SYNTHESIS AND DEVELOPMENT OF PHOSPHORESCENT STRONTIUM ALUMINATES

PH.D. THESIS

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1. Prelude and objective

Light and color phenomena inspire humankind since the historical ages. Amongst the several known luminescence types, phosphorescence – firstly recognized in alkali sulphides contaminated with d-metals – has been studied since the 17th century. The exploration was followed by the identification of the necessity for specific contaminant elements in several inorganic phosphors. By now, the synthesis, characterization, development, and application of both organic and inorganic luminescent materials became a new, individual branch of the industry. Nowadays, we can synthesize artificial crystals, superior to natural ones in all of their luminescent parameters. In these artificial materials, luminescent properties and qualities are plannable and tunable by modification of their dopant quality and concentration, as well as by tuning the lattice parameters of the host. Fine-tuning of luminescent properties of inorganic crystallic phosphors to meet a broad scale of industrial demands is a major current trend in the development of these materials. On the other hand, a secondary trend aims the deeper understanding of energy transfer mechanisms during phosphorescence, as these processes have been only partially clarified.

The application of luminescent materials is already widespread. However, the number of applications may be increased further by new methods, which can take advantage of the most important abilities of phosphors, namely: the capability to be excited by both artificial light sources and natural sunlight, and the emission of visible light up to 30 hours with sufficient intensity to be seen by the naked human eye in the dark. Amongst the possible applications, using phosphorescence as an alternative energy storage method can also be considered. So-called long persistent phosphors are already present in many ordinary indoor and outdoor applications, such as in parts of buildings without access to natural light, traffic marks on roads without public lighting, or in banknotes. Developments in advanced applications are in progress for auxiliary layers in solar cells and assistant light sources in photocatalitic reactions. Special types of long persistent phosphors, emitting in the IR range, can be used as biomarkers. Furthermore, phosphors in general can be used as absorbing and detecting agents for radioactive radiations or acoustic phenomena. The advanced applications project that there is a demand for development on special characteristics (e.g. color change, emission wavelength tuning) of inorganic phophors, as well as for optimization of persistence and processibility parameters.

During the preparation of my thesis, I managed to expand knowledge in the field on the following topics:

1. Investigation on the effect of homogenization methods, flux and activator contents on the synthesis of $SrAl_2O_4$:Eu,Dy and $Sr_4Al_{14}O_{25}$:Eu,Dy strontium aluminate phosphors. The products were characterized by their crystallinity, luminescence, and phosporescence decay intensities, performed via X-Ray powder diffrectometry (XRD) photoluminescence spectroscopy (PL) and

phosphorescence afterglow intensity measurement (AG) techniques, in order to find the optimal synthesis parameters.

2. Post-process manipulation of particle size properties of both strontium aluminates and investigation on the effect of their other properties. Determination of particle size reduction trends by solid-state milling method. Changes in particle sizes were followed by scanning electron microscopy (SEM), crystallinity by XRD, luminescent properties by PL and AG. Invested energies by milling were calculated and the established properties of the two phosphors were compared.

3. Investigation on the regeneration of structurally damaged strontium aluminate phosphors. Discovery of the factors affecting the regeneration process in both strontium aluminates, including dependence on the extent of damage in the initial material and various regeneration methods. Observation of the regeneration of the Eu^{2+} luminescence center by XPS technique. Characterization and comparison of crystallinity and luminescence properties of $SrAl_2O_4$:Eu,Dy and $Sr_4Al_{14}O_{25}$:Eu,Dy phosphors by XRD, PL, AG and thermoluminescence (TL) techniques, regenerated by the same methods and initiated from the same level of damage. Explanation of results according to phosphor type and regeneration method.

4. Investigation on the optical, luminescent and structural properties of the mixed co-activated $SrAl_2O_4$:Eu^{2+}, Dy^{3+} , Ho^{3+} and $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} , Ho^{3+} with explanation of the effects and their differences in the two types of phosphors.

5. Expansion of knowledge about the excitation and storage of charge carriers in $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} phosphor. Calculation of energy levels and quantity of trapped charge carriers, excited by sources with different characteristics and intensities.

6. Structural characterization of the newly developed $Sr_4Al_{14}O_{25}$:Eu^{2+}, Dy^{3+} assisted ZnO:Co+AgNP photocatalyst composite by (energy dispersive X-Ray spectroscopy) SEM-EDS, TEM, UV-Vis, (dynamic light scattering) DLS and XRD methods. Investigation on the effectiveness of the photocatalyst in a common dye decomposition model reaction. Presentation of energy saving and safe arrangements of photocatalytic reactions and their effectiveness.

2. Experimental and investigation methods

Strontium aluminate samples were prepared in 6.25 mmol quantities by solid-state and combustion homogenization methods. The synthesis was performed in two steps every time. In case of solid-state homogenization, carbonates and oxides of metals were mixed for 1 hour in a high energy planetary ball mill. In case of the combustion method, raw strontium aluminates were prepared by combustion from nitrates of the metals and urea fuel dissolved in water. In both cases, the homogenous precursors were heat treated at 1200 °C in slightly reducing atmosphere. The prepared samples were grinded in a mortar. Activator and co-activator rare earth elements are substituting elements of the host crystal, therefore, the contents are given in at.% relative to the element substituted.

In the post-process physical stress endurance investigations, strontium aluminates were milled in a planetary ball mill using Si_3N_4 grinding vessel and balls. Energy investment of the milling process was adjusted by time and rotation speed control, between 200-500 rpm and 0-120 minutes ranges.

In order to explore the assistance of strontium aluminate in photocatalytic reactions, the composite catalyst was prepared in multiple steps. The ZnO and ZnO:Co (Zn:Co = 93:7) cores were prepared by combustion synthesis from urea fuel and nitrates of the metals dissolved in water. Silver nanoparticles (Ag NPs) were photodeposited onto the ZnO and ZnO:Co core catalysts. The deposition was performed from a suspension, where 4 grams of ZnO and ZnO:Co cores were suspended in 500 ml water, and after that $AgNO_3$ was dissolved in Zn:Ag 1:0.2 ratio. Photodeposition was driven by 3 hours of UV irradiation to the suspension. PDMS embedding of strontium aluminate was performed by mixing the polymer precursor and the phosphor in PDMS to phosphor 1 to 0.02-0.12 weight ratios, then crosslinking the material by a catalyzing agent. The photocatalytic performance of the as-prepared composite catalyst was verified by a dye decomposition model reaction of 10 mg/l methyl orange dye solution, with and without phosphor assistance. The photocatalytic dye decomposition reactions were performed in fixed bed reactions, without mixing, activated by LED irradiation.

The charging and afterglow processes of $Sr_4Al_{14}O_{25}$:Eu,Dy were performed on 300 mg samples, when followed by AG only, and 20 mg samples, when charged by α, β and UV and followed by TL and AG. With the constant and known irradiation powers of sources, irradiation times were adjusted to different phosphorescence performances.

The characterisation of stontium-aluminate and catalyst particles, such as morphology, size and macro strucure was performed via electron microscopy methods (TEM, SEM), while elemental analysis and distributions were defined via energy dispersive X-Ray spectroscopy (SEM-EDS) method. Structural parameters of phosphors and catalysts were obtained via X-ray diffractometry (XRD). The oxidation state of the luminescence center was investigated via X-ray photoelectron spectroscopy (XPS) method. Color and luminescence performances of phosphors were determined via UV-Vis diffuse reflectance spectroscopy. Energy levels of trapping positions in phosphors, created by different dopant contents were determined by thermoluminescence (TL) method and calculations using Chen's method. The phosphorescence decay of strontium aluminates were measured via photonmultiplier tubes with a complex auxiliary system for afterglow (AG) measurements.

3. New scientific results

1. Exploration of mechanical stress endurance, post-process particle size reduction trend and regeneration of damaged strontium aluminates

1.1 We showed that the optimal flux content is Al:B 9:1 and the optimal dopant content is Sr:Eu:Dy 0.88:0.04:0.08 for the synthesis of both $SrAl_2O_4$: Eu^{2+}/Ln^{3+} és $Sr_4Al_{14}O_{25}$: Eu^{2+}/Ln^{3+} phosphors. Besides, the optimal homogenization for the two step synthesis can be achieved by milling the precursors for 1 hour on 450 rpm, and the high temperaure heat treatment needs no more than 4 hours of reaction (at 1200 °C, H_2/N_2 10 v/v% atm.) [1].

1.2 We demonstrated that the energy invested during a post-process grinding has a critical energy level (~10 J/g), over which both strontium aluminates degrade in both particle size and crystallinity. In addition, lower than 0,5 μm average diameter size cannot be achieved by grinding. We have also proven that size and luminescence degradation trends were different for the two phosphors under the same milling conditions, via their difference in aggregation status. The XRD, PL és AG és TL measurements proved that photoluminescent and phosphorescence powers are both dependent mainly on the crystallinity factor in both phosphors [2].

1.3 We achieved partial regeneration of highly damaged strontium aluminate phosphors by providing a reaction environment equivalent to their original heat treatment (4 h, 1200 °C, H_2/N_2 10 v/v% atm.). The result of the regeneration depended mainly on the level of damage in the initial phosphor samples. As a result of our investigation via XRD, XPS and TL methods, we could confirm the oxidation of the luminescence center under physical stress and reversed ($Eu^{3+} \rightarrow Eu^{2+}$) state after regeneration process. The reason of the partial regeneration was identified as the partial re-crystallization of the phosphors with a large number of killer traps remaining in their structures [2].

2. Investigations on the optical and structural properties of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} , Ho^{3+} and $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+} , Ho^{3+} mixedly co-activated phosphors

2.1 It has been shown that when the Ho^{3+} was added as co-activator element or replaced the Dy^{3+}, the photoluminescence intensity of phosphors increased on their emission peaks in both strontium aluminates. Related to the Dy^{3+} co-activated originals, the emisson intensity increased 100% and 60% for $SrAl_2O_4:Eu^{2+}$, Ho^{3+} and +100% $Sr_4Al_{14}O_{25}:Eu^{2+}$, Ho^{3+} respectively. The $Dy^{3+}\rightarrow Ho^{3+}$ replacement caused the shift of the phosphorescence intensity already, whereas the intensity increased in the first 10 s of decay, but decreased in the later stage [1,3].

2.2 It has been determined that in case of $SrAl_2O_4:Eu^{2+}$, RE^{3+}, when RE^{3+} is one element only, various Ln-alumino-garnets emerged as secondary phases during the original synthesis of the phosphors. These garnets occurred less when the phosphor was co-activated with two RE elements. $SrAl_2O_4:Eu^{2+}$, Dy^{3+} , Ho^{3+} exhibited the best performance (+45% PL intensity and -12% phosphorence lifetime) when the Eu^{2+}:Dy^{3+}:Ho^{3+} content setted to 1:1:1, for the above-mentioned reason. The $Sr_4Al_{14}O_{25}:Eu^{2+}$, RE^{3+} phosphor acted differently, as its garnet content was negligible. Therefore, mixed co-activation caused a gradual shift of the photoluminescence intensity and phosphorescence lifetime, between single co-activated variants, without a highlighted optimum [1,3].

2.3 It has been investigated that in case of $Sr_4Al_{14}O_{25}:Eu^{2+}$, RE^{3+} and $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+}, RE^{3+} (RE = Gd, Tb) single and mixed co-activations, increased photoluminescence intensity (to similar level as Ho^{3+}) can be achieved without phoshorescence lifetime degradation. Based upon TL studies, the occurred energy levels by Dy, Gd, Tb, Ho, Ce, Nd co-activations have been calculated. The elements: Gd, Tb, Ho, and Ce showed similar dominant energy levels related to Dy, however their stability in charge carrier storage was somewhat different. In contrast, Nd co-activation introduced deep killer traps in the host strucure.

3. Investigation on the possible safe and energy-efficient applications of $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+} supported ZnO:Co+AgNP in photocatalityc systems

3.1 Phosphorescence was successfully used as an alternative energy storage method. For this application, a ZnO:Co+AgNPs photocatalyst was made, where ZnO:Co was sensitized to the emission wavelength of the phosphor (450-550 nm) and photopedosited AgNPs increased the catalytic activity. Two main arrangement types of phosphors and catalysts have been presented in order to find the best application method. We showed that a PDMS-embedded phosphor (0.12:1 phosphor:PDMS weight ratio) as background support is safer, but phosphor/catalyst (1:1 weight ratio) mixtures cause faster elimination of the dye molecules [4].

3.2 The additional light of the phosphor was effective under energy saving, flickering excitation of the photocatalyst in both arrangements. In best cases, the dye decomposition slowed by 2% only while 50% energy saving was achieved. In case of the phosphor catalyst mixture used in larger quantities, adsorption and self-screening effects were also discovered besides the normal photocatalytic dye decomposition process [4].

4. Examination on the trapping, storage and de-trapping processes of charge carriers in $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+}

4.1 We investigated the differences in phosphorescence lifetime, as well as trapping, storage, and de-trapping tendencies of the charge carriers in $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+} after being excited by alpha, beta, and UV light sources. It has been determined that the effectiveness of the charging process is much more dependent on irradiation flux and charge than on the energy of the irradiating photon or particle. Saturation tendencies were shown for all excitation sources [5].

4.2 It has been determined via thermoluminescence measures that excitation by ionizing and UV irradiation sources results in different trapping/de-trapping mechanisms in the $Sr_4Al_{14}O_{25}:Eu^{2+}$, Dy^{3+} phosphors. The difference originated from the possibility of direct trapping, excluding the luminescence center [5].

4. Publications related to this thesis

[1] Luminescence properties of Ho^{3+} co-doped $SrAl_2O_4:Eu^{2+}$, Dy^{3+} long-persistent phosphors synthesized with a solid-state method

Z. Győri, V. Havasi, D. Madarász, D. Tátrai, T. Brigancz, G. Szabó, Z. Kónya, Á. Kukovecz

Journal of Molecular Structure 1044 (2013) 87.

$IF_{(2013)}$:1,60; $citation_{(2021)}$: 16

[2] Photocatalytic performance of $Sr_4Al_{14}O_{25}$:Eu, Dy phosphor assisted ZnO:Co+Ag nanocomposite under continuous and pulsed illumination

V. Havasi, B. Vödrédi, Á. Kukovecz

Catalysis Today 284, (2017) 107-113.

$IF_{(2017)}$:4,03; $citation_{(2021)}$: 13

[3] On the effects of milling and thermal regeneration on the luminescence properties of Eu^{2+} and Dy^{3+} doped strontium aluminate phosphors

V. Havasi, D. Tátrai, G. Szabó, E. Varga, A. Erdőhelyi, Gy. Sipos, Z. Kónya, Á. Kukovecz

Journal of Luminescence 219 (2020) 116917.

$IF_{(2019)}$:3,28; $citation_{(2021)}$: 15

[4] Luminescence and color properties of Ho^{3+} co-activated $Sr_4Al_{14}O_{25}$: Eu^{2+}, Dy^{3+} phosphors

V. Havasi, G. Sipos, Z. Kónya, Á. Kukovecz

Journal of Luminescence 220, (2020) 116980.

$IF_{(2019)}$:3,28; $citation_{(2021)}$: 9

[5] Systematic comparison of saturation effects and afterglow properties of $Sr_4Al_{14}O_{25}$:Eu, Dy phosphor excited by alpha and beta ionizing sources and UV light

V. Havasi, D. Tátrai, G. Szabó, Gy. Sipos, Z. Kónya, Á. Kukovecz

Journal of Molecular Structure 1140, (2017) 89-98.

$IF_{(2017)}$:1,78; $citation_{(2021)}$: 3

5. Presentations, posters and attendance at conferences

- 31th European Congress on Molecular Spectroscopy (EUCMOS)

Kolozsvár, 2012. aug. 26 - 31.

The influence of synthesis methods, different dopant ions and ratios on the luminescence of $SrAl_2O_4$ nanoparticles

Győri Zoltán, Havasi Viktor, Pusztai Péter, Madarász Dániel, Kukovecz Ákos, Kónya Zoltán

- XXXI. OTDK Kémia és Vegyipari Szekció, Eger, 2013. április 4-6.

Holmiummal ko-aktivált stroncium-aluminátok szintézise és fotolumineszcens tulajdonságainak vizsgálata

- A Magyar Mikroszkópos Társaság éves konferenciája, Siófok, 2013. máj. 23-25.

Havasi Viktor, Győri Zoltán, Kukovecz Ákos, Kónya Zoltán

Synthesis and characterization of Ho^{3+} co-doped $SrAl_2O_4:Eu^{2+}$,Dy^{3+} phosphors in order to using them as downconverter composites with quantum dots

- XXXVI. Kémiai előadói Napok, Szeged, 2013. okt. 28-30.

Havasi Viktor, Győri Zoltán, Kukovecz Ákos, Kónya Zoltán

Hosszantartóan foszforeszcens stronciuam-aluminátok előállítása és jellemzése

- The Conference for Young Scientists in Ceramics, 10th Students Meeting, 2013. nov. 6-9.

Havasi Viktor, Győri Zoltán, Kukovecz Ákos, Kónya Zoltán

Synthesis and characterization of Strontium aluminate phosphors and CdSe Quantum Dot based composites

- XX. Nemzetközi Vegyészkonferencia, Kolozsvár, 2014. november 6-9

Bogya Erzsébet Sára, Havasi Viktor, Kukovecz Ákos

Ülő csepp-párolgás tanulmányozása makropórusos szén nanocső filmekről

- 12th Multinational Congress on Microscopy, Eger, 2015. aug. 23-28.

Synthesis and characterization of oversized porous ZnO flakes deposited directly on conductive metallic substrates (poszter)

Havasi Viktor, Kónya Zoltán, Kukovecz Ákos

- 33th European Congress on molecular Spectroscopy (EUCMOS)

Szeged, 2016. júli. 30 - aug. 4.

Charging-up effects on long persistent luminescence properties of visible light and ionizing irradiated Sr4Al14O25:Eu, Dy phosphors

Havasi Viktor, Tátrai Dávid, Szabó Gábor, Sipos György, Kónya Zoltán, Kukovecz Ákos

- 7th International Workshop on Photoluminescence in rare earths: photonic materials and devices (PRE'17) Rome, 2017 nov. 30- dec. 2.

Luminescence and color tuning of $Sr_4Al_{14}O_{25}$: Eu^{2+}, Dy^{3+}, Ho^{3+} phosphors by mixed lanthanide co-activation (előadás)

Havasi Viktor, Sipos György, Kónya Zoltán, Kukovecz Ákos

6. Other publications

1. Synthesis, characterization and photocatalytic activity of crystallineMn (II) Cr (III)-layered double hydroxide

Z. Timár, G. Varga, Sz. Muráth, Z. Kónya, Á. Kukovecz, V. Havasi, A. Oszkó, I. Pálinkó, P. Sipos

Catalysis Today 284, (2017) 195-201.

$IF_{(2017)}$: 4,03; $citation_{(2021)}$: 21

2. Exploring Pd/Al_2O_3 Catalysed Redox Isomerisation of Allyl Alcohol as a Platform to Create Structural Diversity

A. Dékány, E. Lázár, B. Szabó, V. Havasi, Gy. Halasi, A. Sápi, Á. Kukovecz, Z. Kónya, K. Szőri, G. London

Catalysis Letters 147, (2017) Issue 7, 1834–1843.

$IF_{(2017)}$: 2,79; $citation_{(2021)}$: 3

3. Pulse electrodeposition and characterization of non-continuous, multi-element-doped hydroxyapatite bioceramic coatings

M. Furko, Z. May, V. Havasi, Z. Kónya, A. Grünewald, R. Detsch, A. R. Boccaccini, Cs. Balázsi

J. Solid State Electrochem 22, (2018) Issue 2, 555–566.

$IF_{(2017)}$: 2,31; $citation_{(2021)}$: 9

4. Development and characterizationof multi-element doped hydroxyapatitebioceramic coatings on metallic implantsfor orthopedic applications

M. Furko, V. Havasi, Z. Kónya, A. Grünewald, R. Detsch, A.R. Boccaccini, Cs. Balázsi

Boletín de la Sociedad Española de Cerámica y Vidrio 57, (2018) Issue 2, 55-65.

$IF_{(2017)}$: 1,05; $citation_{(2021)}$: 33

5. The aggregation behaviour of 2H-imidazole-2-thione derivatives in solution, the solid state and over polycrystalline gold surface

T.N. Hung, G. Varga, Z. Kónya, Á. Kukovecz, G. Kozma, V. Havasi, P. Sipos, G. Mlostoń, I. Pálinkó

Journal of Molecular Structure 1180, (2019) 26-30.

$IF_{(2018)}$: 2,01; $citation_{(2021)}$: 0

6. Cross-Calibration of an α-Source Used for Luminescence Dating by Applying Different Samples and Procedures

G. Sipos, C. Schmidt, T. Bartyik, D. Filyó, G. Magyar, V. Havasi, Á. Kukovecz

Geochronometria 48 (1), 61-72

$IF_{(2021)}$: 1,51; $citation_{(2021)}$: 0

Peer-reviewed papers total: **11**	out of these, related to the topic of this thesis: **5**
Cumulative impact factor: **27.67**	out of these, related to the topic of this thesis:**13.97**
Summary of independent citations: **106** Not independent citations: **9**	out of these, related to the topic of this thesis: **45**