

TLS 20A1 BM – (H-SGM) XAS**TLS 05A1 EPU – Soft X-ray Scattering**

- XANES, RIXS
- Material Science, Chemistry, Condensed Matter Physics

References

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Fluoride Phosphors Illuminate a White LED

A fluoride phosphor that forms a zero-phonon line and exhibits high quantum efficiency was applied successfully in diodes emitting white light.

To enhance the color-rendering index (CRI) of a device, red-light phosphors are necessary to enrich the red region of the spectrum. As the human eye is least sensitive to red light within the visible region, we barely detect light emitted above wavelength 650 nm. As a result, the broadened band-emission maximum at approximately 650 nm might cause a loss of high energy in the usage of diodes emitting white light (WLED). A fluoride phosphor with high intensity and a line spectrum, with maximum at 630 nm, can be detected by a human eye. Fluoride phosphors show no excitation at 550 nm, which can assist WLED devices to avoid re-absorption, thus making a fluoride phosphor a suitable candidate for use in WLED devices. At present, fluoride phosphors are synthesized with varied chemical compositions. To modify the spectra from fluoride phosphors, a distortion of the crystal is necessary, to cause the formation of the zero-phonon line that gains another line with maximum about 620 nm.

In the study¹ done by Ru-Shi Liu (National Taiwan University) and his co-workers, a new fluoride phosphor, namely, $\text{Rb}_2\text{GeF}_6\text{:Mn}^{4+}$ (RbGF), was synthesized with the formation of a zero-phonon line (ZPL), which can further improve the color-rendering index of WLED devices. The fabricated RbGF phosphor was applied in a LED, and the performance was compared with the commercial phosphor. The authors applied synchrotron-based X-ray diffraction (XRD) techniques at **TPS 09A** to clarify the detailed structural information of the RbGF samples.

The XRD pattern of RbGF, in which all diffraction signals can be indexed to hexagonal RbGF, indicates that pure single-phase RbGF can be obtained in a hexagonal system with particle size about 30–50

μm . The authors performed a Rietveld refinement to obtain further information about RbGF (**Fig. 1(a)**); this refinement indicates that $R_p = 2.55\%$ and $R_{wp} = 4.80\%$ adequately represent real data, with crystal parameters $a = 5.958715(8) \text{ \AA}$ and $c = 9.67058(2) \text{ \AA}$ belonging to the hexagonal system with space group $P6_3mc$. The geometry of the GeF_6^{2-} site has been simulated (**Fig. 1(b)**); the results of the fit show that the F–Ge–F bond angle is slightly distorted by the

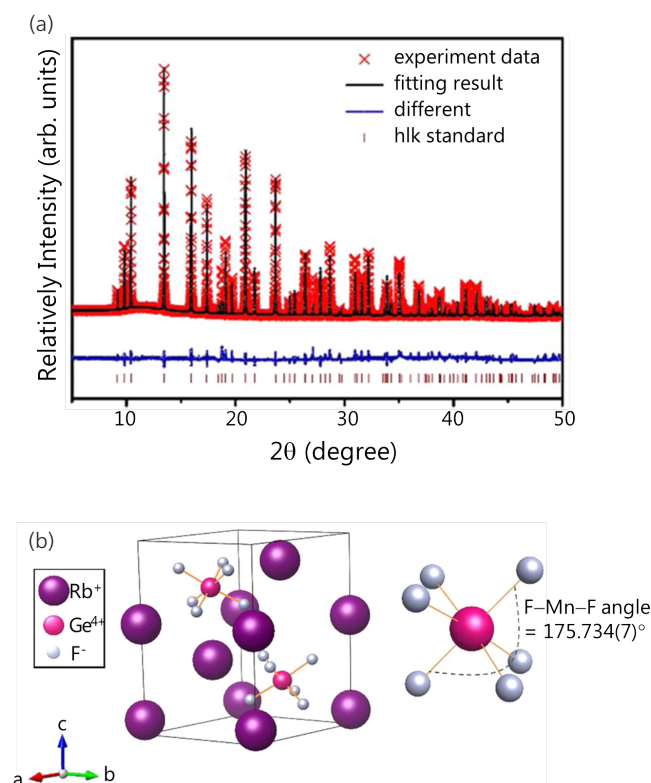


Fig. 1: (a) XRD refinement results of $\text{Rb}_2\text{GeF}_6\text{:Mn}^{4+}$ as prepared, with one pure-phase fit. (b) Simulated refinement model of the GeF_6^{2-} site into which activator Mn^{4+} was doped. [Reproduced from Ref. 1]

crystal structure, with angle equal to $175.734(7)^\circ$. This angle differs from that of a commercial fluoride phosphor, such as $\text{K}_2\text{SiF}_6\text{:Mn}^{4+}$ (KSF) that has an F–Si–F angle equal to 180° with point group O_h of the SiF_6^{2-} site. Consequently, once the MnF_6^{2-} activator becomes doped into RbGF in the GeF_6^{2-} site, the MnF_6^{2-} geometry might also become distorted; the MnF_6^{2-} point group might alter to C_3 , which would directly affect the RbGF spectra.

In summary, the authors synthesized a fluoride phosphor (RbGF) of a new chemical composition that exhibits a ZPL and high quantum efficiency (external quantum efficiency = 58%) that is almost equal to that of the commercial phosphor (KSF). The mechanism of the ZPL formation, and the relation between the ZPL and its sideband, were studied under various conditions such as low temperature and high pres-

sure. This new fluoride phosphor might be a critical material in revolutionizing WLED. (Reported by Yan-Gu Lin)

*This report features the work of Ru-Shi Liu and his co-workers published in Chem. Mater. **29**, 935 (2017).*

TPS 09A Temporally Coherent X-ray Diffraction

- XRD
- Material Science, Surface, Interface and Thin Films, Condensed Matter Physics

Reference

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Dual Doping Strengthens Metal-Support Interactions

Dual-doped TiO_2 provides an enhanced electron conductivity and improved activities in fuel cells.

As a proton-exchange-membrane fuel-cell catalyst, platinum (Pt) has the best performance among catalytic metals, but its great cost and the small rate of reaction at the cathode, which is the site of the oxygen reduction reaction (ORR), limit the widespread use of proton-exchange-membrane fuel cells. Moreover, Pt sintering and support degradation remain unresolved problems in acidic solutions. The most commonly used support (as a Pt carrier) is TiO_2 , because of its electrochemical stability and its resistance to dissolution in acidic media, as found in working fuel cells. Although TiO_2 allows for some degree of electron transfer from Pt to the electrode, its conductivity is much less than that of carbon. This decreased conductivity effectively limits the activity of a Pt/ TiO_2 catalyst, such that it is not comparable to a Pt/C catalyst. One common approach to enhance the conductivity of TiO_2 , and thus to increase the activity of the catalyst, is to dope other elements (cationic or anionic) into the TiO_2 lattice. In addition to single-ion doping, the TiO_2 lattice can simultaneously accommodate both cationic and anionic dopants. An intriguing question naturally arises as to the utility, application and activity of dual-doped supports for Pt catalysts in fuel-cell applications.

In the study¹ conducted by Bing-Joe Hwang (National

Taiwan University of Science and Technology) and his team, electrochemical and spectral data together with ORR activity studies indicated that $\text{Ti}_{0.9}\text{Nb}_{0.1}\text{N}_x\text{O}_y$ and $\text{Ti}_{0.8}\text{W}_{0.2}\text{N}_x\text{O}_y$ synthesized as dual-doped catalytic supports for Pt nanoparticles offer considerable promise as a new class of catalytic support for use in fuel cells. The authors recorded synchrotron-based X-ray absorption spectra (XAS) at **TLS 17C1** to demonstrate how the defect formation affects the interactions between Pt and the singly or doubly doped TiO_2 supports, and manipulates the physical and chemical properties of the resulting catalysts.

To investigate the electronic properties of Pt nanoparticles on $\text{Ti}_{0.9}\text{Nb}_{0.1}\text{N}_x\text{O}_y$ and to verify the strong metal-support interaction (SMSI) state, Pt L_{3-} edge X-ray absorption near-edge structure (XANES) spectra were recorded. The spectrum was plotted and compared with those of the Pt/ TiN_xO_y and Pt/ $\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_y$ catalysts; Pt foil and Pt/C were measured as references (**Fig. 1(a)**). In XANES spectra, the intensity of the white line is a direct measure of the d-band vacancy. The decrease in the white-line intensity can be attributed to SMSI that in turn lead to an electron transfer from the support to Pt. Additionally, the SMSI decrease the adsorption strength of the oxygen intermediates that are formed during