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Thermal expansion and solubility limits of plutonium-doped lanthanum zirconates

Satoshi Yamazaki [a], Toshiyuki Yamashita [b], Tsuneo Matsui [a,*], Takanori Nagasaki [a]

[a] *Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

[b] *Department of Material Science, Japan Atomic Energy, Research Institute, Tokai, Ibaraki 319-1195, Japan*

Abstract

Plutonium-doped and undoped lanthanum zirconates were prepared by solid state reaction. The solubility limit of Pu in $La_2Zr_2O_7$ was studied by X-ray diffraction, and the solubility limits of Pu in pyrochlore-type phase prepared in air, vacuum and Ar–8%H_2 atmospheres were determined to be 10, 35 and 100 mol%, respectively. The compound with 80 mol% Pu prepared in air and the compounds with 80 and 100 mol% Pu prepared in vacuum showed single fluorite-type phases. Thermal expansion coefficients of $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$ ($x = 0$, 0.05, 0.10 and 0.80) were also measured by high-temperature X-ray diffraction at temperatures between room temperature and 1273 K in air and He–8%H_2 atmospheres and were found to increase with increasing Pu content. The dependence of the linear thermal expansion coefficients on Pu content is discussed from the point of view of the radii of both tetravalent Pu in air and trivalent Pu in He–8%H_2.

1. Introduction

Ceramic waste forms that are natural mineral analogues are promising candidates for the disposal of high-level nuclear waste (HLW), especially for long half-life transuranium (TRU) elements, because of their thermodynamic stability for long time. Lanthanum zirconate $La_2Zr_2O_7$ with a pyrochlore structure, which is similar to a fluorite structure with twice the lattice parameter [1], is one of the important host phases with wide solubility of simulated constituents of TRU elements and good durability in water [2]. The relationship between the leaching rate and the local crystal structure of $(La_{1-x}Ln_x)_2Zr_2O_{7+y}$ (Ln = Nd and Ce) has been studied [3]. Since plutonium, a long half-life TRU element, is thought to exist in HLW in some cases, it is important to understand the phase equilibrium and thermophysical properties of $La_2Zr_2O_7$ containing Pu. In this study, undoped and plutonium-doped lanthanum zirconates $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$ ($x = 0$–1.00) were prepared by solid state reaction in various environmental conditions, and the solubility limit of Pu in $La_2Zr_2O_7$ was determined by X-ray diffraction (XRD). Thermal expansions of $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$ ($x = 0$, 0.05, 0.10 and 0.80) were also measured by high-temperature XRD at temperatures between room temperature and 1273 K in air and He–8%H_2 atmospheres.

2. Experimental

2.1. Sample preparation

Powdered samples of $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$ ($x = 0$, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.40, 0.50, 0.60, 0.80 and 1.00) were prepared by heating pellets made of the mixtures or mixtures of La_2O_3, ZrO_2 and PuO_2 powders in proper ratios at 1773 K for 34 h in air, vacuum (3×10^{-5} Torr) and Ar–8%H_2 atmospheres and then pulverizing them with an agate mortar and a pestle. Heating and pulverizing processes were repeated several

* Corresponding author. Tel.: +81-52 789 4682; fax: +81-52 789 4691.

E-mail address: t-matsui@nucl.nagoya-u.ac.jp (T. Matsui).

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times. An additional heat treatment at 1973 K for 5 h in Ar–8%H_2 was carried out on the samples prepared in an Ar–8%H_2 atmosphere at 1773 K to reduce the plutonium valence in the samples.

2.2. X-ray diffraction

High temperature XRD study was done using a Rigaku RAD-3C diffractometer system with an attached furnace unit. Furnace temperature was controlled by a PID-type temperature controller unit to within ±1 K during the XRD measurements. Temperatures of samples, heated by the radiation from the furnace, were determined by the lattice parameter of the Pt sample holder and the thermal expansion data of platinum [4]. This determination procedure of the sample temperature has been used for the determination of the thermal expansions of several oxides such as Pu-doped $CaTiO_3$ [5] and $(U, Np)O_2$ [6]. The estimated error in temperature was ±10 K, most of which came from uncertainties in determination of the lattice parameter of platinum.

Each specimen was annealed first at 1273 K in air or in a He–8%H_2 atmosphere for 1 h in order to recover any lattice distortions in crystallites from self-irradiation damage. Then the furnace temperature was changed to the programmed temperature and kept at that temperature for 1 h before the XRD measurements were carried out. Although the samples had been prepared in Ar–8%H_2, He–8%H_2 gas was used for the XRD measurements to prevent argon from absorbing X-rays and thus keeping high X-ray intensities at high temperatures.

Lattice parameters were calculated from X-ray reflections employing the least-squares method for the Nelson–Riley extrapolation. The estimated standard errors of the calculated lattice parameters were less than ±0.0002 nm.

3. Results and discussion

3.1. Solubility limit

The lattice parameters of $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$ are shown in Fig. 1 as a function of Pu concentration. As seen in this figure, the lattice parameter of the pyrochlore phase heated in air decreases with Pu concentration up to 10 mol% ($x = 0.10$), and then becomes constant. This indicates that the solubility limit of Pu in the pyrochlore phase had been reached; further addition of Pu was absorbed by the growth (amount and Pu content) of the fluorite phase. Thus, the solubility limit of Pu was estimated to be 10 mol%. Since the oxidation state of Ce doped in $La_2Zr_2O_7$ prepared in air is tetravalent [3], Pu ions were inferred to be predominantly tetravalent-Pu^{4+} ions in the Pu-doped $La_2Zr_2O_7$ prepared in air. Then, the oxygen nonstoichiometry, y, in $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$

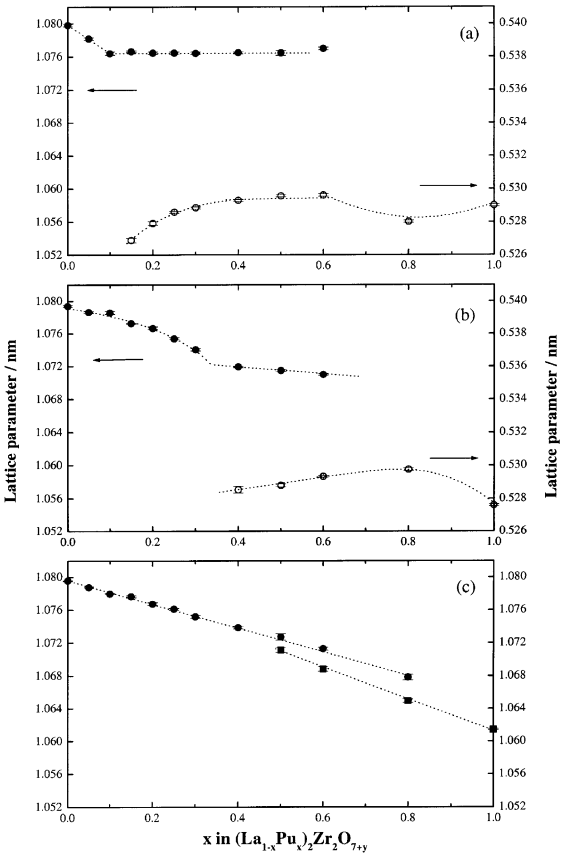

Fig. 1. Lattice parameters of the pyrochlore-type phase (closed symbols) and the fluorite-type phase (open symbols) of $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$ heated in air (a), vacuum (b) and Ar–8%H_2 (c).

can be estimated as $y = x$. When two Pu^{4+} ions are substituted for two La^{3+} sites in $La_2Zr_2O_7$, an O^{2-} ion should enter a vacancy site adjacent to Zr^{4+} ions in order to keep electrical neutrality. It was presumed that the lattice parameter of the pyrochlore phase increases by the introduction of the O^{2-} ion in a pyrochlore crystal structure [1]. On the other hand, the substitution of Pu^{4+} ions for the La^{3+} sites makes the lattice parameter shrink because the ionic radius of Pu^{4+} (0.096 nm, 8-coordinated [7]) is smaller than that of La^{3+} (0.116 nm, 8-coordinated [7]). Though these two effects work competitively in the same lattice, the lattice parameter of the pyrochlore phase decreases by the substitution of Pu as shown in Fig. 1(a), indicating that the effect of ionic radius is larger than that of interstitial O^{2-} ions. The XRD pattern of the sample doped with 80 mol% ($x = 0.80$) Pu heated in air showed a single fluorite phase, while that of the samples doped with 100 mol% ($x = 1.00$) showed a two-phase mixture of a fluorite-type phase and a tetragonal ZrO_2 solid solution.

The lattice parameter of the pyrochlore phase heated in vacuum (Fig. 1(b)) also decreased with Pu concentration up to about 35 mol% ($x = 0.35$), and then became almost constant, indicating that the solubility limit of Pu in the pyrochlore phase had been reached and that further Pu addition was associated with the formation of a fluorite phase. In vacuum, some of Pu^{4+} ions may be reduced to Pu^{3+} ions, which can substitute for La sites in $La_2Zr_2O_7$ without introducing interstitial O^{2-} ions, resulting in an increase of the solubility limit of Pu. A slight change of the lattice parameters in the two-phase region was seen in Fig. 1(b); this may have been caused by the differences in the relative amounts of Pu^{4+} and Pu^{3+} in these samples. Since this could not be confirmed, we could not verify the reason for the slight change of the lattice parameters in the two-phase region and also could not estimate the nonstoichiometry y in this case. The samples with Pu concentration 80 and 100 mol% ($x = 0.80$ and 1.00) heated in vacuum showed only a single fluorite phase.

The lattice parameter of the pyrochlore phase heated in Ar–8%H_2 decreases with increasing Pu concentration through the whole Pu concentration range, as shown in Fig. 1(c). The XRD patterns of samples with Pu concentration 0–40 and 100 mol% ($x = 0$–0.40 and 1.00) heated in Ar–8%H_2 showed a single pyrochlore-type phase. The lattice parameter of $Pu_2Zr_2O_{7+y}$ ($x = 1.00$) was confirmed to be 1.0614 nm. The samples with Pu concentration 50–80 mol% ($x = 0.50$–0.80) showed both the pyrochlore-type phase and the cubic-type one. Since the end members of this system heated in Ar–8%H_2 were both pyrochlores, the cubic-type phases observed in the samples were also thought to be pyrochlore-type phases, although the characteristic diffraction peaks of the pyrochlore structure were weak and the cubic-type phase could not be well confirmed as a pyrochlore-type phase. These pyrochlore phases were anticipated to be composed of a La-rich pyrochlore and a Pu-rich pyrochlore.

The oxidation state of Pu was determined by applying to $Pu_2Zr_2O_{7+y}$ the relationship between the lattice parameter and the oxidation state of Ce in $Ce_2Zr_2O_{7+y}$. The relationship between the lattice parameters and the radii of A-site ions in $A_2Zr_2O_7$ pyrozirconates is shown in Fig. 2. As seen in the figure, the lattice parameter of the stoichiometric $Pu_2Zr_2O_7$ pyrochlore was calculated to be 1.070 nm by interpolation of the radius, 0.112 nm, of Pu^{3+} ion with coordination number 8 given by Morss [8]. Then, the lattice parameter of the present $Pu_2Zr_2O_{7+y}$ was smaller than the calculated one for the stoichiometric $Pu_2Zr_2O_7$ by 0.0086 (1.070–1.0614) nm. Cerium zirconate, $Ce_2Zr_2O_{7+y}$ ($y = 0$–0.36), has a pyrochlore structure and its lattice parameter decreased with increasing oxygen content caused by the oxidation of Ce ions from trivalent to tetravalent [9]. When the lattice parameter of $Ce_2Zr_2O_{7+y}$ decreased by 0.0086 nm from that of $Ce_2Zr_2O_7$ ($y = 0$), the oxygen non-stoichiometry of $Ce_2Zr_2O_{7+y}$ was obtained to be about 0.22, corresponding to $CeO_{1.61}$–ZrO_2, from the literature [9]. Then, the oxidation state of $Pu_2Zr_2O_{7+y}$ heated in Ar–8%H_2 is inferred to be corresponding to $PuO_{1.61}$ and the nonstoichiometry can be determined to be about $y = x/4.5$.

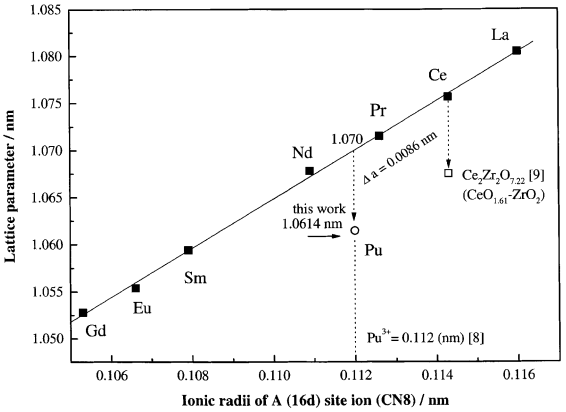

Fig. 2. Relationship between the lattice parameters [1] and the radii of A site ions with coordination number 8 in $A_2Zr_2O_7$ pyrozirconates.

3.2. Thermal expansion

The lattice parameters of $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$ ($x = 0$, 0.05, 0.10 and 0.80 in air, $x = 0$ and 0.10 in He–8%H_2) are plotted against temperature in Figs. 3(a) and (b). All lattice parameters are seen to increase smoothly with temperature up to about 1300 K, indicating that no phase transitions occur in this temperature range. The measured lattice parameters were fitted as a function of

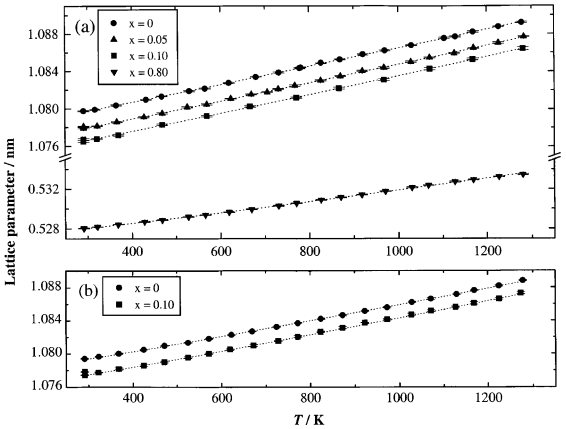

Fig. 3. Lattice parameters of $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$ obtained in air as a function of temperature ($x = 0$, 0.05, 0.10; pyrochlore-type phase, $x = 0.80$; fluorite-type phase) (a), and obtained in He–8%H_2 atmosphere ($x = 0$ and 0.10) (b).

Table 1
Regression data for $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$[a]

x Value	Atmosphere	b_0 (nm)	b_1 ($\times 10^6$ nm/K)	b_2 ($\times 10^{10}$ nm/K^2)	b_3 (nm K)
0.00	Air	1.07685	9.1805	4.1621	0.04230
0.00	He–8%H_2	1.07656	8.9347	4.0747	0.03804
0.05	Air	1.07509	9.1298	4.8997	0.02747
0.10	Air	1.07367	9.3027	4.9501	0.03623
0.10	He–8%H_2	1.07437	9.5373	3.6051	0.07010
0.80	Air	0.52633	4.9934	4.9103	0.05480

[a] a_T (nm) $= b_0 + b_1T + b_2T^2 + b_3/T$.

temperature in the form of $a_T = b_0 + b_1T + b_2T^2 + b_3/T$ where a_T is the lattice parameter at the absolute temperature T. The regression results are listed in Table 1. Linear thermal expansion coefficients (α) at temperature T were calculated by the relation

$$\alpha(T) = \frac{1}{a_{298}} \frac{da_T}{dT},$$

where a_T and a_{298} are the lattice parameters at T and 298 K. Calculated results are plotted against temperature in Figs. 4(a) and (b). In both heating atmospheres, air and He–8%H_2, the linear thermal expansion coefficients of $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$ increased with increasing Pu concentration. Comparing the linear thermal expansion coefficients of the sample prepared in air and that in Ar–8%H_2 with the same Pu concentration, the value of the linear thermal expansion coefficient of the former was larger than the latter. As seen from Fig. 4(a), the temperature dependence of the linear thermal expansion coefficient of the sample with $x = 0.80$ heated in air was different from the others. This difference may be caused by the structural difference between this sample with fluorite-type structure and others with pyrochlore-type one.

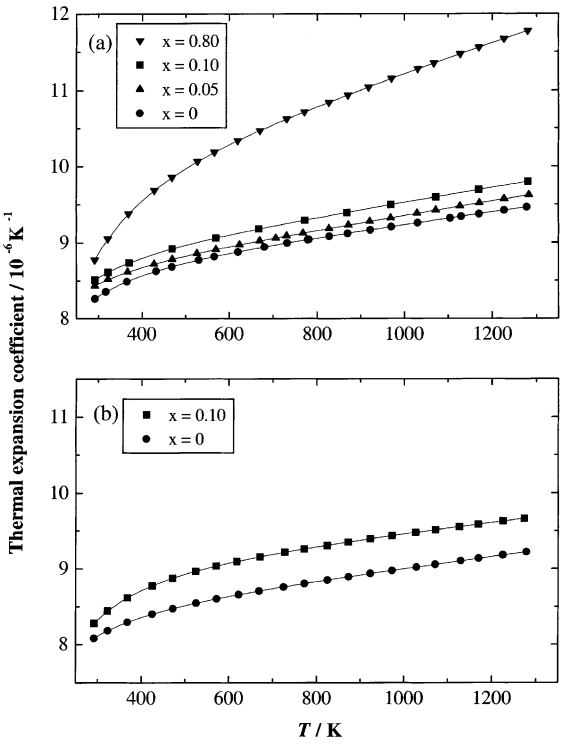

Fig. 4. Calculated linear thermal expansion coefficients of $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$ in air ($x = 0$, 0.05, 0.10 and 0.80) (a), and in He–8% H_2 ($x = 0$ and 0.10) (b).

The linear thermal expansion coefficients of $Ln_2M_2O_7$ (Ln = La–Gd, M = Zr and Hf) have been studied previously and increased from the La-sample to the Gd-sample with decreasing ionic radius of Ln [10]. This decreasing trend was explained by the concomitant decrease of Madelung energy with increase of 48f oxygen positional parameter of the pyrochlore related to the radii of cations. The 48f oxygen parameter of $A_2B_2O_7$ pyrochlore increases with decrease of the radius of A cation when B cation is fixed [11]. Then, the linear thermal expansion coefficient increases with decrease of the ionic radius of A site. Since the ionic radius with coordination number 8 decreases in the order of $La^{3+} > Pu^{3+} > Pu^{4+}$, the average ionic radius of $(La_{1-x}Pu_x)$ site decreases with increasing Pu concentration in any heating atmosphere. For the same Pu concentration, the average ionic radius of $(La_{1-x}Pu_x)$ site heated in air is smaller than that of prepared in Ar–8%H_2. This relation of the average ionic radius of $(La_{1-x}Pu_x)$ in $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$ is consistent with the present results on the dependencies of linear thermal expansion coefficients on Pu content and heating atmosphere.

4. Summary

The phase equilibrium of $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$ ($x = 0$–1.00) was studied by X-ray diffraction, and the solubility limits of Pu in pyrochlore-type phase prepared in air, vacuum and Ar–8%H_2 atmospheres were determined to be about 10, 35 and 100 mol%, respectively.

Lattice parameters of $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$ ($x = 0$, 0.05, 0.10 and 0.80 in air, $x = 0$ and 0.10 in He–8%H_2)

were measured by high-temperature X-ray diffraction at temperatures between room temperature and 1273 K in air and He–8%H_2 atmospheres. The linear thermal expansion coefficients of $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$, prepared both in air and in Ar–8%H_2, increased with increasing Pu content. For the same Pu concentration, the linear thermal expansion coefficient heated in air was larger than that heated in He–8%H_2. These results can be explained by the Madelung energy related to the average ionic radius of $(La_{1-x}Pu_x)$ in $(La_{1-x}Pu_x)_2Zr_2O_{7+y}$.

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