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The Study of Effect of different Doping on the Structural, Morphological, Optical and Spectral Properties of Magnesium Aluminate Spinel

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Abstract: A scientifically important material that has been widely studied because of its numerous useful properties and applications is Magnesium aluminate. It has been used for a variety of transition metals and lanthanide ions as a phosphor host to study different properties and to explore possible applications. Hence the present study in this review paper deals with the current developments in the effect of doping on different properties of magnesium aluminate spinel.

INTRODUCTION

Magnesium aluminate with spinel structure have general formula AB_2O_4 with one divalent cation (A^{2+}) and two trivalent cations (B^{3+}). Unit cell consists of a face centered cubic close packed arrangement of thirty two oxygen (O^{2-}) ions. One-eighth of the tetrahedral voids (64) and half of the octahedral voids (32) have been found to be occupied by Mg^{2+} and Al^{3+} cations with eight formula units i.e., $[AB_2O_4]_8$ [1]. $MgAl_2O_4$ exhibits distinctive properties like high chemical inertness, high melting point (2135°C), low dielectric constant (ε = 7.5), thermal stability, hydrophobicity, high resistance to radiation damage, high mechanical strength at elevated temperatures, low surface acidity, relatively low coefficient of thermal expansion, low density, good photonic efficiency, high electrical resistivity, wide band gap energy, catalysis etc. As a result they used in different capacities, like in humidity sensors [2], Nano devices [3], as insulating material [4], fusion technology [5], high temperature applications [6], for low electrical losses [7], photo luminescent material [8], catalysts for many reactions [9, 10], refractory materials, transparent ceramics [11], spinel-bonded castables [12], metallurgical, electrochemical, [13] radio technical [14] and chemical industrial fields [15]. Several techniques such as, conventional solid-state-reaction (SSR) including mechanical oxide and/or salt mixtures calcination, organic gel-assisted citrate complexation, and spray drying (atomization) have been extensively employed [16–20]. A number of non-conventional methods such as co-precipitated method [21], aerosol method [22], citrate–nitrate route [23], sol–gel method [24, 25], modified sol–gel route [26, 27], self -heat-sustained (SHS) technique [28] have been exploited. Purity, particle size, morphology, synthesis temperature, reactivity and physical properties of the MgAl2O4 spinel are influenced by both the precursors used and synthesis method [29, 30].

Both magnesium and aluminum cations can be replaced by other cations having similar size, keeping the electrochemical balance. Herein, I review the effect of doping of magnesium aluminate spinel on different properties.

EFFECT OF DIFFERENT DOPING OF MAGNESIUM ALUMINATE ON ITS VARIOUS PROPERTIES

The effect of doping of $MgAl_2O_4$ by a binary mixture of Co and Zn ions on the absorbance, capacitance, heat capacity, electrical resistivity, thermal conductivity, and thermal diffusivity have been studied by Iqbal *et al.* [31]. They have synthesized materials with composition $Mg_{1-2}x$ (Co, Zn) xAl_2O_4 (x = 0.0–0.5) by solution combustion synthesis assisted by microwave irradiation. The substituted spinels with a Scherer crystallite size of 18-23 nm and 45 nm undoped samples were formed, as observed from X-ray diffraction and established by transmission electron microscopy. There have been observed

three strong absorption bands at 536, 577 and 630 nm for the doped samples due to the three spin allowed ($^4A_2$ (F) $\rightarrow$ $^4T_1$ (P)) electronic transitions of Co^{2+} at tetrahedral lattice sites, whereas the pure magnesium aluminate remained transparent in the whole spectral range. The semiconducting behaviour of the materials have been marked by their temperature dependent electrical resistivity. In the doped materials the heat capacity have been reported to get increased while thermal conductivity and diffusivity got lowered. The dielectric constant increased due to doping. The doped materials have been observed to show better thermal stability in 298-1773 K temperature range.

The effect of doping on surface structure of $MgAl_2O_4$ spinel has been reported by Hasan et al. via atomistic calculations [32]. They have used high temperature annealing to study the potential energy changes and produced more stable surface structures. Then doping of the surfaces were done with three trivalent cations, Y^{3+}, Gd^{3+}, La^{3+} and one tetravalent cation Zr^{4+} and then determined the surface segregation energies of the dopants (cations) and surface energies of the doped surface. The surface energy of spinel has been observed to be reduced by all the dopants and this reduction in energy has been found to be related to both the size and valence of the dopant with the dopant charge playing a larger role in segregation of the surface and hence reduction of the surface energy than the dopant size. The lowest energy surface has been found the (100) surface, whereas the highest energy surface is (111). The expected crystal shape has been found to be dominated by (100) surfaces for both the undoped and doped spinels, but the relative proportion of the various surfaces varied with doping because of the unequal changes in energy, which has impacts on shapes of equilibrium nanoparticles and on applications sensitive to surface properties.

The effect of size of nanocrystals on optical properties of Cr^{3+} doped $MgAl_2O_4$ spinels have been reported by G³uchowski et al.[33]. From the luminescence, excitation and lifetime measurements, the optical properties of Cr^{3+}:$MgAl_2O_4$ nanocrystals have been found to significantly depend on their size. Blaakmeer et al have synthesized lithium-doped $MgAl_2O_4$ spinels and have reported the investigation of morphology of these spinels along with the structural changes that occur due to lithium doping, with the help of advanced solid state ^{7}Li, ^{25}Mg, and ^{27}Al NMR [34]. The spinel structure has been observed to be well retained, while the quantity of tetrahedral aluminum increased with increase in lithium content. The presence of two tetrahedral sites has been discovered in both doped and undoped spinels with the help of MQMAS experiments. The ^{25}Mg spectra obtained with the quadrupolar-Carr-Purcell-Meiboom-Gill (QCPMG) and side band selective Double Frequency Sweep-QCPMG (ssDFS-QCPMG) pulse sequences have been found to have heterogeneity. With static variable temperature ^{7}Li NMR experiments lithium mobility was measured. In these magnesium spinels a low fraction of mobile lithium (3-4%) has been established. The lithium-doped spinels may be used as solid state electrolytes in batteries in which all constituents have the spinel structure.

The effect of Ti doping in Ti-doped $MgAl_2O_4$ have been reported by Kim et al. who produced Ti-doped $MgAl_2O_4$ spinels by combining possible Ti oxidation states (Ti^{2+}, Ti^{3+}, and Ti^{4+}) using a theoretical thermodynamic approach[35]. Crystal models having each doping type were prepared and by considering them as independent phases, phase diagrams of the Mg–Al–Ti–O system have been replicated based on first-principle's calculations, thus enabled the investigation of stable doping types as a function of their synthesis conditions and chemical compositions. A quantitative analysis model has been established for calculating the proportions of certain doping types based on the considerations of formation energy and mixing entropy, and the fractions of doping kinds have been calculated. Variations in the ratios of Ti^{3+}:Ti^{4+} have been replicated and the effects of temperature, oxygen partial pressure, Mg/Al ratio and surface on these have been examined. This study provides guidelines to the design Ti-doped $MgAl_2O_4$ phosphors for LED applications.

The structural and dielectric characteristics of Zn-doped MgAl2O4 spinels have been reported by Hussain et al. They synthesized $MgAl_2O_4$ ceramics by sol-gel based microwave assisted combustion process at low temperature [36]. In order to investigate the effect of doping with Zn on the structural and dielectric statistics of MgAl2O4 spinels, Zn has been substituted at Mg site. The crystal structure has been confirmed and evaluated for its structural parameters using X-ray diffraction. Scanning electron microscope has

been used to determine the surface morphology. The effects of substitution of Zn at Mg-site on frequency dependent dielectric constant and tangent loss have been reported in detail.

The luminescence behavior of Ce doped MgAl2O4 spinels have been reported by Tabaza et al. [37]. They have produced Ce doped $MgAl_2O_4$ nanocrystals by a simple combustion method in which metal nitrates were used as predecessors and urea as a fuel in a preheated furnace at 520°C, followed by annealing in a hydrogen atmosphere. Various characterization studies such as X-ray diffraction (XRD), UV-Visible spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy and photoluminescence spectroscopy (PL) have been reported. In PL spectra of Ce doped $MgAl_2O_4$ using an excitation wavelength of 350 nm broad green emission bands centered at 500 nm have been produced. The sample doped with 0.75 mol% Ce has produced maximum green emission.

The luminescence behavior of (Mg, Zn)Al_2O_4:Tb mixed spinel thin films have been reported by Kroon et al [38]. At first, the optimum Mg:Zn ratio and Tb concentration have been determined for green luminescence from the $^5D_4$ - $^7F_5$ transition of Tb^{3+} ions using nanocrystalline samples obtained by combustion synthesis. Thin films with x = 0.75 and 0.5 mol% Tb using a solution of the nitrates of Mg, Zn, Al and Tb in ethanol, with ethylene glycol as complexing agent, have been spin-coated on Si (100) substrates followed by annealing for 1 h in air. X-ray diffraction of the sample annealed at 600 °C has shown the thin film having strong (111) preferential orientation. The luminescence has been found to be increased, with an increase in annealing temperature up to 1000°C, whereas the surface became somewhat rougher and the layer-substrate interface more inter diffused. On annealing the samples at 1200°C, the diffusion of Si through the layer takes place resulting in the formation of an additional phase. As a result the green Tb emission has been observed to be slightly reduced, whereas blue emission from the $^5D_3$ level of Tb^{3+} has been found to be considerably increased in these samples.

The effect of Cr doping on the electrical properties of $MgAl_2O_4$ nanoparticles have been reported by Saha et al. [39]. They have synthesized Magnesium aluminate nanoparticles with different chromium concentration in the range 0–12% with crystal size ranging from 8.5 to 19.8 nm using a citrate-nitrate sol-gel route. Their surface morphology has been studied with the help of a field emission scanning electron microscope which has shown the existence of both grain and grain boundary along with their aggregates. The dielectric constant, dielectric loss and ac conductivity as a function of frequency of the applied electric field at different compositions have been studied and their variation with frequency has been explained on the basis of Maxwell–Wagner interfacial model. The effect of grain and grain boundary on the electrical properties of this spinel oxide has been studied using impedance spectroscopy technique. With the increase of doping concentration all the electrical parameters have been observed to change gradually.

The structural and spectroscopic properties of Yb^{3+}doped $MgAl_2O_4$ spinels have been reported by Wiglusz et al. [40]. They have synthesized Yb^{3+}doped $MgAl_2O_4$ nanoparticles in the range of 10–30 nm as a function of the dopant concentration and sintering temperature by a sol–gel method followed by heat-treatment in the range of 700-1000°C. The main Yb^{3+} zero-phonon line has been found at 976 nm. The broad absorption spectroscopy and emission spectroscopy have been used to characterize the spectroscopic properties of the Yb^{3+} ions. There is the high inversion speed between Mg^{2+} tetrahedral sites and Al^{3+} octahedral sites so even at low temperature, the spectra have shown a strong distorted spinel lattice. It has been observed in the cooperative luminescence spectra at around 500 nm that the substitution of Mg^{2+} ions by Yb^{3+}ions favored the formation of Yb^{3+} ion pairs. The declines in luminescence depend on the Yb^{3+} content, the energy transfer between ions and the presence of ion pairs and aggregates.

The effect of Cr^{3+} doping on photoluminescence properties of $MgAl_2O_4$ spinel have been reported by Phan et al. from their study of photoluminescence spectra in wavenumber range between 26,300 and 12,500 cm^{-1}. With the help of a number of excitation sources, a broad band, namely K, with a peak at 15,547 cm^{-1} and the transition process of luminescence lines between the electronic levels of the Cr^{3+} ion, such as R, Ni (i = 1-4) lines have been observed. The K-band has been suggested to be obtained from the electric dipole transition $^2Eg \rightarrow {}^4A_{2g}$, in a strong crystal field having $D_q/B > 2.3$.

The structural and spectroscopic properties of red light emitting Li^{+} co-doped $MgAl_2O_4$: Eu^{3+} nanophosphors have been reported Faizan et al. They have synthesized it by combustion synthesis method [42] and characterized these phosphors by XRD, FTIR, UV-visible and photoluminescence (PL) spectroscopy. The band gap of pure Eu^{3+}doped and Li^{+} co-doped MgAl2O4 phosphor have been found from the DR spectra by means of the K-M function F (R_{∞}). The photoluminescence spectra of $MgAl_2O_4$: $Eu^{3+}$and Li^{+} co-doped $MgAl_2O_4$:Eu^{3+} phosphors have been defined by $^5D_0$ - ^7F_j transitions (J=0, 1, 2, 3, 4). With Li^{+} codoping the emission intensity of these phosphors has been observed to increase.

The spectroscopic properties of Ti and Mn-doped MgAl2O4 spinels have been investigated and reported by Jouini et al. They have grown these Ti and Mn-doped MgAl2O4 spinels by the micro-pulling-down method and studied these due to its potential use as a short-wavelength tunable solid-state laser [43]. Ti-doped MgAl2O4 have been found to give strong blue emission and green emission is observed from Mn-doped spinel. By changing the doping concentration the optimum conditions to obtain the strongest emission have been studied. The two broad emission bands around 455 nm for Ti (decay time of 5.7 µs) and 518 nm for Mn (decay time of 6.11 ms) have been obtained when pumped in the UV region at 266 nm and 355 nm, respectively. Ni^{2+}-doped crystals have shown a broad absorption band at about 980 nm suitable for InGaAs laser diode pumping and a broad emission band in the near infrared with two decay times at 210 µs and 850 µs respectively.

Dose dependence of mechanoluminescence (ML) properties of $MgAl_2O_4$:Dy Phosphor have been reported by Satapathy et al. They prepared it by using solution combustion technique [44]. Two distinct ML peaks have been observed for all the samples of ML which has been excited impulsively by dropping a load of mass 0.7 kg onto the phosphors from various heights. The MgAl2O4:Dy phosphor has been observed to show linear response to gamma-ray dose and low fading. This property of MgAl2O4:Dy phosphor can be used for dosimetric purpose. Satapathy et al. have investigated the dose dependant ML (mechanoluminescence) and TL (thermoluminescence) behavior of polycrystalline powder samples of MAl2O4:Dy (M= Ba, Mg, Ca) phosphors which were prepared by a combustion route in which urea was used as a fuel [45]. The characteristic emission of Dy doped aluminate samples has been observed in Photoluminescence (PL) emission spectrum. TL and ML measurements have been carried out on Dy^{3+} doped aluminates by gamma irradiation in the dose range 0.2-2.2 kGy. The intensity of ML and TL has been observed to increase with increasing dose of gamma ray. MAl_2O_4 (M= Ba, Mg, Ca) doped with Dy phosphors have been found to show linear response up to about1.1 kGy of radiation dose and low fading (5-6% over the period of 15 days) for ML and TL measurement.

The role of cation defect centres in thermoluminescence mechanism of $MgAl_2O_4$:Tb have been investigated by Alagu et al. by relating various techniques such as Electron Spin Resonance (ESR), Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) [46]. TL studies have shown two peaks at 120°C and 340°C. $MgAl_2O_4$:Tb^{3+} stimulated with 470 nm blue light revealed OSL. ESR study has shown two defect centres with g = 2.011 and g = 2.0052 which are given to V^{-} centre and F^{+} centre, respectively. V-centre has been correlated to 120°C TL peak whereas F^{+} centre has been correlated with both the 120 and 340°C TL peaks through step annealing ESR technique.

The photoluminescence and EPR investigations of Mn doped $MgAl_2O_4$ phosphors have been studied by Singh et al. which were produced through combustion route. Photoluminescence studies have shown green emission at 518 nm due to T-4(1) - (6)A(1) transition and red emission at 650 nm due to the charge-transfer de-excitation associated with the Mn^{2+} ion. The EPR spectrum has shown allowed and forbidden hyperfine structure at q = 2.003. The variation of zero-field splitting parameter (D) with temperature has been evaluated.

The fluorescent properties of chromium-doped $MgAl_2O_4$ Nano powders have been studied by Krizan et al. which were prepared by combustion method using urea as a fuel [48]. Fluorescence properties of these products have found the applications in fluorescent sensor and in the formation of transparent polycrystalline ceramic materials for laser and optical applications.

The effect of substitution of K^{+} ions on the structural and electrical properties of $MgKxAl_2O_4$ spinel oxides (x=0.0, 0.25, 0.5, 0.75, 1.0) with

crystallite size between 6 and 8 nm have been studied by Ahmad et al. and $MgKxAl_2O_4$ was produced by the chemical co-precipitation method [49]. Due to its DC electrical resistivity, it has shown a typical semiconducting behaviour. An extra hole is formed in the system due to substitution of a Mg^{2+} ion by a K^+ ion, which formed small polaron. The conduction mechanism in the $MgKxAl_2O_4$ has been reported to be due to the thermally activated hopping of these small polarons.

Ahmad et al. have studied the effect of substitution of Mg^{2+} ions by Co^{2+} ions on the structural and electrical properties of $MgAl_{2-x}CoxO_4$ (x = 0.0, 0.5, 1.0, 1.5, 2.0) with crystallite size between 7 and 19 nm which has been reported to be synthesized by the chemical co-precipitation method [50]. With increase in the Co^{2+} concentration, the lattice constant, X-ray density and bulk density have been observed to rise, whereas percentage porosity have been found to decrese. As expected for a typical semiconductor the dc electrical resistivity has been observed to decrease as a function of temperature. The doping with Co^{2+} ions is supposed to form small polarons and the conduction in the system been reported to be partly due to hopping of these small polarons between the adjacent sites.

The effect of Yb^{3+} doping on structure in $Yb_xMg_{1-x}Al_2O_4$ spinel (where x = 0.00, 0.05 and 0.01) have been investigated by Ali et al. which were synthesized by combustion method using malonic acid dihydrazide as a solid fuel [51]. Thermal analysis has shown that after annealing at 700°C, the crystalline phase of $MgAl_2O_4$ and doping materials are formed. The sheet and spherical shapes for $Yb_{0.1}Mg_{0.9}Al_2O_4$ and $MgAl_2O_4$ samples annealed at 1000 °C have been shown in TEM micrograph. With increasing the amount of Yb^{3+} in the lattice of $MgAl_2O_4$ and calcinations temperatures, the edges of bands have been reported to get shifted to higher wavelength and band energies shifted to lower values.

CONCLUSION

Alkaline earth aluminates have opened a new challenge in the field of phosphor technology by showing their long light persistence property for the past few decades. The most common fluorescent lamp phosphors used these days are the rare earth doped Barium Magnesium Aluminates, Lanthanum Phosphate and Calcium Halo phosphates. As the materials used in the fluorescent lamps are good photo luminescent materials, either the inherent defects present in the phosphor can be used or suitable modifiers can be added to induce thermoluminescence in these phosphors. Cr_2O_3 addition increases the spinel formation and also the densification. Magnesium-aluminate spinel crystals ($MgAl_2O_4$) are potential material for ap-plication in science and technology as ma-trix for fiber-optic temperature sensors, tunable solid state lasers, substrate for mi-croelectronics. This spinel is also very spe-cific in respect to its crystalline structure. The optical spectra of the doped crystals have been found to show intense absorption in the range of 4.5-6.7 eV which is fit with three absorption bands which may be explained by the formation of .F-type centers if doped with Mn ions which results in variations of electronic properties of F^+-centers and formation of complex defects including Mn-ions. The intensity and energy position of these bands vary depending upon the concentration of doping ions. Thus changing the type and concentration of doping ions the various properties and hence applications of these doped magnesium aluminate spinels can be improved according to reduirement.

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