Atomic controllable anchoring of uranium into zirconate pyrochlore with ultrahigh loading capacity†

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Efficient immobilization of actinide wastes is challenging in the nuclear energy industry. Here, we reported that 100% substitution of Zr\(^{4+}\) by U\(^{6+}\) in a La\(_2\)Zr\(_2\)O\(_7\) matrix has been achieved for the first time by the molten salt (MS) method. Importantly, we observed that uranium can be precisely anchored into Zr or La sites of the La\(_2\)Zr\(_2\)O\(_7\) matrix, as confirmed by X-ray diffraction, Raman, and X-ray absorption spectra. This work will guide the construction of site-controlled and high-capacity actinide-immobilized pyrochlore materials and could be extended to other perovskite materials.

Safe disposal of high-level nuclear wastes is a key issue for the development of nuclear power. Over the past three decades, significant efforts have been devoted to exploring the stable solid forms for the immobilization of high-level nuclear wastes in long-term geologic repositories. Zirconate pyrochlore (general formula A\(_2\)B\(_2\)O\(_7\)), which has good thermal stability, chemical durability and strong resistance to radiation damage, has been proposed as a superior host phase for nuclear wastes, especially for long-lived radioactive actinides. Due to their ionic size, actinide ions could substitute on either the A site or B site in the A\(_2\)Br\(_2\)O\(_7\) host, which can directly alter the defect engineering and affect the stability of the immobilization host.

For instance, some A-site doped zirconate pyrochlores such as A\(_{2-x}\)An\(_x\)Zr\(_2\)O\(_7\) (A = La, Nd, Gd; An = Pu\(^{3+}/4+\), U\(^{4+}/5+/6+\)) have been reported. By contrast, Gregg and Zhang et al. reported that the uranium is mainly located on the pyrochlore B-site instead of the targeted A site. Some other B-site substituted La\(_2\)Zr\(_2-x\)An\(_x\)O\(_7\) and Gd\(_2\)Zr\(_2-x\)An\(_x\)O\(_7\) pyrochlores have also been reported. In particular, the U oxidation state can be controlled under different sintering atmospheres. The incorporation of actinides into zirconate pyrochlore is generally achieved via several methods, such as the solid-state (SS) method, MS method, sol–gel method, co-precipitation method, and gel-combustion method. Each method has its own advantages and shortcomings. For example, the conventional SS method normally requires sintering at temperatures above 1400 °C for more than 48 h to obtain pure pyrochlore phase, due to slow diffusion of the reacting constituents. Synthesis in the liquid phase or wet chemical conditions often requires environmentally unfriendly organic/inorganic precursors and solvents, such as chelating agents, and nitrates. Chemical synthesis methods of the materials play a vital role in adjusting the structure, size and phases and reducing the cost for industrial applications. Molten salts are promising synthesis media, because of their meritous features, including environmental friendliness, low cost, being simple to operate, being easy to scale-up, etc. Previous works have reported the synthesis of pure A\(_2\)B\(_2\)O\(_7\) phase by the MS method, suggesting that the MS method is feasible. Recently, we reported that uranium can precisely occupy the Nd or Zr sites to form Nd\(_{2-x}\)U\(_x\)Zr\(_2\)O\(_7\)\(_{1+}\) (0 ≤ x ≤ 0.2) and Nd\(_{2}\)Zr\(_{2-x}\)U\(_x\)O\(_7\)\(_{1+}\) (0 ≤ y ≤ 0.4) nanoparticles. Here, we performed a systematic study of uranium accommodation in La\(_2\)Zr\(_2\)O\(_7\) pyrochlore oxides via the MS method and achieved 100% substitution for the Zr site.

The synthesis of U-incorporated La\(_2\)Zr\(_2\)O\(_7\) via the MS method is illustrated in Scheme S1 (ESI†). For comparison, we also synthesized the samples by the SS method with a calcination temperature of 1440 °C for 48 h. First, we compared the phase structure of undoped La\(_2\)Zr\(_2\)O\(_7\) via the MS and SS method using conventional XRD (Fig. S1a, ESI†), synchrotron XRD (Fig. S2, ESI†),
and Raman spectra (Fig. S1b, ESI†), supporting a typical pyrochlore structure (space group: Fd3m) in La2Zr2O7 host.

Next, we began to evaluate the solubility of uranium in La2Zr2O7. Two series of U-doped La2Zr2O7 oxides were prepared via the MS and SS method, targeting substitution on either the A-site forming La2-xUxZr2O7+y or B-site forming La2Zr2-xUxO7+y. As it is shown by XRD (Fig. S2c and S3, ESI†), for the series of U-doped La2Zr2O7-SS compounds, the pure pyrochlore phase persisted to \( x \approx 0.1 \), while \( x \approx 0.2 \) resulted in the formation of the second phase, such as ZrO2 in the A-site-doped samples or \( \text{La}_0.8\text{La}_{0.2}\text{LaO}_4 \) impurities in the B-site-doped samples. In contrast, in the La2-xUxZr2O7+y MS samples, the second phases of ZrO2 and UO3 appear only when the U content rises to \( x \approx 0.6 \), while in the La2Zr2-xUxO7+y MS samples, no impurity peaks can be detected even when all B-site atoms are replaced by U atoms, reflecting that there is relatively higher U accommodation in the MS method. In addition, we clearly observed an opposite trend of the shift of diffraction lines shown in the right panel of Fig. 1a and b. In the La2-xUxZr2O7+y-MS samples, the diffraction peaks slightly shift towards higher 2\( \theta \) angles, whereas they shift towards lower 2\( \theta \) angles in the La2Zr2-xUxO7+y-MS samples with increasing uranium content. A systematic shift in the peak position indicates a change in lattice parameters. Because the radius of the uranium ion is between those of La3+ (1.16 \( \text{Å} \), 8-fold coordination) and Zr4+ (0.72 \( \text{Å} \), 6-fold coordination) ions, the shrinkage or expansion of the lattice parameter is easy to understand when substituting \( \text{La}^{3+} \) or \( \text{Zr}^{4+} \) sites with uranium ions. In contrast, the shifts in the peak positions in the spectra of the U-doped La2Zr2O7-MS compounds, the pure pyrochlore phase persisted to \( x \approx 0.1 \), while \( x \approx 0.2 \) resulted in the formation of the fluorite phase. The new broad peak in the XRD patterns for the series of U-doped La2Zr2O7-SS compounds, the pure pyrochlore phase persisted to \( x \approx 0.1 \), while \( x \approx 0.2 \) resulted in the formation of the fluorite phase. The new broad peak in the XRD patterns for the U-doped La2Zr2O7-MS samples, only a single broad Raman active mode in the range of 200–600 cm\(^{-1}\) can be observed (Fig. 2b), supporting the formation of the fluorite phase. The new broad peak in the region of 650–800 cm\(^{-1}\) in the U-doped La2Zr2O7 samples is typical of highly disordered pyrochlore phases, and has been extensively reported in the literature\(^{15}\) on other pyrochlore materials disordered by high temperatures, pressures, and irradiation. In addition, the \( \text{U}^{6+} \) structure with \( \text{UO}_6 \) octahedral species may also contribute to this mode according to previous works.\(^{16}\) Combining XRD and Raman results, we can safely conclude that the MS method is firmly conducive to the higher accommodation of uranium in the La2Zr2O7 pyrochlore phase, and most importantly, can accurately control the substitution position of the matrix.

X-Ray absorption spectra were used to investigate the local and electronic structure information around specific elements.\(^{17}\) First, the valence states of uranium ions in U-doped La2Zr2O7-MS samples are determined by the conventional U-M4 edge X-ray absorption near-edge structure (XANES) spectra (Fig. 2c), in which the energy position of all U-doped samples is the same as that of \( \text{UO}_3 \), indicating a \( \text{U}^{6+} \) oxidation state. In addition, uranium speciation can be evaluated through the comparisons of U-L3 XANES spectra for the U-doped La2Zr2O7 samples and other U-related references including \( \text{UO}_4^{2-} \), \( \text{UO}_2^{2+} \) and \( \text{UO}_3 \) (Fig. S7b, ESI†). The U-L3 white line
is very sensitive to the local coordination chemistry of the absorbing atom. The significant spectral differences between our samples and these references in Fig. S7b (ESI†) rules out the existence of uranium in the form of \(\text{UO}_3^{2-}\), \(\text{UO}_2^{2-}\) and \(\text{UO}_2^+\), indicating that the possible species form is \(\text{UO}_3^{2-}\) in both A-site and B-site doped \(\text{La}_2\text{Zr}_2\text{O}_7\) samples. Hexavalent uranium has an ionic radius of 0.73 Å and 0.86 Å in 6- and 8-fold coordination, respectively; these radii are comparable to that of \(\text{Zr}^{4+}\) (0.72 Å) but significantly smaller than that of \(\text{La}^{3+}\) (1.16 Å). Besides, due to the charge balance, \(\text{U}^{6+}\) doping at the \(\text{La}^{3+}\) sites is much more difficult. Thus, the A-site doped compound is prone to form the second phase at high U contents, which is consistent with the above XRD results. Due to the large lifetime broadening in conventional M\(_4\)-edge XANES, no obvious pattern differences can be observed between \(\text{La}_{2-x}\text{U}_x\text{Zr}_2\text{O}_{7-x}\) and \(\text{La}_2\text{Zr}_{1.9}\text{U}_{0.1}\text{O}_{7.8}\) compounds.

Experimental resolution can be improved by high energy resolution fluorescence detection (HERFD) XANES. Fig. 2d shows the U-M\(_4\) edge HERFD-XANES data of selected \(\text{La}_{1.9}\text{U}_{0.1}\text{Zr}_2\text{O}_{7+x}\) and \(\text{La}_2\text{Zr}_{1.9}\text{U}_{0.1}\text{O}_{7.8}\) samples synthesized by the MS method. The high-valent \(\text{U}^{6+}\) state mainly exists among all the synthesized samples, but significant differences were observed in A-site and B-site doped samples synthesized by the MS method for the first time using HERFD-XANES, whereas the spectral patterns are almost the same in corresponding samples synthesized by the SS method (Fig. S8, ESI†). It is worth noting that compared to the B-sites, which have octahedral \(\text{UO}_6\) geometry, the ideal A site has a pentagonal bipyramidal \(\text{UO}_7\) geometry; this discrepancy indicates a much higher local symmetry of \(\text{U}\) cations in the B-site doped samples. Fig. 2d shows that with increasing symmetry, the high-energy shoulder peak decreases until it disappears in \(\text{La}_2\text{U}_{1.57}\text{Zr}_{0.43}\text{O}_{7+x}\). In addition, a weak high-energy peak (marked by S) originating from the covalency between \(\text{U}^{6+}\) and \(\text{O}\) was observed among all U-doped samples, confirming the presence of a \(\text{U}^{6+}\) oxidation state. To probe the possible bonding between uranium and the oxygen ligand in the U-doped \(\text{La}_2\text{Zr}_2\text{O}_7\), we performed extended X-ray absorption fine structure (EXAFS) analysis at the U M\(_4\) edge using both Fourier transform (FT) and wavelet transform (WT) analyses. The WT-EXAFS analysis can provide the correlated structural information from both the space and \(k\)-space (Fig. 2e). The intensity maximum is well resolved for the \(\text{La}_{2-x}\text{U}_x\text{Zr}_2\text{O}_{7+x}\)-MS (\(\sim 6.5 \text{ Å}^{-1}\)) and \(\text{La}_2\text{Zr}_{2-x}\text{U}_x\text{O}_{7+x}\)-MS (\(\sim 5.8 \text{ Å}^{-1}\)) samples, arising from their differences in U-O bond lengths (Fig. S9b, ESI†). With increasing U doping, the structural disorder increases continuously. In particular, in extreme cases when all Zr atoms are replaced by uranium atoms, that is, \(\text{La}_2\text{U}_{1.57}\text{Zr}_{0.43}\text{O}_{7+x}\), the local structure displays significant changes both in the \(k^2\)-weighted \(\chi(k)\) and FT signals (Fig. S9, ESI†), as well as WT-contour plots (Fig. 2e), supporting the phase transformation in the \(\text{La}_2\text{U}_{1.57}\text{Zr}_{0.43}\text{O}_{7+x}\) compound, although no uranium- or lanthanum-derived oxides are evident from the XRD analysis. Zr-K XANES and EXAFS analysis (Fig. S10, ESI†) reveals that the local structure around the Zr atom remains unchanged with U doping.

To evaluate the relative stability of the possible U substitution in pristine \(\text{La}_2\text{Zr}_2\text{O}_7\), we calculated the defect formation energies \((\varepsilon_d)\) for U substitutional La sites (\(\text{ULa}^\text{3+}\)) and Zr sites (\(\text{UZr}^\text{3+}\)), as shown in Fig. 3. According to the experiment, U-doped \(\text{La}_2\text{Zr}_2\text{O}_7\) is prepared by replacing \(\text{La}^{3+}\) with \(\text{U}^{6+}\) or \(\text{U}^{4+}\), which suggests that \(\text{U}^{6+}\) is the only high-valent state in the U-compounds. The Fermi energy \((\varepsilon_F)\) range corresponds to the calculated fundamental band gap of pristine \(\text{La}_2\text{Zr}_2\text{O}_7\). The slope of the lines represents the charge state of the doping ions.
most stable and has the lowest \( E_d \) when the \( E_p \) is above 2.28 eV, suggesting that \( U_{\text{La}}^{3+} \) tends to combine with \( O_{\text{La}}^{2-} \) to form defective pairs with increasing \( U \) doping concentration. In Fig. 3b, \( U_{\text{La}}^{2+} + O_{\text{La}}^{-} \) is most stable at \( E_p \) above 1.38 eV, implying that the introduction of \( O \) can significantly reduce the formation energy of the whole system when doping with high \( U \) contents. Considering that the MS method is conducive to supplying oxygen due to its faster mass transport ability, it is easier to synthesize pure pyrochlore samples with high \( U \) content using the MS method, as theoretically predicted. Moreover, to investigate the possibility of fluorite phase formation, we also calculated the \( E_d \) of anti-site defects (\( \text{La}_{\text{La}}^{3+} + \text{Zr}_{\text{La}}^{3+} \)) and constructed a \( \text{La}_{\text{La}}^{3+} + \text{Zr}_{\text{La}}^{3+} + U_{\text{La}}^{2+} + O_{\text{La}}^{-} \) defect cluster. As shown in Fig. 3b, the \( E_d \) of \( \text{La}_{\text{La}}^{3+} + \text{Zr}_{\text{La}}^{3+} + U_{\text{La}}^{2+} + O_{\text{La}}^{-} \) was 0.35 eV lower than that of \( U_{\text{La}}^{2+} + O_{\text{La}}^{-} \), indicating that the fluorite phase is more likely to exist when high concentration \( U \) is doped. This conclusion is consistent with the experimental result that fluorite \( \text{La}_{\text{La}}\text{U}_{\text{La}}\text{O}_{\text{La}}7 \) is finally formed.

In summary, we systematically studied the uranium solubility, species, valence state and defects in \( \text{La}_{\text{La}}\text{Zr}_{\text{La}}\text{O}_{\text{La}}7 \) pyrochlore synthesized by the MS method. Compared to the SS method, the MS method is of prime significance for the ultrahigh loading capacity of uranium ions and of precisely controlling the \( U \) substitution into \( \text{La} \) or \( \text{Zr} \) sites in \( \text{La}_{\text{La}}\text{Zr}_{\text{La}}\text{O}_{\text{La}}7 \). This work will guide the construction of site-controlled and high-capacity actinide-immobilized pyrochlore materials and could be extended to other materials (Fig. S12, ESI†).

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Conflicts of interest
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