Tailoring the Magnetic and Optical properties of MgO Nanoparticles by Cobalt doping

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Received: 11 March 2022 Published: 30 June 2022

Abstract

In this work, Cobalt (0-10) % doped MgO nanoparticles are prepared for magnetic and optical studies. X-ray diffraction studies show the particle size increases from 3.10 nm to 9.50 nm with increasing Cobalt concentration in MgO samples. The secondary phases are observed beyond 5% Cobalt in the host MgO which indicates the solubility limit of dopant in this material. SEM analysis further reconfirms the purity and spherical morphology of nanoparticles in all samples. Its result also reveals that the smallest particles have the largest oxygen vacancy concentration as compared to other samples. The dopant and size-induced effects are observed for electronic absorption spectra and bandgap of the samples. UV-visible absorption spectra show a quantum confinement effect as the optical band gap decreases with the increase of the particle size. The optical band gap of the nanoparticles ranges from 4.68 eV to 3.15 eV which is very less in comparison with the bulk MgO band gap up to 7.2eV. Vibrating sample magnetometer studies at room temperature clearly show the ferromagnetic behavior for pure MgO nanoparticles in contrast with the paramagnetic behavior for other samples. It is suggested that the presence of the ferromagnetic behavior in pure MgO nanoparticles are due to the presence of oxygen vacancies.

Key words: Nanoparticles, Co doped MgO, quantum confinement, ferromagnetic.

DOI Number: https://doi.org/10.52700/jn.v2i2.56

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Introduction:

Dilute magnetic semiconducting and insulating oxides have gained significant prominence as a result of technical advances in the field of spintronic. This intriguing combination of spin and charge degrees of freedom in the same material has sparked a whirlwind of research and the creation of new spintronic devices with improved functionality. Various metal oxide nanoparticles show magnetic ordering at room temperature such as ZnO, SnO₂, In₂O₃, MgO, etc. with transition metal doping when grown as thin film or in powder form. The presence of ferromagnetism (FM) in these oxides has been reported repeatedly in experiments. Over the past decade, researchers put up tremendous effort to explore the origin of RTFM in these oxides. Some groups reported that RTFM origin is due to the presence of defects. J. F. Hu et al., studied the role of oxygen vacancies in magnetic ordering. Sundaresan et al., reported that this is the intrinsic feature of wide band gap oxides.

The present work is focused on a wide band gap insulating oxide MgO. It is an essential material from both an applied and fundamental standpoint. MgO nanomaterials have a wide range of industrial applications due to its environmental compatibility and significant thermal stability. It is used in superconducting goods, steel hazardous waste remediation, in refractory materials paints and in magnetoresistive devices. Magnesium Oxide is a wide band gap insulator having a wide band gap of 7.2 eV and possesses diamagnetic behavior at the bulk level. It has been reported that optical bandgap of MgO can be tuned from 7.2 eV to 3.37 eV by doping it with Zn. MgO nanoparticles also exhibit room temperature ferromagnetism under some conditions. It was previously proposed that neutral Mg vacancies cause a large magnetic moment on nearby oxygen ions.

The origin of Ferromagnetic order in insulating oxides has been of great interest and is still unclear. Notably, more research is needed in the understanding of ferromagnetism origin in these nanoscale oxides. This would lead not only to the creation of new systems with simple structures but also enable monitoring the incorporation and distribution of impurities in it as well. Various research work has been carried out to improve the magnetic properties MgO by doping it with Fe, Ni, Mn, Cr. The effect of Co doping in MgO samples is still unclear. Therefore, Cobalt doped Magnesium oxide samples (Co=0.00, 0.01, 0.03, 0.05, 0.08, 0.10) are synthesized to study the magnetic and optical properties in Co doped MgO materials.
Materials and method:

Magnesium and Cobalt nitrates (hydrated) of analytical grade were used for the preparation of the samples. NaOH was used as a precipitating agent for the formation of nanoparticles. The desired amount of metal precursors and NaOH were dissolved in deionized water. These samples were synthesized with the same procedure which has been reported in our previous work. The obtained samples were dried in oven at 100 °C for 24 hours and then annealed at 500 °C in oven for 05 hours.

All samples (powder form) were characterized by X-ray diffraction (D8 an advanced X-ray diffractometer (Bruker Axis) by UK) with Cu Kα (λ=1.5405 A) radiation. Morphology and purity of the samples were further confirmed by the Scanning electron microscope (JSM 6380A JEOL a Japanese System) equipped with EDX. The optical band gap of the samples was analyzed by UV-Visible spectrometer (An Ultraviolet Spectrophotometer by Beckman coulter DU-730 made by USA). Magnetic measurements at room temperature were performed using vibrating sample magnetometers VSM.

Results and Discussion:

The X-ray diffraction patterns for pure and Co doped MgO nanoparticle samples are shown in Figure 1. All diffraction peaks of pure and Co doped MgO samples were found to be well consistent with the cubic structure with the standard JCPDS file No. 89-7746. Tiny peaks suggest the appearance of secondary phases of Co₃O₄ (JCPDS file No. 42-1467) and CoO (JCPDS card no. 43-1004 for the samples with Co concentrations >5%. The presence of secondary phases shows that Co has a solubility limit (Co=5%) in the host material. The particle size is estimated from X-ray line broadening by the using Debye-Scherrer formula.

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]

where D denotes particle size, λ denotes wavelength, β denotes full-width half maxima (FWHM) and K is 0.9 for spherical particles. Crystallite size (D), and lattice parameter “a” of all samples are calculated from the (200) peak. These estimated values of particle size are 3.10 nm, 5.00 nm, 6.70 nm, 8.40 nm, 8.80 nm, and 9.50 nm for all samples with increasing Co concentration for 0% to 10% in MgO respectively. The lattice parameter for these cubical crystal structures is found to increase from 4.97 Å to 5.63 Å for all samples. This increment in the particle size and lattice
parameter is due to the larger ionic radius of Co$^{+2}$ (0.745 °A) as compared to the Mg$^{+2}$ (0.72 °A). These systematic variations in the samples confirmed that cobalt atoms are well incorporated in MgO samples.

Morphology of the samples was investigated by Scanning electron microscopy. All the samples were taken at 20 kV and 55000 X indicating various size aggregates. SEM images of all samples are shown in Fig 2 (a-f). In all samples, nanoparticles seem to be spherical in shape having uniform and narrow size distribution. In order to check the composition of samples, energy dispersive X-rays were performed. Figure 3 shows the spectral analysis of EDX which confirmed that all
samples are composed of Magnesium, Cobalt, and oxygen only. No additional peak for any other element has been found in the spectrum which confirms that our samples are pure. The estimated ratio of O vs metals in the pure MgO sample is found to be 0.576 which is very low as compared to the other samples. This ratio in other samples is found to be in the range of 0.8-0.9. In the pure MgO sample, this small ratio reflects a high concentration of Oxygen vacancies as compared to other samples.

Figure: 2 SEM images of pure (a) and (b) 1%, (c) 3%, (d) 5%, (e) 8%, and (f) 10% Co doped MgO nanoparticles.
The synthesized nanoparticles were dispersed in isopropanol to obtain the electronic absorption spectra of the samples as shown in Figure 4. Several peaks were observed within the detection limit of the UV-VIS spectrometer which arises due to the defects, anions on the surface, and low coordinated cations. Interestingly, the peaks in the UV region which are very close to each other formed discrete transitions, whereas a broad peak in each spectrum is responsible for the band-to-band transitions. This effect is more clearly shown when the absorption coefficient $\alpha$ is plotted against energy.

$$\alpha h\nu = C (h\nu - E_g)^{\frac{1}{2}}$$
where $\alpha$ = absorption coefficient, $h$ = Planck’s constant, $\nu$ = frequency of light and $E_g$ = bandgap.

The plot of $(\alpha h \nu)^2$ vs incident photon energy for all samples is inserted in Figure 4 for each sample and the bandgap energy of the samples was determined using a fitting procedure.

The calculated bandgap values decrease from 4.68 eV (for pure MgO) to 3.15 eV. (for 10 percent Co-doped MgO).

**Figure 4:** Absorption spectra of all samples along with optical band gap plot (inset)

Figure 5 shows the influence of Co concentration in MgO samples for optical bandgap and crystallite size. This is in line with the fact that transition metal additives have an impact on the optical band gap of host metal oxides. Increased dopant concentration in the host lattice is
responsible for the observed decreasing trend in band gap values. The observed decrease of the band gap as Co concentration increases leads to an increase in particle size. This decrease in band gap energy of the pure MgO nanoparticle indicated that this material transformed from insulating to semiconductor with the addition of Co content.

The lattice distortion caused by the inclusion of Co on the host MgO lattice is responsible for the observed narrowing of the band gap. The structure and intensity of the interaction between donors and the host lattice change as a result of this distortion, resulting in the observed band gap reduction as a function of increasing dopant concentration. The decrease in band gap with increasing Co concentration can also be explained by the existence of mixed valance states of Co in the host MgO lattice, i.e. Co$^{2+}$, Co$^{3+}$. The researcher reported that color centers were observed in these mixed valance states due to unpaired electrons in the d orbital, which narrows the band gap.

![Figure 5](image)

**Figure 5:** This graph shows that the band gap decreases with increasing Co concentration, whereas size of particle increases monotonically.

Magnetic characterization of the samples was done at room temperature by VSM. Magnetization curves for all the samples that were studied show interesting magnetic behavior. M(H) Loop of
undoped MgO sample has two components, one is Ferromagnetic and the other is Diamagnetic at a higher magnetic field as shown in Figure 6. By subtracting the diamagnetic behavior, the net Magnetization pattern is obtained by the equation \( M_f = M - \chi_d H \) where \( M_f \) is the Ferromagnetic component and \( \chi_d \) is the slope at a high field as shown in Figure 7 for pure MgO sample. This ferromagnetic behavior could be due to the high concentration of oxygen vacancies present in the samples. From EDX results it is already mentioned that there is a large concentration of oxygen vacancies present in pure MgO samples. Oxygen vacancy-mediated magnetic behavior has also been reported by another group. These vacancies enhance the direct interaction between the neighboring spins resulting in the long-range ferromagnetic order. From Figure 7, it is shown that the saturation magnetization value is 0.036 emu/g and the coercive field is \( H_c = 67.889 \) Oe. It has been reported that particle having a smaller size less than \( \approx 18 \) nm exhibits low coercivity values typically around a few tens of Oersted.

M(H) loops of other cobalt-doped (1-10) samples are shown in Figure 7. It is evident from the diagram that the incorporation of cobalt of either concentration in the MgO host matrix minimizes the ferromagnetic effect present in pure MgO nanoparticles. M(H)- loops show a Paramagnetic pattern. We suggest this behavior could be due to less concentration of oxygen vacancies in these samples as confirmed from EDX results. Magnetic susceptibility of all the samples shows that 1% has \( \chi_p \) value as \( 5.08 \times 10^{-5} \), 3% has \( 3.6 \times 10^{-6} \), 5% has \( \chi_p \) value as \( 2.75 \times 10^{-5} \), 8% has \( 3.4 \times 10^{-5} \) and the last one having 10% concentration of Co in MgO has \( \chi_p \) value as \( 3.25 \times 10^{-5} \). All values are in emu/gOe.
Figure 6: M(H) Loop of undoped MgO showing ferromagnetic and diamagnetic behavior

Figure 7: M(H) Loop of pure and Co doped MgO samples
Conclusion:

Cobalt (0-10)% doped MgO nanoparticles were synthesized for tuning the magnetic and optical properties. The optical band gap of the nanoparticles was found in ranging from 4.68 eV (for pure MgO) to 3.15 eV (for 10% Co in MgO). The electronic absorption spectra revealed that bandgap of the samples was decreased due to size-induced effects, as the optical band gap decreases with the increase of the particle size. The secondary phases were observed beyond 5% Cobalt in the host MgO which indicated the solubility limit of dopant in this material. The morphology of the samples was found to be spherical in shape and EDX analysis further reconfirmed the purity of the samples. The obtained results also revealed that the smallest particles have the largest oxygen vacancy concentration as compared to other samples. Vibrating sample magnetometer studies at room temperature clearly indicated the ferromagnetic behavior for pure MgO nanoparticles in contrast with the paramagnetic behavior for other samples. The ferromagnetic behavior in pure MgO nanoparticles was observed due to the presence of oxygen vacancies.

References

Mathon, J., & Umerski, A. Theory of tunneling magnetoresistance of an epitaxial Fe/MgO/Fe (001) junction. Physical Review B, 63(22), 220403, (2001).

Parkin, S. S., Kaiser, C., Panchula, A., Rice, P. M., Hughes, B., Samant, M., & Yang, S. H. Giant tunnelling magnetoresistance at room temperature with MgO (100) tunnel barriers. Nature materials, 3(12), 862-867, (2004).

Yuasa, S., Nagahama, T., Fukushima, A., Suzuki, Y., & Ando, K. Giant room-temperature magnetoresistance in single-crystal Fe/MgO/Fe magnetic tunnel junctions. Nature materials, 3(12), 868-871, (2004).

Stoneham, A. M., Pathak, A. P., & Bartram, R. H. The ground state of two-hole centres in oxides. Journal of Physics C: Solid State Physics, 9(1), 73, (1976).

Ishizaki, T., Cho, S. P., & Saito, N. Morphological control of vertically self-aligned nanosheets formed on magnesium alloy by surfactant-free hydrothermal synthesis. CrystEngComm, 11(11), 2338-2343, (2009).

Raza, S. M., Uddin, Z., Tahir, A., & Raza, S. M. Synthesis, tailoring the optical properties of insulating alkaline-earth metal oxide (MgO) with dopants of transition metal (Cu) and
vibrating sample magnetometer measurements. Solid State Communications, 346, 114634, (2022).

Sundaresan, A., Bhargavi, R., Rangarajan, N., Siddesh, U., & Rao, C. N. R. Ferromagnetism as a universal feature of nanoparticles of the otherwise nonmagnetic oxides. Physical Review B, 74(16), 161306, (2006).

Kinge, S., Crego-Calama, M., & Reinoudt, D. N. Self-assembling nanoparticles at surfaces and interfaces. ChemPhysChem, 9(1), 20-42, (2008).

Tian, Y. F., Antony, J., Souza, R., Yan, S. S., Mei, L. M., & Qiang, Y. Giant positive magnetoresistance in Co-doped ZnO nanocluster films. Applied Physics Letters, 92(19), 190109, (2008).

Singh, J. P., Dixit, G., Srivastava, R. C., Agrawal, H. M., Reddy, V. R., & Gupta, A. Observation of bulk like magnetic ordering below the blocking temperature in nanosized zinc ferrite. Journal of magnetism and magnetic materials, 324(16), 2553-2559, (2012).

Chetri, P., Choudhury, B., & Choudhury, A. Room temperature ferromagnetism in SnO 2 nanoparticles: An experimental and density functional study. Journal of Materials Chemistry C, 2(43), 9294-9302, (2014).

Diaz-Gallifa, P., Fabelo, O., Pasan, J., Canadillas-Delgado, L., Lloret, F., Julve, M., & Ruiz-Perez, C. Two-Dimensional 3d–4f Heterometallic Coordination Polymers: Syntheses, Crystal Structures, and Magnetic Properties of Six New Co (II)–Ln (III) Compounds. Inorganic Chemistry, 53(12), 6299-6308, (2014).

Venkatesan, M., Fitzgerald, C. B., & Coey, A. J. Unexpected magnetism in a dielectric oxide. Nature, 430(7000), 630, (2004).

Si, M. S., Gao, D., Yang, D., Peng, Y., Zhang, Z. Y., Xue, D., & Zhang, G. P. Intrinsic ferromagnetism in hexagonal boron nitride nanosheets. The Journal of Chemical Physics, 140(20), 204701, (2014).

Wang, Y., Li, L., Prucnal, S., Chen, X., Tong, W., Yang, Z., & Zhou, S. Disentangling defect-induced ferromagnetism in SiC. Physical Review B, 89(1), 014417, (2014).

Sundaresan, A., Bhargavi, R., Rangarajan, N., Siddesh, U., & Rao, C. N. R. Ferromagnetism as a universal feature of nanoparticles of the otherwise nonmagnetic oxides. Physical Review B, 74(16), 161306, (2006).
Hu, J., Zhang, Z., Zhao, M., Qin, H., & Jiang, M. Room-temperature ferromagnetism in MgO nanocrystalline powders. Applied physics letters, 93(19), 192503, (2008).

Sundaresan, A., Bhargavi, R., Rangarajan, N., Siddesh, U., & Rao, C. N. R. Ferromagnetism as a universal feature of nanoparticles of the otherwise nonmagnetic oxides. Physical Review B, 74(16), 161306, (2006).

Shalimov, A., Potzger, K., Geiger, D., Lichte, H., Talut, G., Misiuk, A., & Fassbender, J. Fe nanoparticles embedded in MgO crystals. Journal of Applied Physics, 105(6), 064906, (2009).

Ramachandran, S., Narayan, J., & Prater, J. T. Magnetic properties of Ni-doped MgO diluted magnetic insulators. Applied physics letters, 90(13), 132511, (2007).

Azzaza, S., El-Hilo, M., Narayanan, S., Vijaya, J. J., Mamouni, N., Benyoussef, A., & Bououdina, M. Structural, optical and magnetic characterizations of Mn-doped MgO nanoparticles. Materials Chemistry and Physics, 143(3), 1500-1507, (2014).

Stavale, F., Nilius, N., & Freund, H. J. Cathodoluminescence of near-surface centres in Cr-doped MgO (001) thin films probed by scanning tunnelling microscopy. New Journal of Physics, 14(3), 033006, (2012).

Sharma, U., & Jeevanandam, P. Synthesis of Zn2+-doped MgO nanoparticles using substituted brucite precursors and studies on their optical properties. Journal of Sol-Gel Science and Technology, 75(3), 635-648, (2015).

Raza, S. M., Uddin, Z., Tahir, A., & Raza, S. M. Synthesis, tailoring the optical properties of insulating alkaline-earth metal oxide (MgO) with dopants of transition metal (Cu) and vibrating sample magnetometer measurements. Solid State Communications, 346, 114634, (2022).

Mathon, J., & Umerski, A. Theory of tunneling magnetoresistance of an epitaxial Fe/MgO/Fe (001) junction. Physical Review B, 63(22), 220403, (2001).

Parkin, S. S., Kaiser, C., Panchula, A., Rice, P. M., Hughes, B., Samant, M., & Yang, S. H. Giant tunnelling magnetoresistance at room temperature with MgO (100) tunnel barriers. Nature materials, 3(12), 862-867, (2004).

Stoneham, A. M., Pathak, A. P., & Bartram, R. H. The ground state of two-hole centres in oxides. Journal of Physics C: Solid State Physics, 9(1), 73, (1976).
Choudhury, B., Basyach, P., & Choudhury, A. Monitoring F, F+ and F22+ related intense defect emissions from nanocrystalline MgO. Journal of luminescence, 149, 280-286, (2014).

Pathak, N., Ghosh, P. S., Gupta, S. K., Kadam, R. M., & Arya, A. Defects induced changes in the electronic structures of MgO and their correlation with the optical properties: a special case of electron–hole recombination from the conduction band. RSC advances, 6(98), 96398-96415, (2016).

Feng, S. H., & Li, G. H. Hydrothermal and solvothermal syntheses. In Modern inorganic synthetic chemistry (pp. 73-104). Elsevier, (2017).

Basu, S., Chen, Y. B., & Zhang, Z. M. Microscale radiation in thermophotovoltaic devices—a review. International Journal of Energy Research, 31(6-7), 689-716, (2007).

Rodriguez, J. A. Electronic and chemical properties of mixed-metal oxides: basic principles for the design of DeNOx and DeSOx catalysts. Catalysis today, 85(2-4), 177-192, (2003).

Naseem Shah, S., Naeem, M., Rizwan Ali, S., Mahmood, S., Imran Ali, S., Bibi, Y., & Ul Hassan, N. Morphological Change in Cu-DOPED ZnO from Rod-Like to Flowers-Like Nanostructures: a Vital Role for the Optical Band Gap Tuning. Surface Review and Letters, 24(Supp01), 1850001, (2017).

Kumari, L., Li, W. Z., Vannoy, C. H., Leblanc, R. M., & Wang, D. Z. Synthesis, characterization and optical properties of Mg (OH) 2 micro-/nanostructure and its conversion to MgO. Ceramics International, 35(8), 3355-3364, (2009).

Kumar, N., Sanyal, D., & Sundareshan, A. Defect induced ferromagnetism in MgO nanoparticles studied by optical and positron annihilation spectroscopy. Chemical physics letters, 477(4-6), 360-364, (2009).

Vrancken, B., Thijs, L., Kruth, J. P., & Van Humbeeck, J. Heat treatment of Ti6Al4V produced by Selective Laser Melting: Microstructure and mechanical properties. Journal of Alloys and Compounds, 541, 177-185, (2012).

Arshad, M., Ansari, M. M., Ahmed, A. S., Tripathi, P., Ashraf, S. S. Z., Naqvi, A. H., & Azam, A. Band gap engineering and enhanced photoluminescence of Mg doped ZnO nanoparticles synthesized by wet chemical route. Journal of Luminescence, 161, 275-280, (2015).

Naeem, M., Qaseem, S., Gul, I. H., & Maqsood, A. Study of active surface defects in Ti doped ZnO nanoparticles. Journal of applied physics, 107(12), 124303, (2010).
Li, F., Zhang, C. W., & Zhao, M. First-principles study of electronic structure and magnetic properties of Cu-doped CeO2. Journal of Applied Physics, 112(8), 083702, (2012).

Lee, H. J., Jeong, S. Y., Cho, C. R., & Park, C. H. Study of diluted magnetic semiconductor: Co-doped ZnO. Applied Physics Letters, 81(21), 4020-4022, (2002).

Mishra, D., Mandal, B. P., Mukherjee, R., Naik, R., Lawes, G., & Nadgorny, B. Oxygen vacancy enhanced room temperature magnetism in Al-doped MgO nanoparticles. Applied Physics Letters, 102(18), 182404, (2013).