Host-Guest Prospects of Neodymium and Gadolinium Ultraphosphate Frameworks for Nuclear Waste Storage: Multi-Temperature Topological Analysis of Nanoporous Cages in RP₅O₁₄

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ABSTRACT

Rare-earth ultraphosphate (RP₅O₁₄) framework materials are potential host media for nuclear waste storage, since cages within their nanoporous structures have volumes that match well those of prospective guests such as uranium or plutonium ions. Good volume matches of host cages and guest compounds are nonetheless not the only structural requirement for ensuring viable nuclear waste storage. Host structures also need to be stable enough to withstand the typical environmental conditions of long-term storage of spent nuclear fuel. To this end, the nanoporous cage topologies of neodymium and gadolinium ultraphosphate, NdP₅O₁₄ and GdP₅O₁₄, are investigated as a function of temperature. Topological analysis shows that, while both compounds are essentially isostructural, thus displaying the same type of cage structures, the cage volumes of NdP_5O_{14} are significantly larger than those of GdP_5O_{14} , with one stark exception. This exception concerns the smallest cage of NdP₅O₁₄, whose 8/4 topology lacks structural cross-linking that would otherwise give it much more strength. This 'squashed' cage appears to owe its origins to the specific nature of crystallographic twinning in NdP₅O₁₄, which causes strain that needs alleviating; squashing the 8/4 cage in NdP₅O₁₄ would be the most susceptible option towards this end, since its cage manifests the weakest structural construct. GdP_5O_{14} succumbs to a gradual contraction of its 8/4 cage only with increasing temperature above 300 K; this is well below its second-order monoclinic-toorthorhombic phase transition at 420-430 K; which is 420 K for NdP₅O₁₄. Fortunately, the volumes of heavy metal ions that arise from spent nuclear fuels do not match the size requirements of cages with 8/4 topology in RP₅O₁₄ hosts needed for encapsulation; otherwise, radiation leakage of such containment would present a risk. Both NdP_5O_{14} and GdP₅O₁₄ would therefore seem to offer good prospects as host media for nuclear waste storage.

KEYWORDS

Rare-earth ultraphosphate; nuclear waste storage; temperature-dependent nanoporous cage topology; crystallographic twinning

1. INTRODUCTION

Nuclear waste containment is an important field of environmental science given the desperate need to find cleaner, safer, and more sustainable ways to store spent nuclear fuel. Host-guest media is one possible option whereby crystalline materials that contain nanoporous framework structures act as hosts for encapsulating radioactive ions and oxides from nuclear waste streams [1]. Rare-earth ultraphosphates were recently identified as possible host media for nuclear waste storage, in a screening study of a wide range of nanoporous framework materials [2]. The screening study determined the volumes of empty cages in 628 phosphate framework structures, to pinpoint potential host materials that could encapsulate environmentally important guests with similar volumes, such as UO_2 and PuO_2 . Cage volume alone is nonetheless not a sufficient criterion to fully assess the prospects of host media for nuclear waste storage applications. This predictive type of materials screening process accordingly needs to be supplemented by detailed experimental studies on host media that have been short-listed by this materials discovery workflow. In particular, the stability of the cages that are prospected for guest encapsulation needs to be assessed as does any structural characteristic that may perturb the host framework structure in a way that risks the leaching of nuclear waste.

To this end, we herein investigate the topological stability of all cage structures in two rareearth ultraphosphates, neodymium and gadolinium ultraphosphate, NdP₅O₁₄ and GdP₅O₁₄. This includes a temperature-dependent profiling of these cages in the range T = 120 - 480 K, given that rare-earth ultraphosphate crystal structures, RP₅O₁₄ (R = lanthanide), are well known to undergo monoclinic-to-orthorhombic second-order phase transitions with transition temperatures rising with increasing lanthanide atomic number, from approximately 390 K (LaP₅O₁₄) to 447 K (TbP₅O₁₄) [3-7]. This temperature range naturally contains the typical environmental conditions of nuclear waste storage.

Understanding how the cage structures within RP_5O_{14} frameworks may be perturbed as a consequence of the overarching structural transition of the material is thus crucial for ensuring safety from disastrous incidents such as radiation leakage.

Reports of specific transition temperatures can vary widely owing to differences in factors such as crystal fabrication, or the experimental analysis probe used (e.g. X-ray diffraction, neutron diffraction, or optical assessment) [8]. The well-documented ferroelasticity of RP_5O_{14} below the Curie temperature demonstrates an additional complication [3-5,9,10], particularly in NdP₅O₁₄, where twin boundaries may be introduced, or moved, by applying surprisingly low amounts of localized pressure (14 ± 3 kNm⁻²) [3,5]. Above the Curie temperature, RP_5O_{14} crystals become paraelastic [4,9]. The tendency of NdP₅O₁₄ toward twinning in the ferroelastic phase has been extensively investigated, and it has been shown that the natural twin boundaries are of two orientations. The more commonly found a twin corresponds to a change in the crystallographic *c*-axis, while the higher-energy *b*-type twin displays changes in the crystallographic *a*-axis [3,10]. Even though GdP₅O₁₄ also exhibits a ferroelastic twin boundary on the (100)-plane [9], studies on this compound remain sparse. Accordingly, the effect of crystallographic twinning on the cage structures of these two subject compounds is studied in detail, using single-crystal X-ray diffraction, with particular attention being directed at the pseudo-merihedral twinning below the transition temperature.

2. MATERIALS AND METHODS

2.1 Data collection

High quality single crystals of NdP_5O_{14} and GdP_5O_{14} were grown according to the procedure reported by Danielmeyer and co-workers [11]. In each instance, a suitable single crystal was mounted onto a nylon fibre using an epoxy resin. Samples were placed onto a Rigaku Saturn 724+ CCD single-crystal X-ray diffractometer and probed from 120 K to 480 K using an Oxford Cryosystems CryostreamPlus N₂ cooling device. A full dataset suitable for crystal structure determination was collected for each compound at 5 K or 10 K heating intervals. The samples were held at each new temperature for a minimum of 15 minutes. The GdP_5O_{14} sample was also subsequently cooled within the same temperature range using 5 K or 10 K increments, whereupon data collections were acquired to investigate potential hysteresis effects. All data were acquired assuming the lowest possible (either monoclinic or triclinic) crystal symmetry so as to ensure that sufficient data were collected at all temperatures. Cell refinement, data collection, and data reduction were carried out using the Rigaku CrystalClear-SM Expert 2.0 software [12]. The absorption correction was implemented using ABSCOR [13]. All structures were solved using direct methods and refined by full-matrix least-squares methods on F2 using SHELXL-97 [14]. Structures at all temperatures were solved with monoclinic symmetry; higher-temperature structures (≥ 340 K) were also solved with orthorhombic symmetry. Thus, the pattern of the twin fraction (BASF) through the transition could be followed through the monoclinic structural refinement. This dual refinement option also allowed pinpointing of the transition temperature by observing at which temperature the structure solutions changed from a preference for monoclinic to orthorhombic symmetry, as indicated by statistical figures-of-merit, such as the R1 factor, and the refined twinning fraction. A detailed summary of the crystal, data collection and crystal structure refinement details of NdP₅O₁₄ and Gd_P5O₁₄ at each temperature is given in the Crystallographic Information Files that comprise the Supporting Information.

2.2 Crystallochemical analysis

The crystallographic topological analysis program package TOPOS15 (version 4.0 Professional) was used to identify cages in the RP_5O_{14} structures and to determine the respective void spaces within. For a comprehensive crystallochemical analysis, TOPOS utilizes graph theory; void space analysis is accomplished via a two-step process: i) the determination of all cages found within each structure, prior to ii) calculating the void space volume within each cage using Voronoi-Dirichlet polyhedra (VDP). This procedure establishes a basis for the comparison of the cavity volumes in each structure. The workflow that used TOPOS to ascertain void space contained within individual cages of GdP₅O₁₄ and NdP₅O₁₄ is shown in Figure 1.



Figure 1. The process of determining void space volumes within cages, using TOPOS.

The framework structures of GdP_5O_{14} and NdP_5O_{14} contain tiles, defined as generalized polyhedra (cages), which contain at least two edges incident upon each vertex and two faces incident upon each edge [16,17]. Tiles are characterized by how many faces a given tile

possesses. Each face is defined by its *m*-membered rings, and the tiles are described by face symbols [M^m . N^n ...], which denominate *m* faces that are *M*-rings, and *n* faces that are *N*-rings [16]. The topological representation of nodes and tiles is illustrated in Figure 2 using the example of NdP₅O₁₄. Physically, tiles correspond to minimal cages within a net, from which larger tiles can be constructed by merging the faces of minimal cages, giving rise to maximal proper tiles. For the purposes of this study, 'cages' refer to maximal proper tiles. For an indepth discussion of cages and tiling, see Delgado-Friedrichs and O'Keeffe, and Blatov *et al.* [16,18]. In order to analyze the cavity size of individual cages within GdP₅O₁₄ and NdP₅O₁₄, cages were isolated, and void nodes were generated from the atoms forming the cages. Consequently, VDP were generated for these void nodes, and their volumes were calculated.



Figure 2. An example of a 16/8 cage using NdP₅O₁₄ defined as a [4⁴.7⁴] tile; 16/8 denominates the total number of nodes/faces; [4⁴.7⁴] indicates the presence of four faces consisting of 4-membered rings (e.g. pink plane), and four faces consisting of 7-membered rings (e.g. yellow plane). Reprinted with permission from ref. [2]. Copyright 2016 American Chemical Society.

3. RESULTS

Determination of cage structures in NdP_5O_{14} and GdP_5O_{14} below any phase transition.



The crystal structures of NdP₅O₁₄ and GdP₅O₁₄ at 140 K are shown in Figure 3.

Figure 3. Crystal structures of NdP₅O₁₄ (left), and GdP₅O₁₄ (right), as viewed looking down the (100) crystallographic axis.

A topological analysis of each crystal structure involved an initial determination of the maximal tiles, and an identification of void space volumes for each cage. Both structures exhibit five identified maximal proper tiles: $[4^4]$, $2[4^2.6^2]$, $[4^2.5^4]$, $[4^4.7^4]$, and $2[4^4.5^2.6^2.7^2]$. According to this notation, the first cage, $[4^4]$, consists of four faces that are type-4 rings (where a type *n*-ring has *n* edges). The second cage, $2[4^2.6^2]$, comprises two faces that are type-4 rings, and two faces that are type-6 rings; the '2' in front of the square brackets denominates the cage ratio, i.e., 1:2:1:1:2. Each cage is more easily described as a ratio of the total number of nodes/faces. This way, the maximal proper tiles are identified as 6/4, 8/4, 10/6, 16/8, and 18/10, with respect to the earlier definitions. The shape of each cage is shown in Figures 4-8 together with their cage volume variation as a function of temperature. All data are presented, while data were only fitted up to 440 K above which there is no longer a smooth trend since the materials have well exceeded their phase transition.



Figure 4. Distribution of the void space volumes within the 8/4 maximal proper tile (left); shape of the 8/4 cage (right).



Figure 5. Distribution of the void space volumes within the 8/4 maximal proper tile (left); shape of the 8/4 cage (right).



Figure 6. Distribution of the void space volumes within the 10/6 maximal proper tile (left); shape of the 10/6 cage (right).



Figure 7. Distribution of the void space volumes within the 16/8 maximal proper tile (left); shape of the 16/8 cage (right).



Figure 8. Distribution of the void space volumes within the 6/4 maximal proper tile (left); shape of the 6/4 cage (right).

Trends between cage shape and volume for each compound were first considered using the 120 K data, i.e. before contemplating any possible perturbations from temperaturedependent effects. For all cages, except for the 8/4 cage, NdP₅O₁₄ produces void space volumes that are ~1-3 Å³ larger than those of their GdP₅O₁₄ counterparts. This general trend toward larger cages in NdP₅O₁₄ is perhaps not surprising, as the rare-earth ion coordinates to oxygens, and R…O bond lengths in rare-earth ultraphosphate crystal structures [19-24] are slightly longer for Nd…O (2.44 Å), than for Gd…O (2.41 Å).

The exceptional 8/4 cage is ~0.5 Å³ smaller in NdP₅O₁₄ than that in GdP₅O₁₄ (Figure 4). This anomaly in the 8/4 cage void volume of NdP₅O₁₄ is intriguing. From an 'engineering'

perspective, the 6/4, 10/6, 16/8, and 18/10 cages are relatively sturdy, given the good number of supports to hold their framework, while the 8/4 cage is defined by two diamond-shaped 'caps' supported by only two 'columns' (Figure 4, right). In addition, there are no additional nearby physical supports from the framework surrounding the 8/4 cage within the structure, that would otherwise help to stabilize these 'weaker' edges. Since it is the only type of cage that is even smaller than that of its GdP_5O_{14} counterpart, it would seem that the 8/4 cage in NdP_5O_{14} may be 'squashed' by some means, owing to its structural weakness relative to all other cages. The observation that the 8/4 cage in GdP_5O_{14} is not similarly squashed, at least by the same extent, is especially curious, given the structures of NdP_5O_{14} and GdP_5O_{14} are essentially isomorphous.

4. DISCUSSION

4.1 Rationalizing the 'squashed' nature of the 8/4 cage in NdP₅O₁₄ by comparing twinning effects in NdP₅O₁₄ and GdP₅O₁₄.

The positioning of the 8/4 cage within the structure is pertinent, since its 'weak' edge is located at an angle between the crystallographic *b*- and *c*-axes. Given that the predominant twinning within NdP_5O_{14} crystals is found as a reversal of the c-axis, this consequently puts strain on this cage in such a way as to potentially shorten that particular edge (see Figure 9).



Figure 9. Twinning via a reversal of the c-axis in NdP₅O₁₄. The 8/4 cage is highlighted by the yellow wire frame, showing its position within the cage network. The black arrows show the expected direction of strain, arising from this type of twinning.

While GdP_5O_{14} manifests the same type and extent of crystallographic twinning seen in NdP_5O_{14} , its 8/4 cage is does not appear to be 'squashed' in the same way. Moreover, there is no report of any mechanical way to induce twinning in GdP_5O_{14} , in stark contrast to NdP_5O_{14} where twin boundaries may be introduced or removed by applying very low levels of local stress to the crystal; for example, by stroking the crystal with a needle [3,5]. The low threshold to strain forming in crystallographic twins of NdP_5O_{14} is presumably the cause of the

'squashed' 8/4 cage, in contrast to the case of GdP_5O_{14} whose 8/4 cage is not similarly squashed and there is no evidence of crystallographic strain. This contrast is presumably a result of the relative strengths of the material frameworks. GdP_5O_{14} will form a stronger crystal structure than NdP_5O_{14} , since the smaller ionic radius of Gd^{3+} compared to Nd^{3+} affords shorter (stronger) $Gd\cdots O$ than $Nd\cdots O$ coordination bonds, while the electronegativity of gadolinium is also higher than that of neodymium.

4.2 Phase transitions in NdP₅O₁₄ and GdP₅O₁₄.

Temperature stability is naturally a key material attribute of a prospective host medium for nuclear waste containment. Since RP_5O_{14} compounds are known to undergo monoclinic-to-orthorhombic second-order phase transitions, it seemed pertinent to track these structural changes as a function of temperature, including the concurrent modulation in the cage volumes of these materials. Moreover, the origin of these phase transitions lies in a variation in crystallographic twinning, whereby the monoclinic angle tends to 90°, whereupon the structure transitions to a non-twinned one with orthorhombic crystal symmetry. Since crystallographic twinning in NdP₅O₁₄ below the transition temperature appears to be the cause of the 'squashed' 8/4 cage through local strain effects, a study that shows how these cage volumes evolve through these phase transitions could also provide additional insights into the anomalous behavior of the 8/4 cage in NdP₅O₁₄.

4.2.1 Temperature characteristics of the phase transition.

Previous studies have indicated that the monoclinic-to-orthorhombic transition in RP_5O_{14} is second order, being gradual at first, but becoming quite pronounced nearer to the transition temperature. The generally accepted transition temperature of NdP_5O_{14} is ~ 420 K, while that of GdP_5O_{14} is ~445 K [4-6,10,25]. The results for NdP_5O_{14} from our study agree well with those previous reports, as evidenced by the rise in twinning fraction as a function of temperature (Figure 10).

However, the results of our study suggest that the transition for GdP_5O_{14} occurs at 420-430 K, rather than at the previously reported 440-450 K. In particular, the twin fraction in the monoclinic structural model suddenly increases from approximately 25% at 420 K to approximately 48% at 430 K (Figure 10), whereupon β tends to 90° at the phase transition. This result is corroborated by the trend observed in the R1 factor for the orthorhombic crystal structure model of GdP_5O_{14} which surpasses that of the monoclinic model at 420 K and is maintained at 430 K and beyond (see Supporting Information).

Further corroboration that the GdP₅O₁₄ transition temperature is indeed in the 420-430 K range arises from the evaluation of the extinction coefficient of the crystal, as modeled in the monoclinic structural refinements over the full temperature range. From 120-270 K, the extinction coefficient, EXTI, defined according to Sheldrick [14], steadily rises (EXTI = 0.003-0.016), after which it plateaus at ~0.016; at 420 K, it sharply decreases, reaching 0.009 at 430 K, before rising again to ~0.015 by 450 K. Such a temperature-specific drop of the extinction coefficient is indicative of a temporary decrease in crystal quality, which is required for a change of the phase of the crystal structure at this temperature.

Some hysteresis effects in the twinning of the GdP_5O_{14} crystal were observed upon cooling, reflected in the slightly higher twin fraction observed after returning to low temperatures. As

the temperature increases from 120 K to 310 K, the twin fraction averages ~5%. However, after transitioning to orthorhombic symmetry and subsequently transitioning back to monoclinic symmetry, the approximate average for the twin fraction as the temperature decreases from 310 K to 120 K is ~7%. Unit cell parameters exhibit little or no change, suggesting that any hysteresis is restricted to the twinning fraction. Hysteresis effects for the NdP₅O₁₄ sample were not explored, owing to a weakening of the crystal mount at high temperatures, which rendered the sample unusable after data collection at 480 K.



Figure 10. Twinning fractions for NdP₅O₁₄, and GdP₅O₁₄ as a function of temperature, determined from crystal structure refinements of exclusively monoclinic solutions over the full temperature range. Twinning fractions above the transition temperature are therefore artificial since the orthorhombic crystal structures are not twinned, but these artificial values serve as a sensitive parameter by which the phase transition can be tracked.

4.2.2 Evolution of cage volumes through the phase transitions.

Comparing temperature-dependent modulations in cage volume between the NdP₅O₁₄ and the GdP₅O₁₄ sample, some notable similarities, and distinct differences become evident. Intuitively, one would expect a fairly steady increase in void space volumes with increasing temperature until the phase transition becomes incipient. This expectation is certainly observed experimentally for the all cages except for 8/4 (Figure 4). The rates of thermal expansion for NdP₅O₁₄ and GdP₅O₁₄ are quite different. Very little thermal expansion is observed in the 10/6 (Figure 6), 16/8 (Figure 7), and 6/4 cages (Figure 8) of NdP₅O₁₄, over the full temperature range studied. Meanwhile, cage volumes of GdP₅O₁₄ increase marginally up to ~250 K, beyond which they show greater thermal expansion, with a high degree of fluctuation in view of the incipient phase transition whereby β starts to approach 90°.

Regarding the 8/4 cage, its thermal expansion in NdP₅O₁₄ seems to increase essentially monotonically until about 400 K. In contrast, the 8/4 cage in GdP_5O_{14} appears to start contracting with increasing temperature beyond about 300 K until it approaches the phase transition, whereupon its volume fluctuates substantially; its original volume is recovered upon lowering the temperature back below 300 K but only via a significant level of thermal hysteresis (Figure 4). This level of thermal contraction in GdP5O14 is such that it tends towards the volume of its 'squashed' NdP₅O₁₄ analogue in the region 350-450 K. While it was discussed above that the stronger nature of the GdP₅O₁₄ lattice may allow it to resist the squashed nature of its NdP₅O₁₄ counterpart at low temperatures, these anomalous thermal effects observed above room temperature may suggest that it cannot overcome them at elevated temperatures. This thermal instability suggests a limit to its use in nuclear waste storage, should this result in radiation leakage of an encapsulated ion from this particular cage in GdP₅O₁₄. Meanwhile, the squashed nature of the 8/4 cage in NdP₅O₁₄ indicates that containment of nuclear waste material within the 8/4 cage of RP₅O₁₄ framework materials would be inadvisable. Fortunately, in the aforementioned recent screening study of volumes of empty cages in 628 phosphate framework structures to pinpoint potential hosts for encapsulating guest materials such as the nuclear waste, no 8-nodal cages in any of these possible phosphate structures were of the right size to accommodate uranium, plutonium or caesium ions as guests. It would therefore appear that encapsulation of spent nuclear waste within 8/4 cages of phosphate frameworks is unlikely in any case.

Notwithstanding this structural anomaly in the 8/4 cage, GdP_5O_{14} and NdP_5O_{14} framework materials would seem pretty rigid over a wide temperature range, including the elevated temperatures that are associated with spent fuels that are cooling within nuclear waste streams. They would therefore seem able to encapsulate nuclear waste materials without leakage.

5. CONCLUSIONS

NdP₅O₁₄ and GdP₅O₁₄ have been assessed for their prospects as host media to encapsulate guests, such as UO_2 or PuO_2 , for nuclear waste containment. To this end, the crystal structures of these nanoporous host frameworks were determined, whereupon the topological characteristics of each type of nanoporous cage was classified, and the associated cage volume was calculated. One of these void spaces, classified as an 8/4 cage, appears to be 'squashed' within the structure of NdP₅O₁₄ but curiously not in GdP₅O₁₄ at low temperatures, even though the two compounds are otherwise isostructural. Nonetheless, the 8/4 cage in GdP₅O₁₄ was found to contract at elevated temperatures, seemingly overcoming the stronger nature of the GdP₅O₁₄ lattice, compared with that of NdP₅O₁₄, that presumably withstands contraction forces at low temperatures. A topological analysis revealed that the 8/4 cage is much weaker than the other types of cages in RP₅O₁₄ frameworks, because its structural scaffold contains few cross-links that would otherwise give it more strength. Crystallographic twinning in NdP₅O₁₄, which exposes this 8/4 cage to local strain, also makes its weak character particularly susceptible to local strain effects, to an extent that twinning in NdP₅O₁₄ can be induced by a small mechanical force, such as a crystal of NdP₅O₁₄ being stroked by a needle [3,5]. Multi-temperature single-crystal X-ray diffraction studies of GdP_5O_{14} and NdP_5O_{14} (T = 120-480 K) showed how the strength of the 8/4 cage in GdP₅O₁₄ starts to falter above 300 K,

leading to thermal contraction with increasing temperature such that it tends toward the volume of the 8/4 cage in NdP₅O₁₄ at elevated temperatures. The other types of cages in these RP₅O₁₄ structures exhibited fairly regular behavior in thermal expansion, until the temperature approached the monoclinic-to-orthorhombic second-order phase transitions of NdP₅O₁₄, and GdP₅O₁₄, identified at T ~ 420 K, and 420-430 K, respectively. The multi-temperature studies also enabled the thermal stability of these host frameworks to be assessed in terms of their applicability to the environmental conditions that are typical in processing and storing nuclear waste. Both NdP₅O₁₄ and GdP₅O₁₄ compounds appear to present good prospects as host media for nuclear waste containment pending that the 8/4 cage is not involved in guest encapsulation.

Although it is beyond the remit of this study, further investigations into the suitability of rareearth ultraphosphates for the purposes of nuclear waste storage will also need to take several other factors into account. In particular, physical and chemical considerations from daughter products resulting from continued radioactive decay must be investigated, as well as the effects of extensive radiation exposure on the stability of the host structure, including dose, type of radiation, and decay energies. These additional factors are not trivial, requiring considerable testing and thought, given that the composition of the anticipated radionuclides to be included in the host phosphate material will most likely vary significantly from waste stream to waste stream [1].

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7. SUPPORTING INFORMATION

Supporting Information available: Crystallographic Information Files (CIFs) for NdP₅O₁₄ and GdP₅O₁₄ as a function of temperature (T = 120-480 K) showing both monoclinic and orthorhombic crystal structure refinements in the region of the second-order monoclinic-to-orthorhombic phase transition. CIFs for GdP₅O₁₄ are given for studies on increasing and decreasing temperature, demonstrating its thermal hysteresis above T = 300 K.

8. CONFLICTS OF INTEREST

The authors declare the absence of any potentially competing financial interests.

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GRAPHICAL ABSTRACT

HIGHLIGHTS

- The temperature-dependent cage topologies of RP₅O₁₄ (R = Nd or Gd) were examined
- A topological analysis revealed similar cage structure for RP₅O₁₄ (R = Nd or Gd)
- One exception: the 8/4 cage topology of NdP₅O₁₄ lacks structural cross-linking
- Volume (UO₂ or PuO₂) \gg 8/4 topology in RP₅O₁₄ (R = Nd or Gd)
- RP₅O₁₄ (R = Nd or Gd) are good prospective host media for nuclear waste storage