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Synthesis of cerium-based high-entropy perovskites and their application in the degradation of organic dyes

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INTRODUCTION

Perovskites are materials that have the same crystal structure as the first mineral found with that structure, calcium titanium oxide ($CaTiO_3$). Perovskite compounds have a chemical formula ABX_3 where 'A' are cations with larger radii, 'B' are cations with smaller radii, and 'X' are anions that bond to both 'A' and 'B'. This research aimed to synthesize high-entropy perovskites via the modified citrate sol-gel method. The starting perovskite material $CeNiO_3$ was characterized by powder X-ray diffraction and thermogravimetric analysis. Once the starting material was successfully synthesized the goal was to dope the starting material with transition metals on the B site and lanthanides on the A site to increase entropy which would minimize the Gibbs energy and yield an additional increase in the stability of the material. The method itself used minimal hazardous substances in accordance with green chemistry. The photocatalytic activity of the $CeNiO_3$ and its high entropy forms were tested on the degradation of synthetic dyes: Methylene blue (MB), Naphthol Green B (NG), and Rhodamine B (RDB) respectively. The results indicate a reduction of maximum absorbance of tested dyes in the given time frame and monitored during irradiation at wavelength of maximum absorbance for each dye (663 nm for MB, 734 nm for NG and 554 nm for RDB).

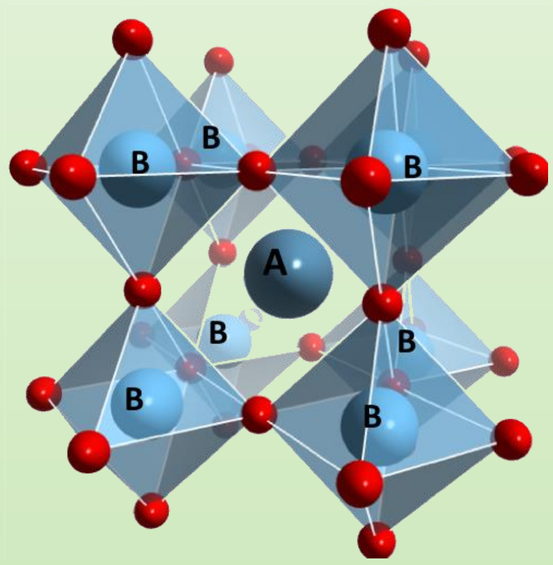

Fig.1. General perovskite structure.

SYNTHESIS

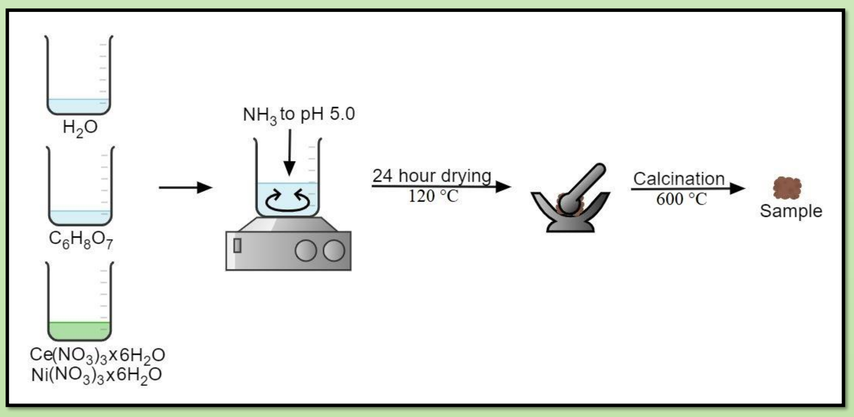

Fig 2. Synthesis pathway for obtaining phase-pure HEOs.

Table 1. Chemical formulae with configuration entropy value for each compound.

Code	Chemical formula	S_{config}
RB1	$CeNiO_3$	0
RB11	$CeNi_{0.25}Cu_{0.25}Mg_{0.25}Zn_{0.25}O_3$	1.386
RB31	$Ce_{0.2}La_{0.2}Pr_{0.2}Sm_{0.2}Eu_{0.2}NiO_3$	1.609

Table 2. Estimated indirect and direct band gap values for each compound from absorbance spectra via the Tauc method.

	Band gap	
Sample	**Direct**	**Indirect**
RB1	5.69	5.16
RB11	5.61	5.18
RB31	5.74	5.21

RESULTS

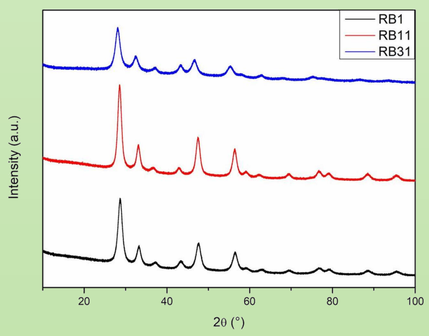

Fig.3. Powder X-ray diffraction patterns (PXRD) of RB1, RB11, and RB31 recorded before thermogravimetric analysis. Given PXRD patterns indicate phase purity of synthesized compounds.

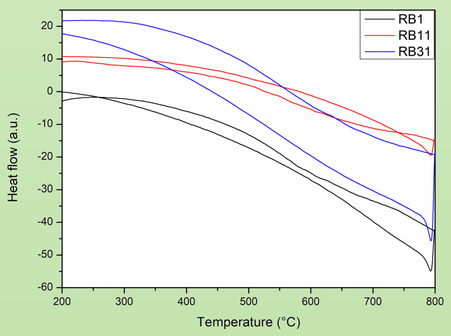

Fig.4. DSC curves of RB1, RB11, and RB31. Given curves describe phase stability of synthesized compounds from 200 °C up to 800 °C. DSC analysis shows no abrupt changes due to heating.

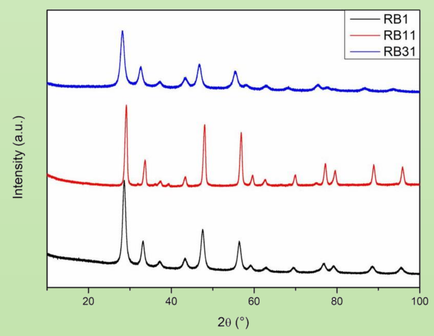

Fig.5. X-ray diffraction patterns of RB1, RB11, and RB31 recorded after TGA/DSC. Peaks are sharper than before the thermal treatment which is the result of additional sintering. RB1 and RB31 are still phase-pure, while RB11 shows additional peaks, probably due to the formation of byphases.

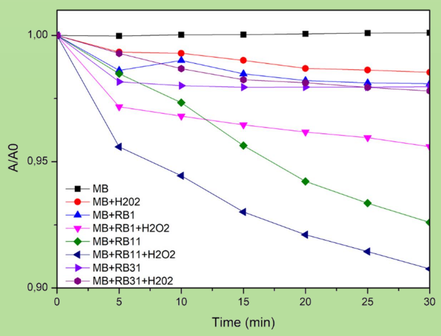

Fig.6. UV-Vis absorption spectra of methylene blue (MB) dye with and without the addition of HEOs monitored at regular intervals of time under halogen lamp (20 W) irradiation at λ = 663 nm.

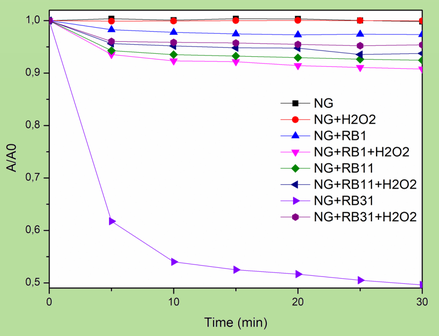

Fig.7. UV-Vis absorption spectra of naphtol green (NG) dye with and without the addition of HEOs monitored at regular intervals of time under halogen lamp (20 W) irradiation at λ = 734 nm.

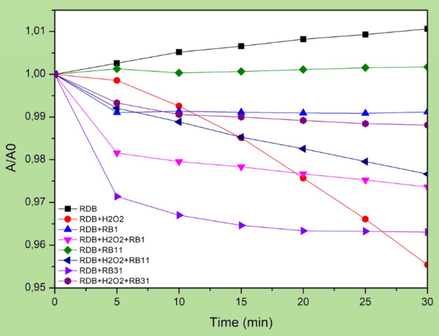

Fig.8. UV-Vis absorption spectra of rhodamine B (RDB) dye with and without the addition of HEOs monitored at regular intervals of time under halogen lamp (20 W) irradiation at λ = 554nm.

CONCLUSIONS

With the above green sol-gel method, phase-pure perovskites were synthesized which was proven by the powder X-ray diffraction analysis. TGA/DSC analysis shows that the compounds are thermally stable. RB1 is more efficient with the addition of hydrogen peroxide as an initiator and co-catalyst. RB11 was the most efficient in MB degradation (9 %), while RB31 was the most efficient for NG (50%) degradation after 30 minutes.