Decoding the structure and properties of near-infrared reflective pigments

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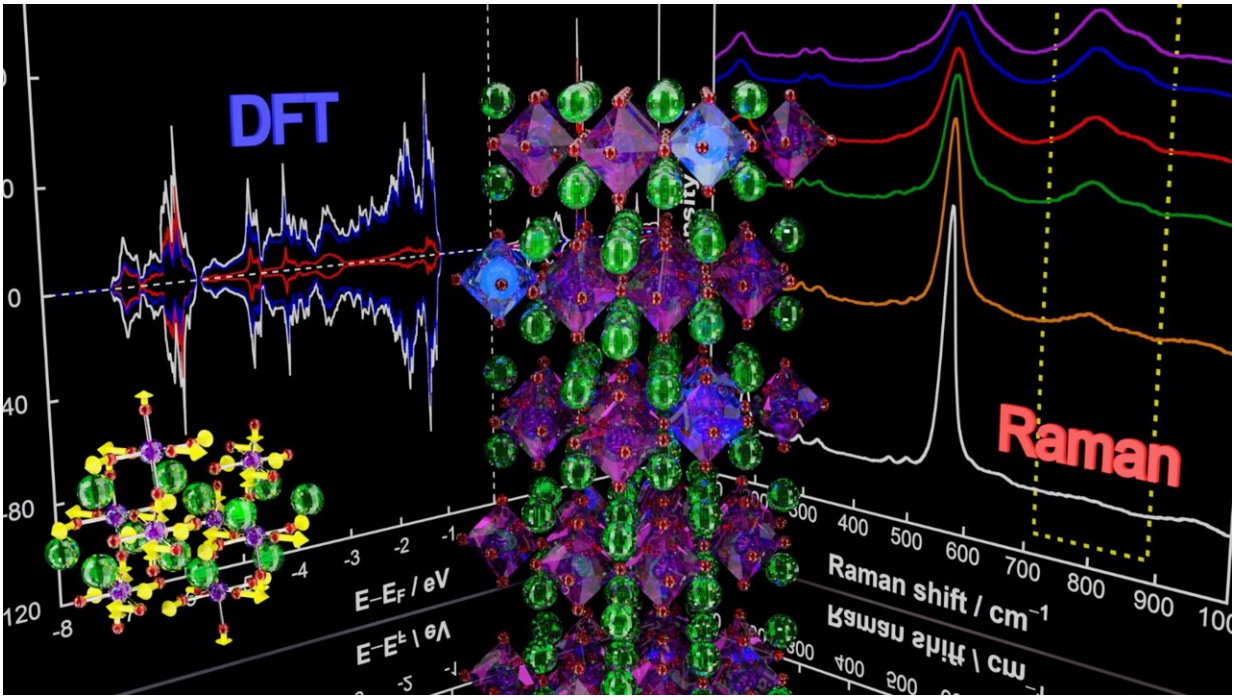

In a new study, researchers from Nagoya Institute of Technology, Japan use a combination of experimental and theoretical approaches to understand the optical, electronic, and magnetic properties of complex solids of layered perovskite compounds, providing valuable insights. The approach is extendable to a wide range of functionalized crystalline ceramic compounds. Credit: Ryohei Oka from Nagoya Institute of Technology, Japan

Urban areas without sufficient tree cover are significantly warmer than

their surroundings. This "urban heat island" effect mainly results from an absorption of near-infrared (NIR) radiation in sunlight. NIR-reflective pigments that can mitigate such heating effects are, therefore, highly desirable.

In particular, functional inorganic pigments are an attractive candidate on this front. In fact, Dr. Ryohei Oka and his colleague from Nagoya Institute of Technology, Japan, have demonstrated that layered perovskite ceramic compounds of the type A_2BO_4 are ideal for reflecting NIR. In his previous study, it was discovered that novel perovskites such as titanium-added calcium manganese oxide ($Ca_2(Mn,Ti)O_4$) ceramics are much better at reflecting NIR radiation than commercially available black pigments. However, the mechanism by which $Ca_2(Mn,Ti)O_4$ achieves this remarkable feat remains unknown.

In a recent study published in *Inorganic Chemistry*, Dr. Oka and his colleague, Dr. Tomokatsu Hayakawa, analyzed the structure and composition of $Ca_2(Mn,Ti)O_4$ using a combination of standard theoretical and experimental techniques to investigate the factors contributing to its enhanced NIR reflectivity. This paper was made available online on April 19, 2022, and published in Volume 61 Issue 17 of the journal on May 2, 2022.

In their work, the duo employed X-Ray diffraction (XRD) and Raman spectroscopy in combination with a computational method called "density functional theory" (DFT) to successfully extract missing details about the crystal structure and electronic states of $Ca_2(Mn,Ti)O_4$. "Few studies so far have conducted Raman spectroscopy of $Ca_2(Mn,Ti)O_4$. Furthermore, they have not provided any detail of its vibrational modes. However, information about its electronic states and vibrational modes is crucial to understand how these perovskites turn out to be such great NIR reflectors," says Dr. Oka, explaining the motivation behind their approach.

The duo analyzed the crystal structure of calcium manganese oxide (Ca_2MnO_4) and tracked the structural changes that occurred with the addition of Ti impurities. Furthermore, they identified how the chemical bonds within the perovskite are modified upon introducing Ti impurities. They found that, compared to Ca_2MnO_4, $Ca_2(Mn,Ti)O_4$ exhibited an additional Raman peak that was likely due to the activation of a "silent mode" caused by the Ti impurities. However, the XRD patterns of Ca_2MnO_4 and $Ca_2(Mn,Ti)O_4$ were identical. The duo attributed this to Ti-Ti correlation at a certain distance.

Another highlight of their study was the striking agreement between computational results from DFT and experimental data. The energy gaps obtained from the three models for $Ca_2(Mn,Ti)O_4$ used by the duo in their calculations agreed with each other as well as the experimental value. Moreover, the result was independent of Ti-substitution or its position in the crystal. Additionally, the calculations revealed that the enhanced NIR reflectivity upon adding Ti ions resulted from a lowering of "density of states" (the number of electronic states per unit volume per unit energy) near the Fermi level (the highest energy level an electron can occupy at absolute zero temperature).

These findings take us a step closer towards unveiling the thermal shielding property of perovskite ceramics. The perfect combination of experimental and theoretical approaches developed in this study provides a general recipe for understanding the structure and properties of not only A_2BO_4 type ceramics but a range of complex perovskite ceramics. As Dr. Oka puts it, "This combinational approach is applicable to a wide range of functionalized crystalline ceramics to understand their optical, electronic, and magnetic properties in a much better way with more reliable structural models obtained computationally."

Indeed, the detailed understanding of the enhanced NIR reflection mechanism would be extremely beneficial as inorganic pigments find

more application as superior thermal coatings for urban buildings.

More information: Ryohei Oka et al, Raman Spectroscopic Investigation and Electronic State Calculation for $Ca_2(Mn,Ti)O_4$ Black Pigments with High Near-Infrared (NIR) Reflectivity, *Inorganic Chemistry* (2022). DOI: 10.1021/acs.inorgchem.2c00254

Ryohei Oka et al, Synthesis and characterization of black pigments based on calcium manganese oxides for high near-infrared (NIR) reflectance, *RSC Advances* (2016). DOI: 10.1039/C6RA21443F

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