

EPR STUDY OF STRUCTURAL PHASE TRANSITIONS IN VARIOUS HYBRID PEROVSKITES

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Hybrid materials, crystallizing into perovskite-like structures with general formula AMX_3 (where A is an organic or inorganic cation, M is a metal center and X is anionic linker connecting A and M), have gained a lot of attention in recent years [1]. The desirable physical and chemical properties include gas adsorption and storage, efficient solar cells, multiferroicity and others [2-4].

Herein we report continuous-wave (CW) EPR study of structural phase transitions in different hybrid perovskite systems. X-band CW EPR experiments of $[(CH_3)_2NH_2]_2KCr(CN)_6$ and $[(CH_3)_3NH]_2KCr(CN)_6$ reveal one and two structural phase transitions, respectively. The phase transition temperatures are 207 K for $[(CH_3)_2NH_2]_2KCr(CN)_6$ and 261 and 179 K for $[(CH_3)_3NH]_2KCr(CN)_6$. Our research of $[TPrA][Cd(dca)_3]:Mn^{2+}$ revealed two structural phase transitions at 230 and 212 K. From the Arrhenius analysis of the temperature dependence of the EPR linewidth (Fig. 1), we obtain the activation energy of 0.12(2) eV, which was assigned to dynamics of the dicyanamide framework.

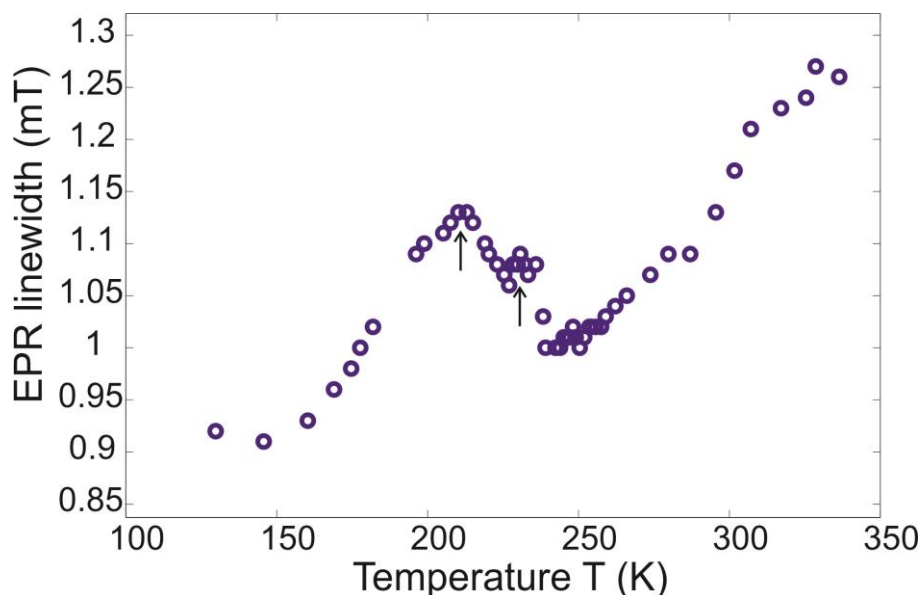


Fig. 1. Temperature dependence of the CW EPR peak-to-peak linewidth of Mn^{2+} centers in $[TPrA][Cd(dca)_3]$. The arrows indicate linewidth anomalies due to the structural phase transitions.

[1] W. Li, Z. Wang, F. Deschler, S. Gao, R. H. Friend and A. K. Cheetham, *Nat. Rev. Mater.*, **2**, 16099, (2017).

[2] Saliba, M.; Matsui, T.; Seo, J.-Y.; Domanski, K.; Correa-Baena, J.-P.; Nazeeruddin, M. K.; Zakeeruddin, S. M.; Tress, W.; Abate, A.; Hagfeldt, A.; Gratzel, M. *Cesium-Containing Triple Cation Perovskite Solar Cells: Improved Stability, Reproducibility and High Efficiency*. *Energy Environ. Sci.* **9**, 1989–1997 (2016)

[3] H.-C. Zhou, J.R. Long, O.M. Yaghi, *Chem. Rev.* **112**, 673–674 (2012)

[4] R. Ramesh, N. A. Spadin, *Multiferroics: progress and prospects in thin films*, *Nature Materials* **6**, 21–29 (2007).