



Gözde Alkan

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

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through Ultrasonic Spray Pyrolysis**

From the Faculty of Georesources and Materials Engineering of the
RWTH Aachen University

submitted by

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from Ankara (Turkey)

in respect of the academic degree of

Doctor of Engineering

approved thesis

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Date of the oral examination: 30. January 2020

Schriftenreihe des IME

Band 64

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Shaker Verlag
Düren 2020

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <http://dnb.d-nb.de>.

Zugl.: D 82 (Diss. RWTH Aachen University, 2020)

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Printed in Germany.

ISBN 978-3-8440-7429-1

ISSN 1610-0727

Shaker Verlag GmbH • Am Langen Graben 15a • 52353 Düren

Phone: 0049/2421/99011-0 • Telefax: 0049/2421/99011-9

Internet: www.shaker.de • e-mail: info@shaker.de

Acknowledgment

I would like to express my sincere appreciation to my advisor Prof. Bernd Friedrich for trusting me and giving me a chance to conduct my PhD studies in his institute, the continuous support of my Ph.D study and related research, for his patience, motivation, and enormous knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor.

This work has been realized thanks to the international collaboration with Serbia; Slovenia, Japan and China under the co-supervision of Prof. Olivera Milosevic and Prof. Rebeka Rudolf. I would like to present my deep thanks to them for their encouragement, continuous, fruitful and constructive comments on my study, widen my research from various perspectives. Beyond, I would like to thank to Dr. Lidija Mancic, Dr. Peter Majeric, Prof. Satoshi Ohara (Osaka University, Japan), , Sayaka Tamura, Koji Tamuta (Tokai University, Japan), Dr. Feifei Sun Dr. Zenquan Tan (Dalian University of Technology, China) for their support in characterization, which enhanced the value of the study.

I also would like to thank my colleagues Claudia Vonderstein, Christoph Vonderstein, Stephan Ludwigs, Marion Thoraval, Fabian Diaz Semiramis Friedrich, Danilo Curtolo, Siran Hassanpour, Jason Zhang, Lillian Peters, Nikolas Borowski for their technical contribution as well as all the precious and good times we spent together, which helped me feel at home in a foreign country. My special thanks would go to, for being my family here. I would like to thank to my students, Carlotta Olsen, Seckin Cakmakoglu, Vijenthana Sojenthana for all their help. I would also like to thank to chemical department, workshop, all technicians and administrative staff at IME but exclusively to Debora Schnabel, Amir Khamoushko and Friedrich Rosen for their support and the good times we spend together. I would also thank to Berfu Göksel and Ilayda Tasci for all the time standing beside me and supporting me mentally.

Last but not least, I would like to thank my mother and father for supporting me every second of my life, even from Turkey never letting me feel alone. Also to my sister, even at the darkest times for making me feel good and never letting me feel alone and finally to my little sunshine Duru.

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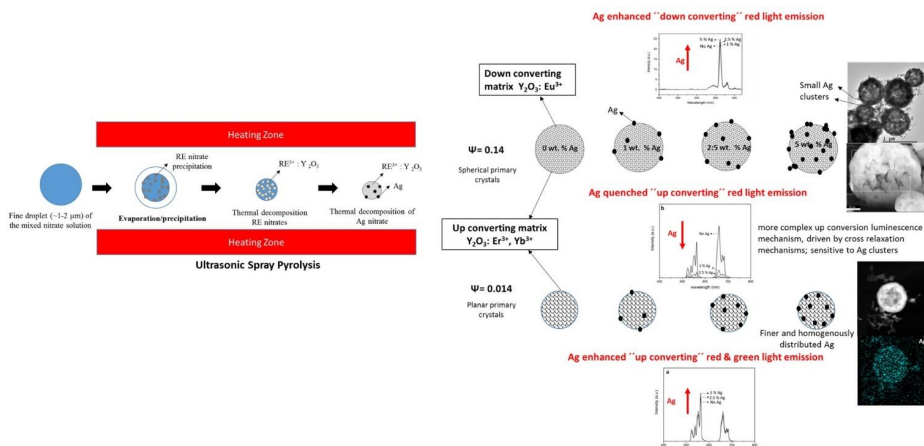
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Abstract

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 $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ and up converting $\text{Y}_2\text{O}_3\text{:Er}^{3+}\text{:Yb}^{3+}$ 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 beinhalten gefährlichen Inhaltsstoffe (im Gegensatz zu Sulfidphosphoren), große Bandlücke (5,8 eV) sowie geringer Phononen Energie ($430\text{--}550\text{ cm}^{-1}$). Die Dotierung der Y_2O_3 -Wirtsmatrix durch Europium (Eu^{3+}) begünstigt die "down-Konvertierung Lumineszenz", 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 Sicherheitstintenwendungen. Der Einbau von Edelmetall-Nanopartikeln in die Oxidstruktur in unmittelbarer Nähe von Emitttern ist eine der vielversprechendsten Methoden zur Steigerung der Photolumineszenz-Effizienz. Daher beschäftigt sich diese Studie mit der Synthese der Abwärtsumwandlung von $\text{Ag@Y}_2\text{O}_3\text{:Eu}^{3+}$ und aufwärts konvertierende $\text{Ag@Y}_2\text{O}_3\text{:Er}^{3+}\text{:Yb}^{3+}$ 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 Diffraction 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.