

confirms the feasibility and great prospects of NASICON-type LZPO coatings for sulfide-based HVASSLB.

In summary, NASICON-type LZPO with high oxidation limits and reasonable ionic conductivity was demonstrated as a proof of concept for a bidirectionally compatible buffering-layer design scheme to overcome the interfacial challenges of sulfide-based HVASSLB. 4.5-V LZPO-LCO/LPSCI/In-Li HVASSLBs could thereby exhibit an initial discharge capacity up to 143.3 mA h g⁻¹ at 0.2 C, and excellent long-cycle performance (95.53% capacity retention after 100 cycles). This work sheds light on the great prospects of sulfide-based HVASSLB with high-rate characteristics, and constitutes a crucial step toward the rational design of the interface and interphase chemistry for high-performance sulfide-based HVASSLB. (Reported by Yan-Gu Lin)

This report features the work of Guanglei Cui and his collaborators published in Adv. Energy Mater. 11, 2100881 (2021).

TLS 16A1 Tender X-ray Absorption, Diffraction

- XANES, EXAFS
- Materials Science, Chemistry, Condensed-matter Physics, Environmental and Earth Science

Reference

1. L. Wang, X. Sun, J. Ma, B. Chen, C. Li, J. Li, L. Chang, X. Yu, T.-S. Chan, Z. Hu, M. Noked, G. Cui, *Adv. Energy Mater.* **11**, 2100881 (2021).

Catching Hidden Structural Evolution in Near-Infrared Phosphors

The random distribution of Ga³⁺ and Sc³⁺ ions at the Ga2 site of Ga₂O₃ greatly affects the photoluminescent properties.

Recently, phosphor-converted IR light-emitting diodes (pc-IR LEDs) have evolved into smart devices with the advantages of large output power, high efficiency and small size. IR phosphor materials are crucial components of these devices, affecting the overall performance of the resulting spectrum. Cr³⁺, as a unique and ideal near-IR emitter that can produce either sharp-line or broadband spectra, has become a promising candidate for producing IR light. Although substantial progress has been achieved in this popular topic, most studies have focused on a single compound or on changing activators without systematically tuning the crystal structure and the luminescent wavelength. Consequently, understanding the control mechanism is considered an important issue in tuning luminescent properties. Some local structural distortions or phase transitions might result in unexpected photoluminescent properties. Moreover, a subtle change in the local structure might tune photoluminescence between sharp-line or broadband emissions. This phenomenon has been seldom discussed in previous studies. The overall tuning mechanism remains vague.

Ru-Shi Liu (National Taiwan University) and his coworkers recently conducted a complete study on the unexpected structure evolution behavior in Cr³⁺-doped phosphors. Ga_{1.994-x}Sc_xO₃:0.006Cr³⁺ (Ga_{2-x}Sc_xO₃:Cr³⁺) phosphors in a series were synthesized; their unique structural

and photoluminescent properties were characterized, demonstrating their high potential in IR-LED applications. Employing X-ray diffraction (XRD) measurements at beamline **TLS 01C2**,¹ the unique partial substitution (~87%) of Sc³⁺ in the octahedral site was demonstrated *via* Rietveld refinement. The synchrotron XRD patterns of Ga_{2-x}Sc_xO₃:Cr³⁺ phosphors with varied Sc³⁺ concentration are shown in **Fig. 1(a)**. The pure phase was obtained at $x = 0-0.8$; Sc₂O₃ impurities existed at $x = 1$ and 1.2. The diffraction signals shifted toward lower angle on incorporation of Sc³⁺ ions because of the ionic size of Sc³⁺ (0.745 Å; CN = 6) larger than that of Ga³⁺ (0.47 Å; CN = 6) (CN denotes coordination number). Unexpectedly, the diffraction peaks did not shift linearly for $x > 0.8$. This finding might indicate the failure of the Sc³⁺ doping when $x > 0.8$. To investigate this unique behavior in-depth, Rietveld refinements of Ga_{2-x}Sc_xO₃:Cr³⁺ were conducted and analyzed. The lattice parameters, namely, a , b , c , and V , linearly increased for $x = 0-0.8$, as shown in **Fig. 1(b)**. The speed of ascent decreased from $x = 0.8-1.0$ and even stopped increasing from $x = 1.0-1.2$. To understand this property, the crystal structure and local coordinated environment of Ga₂O₃ were also carefully examined. Ga₂O₃ possesses a monoclinic structure with space group C2/m. Two distinct Ga³⁺ sites, namely, Ga1 and Ga2, were found in the Ga₂O₃ structure. Ga2 is coordinated with six O²⁻ forming an octahedron; Ga1 is coordinated by four O²⁻ forming a tetrahedron. When introducing Sc³⁺ into

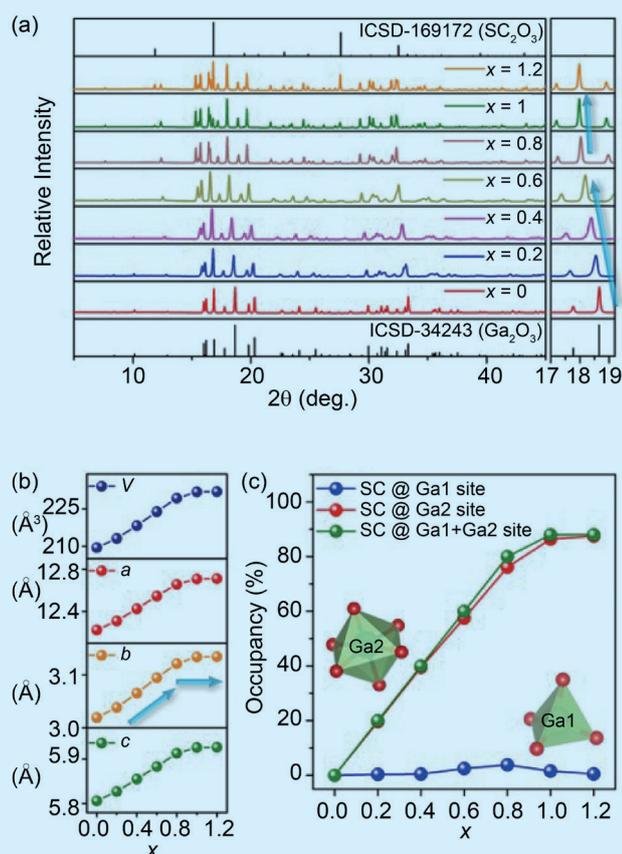


Fig. 1: Structural analysis of $\text{Ga}_{2-x}\text{Sc}_x\text{O}_3:\text{Cr}^{3+}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0,$ and 1.2). (a) Synchrotron XRD patterns, (b) refined lattice parameters and (c) occupancy of Sc^{3+} ions in Ga1, Ga2 and Ga1+Ga2 sites. [Reproduced from Ref. 1]

the Ga1 and Ga2 sites, the actual maximum obtainable amounts of Sc^{3+} in the $\text{Ga}_{2-x}\text{Sc}_x\text{O}_3:\text{Cr}^{3+}$ of $x = 1.0$ and 1.2 were 0.880, as calculated from the Rietveld refinement, proving that Sc^{3+} could no longer be incorporated into the host. Moreover, when Sc^{3+} ions were doped into the Ga_2O_3 structure, a strongly preferred occupation of Sc^{3+} ions at site Ga2 was observed due to the larger polyhedral volume at that site, as shown in **Fig. 1(c)**. The maximum doping occupation value at Ga2 was approximately 0.87, indicating that Sc^{3+} cannot completely occupy the Ga2 site. This result leads to a random distribution of Ga^{3+} and Sc^{3+} ions at the Ga2 site, further affecting the photoluminescent properties.

In summary, synchrotron XRD with Rietveld refinement proved that pure phases were obtained. but lattice parameters were not changed as expected at large Sc^{3+} concentrations. Despite the strongly preferred occupation of Sc^{3+} at the octahedrally coordinated Ga2 site, only partial substitution ($x = 0.87$) was achievable. This work could motivate further research on unexpected partial substitution during the solid solution. (Reported by Yan-Gu Lin)

This report features the work of Ru-Shi Liu and his collaborators published in ACS Energ. Lett. 6, 109 (2021).

TLS 01C2 X-ray Powder Diffraction

- XRD
- Materials Science, Surface, Interface and Thin Films, Condensed-matter Physics

Reference

1. M.-H. Fang, K.-C. Chen, N. Majewska, T. Leśniewski, S. Mahlik, G. Leniec, S. M. Kaczmarek, C.-W. Yang, K.-M. Lu, H.-S. Sheu, R.-S. Liu, ACS Energ. Lett. **6**, 109 (2021).

