One-Step Synthesis and Investigation of Thermal Behaviour of a mixed Mn-Pyrazole-Phosphate and Mn-Oxyhydroxide Nano-Composite.

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Abstract:

The synthesis of novel inorganic-organic hybrid materials has recently gained considerable attention due to their diverse applications. In this context, manganese-oxyhydroxy [1-3] and manganese-pyrazole [4-5] each contribute significantly to electrochemical energy storage, electrochemical devices, solar cells, and as additives for thermal-management coatings**.** In this study, an effort was made to integrate the properties of these materials into a single framework. The composite material was synthesized using a one-step precipitation method. After synthesis, it was divided into two parts and dried using different methods—one at 80°C (SS-1) and the other at room temperature (SS-2). The composition of SS-2 is represented as $Mn(C_3H_4N_2)(OH)_3(HPO_4)\cdot(MnHPO_4)\cdot(Mn\text{-}O\text{-}OH)_2\cdot(NaH_2PO_4)_2\cdot 3H_2O$. It was characterized using ICP-OES and CHNS analysis, with TGA providing further validation. Average crystallite sizes using PXRD were evaluated by Debye-Scherrer formula and Williamson Hall method were found to be 83.5 nm and 60.8 nm for SS1 and SS2 respectively. Structural analysis of SS-1 and SS-2 was carried out using FTIR, UV-Vis-NIR, and SEM, while TGA and DSC were utilized to study their thermal behavior. The UV-Vis-NIR spectrum confirms the presence of Mn-N and Mn-O bonds, whereas the FTIR spectrum identifies various functional groups and linkages, including O-H, C=N, P=O, Mn-O, Mn-N, and H-O-H, validating the molecular composition of the composites. UV-Vis-NIR analysis further indicates that SS-1 has a band gap of 1.46 eV with a refractive index of 2.84, while SS-2 possesses a band gap of 0.50 eV with a refractive index of 3.71. DSC analysis indicates that the specific heat capacity(Cp) of SS-1 and SS-2 is 0.148 J/g·K and 0.167 J/g·K, respectively. The specific heat capacity vs. temperature plot reveals that the average Cp values of these materials are relatively low (see Fig. 1).

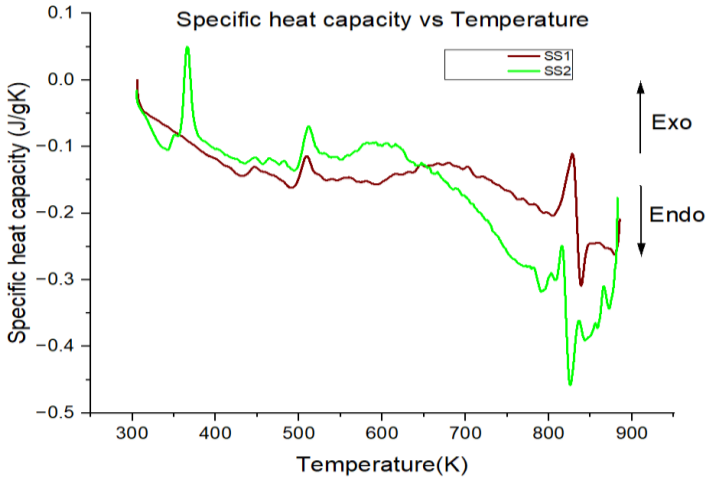

Fig-1: Plot of specific heat capacity of SS-1 and SS-2 versus temperature.

This indicates that materials with a high refractive index and low specific heat capacity exhibit strong light interaction and undergo rapid heating and cooling after the heat source is removed. The presence of nanosized particles can enhance thermal performance through increased surface interactions. Such materials may be beneficial for applications in aerospace, automotive industries, and industrial furnaces.

References:

[1] T.V. Sathyan, Jasmine Thomas, Nygil Thomas, Designing of manganese-based oxides and oxyhydroxides as positive electrode materials and activated carbon from Phyllanthus emblica as negative electrode material for battery type supercapacitor, International Journal of Hydrogen Energy, (2023), 48, 97, 38309-38323. https://doi.org/10.1016/j.ijhydene.2023.06.158

[2] Ghodbane, O., Pascal, J. L., Fraisse, B., & Favier, F. (2010). Structural in situ study of the thermal behavior of manganese dioxide materials: toward selected electrode materials for supercapacitors. *ACS Applied Materials & Interfaces*, *2*(12), 3493-3505. https://doi.org/10.1021/am100669k

[3] Jayaraman Theerthagiri, K. Karuppasamy, C. Justin Raj, Gilberto Maia, M.L. Aruna Kumari, L. John Kennedy, Marciélli K.R. Souza, Eduardo S.F. Cardoso, Soorathep Kheawhom, Hyun-Seok Kim, Myong Yong Choi, Structural engineering of metal oxyhydroxide for electrochemical energy conversion and storage,Coordination Chemistry Reviews,Volume 513,2024,215880, https://doi.org/10.1016/j.ccr.2024.215880

[4] Feng C, Lv CP, Zhao H, Li ZQ, Xie WN, Sun LN, Wang Y. Structural elucidation and supercapacitive performance on a Mn (II)-based MOF. Crystal Growth & Design. 2020 Aug 4;20(9):5682-7. https://doi.org/10.1021/acs.cgd.9b01013

[5] Smernik, Josephine F., et al. "Understanding the structural landscape of Mn-based MOFs formed with hinged pyrazole carboxylate linkers." *CrystEngComm* 25.47 (2023): 6539-6548. https://doi.org/10.1039/D3CE00881A