$ phases are also shown. The Fermi level has been shifted to zero.

3.8 The total DOS and PDOS for the lowest energy configurations of (a) (Al$_2$O$_3$)$_n$ and (b) (Ga$_2$O$_3$)$_n$, with $n = 4$ and 10 clusters. The Fermi level has been shifted to zero.

3.9 The (a) total charge density and (b) ELF for the lowest energy configurations of (Al$_2$O$_3$)$_4$ and (Ga$_2$O$_3$)$_4$ clusters at 75% of the maximum value. The Bader charges on three- and four-fold coordinated Al and Ga atoms and two- and three-fold coordinated O atoms are also shown.

4.1 The lowest energy and some of the low-lying configurations for Mn(GaO)$_n$, ($n = 1$ – 7) clusters. The pink spheres represent the Ga-atoms, the red spheres represent the O-atoms and blue sphere represents the Mn-atom.

4.2 Isodensity surface corresponding to the (HOMO-18) state of Mn(GaO)$_4$, at one-fifth of its maximum isosurface value.

4.3 The lowest energy and some of the low-lying configurations for Mn$_2$(GaO)$_n$, ($n = 1$ – 7) clusters. Other details are same as Figure 4.1.

4.4 The contour plot of the HOMO of the ground state configuration of Mn$_2$(GaO)$_5$, at one sixth of its maximum isosurface value.

4.5 Total spin density [$\rho_\uparrow(\mathbf{r}) - \rho_\downarrow(\mathbf{r})$] isosurface of Mn$_2$(GaO)$_6$ - AFM and FM configurations, at one-sixth of its maximum isosurface value. Red and blue surfaces represent positive and negative spin densities, respectively.
4.6 The total DOS and PDOS associated with Mn atoms for Mn$_2$(GaO)$_6$ AFM and FM configurations. The Fermi level has been shifted to zero.

4.7 Gd$_2$ doped bulk $\alpha$-Al$_2$O$_3$, 3x3x1 supercell. The white, red, and gray spheres represent Al, O, and Gd atoms, respectively.

4.8 The lowest energy and some of the low-lying isomers of GdAl$_{2n-1}$O$_{3n}$ clusters along with the host cluster (Al$_2$O$_3$)$_n$, ($n = 1 - 5$). The white, red, and gray spheres represent Al, O, and Gd atoms, respectively.

4.9 The lowest energy and some of the low-lying isomers of GdAl$_{2n-1}$O$_{3n}$ clusters along with the host cluster (Al$_2$O$_3$)$_n$, ($n = 6 - 10$). Other details are same as in Figure 4.8.

4.10 Bader charge analysis, total DOS, and PDOS associated with Gd, Al, and O atoms for the lowest energy and the low-lying configuration of GdAl$_9$O$_{15}$ cluster. PDOS for Gd-$sd$ contribution is scaled up by a factor of 10. For O atoms, the red and green lines show the PDOS associated with three oxygen atoms bonded with Gd (O$_{Gd}$). The blue and pink lines show the contribution from all O atoms bonded with Al (O$_{Al}$). The Fermi level has been shifted to zero.

4.11 The lowest energy and some of the low-lying isomers of Gd$_2$Al$_{2n-2}$O$_{3n}$, ($n = 1 - 5$) clusters. Other details are same as in Figure 4.8.

4.12 The lowest energy and some of the low-lying isomers of Gd$_2$Al$_{2n-2}$O$_{3n}$, ($n = 6 - 10$) clusters. Other details are same as in Figure 4.8.

4.13 The BE (eV/atom) for the lowest energy configurations of GdAl$_{2n-1}$O$_{3n}$ and Gd$_2$Al$_{2n-2}$O$_{3n}$ clusters along with the host (Al$_2$O$_3$)$_n$, ($n = 1 - 10$) clusters. The BE (eV/atom) for the two Gd doped in the supercell of bulk $\alpha$-Al$_2$O$_3$ configuration is also shown.

4.14 The HOMO-LUMO gap (eV) for the lowest energy configurations of (Al$_2$O$_3$)$_n$, GdAl$_{2n-1}$O$_{3n}$, and Gd$_2$Al$_{2n-2}$O$_{3n}$, ($n = 1 - 10$) clusters. The band gaps (eV) for the bulk $\alpha$-Al$_2$O$_3$, Gd doped $\alpha$-Al$_2$O$_3$, and Gd$_2$ doped $\alpha$-Al$_2$O$_3$ configurations are also shown.

4.15 The total magnetic moments for the lowest energy configurations of (Al$_2$O$_3$)$_n$, GdAl$_{2n-1}$O$_{3n}$, and Gd$_2$Al$_{2n-2}$O$_{3n}$, ($n = 1 - 10$) clusters. The magnetic moments for the Gd and Gd$_2$ doped bulk $\alpha$-Al$_2$O$_3$ configurations are also shown.

5.1 Polarizabilities per atom for (Ga$_2$O$_3$)$_n$ clusters for $n = 1 - 10$ vs the size of the cluster ($n$).

5.2 TDLDA optical absorption spectra of the (Ga$_2$O$_3$)$_n$ clusters for $n = 1 - 10$. A Gaussian convolution of 0.1 eV has been used to simulate a finite broadening of the calculated spectra.

5.3 Total DOS for the lowest energy configurations for (Ga$_2$O$_3$)$_n$ clusters with $n = 1 - 10$. The Fermi level has been shifted to zero.

5.4 Shape dependent optical absorption spectra for cage type configurations of (Ga$_2$O$_3$)$_{10}$ cluster. The first optical gap is also given.