Synthesis and Characterization of Li\(^+\), Ag\(^{2+}\) and Cu\(^{2+}\) metals doped MgO nanostructured in Gel Method

V. Rajendran\(^1\), B. Deepa\(^*\) and R. Mekala\(^1\)

\(^1\)PG Research Department of Physics, Presidency college, Chennai 600 005, Tamilnadu, India.

* Email: b.deepasenthil@gmail.com

Abstract The MgO nano particles doped with alkali, Nobel and transition metals (Li\(^+\), Ag\(^{2+}\), Cu\(^{2+}\)) were synthesized by gel method. The structures, morphologies and size of synthesized samples were characterized and confirmed by Powder X-ray diffraction (PXRD), Scanning Electron Microscope (SEM) and High Resolution Transmission Electron Microscope (HR-TEM). The antibacterial activity for pure and doped MgO nano particles were studied against S. auerus. Among the results, the Li\(^+\) and Cu\(^{2+}\) doped MgO nano particles are best inhibition against the bacterial strains due to the presence of active oxygen species.

Keywords: Nanoparticles, MgO, Strains, PXRD.

1. Introduction

The metal oxides have attracted attention of many applications such as in sensors, optoelectronic, and plasma display panel and as insulating layers\(^1\)\(^3\). Among these material MgO has good inorganic antibacterial agent with cubic periclase structure also high oxygen affinity and low temperature of Mg causes oxide compound easy to synthesis\(^2\). However, many studies have been done to improve the antibacterial activities of various metal oxides such as ZnO, AgO and ZrO\(_2\) by reducing the grain size or by doping transition metal elements\(^4\)\(^5\). Doping of some metal ions into oxide material is effective way
for modifying the physical and chemical properties such as high defect concentrations. These defect concentrations (active oxygen species AOS) played a significant role towards the antibacterial activities of nano crystal. Therefore, we synthesis the bare MgO and various metal doped (Li\(^+/\), Ag\(^{2+}\), Cu\(^{2+}\)) MgO via cost effective sol-gel method. In that Li ions elements has a similar ionic radius (0.76Å) to Mg (0.72Å). These Li ions easily accommodate within the crystal lattice and enhance the antibacterial activity. Second, the Noble metal Ag has bigger ionic radius (1.26Å) than Mg. So that, Ag ions spreading on the surface grain then reduce to Ag\(^{0}\) in higher temperature, it’s inhibit the crystal growth and increases the surface area and generation of hydrogen peroxide. The Cu elements has same ionic radius of Mg. The similarity of ionic radius promotes the substitution incorporation of the dopants. So, these metal ions (Li\(^+/\), Ag\(^{2+}\), Cu\(^{2+}\)) dopants are attributes to the generation and stabilization of AOS. The aim of this work is to clarify the effect of the dopants on antibacterial activity, crystalline size and structure morphology.

2. Experimental

All the chemicals used here were analytical grade and directly used as received without further purification. 0.1 M Magnesium ethonate tetra hydrate was initially dissolved in 50ml of the methanol solvent under constant stirring. The pH of the solution was adjusted to 5 using 1M of BDC. The mixture was continuously stirred until a thick white gel is formed and it is left overnight for further gelation process before been dried in an oven at 100°C for 24 h. The fluffy dried material was grounded to fine powder precursors. The resultant synthesized material was annealed at 600°C for 6 h to form MgO nanostructures. Doped MgO was also prepared by same procedure with addition of dopands. The doping concentration is 2.5mol% for each dopand. In the sol-gel reaction, the magnesium ethonate Mg (CH\(_3\)COO)\(_2\)4H\(_2\)O and benzene -1,2 Dicarboxylic acid (BCD) C\(_8\)H\(_6\)O\(_4\) are hydrolyzed in the methanol to form the mixture of magnesium (Mg\(^{2+}\)) cation and phthalate (C\(_8\)H\(_4\)O\(_4\))\(^-\) anion, respectively. When the reaction medium reaches a pH of about 5, these ions form complexes and are polymerized to give a thick white gel. The gel formed is identified as magnesium phthalate. Besides that, the side products such as acetic acid and water were evaporated during drying at 100 °C for 24 h. Then the Mg (C\(_8\)H\(_4\)O\(_4\)) is decomposed into MgO nanostructures.

2.1 Characterization Techniques

The synthesized samples were subjected into various characterizations. The thermal profiles of the precursors were studied using Thermo gravimetric analysis (TGA Q500 V20.10 Build 36). The Powder X-ray diffraction (PXRD) patterns of the periclase were obtained by the XRD Analytical X’Pert Pro MPD with CuK\(_\alpha\) radiation. The morphology and size of the periclase crystallites were determined using a
scanning electron microscope (SEM; JEOL JSM-7600 F,) and a High resolution transmission electron microscope (HRTEM; JEOL JEM-2100 F).

2.2. Antibacterial studies

The antibacterial activity of the sample was studied by using disc diffusion method. Pure culture of *Staphylococcus aureus* species of bacteria was used for the testing antimicrobial activity of MgO nanoparticles. Nutrient agar medium plates were prepared by suspending 28 g of nutrient agar powder in one liter of distilled water then to sterilize the medium through autoclave at 121°C for 20-25 minutes. Pour 25-35 ml of medium into Petri plate under sterile conditions via laminar air flow chamber. Medium allowed to solidification under room temperature and then the bacterial cultures were swabbed on plates. The sterile discs were dipped as prepared nanoparticles solution at different concentrations (25, 50, 75 and 100 of μg/ml) and kept for incubation at 37°C for 24 hours. Zones of inhibition were measured with Hi Media ruler.

![Fig. 1 Schematic diagram of Bare and doped MgO samples.](image)

3. Result and discussion

Fig (2) shows a XRD diffraction pattern of as prepared samples. The observed pattern for bare and doped MgO sample can be indexed to the cubic phase with periclase structure. As the presence of dopands, one observes that the intensity of the peaks varied and also the diffraction peaks shifted slightly in the (200) plane position, indicating a lattice distortion of the doped catalyst shown in Table. 1. The higher intensity values observed in Li doped MgO sample and lower intensity values for Ag which is due to ionic radius of dopants. The ionic radius is much bigger, smaller and similar than that of Mg$^{2+}$ ions, the
dopants substituting for MgO crystal lattice distortion\textsuperscript{14}. Moreover, the crystallite of doped samples it appears that later decreased from Li to Ag, which indicates changes in crystal strains. The crystalline size of bare and doped MgO nano powder was calculated by Scherer equation. Compare to bare MgO (16.033nm) Li - doped MgO nano structured has largest size and Nobel metal Ag\textsuperscript{2+} has the smallest crystallite size. Then Cu\textsuperscript{2+} doped MgO has nearly similar to the bare MgO. In XRD diffraction pattern, Ag doped peak has some metallic silver elements were detected for exceeding the silver due to its solubility limit of Ag in MgO\textsuperscript{15}.

| Samples      | 2θ(º)  | d-spacing(nm) | FWHM | Crystalline Size (nm) | Lattice Constant (Å) |
|--------------|--------|---------------|------|-----------------------|----------------------|
| MgO          | 42.8167| 0.210951      | 0.5270 | 16.033                | 4.2190               |
| Li-Doped     | 42.7897| 0.211080      | 0.3905 | 21.635                | 4.2216               |
| Cu-Doped     | 42.7892| 0.210536      | 0.5632 | 15.00                 | 4.2107               |
| Ag-Doped     | 42.8187| 0.210942      | 0.7859 | 10.751                | 4.2188               |

Table 1. XRD parameters for Bare and Doped MgO samples.

![XRD Diffraction pattern](image)

**Fig.2** XRD Diffraction pattern (B) Bare MgO (C) Li-doped (D) Cu-doped (E) Ag-doped.

Typical SEM micrographs of different samples were investigated in Fig (3) while considering the doped MgO. The morphological structure was converted from homogeneous agglomerated particle for bare MgO into disc like shapes and ball like shapes besides the dispersed particle for doped MgO sample. The
high resolution TEM image of the as synthesized MgO nano crystalline shown in Fig (4). It clearly shows the lattice fringes, indicating the established crystalline of MgO nano powder. Since a crystallite can be defined by studying the orientation of the lattice fringes, one can see the average grain size in the synthesized MgO nano particle is about 10-20 nm in diameter, which is good agreement with calculated values from XRD analysis. The spacing of a set of fringes is proportional to lattice spacing when the corresponding lattice planes meet the Bragg condition. The distance between the lattice fringes was found to be 0.21 nm, which was good agreement with the lattice spacing of (200) plane in cubic phase of MgO.

![Fig. 3 SEM for (a) Bare MgO (b) Li-doped (c) Cu-doped (d) Ag-doped.](image)

The antibacterial activities of Li\(^+\), Ag\(^{2+}\), and Cu\(^{2+}\) doped MgO nano crystallites are investigated using MBC test and anti bactericidal rate against S.aureus. The MBC values of the as synthesized nano particles towards S.aureus are listed in Table 2. Clearly Li\(^+\) and Cu\(^{2+}\) doped MgO has a lowest
concentration (75μg/ml) observed the best anti bacterial activity followed by standard antibiotic ciprofloxacin. The Li⁺ ions have low valance state and occupy the MgO

crystal lattices which generate the oxygen vacancy to inhibit the bacterial growth\(^{17}\). In the same, Cu\(^{2+}\) ion has similar ionic radius of Mg\(^{2+}\), the similarity of ionic radius promotes substitution incorporation of the dopand, it’s has to increase the number of oxygen vacancies\(^{18}\). However, Ag-doped MgO have relatively less antibacterial activity because of lower susceptibility of gram positive bacteria. The lower susceptibility of gram positive bacteria to silver doped nanoparticles has been attributed to difference in the cell wall structure. Thus, gram positive bacteria may allow less Ag\(^{+}\) ions to reach to cytoplasmic membranes of the bacterial strains. Compared with dopants the bare MgO has a highest antibacterial activity due to high AOS generation in which inhibits the growth of S.aureus.

**Fig. 5** Comparative graph of ZOI and Concentrations of Li, Ag and Cu dopants.

| Microorganism     | Treatment- ZOI of Bare and doped MgO samples. |
|-------------------|-----------------------------------------------|
| **Staphylococcus aureus** | Concentration of MgO Nps (μg/ml) | Li-MgOSamples ZOI (mm) | Cu-MgO Samples ZOI (mm) | Ag-MgO Samples ZOI (mm) |
| Standard Ciprofloxin ZOI (11mm) | 25 | 5 | 5 | 4 |
|                   | 50 | 7 | 6 | 6 |
|                   | 75 | 12 | 10 | 8 |
|                   | 100 | 13 | 11 | 9 |
4. Conclusion

In conclusion, the bare and alkali, Nobel and transition metal (Li\(^{+}\), Ag\(^{2+}\), Cu\(^{2+}\)) doped nanostructured MgO were synthesized by gel method. The Powder XRD, SEM and HRTEM analysis observed that the Periclase cubic structure, disc like and ball like morphologies. The metal dopands obviously influenced the crystallization, various structures and antibacterial activity of nanostructured MgO. The Li and Cu-doped MgO exhibit the good antibacterial activity against S. aureus due to an increase in defect concentration (AOS). However, Ag-doped samples exhibit less antibacterial activity than the other dopands. All these results indicate the ionic radius of dopands is important key factor for the structural, morphological and antibacterial activities of nanostructured MgO.

Acknowledgement

The author is grateful to the Department of Science and Technology (DST) for extending financial assistance to carry out this work.

Reference

[1] T. Abukawa, S. Sato, Y. Matsuoka, 2010 Surface science, 164, 604.
[2] S. Benedetti, H.M. Benia, N. Nilius, S.Valeri, H.J.Freund, 2006 Chemical physics letters 430, 330.
[3] D.S.E. Atanassova, 2002 Microelectronic Reliability 42, 1171.
[4] V.K. Sharma, R.A. Yngard, Y. Lin, 2009 Advanced colloid interface science 145, 83-96.
[5] Neha Sharma, J. Kumar, S. Thakur, S. Sharma, V. Shrivastava, 2013 Drug invention today, 5 50-54.
[6] J.H. He, I. Ichinose, S. Fujikawa, T. Kunitake, A. Nakao, 2002 Chemical Matter 14, 3493-3500.
[7] L. Huang, D.Q. Li, Y.J. Lin, M. Wei, D.G. Evans, X. Duan, 2005 Journal of Inorganic Biochemical, 99, 986-993.
[8] F. Al-Hazmi, F. Alnowaiser, A.A. Al-Ghamdi, M.M. Aly, R.M. Al-Tuwirqi, F. El-Tantaway, 2012 Superlattices Microstructures 52, 200-209.
[9] Y. Rao, W. Wang, F. Tan, Y. Cai, J. Lu, X. Qiao, 2014 Creamics International, 40 14397-14403.
[10] H. E. Chao, Y. U. Yun, H. U. Xingfang, A. Larbot, 2003 Journal of European Creamic Society 23, 1457-1464.
[11] W. Li, S. Iematshah, C.P. Huang, O. Jung, C. Ni, 2002 Material Science Engineering B, 96, 247.
[12] M. Mastuil, N. Kamarulzaman, M. Nawawi, A. Mahat, R. Rusdi, N. Kamarudin, 2014 *Nano. Rsch. Lett.* 9, 134.

[13] J. Yuan, M.X. Chen, J.W. Shi, W.F. shangguan, 2006 *International Journal of Hydrogen energy* 31,1326-1331.

[14] W. Kallel, 2006 *Journal of non-crystalline solids*, 352, 3970-3978.

[15] H. S. Park, D. H. Kim, S. J. Kim, K. S. Lee, 2006 *Journal of Alloys and Compounds*, 415, 51-55.

[16] S. Qiu, S. J. Kalita, 2006 *Materials Science and Engineering A* 435-436, 327-332.

[17] I. Balint, K. Aika, 2001 *Applied Surface Science* 173, 296-306.

[18] S. Egger, R.P. Lehmann, M.J. Height, M.J Loessner, M.Schuppler, 2009 *Applied Environmental Microbiology*, 75, 2973.