Comparative Analysis of Pb-Containing and Pb-Free Perovskite Oxides for Organic Dye Degradation

(Band Alignment and Photocatalytic Efficiency)

Presented by,
Name- Hiranya Ray
Department of Chemistry
Bodoland University

❑ Contents-

❖Introduction

❖Pb-containing perovskite oxides

❖Pb-free perovskite oxides

❖Bond alignment

❖Photocatalytic efficiency

❖Comparison between Pb-containing and Pb-free perovskite oxide

❖Conclusion

❖ References

❑ Introduction-

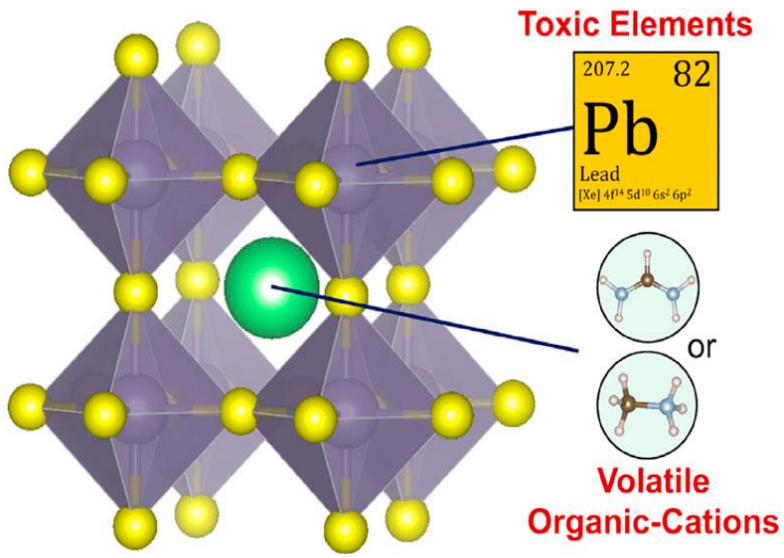
- Perovskite oxides are a large family of mixed-metal oxides that adopt the crystal structure of the mineral perovskite.
- Perovskite oxides have emerged as versatile heterogeneous photocatalysts for degrading recalcitrant organic dyes, such as azo, thiazine, and xanthene dyes.
- Lead-based perovskites eg, $PbTiO_3$ serve as high-efficiency reference catalysts because of how Pb^{2+} shapes their electronic bands and crystal symmetry.
- Pb-free perovskite oxides avoid toxic Pb^{2+} leaching into treated water, making them safe for environmental remediation.



(Fig1)
Count Lev Perovski (1792–1856)

❑ Pb-containing perovskite oxides-

- They adopt the ABO_3 crystal structure with Pb^{2+} at the A-site, including $PbTiO_3$, $PbZr_{1-x}Ti_xO_3$ (PZT), and $PbFe_{0.5}Nb_{0.5}O_3$ (PFN0
- The $Pb^{2+}6s^2$ lone pair hybridizes with O $2p$ states, elevating the valence band maximum and narrowing the bandgap of $PbTiO_3$ to 2.75→2.90 eV for blue-visible light absorption.
- Their conduction and valence band edges straddle aqueous redox potentials, enabling simultaneous production of $\cdot O_2^-$ and $\cdot$ OH radicals.



(Fig-2)

(Source-https://doi.org/10.3389/fmech.2024.1357087)

❑ Pb-free perovskite oxides-

- Pb-free perovskite oxides are mixed-metal oxides with the general formula ABO_3 or $A_2BB'O_6$ that replace toxic Pb^{2+} at the A-site with safer cations such as Ba^{2+}, Sr^{2+}, Ca^{2+}, La^{3+}, or Bi^{3+}
- They fall into wide-bandgap d^0 oxides that absorb UV light and narrow-bandgap bismuth or ferrite oxides ($BiFeO_3$, $LaFeO_3$, $E_g \approx 2.0 \rightarrow 2.6$ eV) that absorb visible light

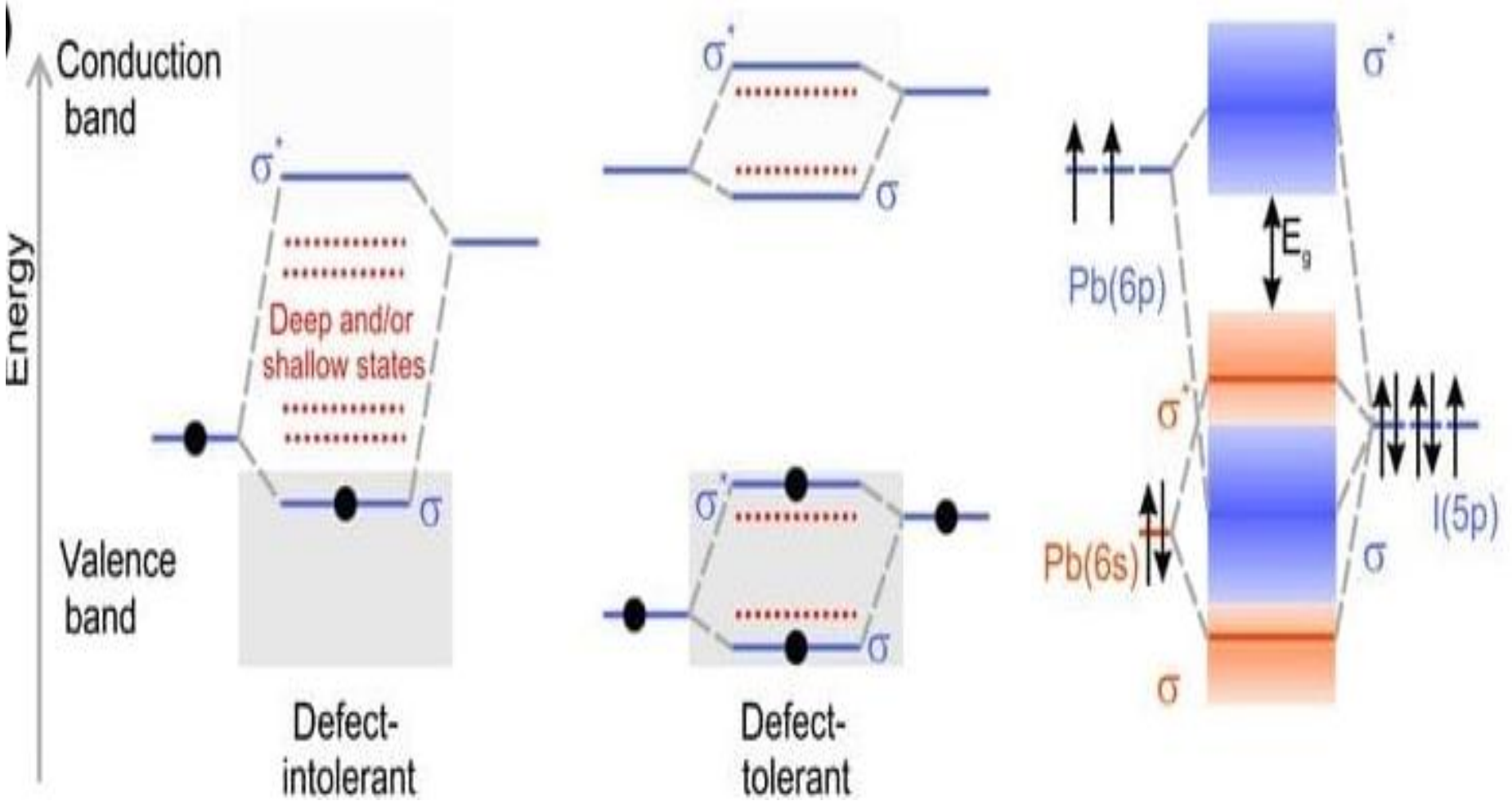
❑ Band alignment-

➢ Orbital Composition of the Valence Band -

- In Pb-based oxides like $PbTiO_3$, occupied Pb $6s^2$orbitals mix with O $2p$ states and raise the valence band edge by roughly 1ev. While Pb-free alkaline-earth titanates rely on pure O $2p$orbitals, keeping their valence band deeper.

➢ Band gap and light absorption-

- That upward valence band shift narrows the band gap of $PbTiO_3$to about 2.75–2.85 eV, allowing visible-light absorption. Pb-free titanates have wide band gaps that restrict them to UV light, while narrow-gap $BiFeO_3$absorbs visible light readily.



(Fig3)

(Source-Huang, H., Bodnarchuk, M. I., Kershaw, S. V., Kovalenko, M. V., & Rogach, A. L. (2017)

❑ Photocatalytic efficiency-

- Pb-based oxides exhibit higher pristine visible-light efficiency . while Pb-free oxides show lower efficiency in unmodified single-phase form.
- Pb-based oxides possess strong spontaneous ferroelectric polarization (P_s), creating a built-in internal electric field .Pb-free oxides generally exhibit weaker room-temperature polarization or higher defect-induced leakage currents.
- Pb-based oxides rely primarily on standard photogenerated e^-/h^+redox pathways because Pb^{2+}lacks facile multivalent redox cycling in water. Transition-metal Pb-free oxides boosting reaction kinetics and total organic carbon (TOC) mineralization well beyond pure photocatalysis.

Pb-containing	Pb-free
• $PbTiO_3$ composites have been studied for degrading dyes such as methylene blue and methyl orange.	• Many oxide catalysts and composites have been tested against dyes.
• Lead-containing ferroelectric materials may help separate photogenerated charges range.	• Avoids lead-related contamination concerns odamine B and azo dyes.
• Lead toxicity and potential release into the environment.	• Avoids lead, but other elements and processing impacts still need assessment.
• Often excellent optoelectronic performance, but durability and lead containment can be concerns.	• Often strong thermal and chemical stability, but performance depends on the material and application processing impacts still need assessment.

❑ Conclusion-

- Pristine Pb-based perovskites ($PbTiO_3$) achieve strong visible-light activity through Pb $6s$–O $2p$band narrowing and internal ferroelectric fields.
- Toxic Pb^{2+}leaching and photocorrosion rule out Pb-based oxides for safe wastewater treatment.
- Unmodified Pb-free oxides split between UV-active titanates ($BaTiO_3$, $SrTiO_3$) and visible-active ferrites ($BiFeO_3$) limited by charge recombination.
- High aqueous stability, zero lead toxicity, and green synthesis compatibility make engineered Pb-free perovskites the practical choice for dye remediation.

❑ References-

- An, J., Zhu, L., Zhang, Y., & Tang, H. (2013). Efficient visible light photo-Fenton-like degradation of organic pollutants using in situ surface-modified $BiFeO_3$ as a catalyst. *Journal of Environmental Sciences, 25*(6), 1213–1225. https://doi.org/10.1016/S1001-0742(12)60172-7

- Bhava, A., Shenoy, U. S., & Bhat, D. K. (2024). Silver-doped barium titanate nanoparticles for enhanced visible-light photocatalytic degradation of dyes. *Environmental Pollution, 344*, 123430. https://doi.org/10.1016/j.envpol.2024.123430

- Bhagwat, U. O., Wu, J. J., Asiri, A. M., & Anandan, S. (2018). Photocatalytic degradation of Congo red using $PbTiO_3$ nanorods synthesized via a sonochemical approach. *ChemistrySelect, 3*(42), 11851–11858. https://doi.org/10.1002/slct.201802303

- Liao, W., Xie, S., Xia, M., Li, Y., & Yin, S. (2026). Surfactant-assisted hydrothermal synthesis of perovskite $PbTiO_3$ superstructure with enhanced PDS activation for azo dye removal. *Journal of Materials Engineering and Performance, 35*, 26767–26776. https://doi.org/10.1007/s11665-026-13956-2

- Nunes, M. J., Lopes, A., Pacheco, M. J., & Ciriaco, L. (2022). Visible-light-driven AO7 photocatalytic degradation and toxicity removal at Bi-doped $SrTiO_3$. *Materials, 15*(7), 2465. https://doi.org/10.3390/ma15072465

- Ruby, S., Rosaline, D. R., Inbanathan, S. S. R., Anand, K., Kavitha, G., Srinivasan, R., Umar, A., Hegazy, H. H., & Algarni, H. (2020). Sunlight-driven photocatalytic degradation of methyl orange based on bismuth ferrite ($BiFeO_3$) heterostructures composed of interconnected nanosheets. *Journal of Nanoscience and Nanotechnology, 20*(3), 1851–1858. https://doi.org/10.1166/jnn.2020.17174

- Zhang, L., Li, X., Chen, J., Jin, D., & Cheng, J. (2022). Enhanced photocatalytic activity in ferroelectric $BiFeO_3$ nanoparticles treated by a corona poling method. *Ceramics International, 48*(11), 15908–15912. https://doi.org/10.1016/j.ceramint.2022.02.131

Thank you