



Solid-Solid Phase Change Material: Towards Heat Dissipation in Next Generation Devices

David Nieto-Castro^{1*}, Claudia Gómez-Aguirre¹, Breogán Pato-Doldán¹

¹CIIAE-Centro Ibérico de Investigación en Almacenamiento energético, Avda de la Universidad, s/n, 10003 Cáceres (www.ciaae.org)

1. ABSTRACT

In this study, we explore the mixed ligand approach, using azide (N_3^-) and formate ($HCOO^-$) in varying ratios with Mn^{2+} to fine-tune the properties and structures of perovskites. Crystals were obtained via the slow diffusion method. FTIR and DSC analysis of the compounds obtained revealed a high dependence between the thermal and structural properties and the ligand ratio used.

2. INTRODUCTION

With the continuous development of electronic devices towards high performance and miniaturization size, heat dissipation problem has become a major obstacle to their development. For this challenge, solid-to-solid Phase Change Materials (ss-PCMs) offer significant potential for thermal energy storage and thermal management through reversible phase transitions.[1] Among these materials, hybrid organic-inorganic perovskites have attracted considerable interest due to their versatility.[2] This family of materials has a general formula of ABX_3 , where A is the guest molecule, B is the transition metal, and X is the ligand bridge. A well-studied family is the formate-perovskites, in which formate ($HCOO^-$) serves as the bridging ligand.[3] These compounds exhibit intriguing properties, such as anomalous thermal expansion and magnetic ordering.[4] Another family is the azide-perovskites, where the azide (N_3^-) acts as the linker, also displaying notable properties and solid-to-solid phase transitions. In this study, we explore the mixed ligand approach, using azide and formate in varying ratios with Mn^{2+} to fine-tune the properties and structures of perovskites.

3. METHODOLOGY

Two mother solutions of sodium formate and sodium azide were mixed in various ratios. Crystals were obtained via the slow diffusion method after one week. The resulting crystals were isolated and washed with methanol several times.

4. RESULTS

FTIR analysis confirmed the presence of both ligands in all the new compounds (Fig. 1, top). The thermal properties of these samples were examined using DSC. For samples with a higher proportion of azide (0:100, 5:95, and 10:90), a decrease in transition temperatures was observed while maintaining similar enthalpy (ΔH) values (Fig. 1, bottom). Samples with higher formate content showed completely different transition profiles. Specifically, samples with a 15:85 and 20:80 azide:formate ratio exhibited multiple phase transition events.

*Corresponding Author: david.nieto@ciaae.org

Samples with a 40:60 and 50:50 azide:formate ratio demonstrated phase transitions at approximately -50°C . Finally, higher proportions of formate did not exhibit phase transition in the temperature range used.

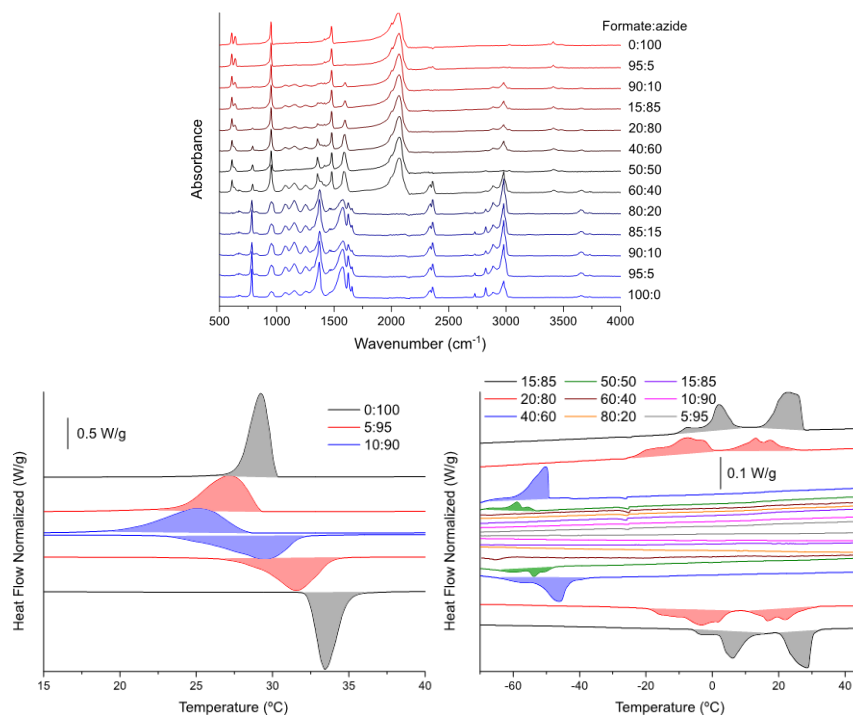


Figure 1. FTIR (top) and DSC(bottom) analysis of all the samples.

5. CONCLUSIONS

A new set of compounds has been synthesised via the ligand mixed approach method. Presence of both of the ligands was confirmed via FTIR measurements. Interestingly, at ratios with higher proportions of azide (< 15 %) a fine tune of the thermal properties. Higher ratios of formate produced a substantial variation in the thermal properties. Crystallographic analysis of all the compounds will be performed to obtain the structure of this new set of compounds and to be better understanding the mechanisms of the thermal transitions.

ACKNOWLEDGMENT

Funded by the European Union - Next GenerationEU

REFERENCES

- [1] A. Fallahi, G. Guldentops, M. Tao, S. Granados-Focil, S. Van Dessel, Review on solid-solid phase change materials for thermal energy storage: Molecular structure and thermal properties, *Applied Thermal Engineering*, 127 (2017), 1427.
- [2] J. M. Bermudez-Garcia, M. Sanchez-Andujar, M. A. Senaris-Rodriguez, M. A. A New Playground for Organic–Inorganic Hybrids: Barocaloric Materials for Pressure-Induced Solid-State Cooling, *The Journal of Physical Chemistry Letters*, 8 (2017), 4419.
- [3] A. Stroppa, P. Barone, P. Jain, J. M. Perez-Mato, S. Picozzi, Hybrid improper ferroelectricity in a multiferroic and magnetoelectric metal-organic framework, *Advanced Materials*, 25 (2013), 2284.
- [4] L. C. Gómez-Aguirre, B. Pato-Doldán, J. Mira, S. Castro-García, M. A. Señaris-Rodríguez, M. Sánchez-Andújar, J. Singleton, V. S. Zapf, Magnetic Ordering-Induced Multiferroic Behavior in $[\text{CH}_3\text{NH}_3][\text{Co}(\text{HCOO})_3]$ Metal–Organic Framework, *Journal of the American Chemical Society*, 138 (2016), 1122.