NDnano
Notre Dame Nanoscience and Technology

NDnano Summer Undergraduate Research
2023 Project Summary

1. Student name & home university:

Hongkai Lou, University of California, Los Angeles (UCLA)

2. ND faculty name & department:

Professor László Forró, Dr. Dávid Beke, Physics and Astronomy

3. Summer project title:

Electron paramagnetic study of spinel oxides.

4. Briefly describe new skills you acquired during your summer research:

Before being granted the opportunity to work in the Stavropoulos Center for Complex Quantum Matter, I first reviewed and acquired the necessary safety training and skills when working in a physics and chemistry lab, especially on topics related to lasers, acids, fire, and potentially dangerous materials, such as Hydrochloric acid. Specifically, I was trained on three new equipment and skills for synthesizing and analyzing the crystal structure of the materials. The first machine is the Hydrothermal synthesis reactor. The material is prepared in the hydrothermal reactor with high pressures and relatively low temperatures (200 °C). The second machine is the Raman spectrometer, which can conduct Raman microscopy and Photoluminescence spectroscopy. The third skill is the electron paramagnetic resonance technique which can identify and analyze paramagnetic centers in the material.

5. Briefly share a practical application/end use of your research:

Currently, there are a lot of different photon-induced therapies with no or limited side effects, making them very promising for the next generation of disease treatment. However, the therapies need visible light. Thus, they only work on the skin since the light does not penetrate into the body. We aim to take these photon-induced therapies to deep tissue therapy, such as cancer treatment. We believe X-ray-induced optical luminescence can solve this problem. Our goal is to find and synthesize materials, especially doped spinel oxides, that can be excited with X-rays and thus generate visible photons inside the body.

6. 50- to 75-word abstract of your project:

Doped spinel oxides can emit visible or infrared light under the excitation of X-ray photons, and the emission can last up to several hours and is called Long Lasting Photoluminescence (LLP). To accomplish a longer period of LLP, our project focuses on synthesizing undoped and doped spinel oxides hydrothermally and analyzes their crystal structure, possible defect, and surface termination using Raman microscopy, Photoluminescence spectroscopy, EPR, and X-ray diffraction analysis.

7. References for papers, posters, or presentations of your research:

References

[1] Dávid Beke et al. “Enhancement of X-ray-Excited Red Luminescence of Chromium-Doped Zinc Gallate via Ultrasmall Silicon Carbide Nanocrystals”. In: *Chemistry of Materials* 33.7 (Apr. 2021). Publisher: American Chemical Society, pp. 2457–2465. ISSN: 0897-4756. DOI: 10.1021/acs.chemmater.0c04671. URL: https://doi.org/10.1021/acs.chemmater.0c04671 (visited on 08/10/2023).

[2] Debasmita Dwibedi et al. “Role of annealing temperature on cation ordering in hydrothermally prepared zinc aluminate (ZnAl2O4) spinel”. en. In: *Materials Research Bulletin* 98 (Feb. 2018), pp. 219–224. ISSN: 0025-5408. DOI: 10.1016/j.materresbull.2017.10.010. URL: https://www.sciencedirect.com/science/article/pii/S0025540817322031 (visited on 08/10/2023).

[3] Shangpan Huang et al. “Optical properties and theoretical study of Mn doped ZnAl2O4 nanoparticles with spinel structure”. en. In: *Journal of Alloys and Compounds* 825 (June 2020), p. 154004. ISSN: 09258388. DOI: 10.1016/j.jallcom.2020.154004. URL: https://linkinghub.elsevier.com/retrieve/pii/S0925838820303674 (visited on 08/10/2023).

[4] S. Sameera et al. “Nanostructured zinc aluminates: A promising material for cool roof coating”. en. In: *Journal of Science: Advanced Materials and Devices* 4.4 (Dec. 2019), pp. 524–530. ISSN: 2468-2179. DOI: 10.1016/j.jsamd.2019.10.003. URL: https://www.sciencedirect.com/science/article/pii/S2468217919302333 (visited on 08/10/2023).

[5] G. G. P. Van Gorkom, J. H. Haanstra, and H. v. d. Boom. “Infrared and Raman spectra of the spinel ZnGa2O4”. en. In: *Journal of Raman Spectroscopy* 1.5 (1973), pp. 513–519. ISSN: 1097-4555. DOI: 10.1002/jrs.1250010510. URL: https://onlinelibrary.wiley.com/doi/abs/10.1002/jrs.1250010510 (visited on 08/10/2023).

Photon-induced therapy (PIT) is a medical treatment that is gaining attention. PIT uses photons to stimulate specific physiological responses in the body for therapeutic purposes. One major type of photon-induced therapy is Photodynamic Therapy (PDT). In PDT, a photosensitive substance known as a photosensitizer accumulates in targeted cells or tissues. When these photosensitized cells are exposed to visible light, they become activated, and this activation leads to the production of reactive oxygen species that can damage or destroy targeted cells, such as cancer cells or abnormal tissues (Figure 1). The advantage of phototherapies is that they can trigger an immune response and have minimal side effects. However, the primary limitation is the requirement of visible light. In order to treat deep-tissue conditions

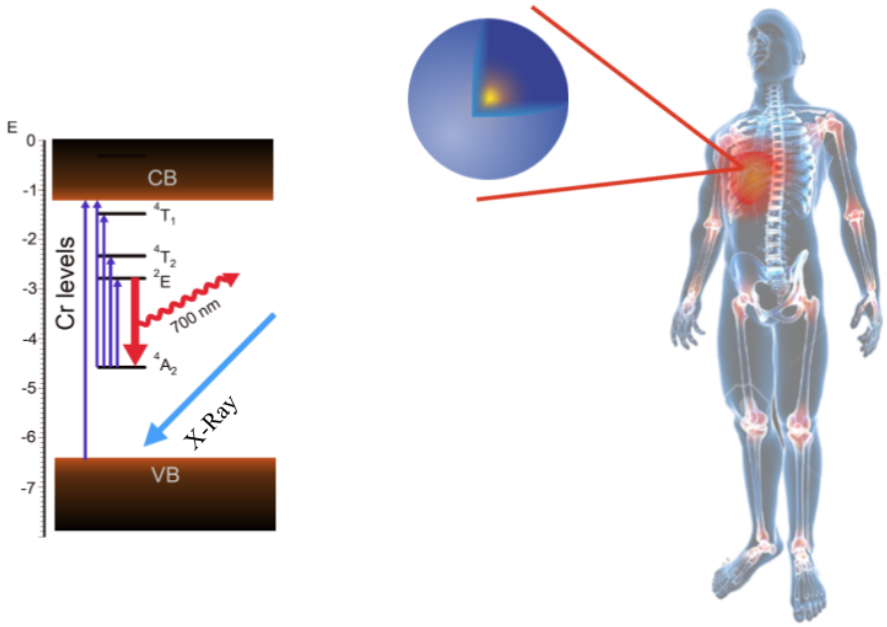


Figure 1: The figure on the left is the energy diagram of ZGO:Cr^{3+}. Doped spinel oxides can be excited by X-ray photons and emit visible or infrared light. Such emission can be used to trigger phototherapy anywhere inside the body.

like cancer, it is necessary to overcome the limitations of light penetration into the human body. We aim to utilize the unique properties of doped spinel oxides to generate visible light inside the body and solve this problem. Zinc Gallate ($ZnGa_2O_4$ or ZGO) and Zinc Aluminate ($ZnAl_2O_4$ or ZALO) are wide band gap semiconductor spinel oxides with interesting physical properties. These materials can convert high-energy photons, such as X-ray photons, into visible or infrared light [1]. When doping spinel oxides with transitional metals like Chromium (Cr), Manganese (Mn), or Nickel (Ni), these materials will emit visible photons with different colors after X-ray excitation, and the photon activation for photo immunotherapy or photodynamic therapy becomes possible locally, independent of the location inside the body (Figure 1). Additionally, the studied materials often contain trap states near the dopants. These trap states can trap the excited photons from returning to the ground state, delaying the relaxation process and causing a delayed light emission lasting for hours or even days. This process is called Long-Lasting Photoluminescence (LLP). Our project goal is to research and understand the possible defects and changes in crystal structures by varying the solution concentration, the doping material and quantity, and the pH values to tune the luminescence intensity and the LLP time.

We used the hydrothermal reaction route to synthesize different spinel oxide nanomaterials. The samples are prepared using high pressure at a moderate temperature (150 to 300 °C). This method has several advantages: it is possible to achieve nanoparticles with sub-10 nm particle size and smaller standard deviations; also, a higher temperature during the synthesis will possibly eliminate possible defects and crystal imperfections, which is not an ideal situation for our research goal as these defects are responsible for the LLP [1]. The sample preparation started by dissolving the soluble salts of the cations (Zn, Ga, Al, and Mn) into aqueous solution [1, 4].

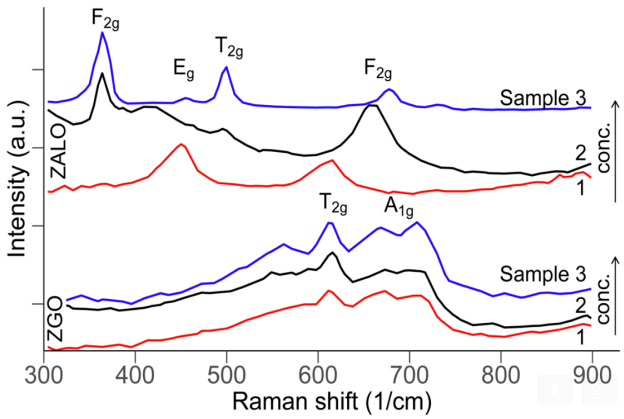
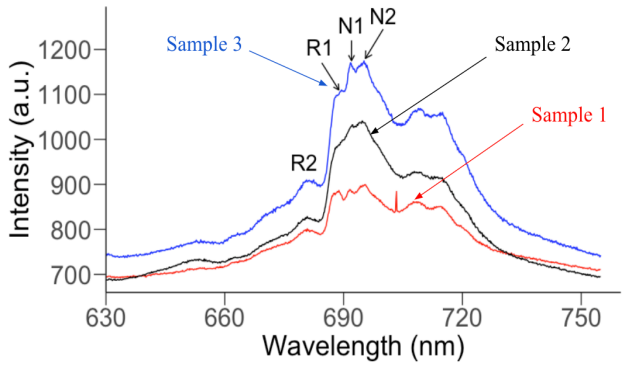


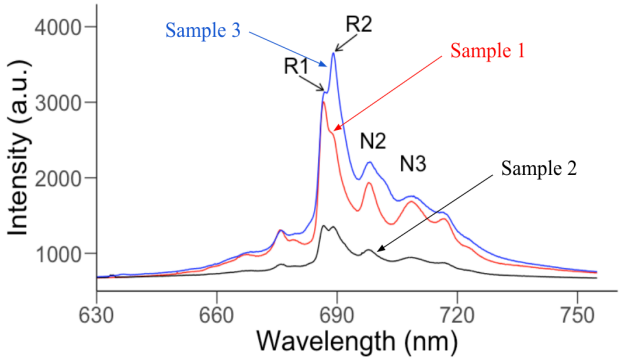
Figure 2: Raman spectra of undoped ZGO and ZALO. The reactant concentration highly affects the peak positions in the ZALO samples.

I varied the reactant concentration and solution pH to examine the effect of those variables on the possible defects and crystal structures. The solution is sealed into a PTFE-lined autoclave and annealed at 220 °C for 10 hours. The white precipitates obtained after the reactions were washed with HCl and DI water to get rid of any unreacted salts.

Raman spectroscopy, X-ray powder diffraction (XRD), and electron paramagnetic resonance spectroscopy (EPR) were used for sample characterization. The Raman can help us to identify if we synthesized the intended nanoparticles and drew us a clearer picture of the crystal structures of the samples. A shift in the Raman peak position and the variation of the half-width signals potential changes in the crystal structure. Note the symmetry of the modes as in Fig 2. Ideally, ZALO has Raman peaks at around 400 cm^{-1} and 660 cm^{-1} [2], and ZGO has its Raman peaks at 611 cm^{-1}, 676 cm^{-1}, and 714 cm^{-1} [5]. The collected Raman spectra (Figure 2) and XRD stated that we produced ZALO and ZGO. A shift in the Raman peaks of our ZALO samples with varying concentrations is also noteworthy. The Raman peaks in the studied materials are so-called phonon modes. The material's symmetry determines which phonon modes are Raman active, and those peaks can be labeled with Mulliken symbols. It can be seen that the reactant concentration highly influences the Raman peak positions in the ZALO samples. Raman spectra suggest that the increase in the reactant concentration changes the crystal symmetry that, changes the selection rules, and makes some forbidden transitions Raman active.



(a) PL Spectra of undoped ZGO



(b) PL Spectra of undoped ZALO

Figure 3: (Photoluminescence) PL Spectra of undoped ZGO and ZALO at room temperature under the excitation of 532 nm. Cr^{3+} dopant is found in both samples from the emission peak around 690 nm. The sharp PL peaks are from the zero phonon lines of diferently perturbed Cr^{3+} ions. The reactant concentration affects the peak intensity and peak ratio as well.

The optical properties are studied with Photoluminescence Spectroscopy (PL). We found a trace of Cr-doping in our undoped samples. We confirmed this result by finding two sharp PL emission peaks at around 690 nm in both ZALO and ZGO at room temperature. It appeared more clearly in ZALO samples (Figure 3a and Figure 3b). The origin of these sharp PL peaks is the Zero Phonon lines (ZPL) from the unperturbed and perturbed Cr^{3+} ions. We identified a possible association between the concentration of reactants and PL Intensity. In the case of ZGO samples, the association is linear: sample 1 possesses the lowest PL intensity, and sample 3 possesses the highest PL intensity.

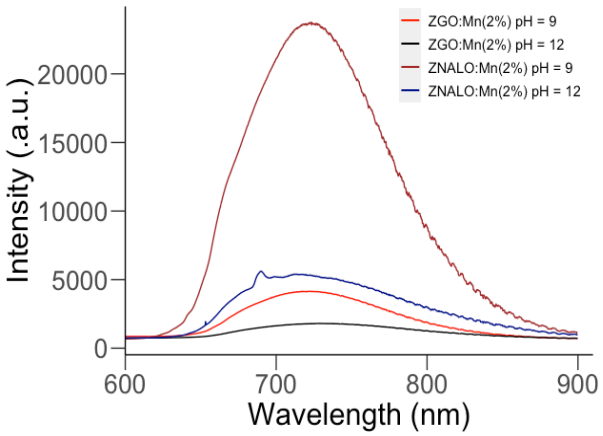


Figure 4: PL Spectra of 2% Mn doped ZGO and ZALO samples with basic pH values under the excitation of 457 nm. The huge and broad PL emission peak at the infrared range is only observed in the basic pH samples.

However, the relationship is nonlinear in the ZALO samples, as sample 2 has the lowest PL intensity. It can also be seen that the peak ratios (the contributions of the ZPLs in the PL spectra) are also affected by the reactant concentration. Since the ZPL is associated with the perturbation of the Cr^{+3} energy levels, we speculate that the concentration of the solutions affects the concentration and types of defects in the crystal. Thus, further research is required to understand how the reaction parameters affect the crystal structure and, later, use this knowledge for defect engineering.

The Raman spectra of ZGO:Mn^{2+} and ZALO:Mn^{2+} are almost identical to the undoped samples suggesting that doping has no macroscopic effect on the crystal structure. The PL spectra were recorded under the excitation of a blue laser at a wavelength of 457 nm. According to the literature, ZALO:Mn^{2+} should exhibit a green luminescence, corresponding to a single PL emission peak at around 510 nm under [3]. However, When we examined the PL spectra of ZGO:Mn^{2+} and ZALO:Mn^{2+}, we only found a very weak green luminescence at 510 nm. Instead, we observed a vas PL emission peak in the infrared range (Figure 4). Furthermore, this red luminescence was only observed in our basic samples (pH = 9 and pH = 12), not in the acidic ones (pH = 2). This unexpected result needs significant research. One possible explanation is that due to the doping of both Mn^{2+} and Cr^{3+} ions, the Mn^{2+} ion transfers its energy to the Cr^{3+} ions and amplifies the emission intensity. However, the significant red-shift and the lack of ZPLs suggest an enormous difference in the crystal field strength if this emission is indeed from the Cr^{3+} levels.

We used hydrothermal synthesis to create undoped and Mn^{2+} doped ZGO and ZALO nanoparticles. The Raman spectra of both nanoparticles under green laser excitation was similar to the literature. Reactant concentration affected Raman peak position. PL spectra showed Cr^{3+} dopant in both undoped samples, and a possible association between concentration and crystal structure was identified. We studied the PL spectra of ZALO:Mn^{2+} and ZGO:Mn^{2+}. Weak green luminescence at 510 nm was observed, and a vast PL emission peak at the infrared range was found only in the basic samples. Further characterizations using Raman, XRD, EPR, and PL spectra are necessary to understand possible defects and differences in crystal structure and field strength. Other dopants, such as Nickel, in ZGO and ZALO nanoparticles will also be studied for the best result.