Sol-gel Synthesis, Structural and Characterization of $Ag_{3(2+x)}Gd_xTi_{4-x}O_{11+\delta}$ Nanocomposites

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Abstract-The $Ag_{3(2+x)}Gd_xTi_{4-x}O_{11+\delta}$ ($0.0 \le x \le 1.0$) (x = 0, 0.25, 0.5, 0.75 and 1.0) nanocomposites were successfully synthesized by sol-gel technique. The surface morphology, structure and the properties of nanocomposites were investigated by SEM, XRD, DTA, IR, UV, EPR and VSM. The XRD result reveals that the composites were formed in Tetragonal lattice type with P42/nnm space group. The average crystallite size of the composites varied from 44 nm to 63 nm. The surface morphology of the samples was evaluated by SEM. The purity of the composites was confirmed through the Energy Dispersive X-ray analysis. Electron paramagnetic resonance lineshapes were recorded at 8 K, 77 K and 300 K which are isotropic in nature. The magnetic susceptibility values of the samples are in ferromagnetic nature at room temperature.

Keywords- Composite Materials; Sol-gel Processes; Electron Paramagnetic Resonance; X-ray Diffraction; Hysteresis Loop

I. INTRODUCTION

In recent years, much attention has been paid on Rare Earth containing Metal (RE) Transition (TM) nanocomposites. This is due to various reasons, in the materials chemist point of view, these materials provide valuable information about basic phenomena like cluster formation and interaction, quantum confinement effects, etc.. However, the application points of view the 4f-3d complexes were used in several fields ^[1] such as optical lasers ^[2], up-conversion luminescence for colour displays ^[3], optical data reading and storage high density Superconductor magnetic materials ^[4] medical, etc.. This is due to extremely high melting points of rare-earth metal ions and transition metal oxides. Recently, chemists pay more attention on Pr^{3+} , Nd^{3+} , Er^{3+} and Gd^{3+} ions doped TM compounds because these materials can be used in the visible spectral region at room temperature. Considering the high coordination number of RE^{3+} ions may render the structural flexibility and increase the stability of the RE³⁺ doped TM composites. The host materials are playing a vital role in developing the rare-earth doped TM composites. The researchers mainly focus on silicates and oxides that are more suitable for practical applications due to their high chemical durability and thermal stabilities. In recent years, ferromagnetic semiconductors have been of great attention scientifically and technologically to both theorists and experimentalists due to potential applications. Doping the RE elements are the better promising alternative to TMs due to its partially filled electronic configuration. Among all the RE ions, Gd³⁺ ion is the only element has both partially filled 4f and 5d orbitals. This can lead a new coupling mechanism via intra ion 4f-5d exchange interaction

followed by inter-ion 5d-5d coupling mediated by charge carriers. The ferromagnetism in Gd^{3+} ions doped ternary alloy Ga-Gd-N films has been observed with a Curie temperature of 400K. There are only a few investigations about the electronic structures and spectroscopic parameters of Gd^{3+} ions in crystals and glasses.

In this report, we describe the sol-gel synthesis and structure-property relations in $Ag_{3(2+x)}Gd_xTi_{4-x}O_{11+\delta}$ (x = 0, 0.25, 0.5, 0.75 and 1.0) nanocomposites using various experimental techniques.

II. EXPERIMENTAL

Sol-gel method has been used to prepare the $Ag_{3(2+x)}Gd_{x}Ti_{4-x}O_{11+\delta}$ (x= 0, 0.25, 0.5, 0.75 and 1.0) nanocomposites. All the reagent grade chemicals were used as received without further purification. Calculated amounts of Gd₂O₃, Ag(NO₃) and TiO₂ were mixed together in 2 M nitric acid medium by stirring for 1 h at pH \approx 4-5, followed by the addition of 30 ml of 1.5 M citric acid solution this was stirred continuously at 60 ° C until it became the transparent gel. Then the gel was dried using an air oven at 200 $^{\circ}$ C for an hour, these processes lead to the formation of light weight porous materials due to the enormous amount of gas evolution, and finally it was sintered at 850 °C for 4 h to get the fine homogeneous dense powder. The powder X-ray diffraction patterns of the samples were identified by using X'Pert (PANalytical) powder X-ray diffract meter. Monochromatic Cu Ka radiation was used as a source with 40 kV/30 mA power. The SEM images were recorded by using Hitchi-S3400 instrument, and EDX was done by a SUPER DRYER II instrument. The concentrations of Ti3+ ions were determined by wet chemistry and the densities were determined by liquid displacement method. The X-band EPR spectral data at 300 and 77 K were recorded with a JEOL JES-TE 100 ESR spectrometer and 8 K were recorded on a Varian EPR spectrometer. The Optical Absorption spectra were recorded by a Varian Cary 5000 UV-VIS-NIR spectrometer in the solid phase. The magnetic moments data were recorded on a LAKESHORE VSM 7404 Vibrating Sample Magnetometer.

III. RESULTS AND DISCUSSION

The powder XRD patterns of the sol gel synthesized $Ag_{3(2+x)}Gd_xTi_{4-x}O_{11+\delta}$ (0.0 $\leq x \leq 1.0$); (A1-A5) samples are shown in Figure 1. In the diffraction patterns, all the major peaks appear in the same diffraction angle, this shows that

the samples (A1-A5) are formed in single phase polycrystalline materials. All the diffraction patterns were indexed perfectly using the least square method to avoid the difference between the experimental and theoretical pattern. Further structural information was carried by Rietveld refinements analysis with the Full Prof software package 2003. The refinement result reveals that all the composites are formed in single phase Tetragonal lattice with P4₂/nnm (Space group no 134) space group. This is good agreement with the standard values. The lattice type and the space group were found to be remaining constant and the Gd^{3+} ion incorporation did not give any structural and the phase changes of the samples within the atomic concentration range $(0.0 \le x \le 1.0)$ studied possibly due to the very low concentration of the Gd³⁺ ion present in the host lattice. The calculated lattice parameters of the composites are given in Table 1.



Fig. 1 Powder x-ray diffraction pattern of $Ag_{3(2+x)}Gd_xTi_{4-x}O_{11+\delta}~(0.0{\le}~x{\le}~1.0)$ nanocomposites

Average crystallite size of the composites was calculated from the full width at half maximum (FWHM) of all the peaks using the Debye-Scherer relation and Williamson-Hall equation. Here, as vary the composition ratio, the average size of the particle is varied from 44 to 63 nm. The crystallite sizes of the samples are increasing with respect to the increasing content of the Gd³⁺ ions. The crystallite sizes of the samples are increasing with respect to the increasing content of the Gd^{3+} ions. The gradual incensement of the crystallite size is due to the small ionic radius of Ti^{3+} (2.0 Å) ions are replaced by higher Gd^{3+} (2.54 Å) ions. The concentrations of Ti^{3+} ions were determined by wet chemistry method. The value of the Ti³⁺ ions gradually decreases as we expect from the composition ratio. This proves that the particular composition of the samples is formed. The densities of the samples were obtained using liquid displacement method (Experimental) and also formed the lattice parameters (calculated). The density of the samples gradually increases from A1 to A5 with increasing content of the Gd³⁺ ionic concentration. This may be due to the higher density of the Gd ion increases. The calculated densities of the samples were coincides with experimental

values. This is another evidence of the powder XRD refinement analysis which is in good agreement with the standard values. The small difference in experimental and calculated densities may be due to porous nature of the sample. In most of the cases, the materials which prepared by sol-gel method is highly porous and this is due to the evolution of gases. The porosity of the samples were calculated using

Porosity (P) =
$$(1-D_E/D_T) \times 100$$
 (1)

where D_E is the experimental density, D_T is the theoretical density. The porosity of the samples first decreases as the x increases from A1 to A3 and then decreases from A4 to A5. The SEM micrographs provide visual proof of the porosity. The crystallite sizes, density and porosity of the samples were reported in Table- 2.

TABLE I LATTICE PARAMETERS AND CHEMICAL ANALYSIS OF $AG_{3(2+x)}GD_x$ TI4- $_xO11+\Delta~(0.0\leq x\leq 1.0;$ A1-A5) Nanocomposites

S.No	a (Å)	b (Å)	c (Å)	Unit cell volume (Å)	No. of Ti ³⁺ ions per g
A 1	7.7535	7.7535	9.1661	551.04	5.321 x 10 ²⁰
A 2	7.2536	7.2536	10.5365	554.38	2.940 x 10 ¹⁹
A 3	6.8565	6.8565	10.1635	477.80	2.766 x 10 ²⁰
A 4	8.0475	8.0475	6.3109	408.71	1.793 x 10 ²⁰
A 5	7.0764	7.0764	8.0492	403.06	1.394 x 10 ²⁰

The DTA cure shows the sharp endothermic peak at 960 °C, This corresponds to the melting point of the composite materials, and the same responses are observed in all the composites. The room temperature FT-IR spectral peaked at 420- 470 cm⁻¹ is due to the Ti- O stretching of the $[TiO_{6/2}]$ octahedron. The band at 440 cm⁻¹ is due to the Gd- O bond and the strong band at 600- 650 cm⁻¹ is ascribed to the Ti-O-Ti stretching mode.

In order to examine the quantitative analysis and distribution of metal ions of randomly selected $Ag_{3(2+x)}Gd_{x}Ti_{4-x}O_{11+\delta}$ nanocomposites at different magnification were performed by SEM-EDX analysis. Figure 2 shows (a) SEM micrographs of A1, A3 and A5 along with (b) Energy dispersive X-ray (EDX) profile (A2) and (c) X-ray mapping of the sample A2. The morphology of the sample A1 shows uneven rod like shape when the Gd ions are incorporated into the samples A2-A5, the samples shows globular in shape. The purity of the samples was confirmed from the EDX profile and quantitative results. The elemental analysis by the EDX results indicating the constituent elements like Ag, Gd, Ti and O are present in the composites. The atomic percentage of the elements were very close to the expected ratio as stated in the synthesis method and no other extra elements were observed this conforms to the formations of pure $Ag_{3(2+x)}Gd_{x}Ti_{4-x}O_{11+\delta}$ nanocomposites. The X-ray mapping of the composites reveals the presence of all the constituent elements, and it is uniformly distributed throughout the surface with resemble of their relative amounts.

TABLE II DENSITY, CRYSTALLITE SIZES AND POROSITY OF $AG_{3(2+x)}GD_xTI_{4-x}O_{11+^5}$ (0.0 $\leqslant x \leqslant$ 1.0; A1-A5) Nanocomposites

Samp	A1	A2	A3	A4	A5	
X-value		0	0.25	050	075	1.0
Density	Experimental	2.7	2.3	2.9	3.2	4.8
(g/clli5)	Calculated	3.0	3.3	5.5	5.5	5.9
Crystallit e sizes	Scherrer	44.0	56.1	59.2	46.4	63.3
(nm)	W-H plot	48±2	54 ± 2	57 ± 2	48 ± 2	52 ± 2
Porosity (%)		11.11	32.29	46.01	41.04	18.09



Fig. 2 (a) The SEM morphology (b) EDX- profile of (c) X-ray mapping of $Ag_{3(2+x)}Gd_xTi_{4-x}O_{11+\delta}$ (0.0 $\leq x \leq 1.0$; A1-A5) nanocomposites.

The EPR technique has been widely employed in this composite characterization due to the existence of the EPR active elements, for example, Ti and Gd are present in this composite. It's a single progress to understand both the electronic and geometrical features of the elements in different chemical environments. The EPR lineshapes of the A1-A5 sample show isotropic lineshapes are centred at g~ 2.01 at the 300 K, 77 K and 13 K. The EPR lineshapes mainly arise from the Gd^{3+} (4f⁷) and Ti³⁺ (d¹) ions. The small extra lines observed on both sides may be due to the superimposed hyperfine features of 158 Gd (I=3/2) or 47 Ti (I=5/2) isotopes. However, the isotropic exchange interaction usually dominates the effects of the spin-orbit coupling, and magnetic dipole interaction of the metal ions. The electron spin resonance of Ti^{3+} (d¹) and Gd^{3+} (4f⁷) ions has been detected only at very low temperature due to rapid spin lattice relaxation^{[5] [6]}.

The optical absorption spectral bands are appeared at 320, 348 and 523 nm. The bands are assigned with the reported data. It reveals the broad band at 320 nm is attributed to the Ti^{3+} ions and the band at 348 nm corresponds to the presence of Ag-TiO₂ nanoparticles. The same results that lead to the samples can be used for photocatalysis^{[7] [8]} The band at 523 nm is correspond to the

f-f transitions of Gd^{3+} ions in the crystal lattice, which are attributed to the ${}^{8}S_{7/2} \rightarrow {}^{6}I_{J}$ transitions of Gd^{3+} ions^[9].

The magnetic properties of the samples were studied by Vibrating Sample magnetometer (VSM) at room temperature. The Magnetization (M) versus Magnetic field (H) shows hysteresis loops in all the cases and the shape of the magnetization curves shows the characteristic of weak ferromagnetism. The Magnetic saturation (Ms) of the samples in the hysteresis loops were not saturated even after the magnetic field of ± 10000 G. The hysteresis loops for the Ag-Gd-Ti nanoparticle show coercivity even at room temperature but the value of Hci is considerably smaller than that would be predicted from the particle size. The coercivity, remanent decreases and the saturation magnetization increases linearly with increasing the content of the Gd³⁺ ions. The hysteresis loops are narrowed without any jerks in the magnetic spins for all the samples. This indicates that magnetic spins are attaining a better homogeneous structure in room temperature. This can be another proof of the single phase formation and purity of the nanocomposites. The magnetic susceptibility (χ) and exchange integral (i) were calculated. The fairly high values of the magnetic susceptibilities in the order of $\sim 10^{-4}$ emu/gG show that the specimens are weak ferromagnetic at 300 K. The calculated Exchange integral of the order of 1013 Hz shows fairly rapid exchange process in the samples. The Weiss constant values do not vary significantly within the composition range studied.

IV. CONCLUSION

The $Ag_{3(2+x)}Gd_{x}Ti_{4-x}O_{11+\delta}(0.0 \le x \le$ 1.0)nanocomposites was successfully prepared by the sol-gel technique and the structural characterization were studied. The main features of their structure analysis were confirmed by power XRD. It reveals that all the samples are formed in Tetragonal lattice with P42/nnm space group. Average crystallize sizes are found to be in the range of 44 nm to 63 nm. The morphology of the samples shows rod like shape to spherical shape. The EDX result shows all the constituent elements present and is distributed homogenously. The EPR lineshapes of the samples at 300, 77 and 13 K are broadened isotropic in nature with $g \sim 2.02$. The magnetic susceptibility ~10⁻⁴ emu/gG shows fairly strong paramagnetic nature of the samples. Exchange integral of the order of 10¹³ fairly rapid exchange process in the samples.

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