

From Average Structure to Local Symmetry: Understanding Cr³⁺ Luminescence in Perovskite Oxides

Jiazheng Li¹, Jian Xu^{1,2,#}, Jumpei Ueda³, Michele Back⁴, Ruilin Zheng^{1,5,6}, Natalia Majewska^{7,8}, Setsuhisa Tanabe^{1,2,#}

1. Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8316, Japan.
2. Graduate School of Global Environmental Studies (GSGES), Kyoto University, Kyoto 606-8501, Japan.
3. Graduate School of Advanced Science and Technology, Japan Advanced Institute of Science and Technology (JAIST), Nomi 923-1292, Japan.
4. Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, Via Torino 155, 30172, Mestre - Venezia, Italy.
5. College of Science, Nanjing University of Posts and Telecommunications, Nanjing, 210023, China.
6. Advanced Laser and Optoelectronic Functional Materials Department, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Science, Shanghai, 201800, China.
7. Institute of Experimental Physics, Faculty of Mathematics, Physics and Informatics, University of Gdańsk, 80-308 Gdańsk, Poland.
8. Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland.

Understanding the luminescence behavior of Cr³⁺ in solid-state hosts requires going beyond conventional descriptions based on average crystal structures. In many oxide phosphors, optical properties are typically interpreted in terms of global symmetry and averaged crystal field strength, which may overlook the complexity of local environments experienced by activator ions.

In this work, Sr_{1-n}Ba_nHfO₃:Cr³⁺ is employed as a model system to investigate how local coordination influences near-infrared (NIR) emission. With increasing Ba content, synchrotron X-ray diffraction reveals a gradual evolution of the average structure toward higher symmetry. Such behavior would suggest a continuous modification of the crystal field environment.

However, X-ray absorption spectroscopy combined with theoretical simulations uncovers a heterogeneous distribution of local Cr³⁺ environments, indicating varying degrees of octahedral distortion. This discrepancy between average symmetry and local coordination plays a decisive role in determining luminescence properties. In particular, excitation characteristics, R-line evolution, and thermal population between the ⁴T₂ and ²E states are found to correlate strongly with local symmetry rather than the average structure.

These findings demonstrate that local structural distortion governs the excited-state dynamics of Cr³⁺, highlighting the limitations of average crystal field models. Ongoing work extends this concept to a broader range of perovskite systems, aiming to establish general principles for tuning Cr³⁺-based NIR emission through local symmetry control.

Jian Xu: xu.jian.3z@kyoto-u.ac.jp; Setsuhisa Tanabe: tanabe.setsuhisa.4v@kyoto-u.ac.jp