

Using Synchrotron X-rays to Investigate the Pb Stabilization for PZT Ceramic Materials

PZT has become popular in the field of industrial applications worldwide, triggered to create a voltage on introducing a mechanical stress on a poled piezoelectric ceramic material so as to induce a change of dipole moment. PZT contains Pb up to 60% of total mass. Because Pb is proved to be accumulated in the food chain and its toxicity causes chronic disease for life, Pb zero-emission and Pb-free piezo-material systems are the next generations of piezo-material because of increasing environmental awareness and more restrictive regulations being made for environmental protection. Kaimin Shih et al. have recently developed a novel chemical Pb-stabilization to incorporate Pb into $\text{PbZr}(\text{PO}_4)_2$ to enhance the Pb stabilization effect through the formation of $\text{PbZr}_{x}\text{Ti}_{(1-x)}(\text{PO}_4)_2$ solid solutions. Synchrotron X-ray experiments demonstrated that the newly robust crystalline structure, developed through a well designed thermal treatment, provides an effective strategy to treat Pb frequently encountered in electronic wastes.

PbZrO_3 is a Pb zirconate titanate (PZT) ceramic of the perovskite family. The site of the Pb–O bond can be easily broken with an acidic attack because the bond Pb–O (2.5 Å) is longer than that of Zr–O (1.9 Å), giving rise to substantial free Pb(II) ions found in an acidic condition of landfill. An insufficient management of PZT-containing ceramic waste disposed of in landfill sites hence promotes a release of Pb(II) ions and poses a severe threat to the landfill operation and the surrounding environment. Herein, Kaimin Shih (The University of Hong Kong, China) focused on the treatment of waste PZT-based ceramics using a novel treatment and synchrotron X-rays to investigate the structural stabilization of PZT, in an effort to find more effective treatment techniques to remediate Pb-laden waste.

$\text{PbZr}(\text{PO}_4)_2$ can be obtained through sintering at 1000 °C for 96 h and a HNO_3 wash (2% v/v) to remove poorly crystallized

materials on the surface to decrease any interference. Based on the Fourier-transform infrared spectral analysis, the wavenumbers for the phosphate normal mode were identified to assure the orthophosphate group in the designed structure. The diffraction signals were also matched with the X-ray Diffraction (XRD) patterns, indicating that crystalline $\text{PbZr}(\text{PO}_4)_2$ was obtained in the process of heat and acid treatment. According to the extinction rule, the space group for crystal $\text{PbZr}(\text{PO}_4)_2$ was assigned to P3c1, which is consistent with the indices ($a = 8.7455$ Å and $c = 32.4963$ Å) confirmed with synchrotron X-ray diffraction (SXRD) using **TPS 09A** at the NSRRC.

The atomic structure (short-range order) around the target ions was further demonstrated for the local bonding environment of $\text{PbZr}(\text{PO}_4)_2$ based on the X-ray absorption spectral measurements at the Zr K-edge and Pb LIII-edge. The Zr

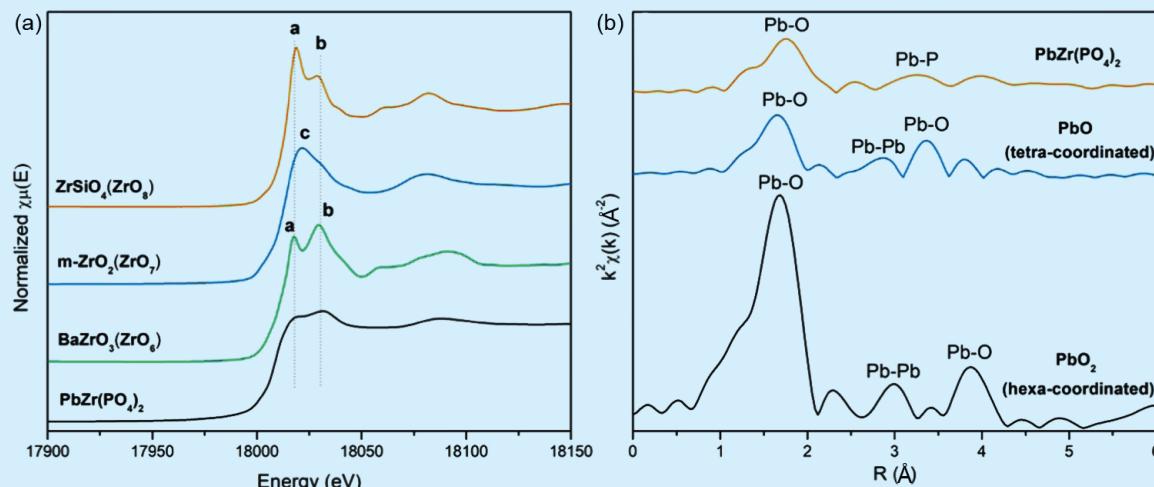


Fig. 1: Normalized Zr K-edge XANES spectra; (a) two main features of BaZrO_3 and ZrSiO_4 were labeled as a and b with different relative intensities, showing octahedral and dodecahedral arrangements of oxygen neighbors around Zr; the spectrum of m-ZrO_2 exhibits a broad feature at c and Fourier transform k^2 -weighted EXAFS spectra in the R space of Pb; (b) the intensity of the first shell was in accordance with the signal from PbO , indicating that the Pb atom was tetra-coordinated to oxygen in the target structure. [Reproduced from Ref. 1]

X-ray absorption near edge structure (XANES) spectrum of $\text{PbZr}(\text{PO}_4)_2$ was compared with the standard references (BaZrO_3 , m-ZrO₂ and ZrSiO₄) to fingerprint the Zr coordination, showing that the Zr K-edge XANES spectrum of $\text{PbZr}(\text{PO}_4)_2$ closely resembles that of BaZrO_3 and Zr is strongly considered to be six-fold coordinated with oxygen in the target structure shown in **Fig. 1**. The peak intensity from $\text{PbZr}(\text{PO}_4)_2$ was then compared with those of the standard references— PbO and PbO_2 , which corresponded to PbO_4 and PbO_6 coordination, respectively. These results indicated that Zr ions were located in octahedral and pentagonal bipyramidal sites; Pb ions were found to be in tetrahedral sites in the local structural environment, indicating the stability of the coordination polyhedra in the target structure. Based on these findings, Shih *et al.* suggested that Zr ions locate in octahedral and pentagonal bipyramidal sites and Pb ions in tetrahedral sites in the local structural environment.

A comparison of the evaluation of the effect of phosphate treatment on Pb stabilization for PbZrO_3 and $\text{PbZr}(\text{PO}_4)_2$ was performed after a long contact time; a continuous increase of Pb leachability was observed from the PbZrO_3 sample. Higher Pb concentrations and pH variations revealed substantial cation dissolution more from PbZrO_3 than from $\text{PbZr}(\text{PO}_4)_2$, as they were more vulnerable to proton-mediated dissolution; the pH values slightly increased from the original 2.85 to 3.03 by the end of the leaching period (**Fig. 2**).

After a long-term durability test, Shih and his collaborators suggested that $\text{PbZr}(\text{PO}_4)_2$ possessed a strong structural stability of the target phase and still maintained high crystallinity, as no new XRD diffraction signal was observed. Furthermore, the Pb stabilization mechanism was suggested as the oxygens play a crucial role in the first coordination shell for the $\text{PbZr}(\text{PO}_4)_2$ sample and the reference compounds herein, whereas the second coordination shell varied among the standards shown in **Fig. 3(a)**. The second shell of Zr in the $\text{PbZr}(\text{PO}_4)_2$ sample was strongly related to the Zr–P bonding environment because of the intensity

and position of signals of zircon from $\text{PbZr}(\text{PO}_4)_2$ in the range 2.5–3.2 Å of R space. Consequently, a Zr–O–P bond was highly possibly formed in the crystalline phase; the structural alteration might improve the product durability. The Pb–O bond length in $\text{PbZr}(\text{PO}_4)_2$ was near that of a free PbO molecule based on the extended X-ray absorption fine structure (EXAFS) data, indicating that oxygens be considered as a hard-sphere atom showing a strong electronegativity so that only a slight difference was induced in the first coordination shell. The O signal was assigned to the lattice oxygen and surface oxygen; a decreased intensity was observed for the O lattice after leaching, indicating depletion of the mineral phase by the acidic attack shown in **Fig. 3(b)**. The variation of surface element composition indicated that an amorphous Zr(OH)_4 layer might have been formed on the outer surface of $\text{PbZr}(\text{PO}_4)_2$, as crystalline Zr(OH)_4 was easily transformed into an amorphous structure on incorporating water molecules into the polymerized structure.

Materials with perovskite structures, of general formula of ABX_3 , have been widely used in the field of piezoelectric ceramics and optoelectronic devices, but increasing environmental awareness and more restrictive regulations have been made for environmental protection. Accordingly, the decreased Pb leachabilities in $\text{PbZr}(\text{PO}_4)_2$ solid solutions show the effectiveness of a phosphate treatment in stabilizing Pb from all forms of waste PZT ceramics and provide insight into waste form design for environmental remediation. Through alteration of the local coordination in the matrix and elemental doping in the solid solutions, heavy metals could be effectively stabilized in a robust structure. In the real wastes, however, a challenge will be to prevent the competitive effect of the heteroatom from entering the coordination sites designed for the target hazardous metals. Pb zero-emission and Pb-free piezo material systems are thus definitely the next generations of piezo material; further efforts should be made to investigate the metal-incorporation affinities in a complicated system. (Reported by Yao-Chang Lee)

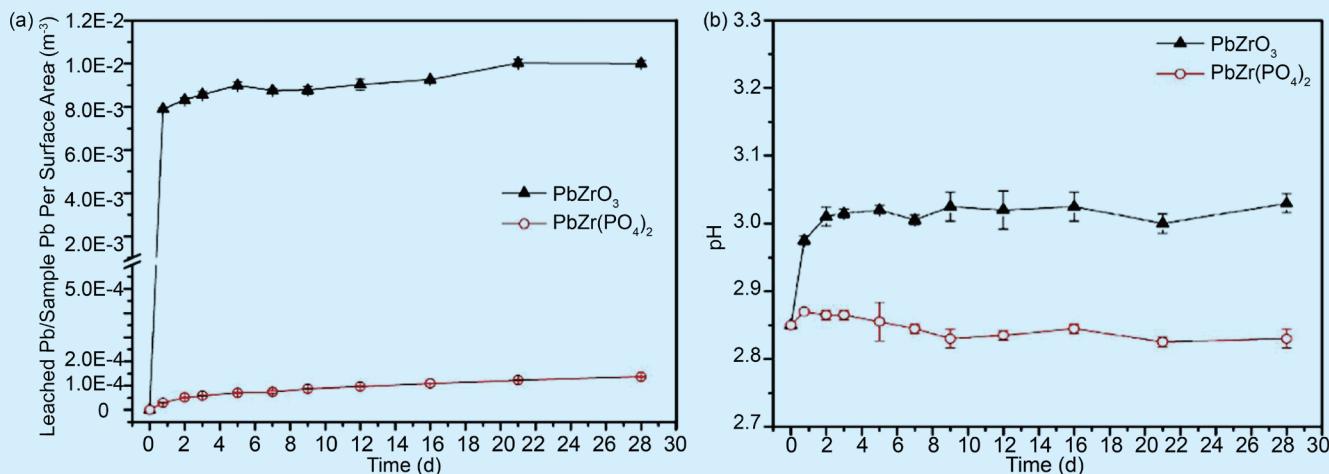


Fig. 2: Normalized lead concentrations (a) and pH variations (b) of PbZrO_3 and $\text{PbZr}(\text{PO}_4)_2$ leachates. [Reproduced from Ref. 1]

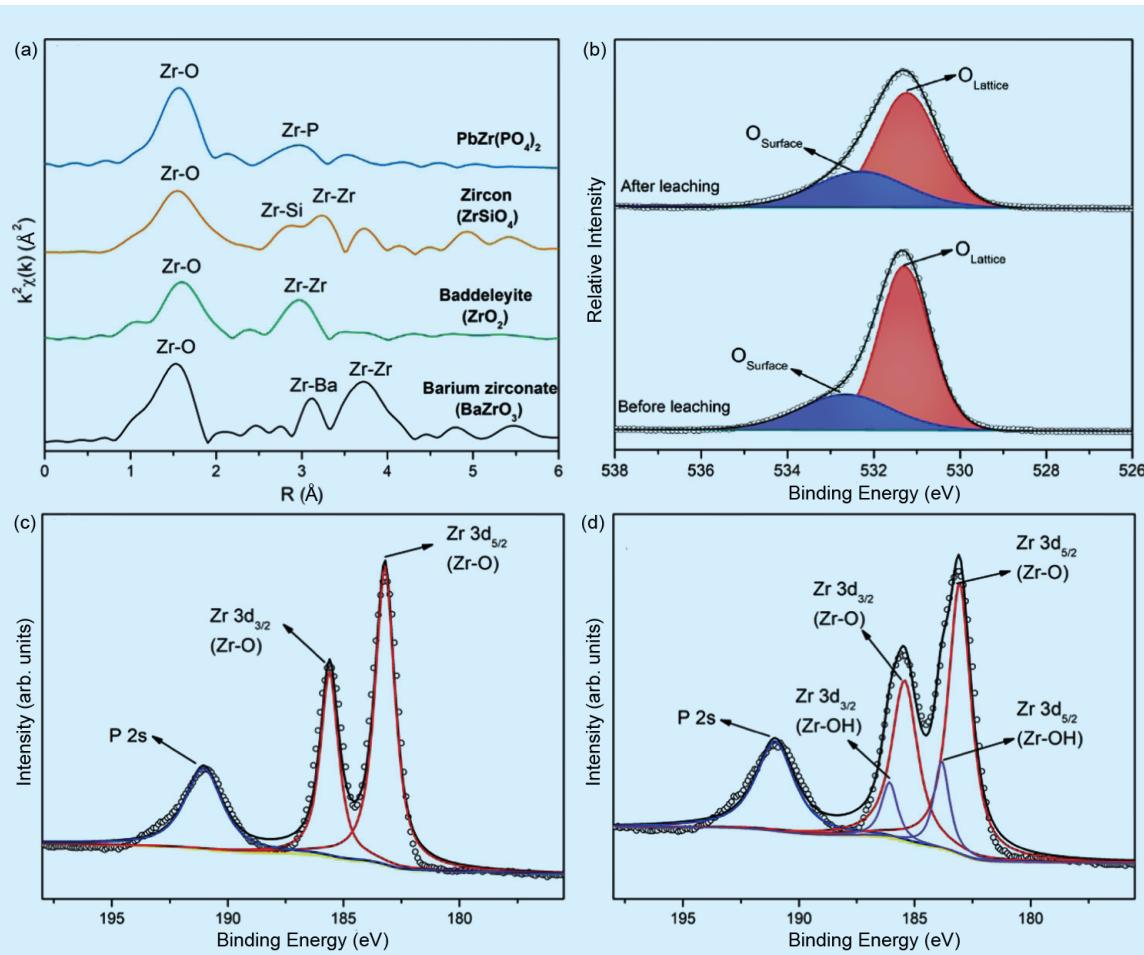


Fig. 3: Fourier transform k^2 -weighted EXAFS spectra in the R space of Zr—the peak positions are uncorrected from the backscattering phase shift; (a) high-resolution X-ray photoelectron spectroscopy (XPS) of O 1s (b) and Zr 3d spin–orbit doublet signals of the $\text{PbZr}(\text{PO}_4)_2$ sample (c) before and (d) after leaching for 28 days. [Reproduced from Ref. 1]

This report features the work of Kaimin Shih and his collaborators published in *Environ. Sci. Technol.* **54**, 6937 (2020).

TPS 09A Temporally Coherent X-ray Diffraction

- XRD, XPS, EXAFS, XANES
- Environmental and Earth Science

Reference

1. Y. Zhou, J. Zhang, C. Liao, T.-S. Chan, Y.-R. Lu, Y.-C. Chuang, C.-K. Chang, K. Shih, *Environ. Sci. Technol.* **54**, 6937 (2020).