Gözde Alkan

Synthesis of photoluminescent rare earth metal oxide based nanocomposites through ultrasonic spray pyrolysis

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Synthesis of photoluminescent rare earth metal oxide based nanocomposites through Ultrasonic Spray Pyrolysis

From the Faculty of Georesources and Materials Engineering of the
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submitted by

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from Ankara (Turkey)

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approved thesis

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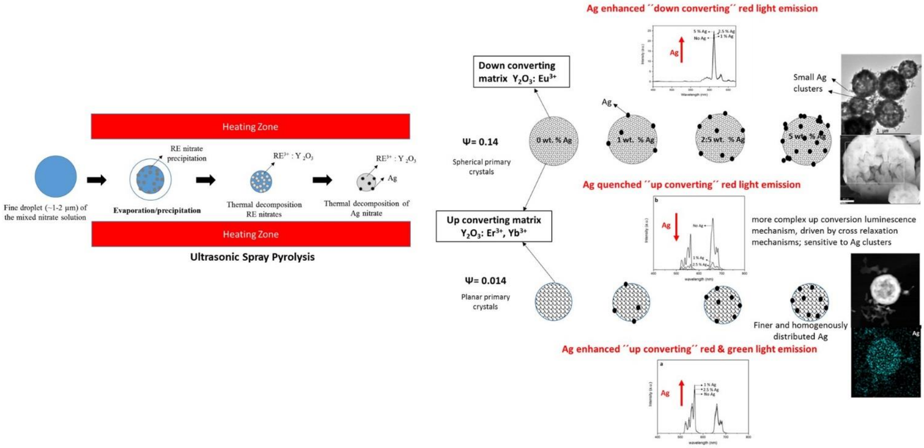
Abstract

Noble metal nanoparticles` incorporation into an oxide structure through methods such as sol-gel, chemical synthesis and laser ablation, has been proven a promising strategy to enhance photoluminescence efficiency. Owing to their surface plasmons, noble metal nanoparticles in close proximity to emitters, improve the light interaction of oxide, and result in higher absorption, also enhancing the energy transfer mechanisms. Among other methods, Ultrasonic Spray Pyrolysis holds the advantages of ensuring the formation of fine particles with uniform hierarchic structures, where the mix of all constituents are atomised and experience reaction together in the ultrafine droplets, acting as a micro reactors. When the importance of uniform distribution of fine emitters and plasmonic surfaces are considered, USP may be a promising method to synthesise those hierarchical spherical particles comprised of primary fine crystals for the enhanced luminescence. However, in the literature, there is not a clear finding about plasmon enhanced luminescence of Y_2O_3 based oxides by synthesised by one step USP. Therefore, the hypothesis of this thesis was the enhancement of down converting Y_2O_3: Eu^{3+} and up converting Y_2O_3: Er^{3+}: Yb^{3+} luminescence emissions by Ag nanoparticle incorporation. Moreover, it was also aimed to fill the lack of knowledge in the literature. Based on the hypothesis, and to confirm it, various amounts of silver (1- 10 wt. %) were incorporated into the Y_2O_3 based oxide, which is exposed to various heat treatment conditions (0-48 h) to ensure uniform distribution and crystal quality of the nanocomposite for both up and down conversion systems. In addition to those, for the up conversion system, a different starting precursor concentration was examined, while keeping the partial ratio of Ag constant to reveal the importance of the composition. The effect of Ag incorporation was evaluated in the as prepared and heat treated state on the material and luminescence properties and mechanisms. The microstructure and semi-quantitative analysis of the chemical composition of synthesised nanoparticles were analysed by Scanning Electron Microscopy (SEM) in combination with Energy Dispersive X-ray Analysis. Quantitative and qualitative phase structure analyses were performed by the X-Ray Diffraction method. Moreover, crystallographic properties such as; ion occupancy, lattice parameters, and microstrain were evaluated by line profile analysis through Topas software. Selected samples were examined by the Transmission Electron Microscopy, Selected Area Diffraction for the structural and Focus Ion Beam techniques. Nanoindentation load-sensitive experiments were performed to evaluate the mechanical properties. In light of the structural and morphological investigations, promising samples were analysed in terms of their up and down conversion luminescence efficiencies by luminescence spectrometer using a Xenon lamp and laser diode; respectively. Emission and excitation peaks were analysed in terms of peak positions and integrated areas to reveal the changes in the luminescence efficiencies. It was revealed that noble metal incorporation up to an optimum Ag loading enhanced the red light emission of the down converting phosphor in the heat treated condition, as proposed in the hypothesis, due to enhanced interaction with the light. Defected microstructures revealed by mechanical tests and also HRTEM analyses are responsible from the poor luminescence efficiencies of the as prepared nanocomposites. However, further Ag incorporation, due to the coalescence of Ag islands, quenched the photoluminescence efficiency. It was found out that a more complex up conversion luminescence mechanism, which was driven by cross relaxation mechanisms, resulted in most of the Ag loadings ending up in deterioration of the up conversion efficiency by Ag incorporation, in contrast to our hypothesis. Only 1 wt. % Ag incorporation with lower precursor concentration enhanced the slightly green light emission of the heat treated nanocomposites. Moreover, it was found out that green to red light emission control can be achieved by adjusting partial Ag concentration and total precursor concentrations, where precursor concentration with 1 wt. % Ag incorporation low favors the green light emission.

Graphical Abstract



Kurzfassung

Momentan steht Yttrium Oxid (Y_2O_3) im Vergleich zu anderen Phosphormaterialien im Mittelpunkt der Aufmerksamkeit aufgrund seiner hervorragenden Eigenschaften wie hohe Korrosionsbeständigkeit, ausgezeichnete Witterungsstabilität, niedrige Degradation unter Spannung, hohe Quanteneffizienz, kaum beinhaltete gefährlichen Inhaltsstoffe (im Gegensatz zu Sulfidphosphoren), große Bandlücke (5,8 eV) sowie geringer Phononen Energie (430-550 cm^{-1}). Die Dotierung der Y_2O_3-Wirtsmatrix durch Europium (Eu^{3+}) begünstigt die "down-KonvertierungLumineszenz", während Erbium (Er^{3+}) Ytterbium (Yb^{3+}) Co-Doping die ´´up-Konvertierung Lumineszenz´´ aufgrund ihrer leiterartigen Energieniveaus fördert. Trotz der enormen Anstrengungen zur Entwicklung hochwirksamer Phosphormaterialien mit Hochleistungs-Synthese sind weitere Verbesserungen erforderlich, um die steigende Nachfrage zu decken, aufgrund breiter Anwendungsbereiche wie Mobiltelefone, LEDs, Verkehrsanzeigen und Sicherheitstintenanwendungen. Der Einbau von Edelmetall-Nanopartikeln in die Oxidstruktur in unmittelbarer Nähe von Emittern ist eine der vielversprechendsten Methoden zur Steigerung der Photolumineszenz-Effizienz. Daher beschäftigt sich diese Studie mit der Synthese der Abwärtsumwandlung von Ag@ Y_2O_3: Eu^{3+} und aufwärts konvertierende Ag@ Y_2O_3: Er^{3+}: Yb^{3+} Nanokomposites von USP zur Verbesserung der Lumineszenz Effizienz von Y_2O_3-basierten Phosphoren. Die Ultraschallsprühpyrolyse ermöglicht die Bildung feiner Partikel mit einheitlichen hierarchischen Strukturen, da alle Bestandteile gleichmäßig zerstäubt werden und eine gemeinsame Reaktion in ultrafeinen Tröpfchen als Mikroreaktor stattfindet. Der Einfluss der Ag-Einlagerung im präparierten und wärmebehandelten Zustand auf die Material- und Lumineszenz Eigenschaften und -mechanismen wurde detailliert untersucht. Die Mikrostruktur- und semi-quantitative Analyse der chemischen Zusammensetzung synthetisierter Nanopartikel wurde mittels Rasterelektronenmikroskopie (REM) in Kombination mit der energie dispersiven Röntgenanalyse analysiert. Quantitative und qualitative Phasenstrukturanalysen wurden mit der Röntgenbeugungsmethode durchgeführt. Ausgewählte Proben wurden mittels Transmissionselektronenmikroskopie, Selected Area Diffraktion und Focus Ion Beam Techniken untersucht. Im Laufe der strukturellen und morphologischen Untersuchungen wurden vielversprechende Proben hinsichtlich ihrer ´´up´´ und ´´down´´ Konvertierung und Lumineszenz-Effizienz analysiert. Das vielversprechendste Materialsystem mit den gewünschten Synthesebedingungen wurde zur praktischen Anwendung vorgeschlagen.