

The High Temperature Oxidation Behavior of 10wt%Gd₂O₃-Doped UO₂

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Abstract

The changes of weight gain, structure, morphology and uranium oxidation states in 10wt% Gd₂O₃-doped UO₂ during the oxidation below 475°C and heat treatment at 1300°C in air were investigated using TGA, XRD, SEM, EPMA and XPS. The room temperature (U_{0.86}Gd_{0.14})O₂ cubic phase converted to highly distorted (U_{0.86}Gd_{0.14})₃O₈-type single phase by oxidation at 475 °C in air. This oxidized phase was reduced by annealing at 1300°C in air. The room temperature XRD pattern of the 1300°C annealed powder revealed that (U_{0.86}Gd_{0.14})₃O₈-type single phase was separated into Gd-depleted U₃O₈ and Gd-enriched (U_{0.7}Gd_{0.3})O_{2+x} type cubic phase. The reduction and phase separation by the high temperature annealing of kinetically metastable and highly deformed (U_{0.86}Gd_{0.14})₃O₈-type phase are interpreted in terms of cation size difference between Gd³⁺ and U according to the oxidation state of U.

Key Words : Ceramic, LWR fuel, Burnable absorber, Gd₂O₃, High temperature oxidation, UO₂, U₃O₈

1. Introduction

Lanthanide rare earth oxides such as gadolinia or erbia have been widely used as a burnable absorber in LWR fuels. They are mixed with UO₂ powder and then pressed and sintered to make (U,Gd)O₂ or (U,Er)O₂ pellets. The effect of dopants on the UO₂ oxidation process has been studies for many years [1, and references therein]. One of the most prominent properties of low-valence-cation doped UO₂ is the enhanced kinetic stability of the cubic U₄O₉-type structure with

respect to U₃O₈-type structure formation. The doped UO₂ retains the fluorite structure to higher temperatures and higher O/M ratios than undoped UO₂ during oxidation.

Recently, theoretical approaches to explain the oxidation behavior of doped UO₂ have been made. Catlow [2] qualitatively shows that the effect of low valence cations addition on the oxygen potential changes with O/M ratio, based on the defect chemistry and thermodynamics. Park [3] set up defect cluster models in Lanthanide-doped UO₂ in order to explain the increase of oxygen

potential compared to pure UO_2 . Park [3] and Janeczek [4] suggested that the principal reason for the increase in the oxygen potential or stability of the cubic phase in the oxidation of doped urania or uraninite compared to pure urania is the blockage of oxygen interstitial sites by the doped cations, which are inert to oxidation. However, until now, most theoretical concerns were limited to the interactions between various defects caused by doped cations. So further work is required to fully understand the oxidation mechanism of doped UO_2 .

Phase relationships between lanthanide oxide and uranium oxide were investigated in the region of high oxygen partial pressure by several researchers [5,6,7]. They found that the solubility of lanthanide elements in UO_{2+x} decreased with increasing x and lanthanide elements did not dissolve in the U_3O_8 phase. Under a thermodynamically equilibrium state, lanthanide elements is insoluble in U_3O_8 phase. However, Taylor et al.[8] and You et al. [9] found that a kinetically metastable $(\text{U,RE})_3\text{O}_8$ can be formed by the oxidation of $(\text{U,RE})\text{O}_2$. A metastable $(\text{U,RE})_3\text{O}_8$ -type phase is separated into an RE-rich fluorite phase and RE-poor U_3O_8 phase by the heating at high temperature[8]. This phase separation process can be applied to mechanical removing of rare earth elements from spent nuclear fuel[8].

In this work, the oxidation behavior of Gd-doped UO_2 at temperatures up to 1300°C in air investigated. Our main concern was focused on the behavior of the Gd cation distribution and the oxidation state of uranium cations during high temperature annealing in air. In addition, the reason for the relative structural stability of the cubic phase in Gd-doped UO_2 is suggested considering the ionic size change of uranium cations with valence.

2. Experimental

In order to precisely and quantitatively analyze the effect of Gd cations on UO_2 oxidation, the achievement of complete chemical homogenization of $\text{UO}_2\text{-Gd}_2\text{O}_3$ solid solution is important. Ball-milled powder of $\text{UO}_2\text{-10wt\%Gd}_2\text{O}_3$ was pressed into cylindrical pellets and sintered at 1720°C for 4h in a H_2 atmosphere. The sintered pellets were held at 1650°C for 20h in an atmosphere with $\text{CO}_2/\text{H}_2=0.3$ for the purpose of chemical homogenization. The final composition of pellets was $(\text{U}_{0.86}\text{Gd}_{0.14})\text{O}_2$.

The oxidized sample was obtained by oxidizing the homogenized pellets at 475°C for 6h in air, and it was further annealed at 1300°C for 4h in air. The weight changes during oxidation and annealing were measured by TGA(TA). The X-ray diffraction profiles were obtained using a MXP (MAC science) diffractometer equipped with a curved graphite monochromator for the investigation of structural change during oxidation and annealing. The oxidation states of uranium cations in the oxidized and annealed samples were measured by X-ray photoelectron spectroscopy. The relative amounts of uranium cations with different valence states were acquired by the deconvolution of the $\text{U}4f_{7/2}$ binding energy peak. The morphology and cation concentration profiles were investigated by SEM and EPMA (Camebax SXR).

3. Results and Discussion

Fig. 1 shows weight gain changes during the oxidation and subsequent annealing of $(\text{U}_{0.86}\text{Gd}_{0.14})\text{O}_2$. The equivalent O/M ratio gain and heating procedure are also given in this figure. The weight gain increases to about 4% by oxidation at 475°C for 3h. As the temperature

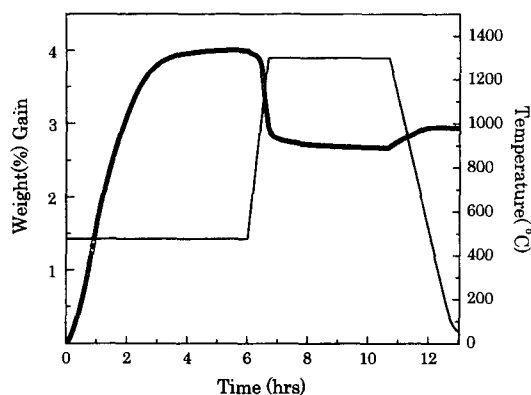


Fig. 1. Weight Changes During Oxidation at 475 °C for 6h, Annealing at 1300°C for 4h and Then Cooling to Room Temperature in Air

increases from 475 to 1300°C, a weight gain rapidly decreases to about 2.69%. And during subsequent cooling, the weight gain increases only to 2.94% but not to the original value (4%). This result suggests that the change in O/M ratio of the (U,Gd)₃O₈-type phase is irreversible.

According to the $p(\text{O}_2)$ -C-T phase diagram of U-O system[10], the equilibrium O/M ratio decreases with increasing temperature under a constant oxygen partial pressure. Therefore, the U₃O₈-type phase is reduced as the temperature increase in constant oxygen partial pressure. This reduction should be thermodynamically reversible. In the TGA curve during the oxidation of the Gd-doped U-O system, the decrease of weight gain in high temperature is partly explained as reduction process. However, it is not fully recovered during the cooling. It suggests that another irreversible reduction occurs during annealing at 1300°C.

Fig. 2 shows the room temperature X-ray diffraction patterns of the 1300°C annealed powder in comparison with the room temperature XRD pattern of oxidized powder at 475°C. There are two distinct differences in the

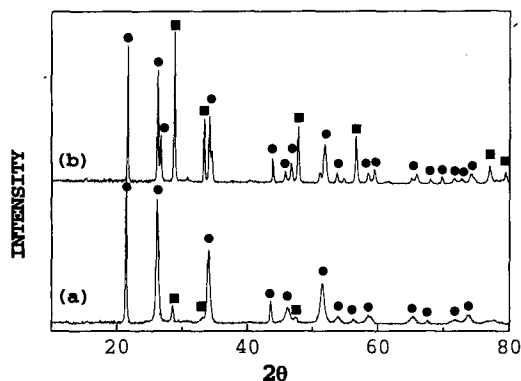


Fig.2. The Room Temperature XRD Profiles of (a) Oxidized Powder at 475°C for 6h in Air and (b) Annealed Powder of (a) at 1300°C for 4h in Air. Diffraction Lines Denoted by ● Originated from U₃O₈ Type Phase, and ■ from UO_{2+x} Type Cubic Phase

XRD patterns between oxidized powder and annealed powder; (1) the amount of UO_{2+x} type cubic phase abundantly increases in the annealed powder, and (2) the FWHMs of the diffraction peaks of the remaining U₃O₈-type phase decrease in the annealed powder. The (U,Gd)₃O₈-type phase produced by oxidizing at 475°C in air is supposed to have severe lattice strain in its lattice. The lattice strain is relaxed during the annealing at 1300°C, with a considerable amount of the U₃O₈-type phase changed to UO_{2+x}-type cubic phase.

Figs. 3(a) and 3(b) show the SEM micrographs of the U₃O₈ and (U,Gd)₃O₈ powders, respectively. The (U_{0.86}Gd_{0.14})₃O₈ powder (Fig. 3(b)) has the same morphology as the U₃O₈ powder (Fig. 3(a)) except for the particle size. Due to the volume expansion during oxidation from the UO₂ phase to the U₃O₈ phase, the powder has many cracks on its surface. Surface cracks in U₃O₈ powder can be healed to reduce the surface energy when sufficient energy for materials transport is

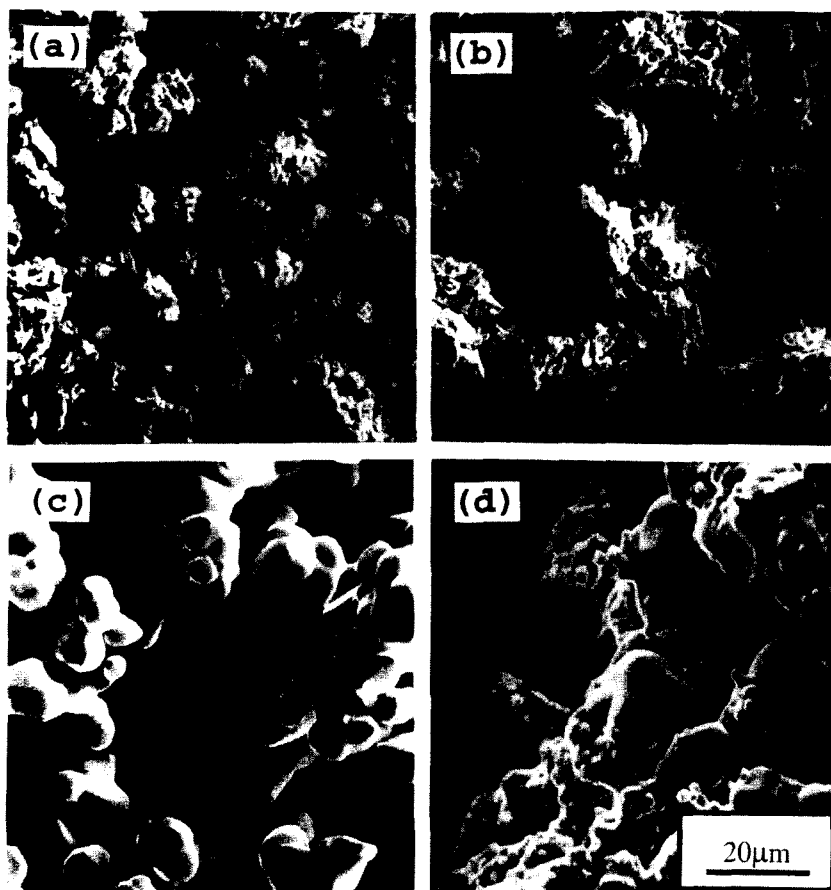


Fig. 3. SEM Powder Morphology of Oxidized Powder at 475°C for 6h [(a) U_3O_8 , (b) $(\text{U}_{0.86}\text{Gd}_{0.14})_3\text{O}_8$] and Respectively Annealed Powder at 1300°C for 4h [(c) Annealed U_3O_8 , (d) Annealed $(\text{U}_{0.86}\text{Gd}_{0.14})_3\text{O}_8$] in Air

provided. Figs. 3(c) and 3(d) show the annealed U_3O_8 and $(\text{U}_{0.86}\text{Gd}_{0.14})_3\text{O}_8$ powders, respectively. After annealing, U_3O_8 powder becomes dense with a smooth surface (Fig. 3(c)). However, interestingly enough, the morphology of the annealed powder of $(\text{U}_{0.86}\text{Gd}_{0.14})_3\text{O}_8$ in Fig. 3(d) differs from that of pure U_3O_8 . The annealed U_3O_8 powder seems to be regular in grain size, but the annealed $(\text{U}_{0.86}\text{Gd}_{0.14})_3\text{O}_8$ powder seems to be irregular, a mixture of large and small grains.

Fig. 4 shows the results of EPMA analysis on the small and large grains. The average

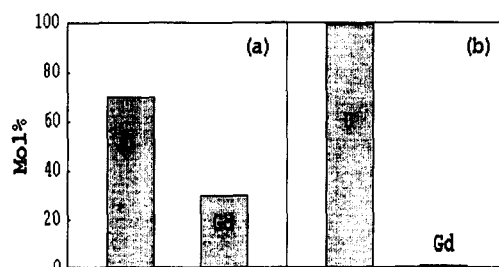


Fig. 4. Relative Cation Concentrations in (a) Small Grains and (b) Large Grains of Annealed $(\text{U}_{0.86}\text{Gd}_{0.14})_3\text{O}_8$ Powder. Cation Concentration is Obtained by EPMA

Table 1. Ionic Radius Change According to Valence and Coordination Number

Element	Valence	Coordinate number	Ionic radii(Å)
U	+3	6	1.165
U	+4	6	1.03
U	+4	8	1.14
U	+5	6	0.90
U	+6	4	0.66
U	+6	6	0.87
U	+6	8	1.00
O	-2	4	1.24
O	-2	8	1.28
Gd	+3	6	1.078
Gd	+3	8	1.193

concentration of Gd cations before annealing is 14% by atom. After high temperature annealing, the Gd cations in the large grains are almost depleted, but those in the small grains are enriched. Depleted Gd cations from large size grains pile up in small grains, and thereby the average Gd concentration increases up to 30% in the small grains. As shown in Fig. 2, the product annealed at 1300°C consists of two phases, orthorhombic and cubic phases. The large grains have either of the two phases. Since Gd is known to be insoluble in the U₃O₈ phase, the large grains have the U₃O₈ phase and the small grains the (U,Gd)O_{2+x} phase. The results indicate that the state of Gd cation settling in the (U,Gd)₃O₈-type lattice is thermodynamically unstable. When sufficient thermal energy is provided, Gd cations diffuse out from the (U,Gd)₃O₈-type lattice to reach a stable state.

The relative structural stability between (U,Gd)₃O₈ and (U,Gd)O_{2+x} can be understood when we consider the ionic size change with the valence state of U cations and the consequent geometrical change of the oxygen coordination polyhedron. A uranium cation has a multivalent character and

can exist in the U⁴⁺, U⁵⁺, and U⁶⁺ states. The effective ionic size of a uranium cation according to the valence state and coordination number is represented in table 1[11]. In contrast to a uranium cation, a Gd cation has a fixed valence of 3+ and hence a fixed ionic radius. When we assume the same coordination number, the ionic volume of a Gd³⁺ cation is about 15% larger than that of U⁴⁺. However, the ionic volume of a Gd³⁺ cation is about 70% larger than that of U⁶⁺. Consider the geometrical situations that a Gd³⁺ cation substitutes for a U cation in the U₃O₈ lattice and the UO_{2+x} lattice. In the case of UO_{2+x}[12,13], the main chemical state of the uranium cation is U⁴⁺ and its ionic volume is compatible with Gd³⁺. Therefore, a Gd³⁺ cation could easily substitute for a U cation in UO_{2+x} without creating severe lattice strain. In the case of U₃O₈[14], the circumstances are different. The main chemical state of a uranium cation is U⁶⁺, and its ionic volume is much smaller than that of Gd³⁺. Therefore, the coordination polyhedron in U₃O₈ has to be enlarged for the Gd³⁺ ion to substitute for a U⁶⁺ ion, and thereby offers sufficient room for the Gd ion. Consequently, an oxygen framework near the substituted Gd cation is severely perturbed. The lattice strain caused by the larger sized cations increases the lattice energy in (U,Gd)₃O₈. This is the main reason for cubic phase stability (or the difficulty of achieving (U,Gd)₃O₈ phase) during the oxidation of rare-earth oxide doped UO₂. That is, when the amount of Gd₂O₃ increases, it is difficult to oxidize (U,Gd)O₂ to the (U,Gd)₃O₈ type phase, with lattice strain overcome. In addition, even if the oxidization to the (U,Gd)₃O₈ phase may occur, this phase readily separates into two strain-free Gd-depleted U₃O₈ and (U,Gd)O_{2+x} cubic phases in order to reduce the lattice energy during high temperature annealing

By summarizing the above results, the TGA curve of Fig. 1 can be explained as follows. The

Table 2. U4f_{7/2} Photoelectron Peak Analysis of Oxidized and Annealed Powder

Oxide	Thermal History	Chemical State	Binding Energy(eV)	FWHM(eV)	Area(%)
U ₃ O ₈		U ⁴⁺	380.1	1.6	40
		U ⁶⁺	381.2	1.6	60
UO ₂ -10wt%Gd ₂ O ₃	Oxidized	U ⁴⁺	380.1	1.9	16.5
		U ⁶⁺	381.0	1.9	83.5
	Annealed	U ⁴⁺	380.2	1.7	61.3
		U ⁶⁺	381.3	1.7	38.7

(U,Gd)O₂ phase is forced to oxidize to the (U,Gd)₃O₈-type phase in spite of the instability of the (U,Gd)₃O₈-type phase, when it is heated in fair amount of oxygen at intermediate temperatures which is sufficiently high for oxidizing but low for cation diffusion. However, oxidized (U,Gd)₃O₈-type powder at 475°C is in an unstable state due to the severe lattice strain caused by Gd cations. Therefore, when sufficient thermal energy is acquired, this unstable (U,Gd)₃O₈ phase drives away the Gd cations to thereby reduce the lattice strain. In the region where Gd cations pile up, the thermodynamic equilibrium phase is changed from the (U,Gd)₃O₈ phase to the (U,Gd)O_{2+x}-type cubic phase. Excess oxygen is then released from this region in order to satisfy the mass balance. This is the irreversible reduction which occurs during high temperature annealing. The Gd-enriched (U,Gd)O_{2+x} type cubic phase cannot be oxidized up to (U,Gd)₃O₈ type phase upon cooling. Therefore, the weight loss from 475°C to 1300°C is not fully recovered although the temperature reverts to 475°C.

The irreversible reduction during the high temperature annealing can be confirmed by X-ray photoelectron spectroscopy (XPS), which gives the oxidation state of uranium cations. The chemical shift in the U4f_{7/2} peak position of binding energy is directly related to the oxidation state of uranium[15]. The relative amounts of

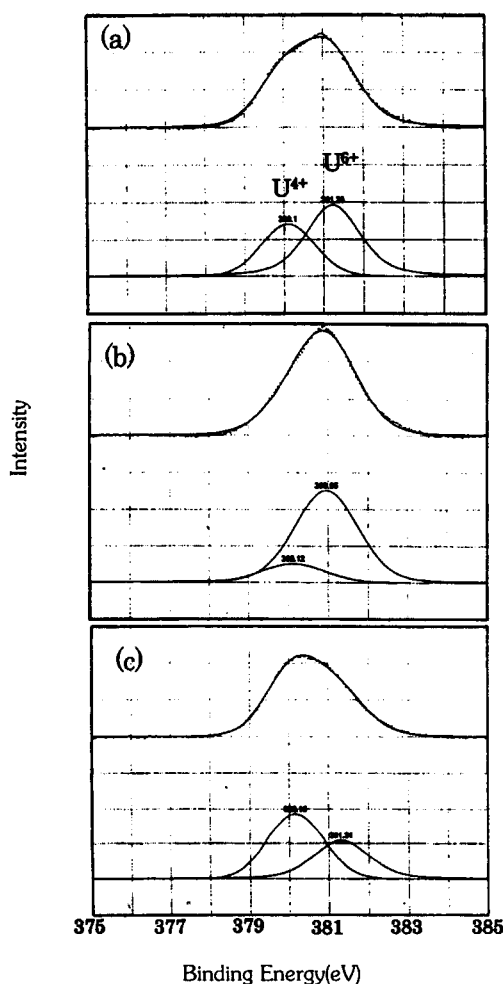


Fig. 5. XPS and Deconvolution of U_{4f7/2} Photoelectron Peaks from (a) Pure U₃O₈, (b) Oxidized Powder of (U_{0.86}O_{0.14})O₂ at 475°C for 6h, and (c) Annealed Powder of (b) at 1300°C for 4h

U⁴⁺(380eV) and U⁶⁺ (381eV) were obtained by deconvolution of the intensity peak near 380eV using the Gauss+Lorentz amplitude distribution function. It was found that in U₃O₈, uranium cations exist in the state of a mixture of U⁴⁺ and U⁶⁺ by the ratio of 1:2 to fit charge balance [16]. Figs. 5(a) and 7(b) respectively show the obtained XPS curves and deconvolution results for the U₃O₈ and (U_{0.86}Gd_{0.14})₃O₈ type phase which were oxidized at 475°C. The binding energy, FWHM and relative area are given in table 2. The relative portion of U⁶⁺ in the (U_{0.86}Gd_{0.14})₃O₈ -type phase is larger than that in U₃O₈. This result clearly reveals that in order to preserve the charge neutrality, which is perturbed by low valence Gd³⁺ substitution, U⁴⁺ cations are further oxidized to U⁶⁺ cations in the (U,Gd)₃O₈ type phase. Gd cations are depleted from the U₃O₈ matrix and pile up somewhere in the surroundings during the annealing of the (U,Gd)₃O₈ phase at high temperatures in air. In Gd depleted regions, the ratio of U⁴⁺/U⁶⁺ cations then recovers the value of 0.5. But the ratio of U⁴⁺/U⁶⁺ in Gd piled-up regions, in which the structure changed to the (U,Gd)O_{2+x} -type cubic phase, is inevitably larger than that in pure U₃O₈. That is, U⁶⁺ cations are reduced during the annealing procedure. This means that the total ratio of U⁴⁺/U⁶⁺ in an annealed sample must be larger than that in pure U₃O₈ after sufficient thermal annealing. Fig. 5 (c) shows the XPS and corresponding deconvolution results of the annealed sample at 1300°C. The obtained binding energy, FWHM and relative area are also given in table 2. The ratio of U⁴⁺/U⁶⁺ reversed by thermal annealing as we expected. The increase of U⁴⁺ amount during annealing reveals that spontaneous reduction occurs. Considering the charge neutrality, excess lattice oxygen atoms produced by spontaneous reduction are diffused out. Thus, the mass of the (U,Gd)₃O₈ phase is diminished after annealing as

shown in Fig. 1.

5. Conclusions

We have shown that the metastable (U,Gd)₃O₈ phase, which is obtained by oxidization of (U,Gd)O₂ at intermediate temperature in air, is spontaneously separated into U₃O₈ and (U,Gd)O_{2+x} phase during the high temperature annealing in air. This phase separation in high temperature is irreversible reducing process. The strain energy in (U,Gd)₃O₈ phase, which is caused by a large ionic size difference between U⁶⁺ and Gd³⁺ is the driving force of phase separation. The relative structural stability in Gd-doped uranium oxides is closely tied with the strong coupling between structure and ionic size difference according to the chemical state of the cations therein. Geometrical coordinate modification near the Gd-cation centered polyhedron incorporated with an adjacent polyhedron inhibits the oxidation of uranium.

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References

1. R.J. McEachen and P. Taylor, J. Nuclear Mat., 254, 87-121(1998).
2. C.R.A. Catlow, J. Nuclear Mat., 79, 432-434 (1979).
3. K. Park and D.R. Olander, J. Nuclear Mat., 187, 89-96(1992).
4. J. Janeczek, R.C. Ewing and L.E. Thomas, J. Nuclear Mat., 207, 177-191(1993).
5. D.C. Hill, J. Am. Ceram. Soc., 45, 258(1962).
6. U. Berndt, R. Tanamas and C. Keller, J. Solid

- St. Chem., 17, 113(1976).
7. I.B. De Alleluia, M. Hoshi, W.G. Jocher and C. Keller, J. Inorg. Nucl. Chem., 43, 1831(1981).
 8. P. Taylor and R.J. Mceachern, WO 96/36971 (1996).
 9. G.S. You, K.S. Kim, D.K. Min and S.G. Ro, J. Nuclear Mat., 277, 325(2000).
 10. Y.S. Kim, J. Nuclear Mat., 279, 173(2000).
 11. O. Muller and R. Roy, The major Ternary Structural Families, Springer-Verlag, Berlin, 5-7(1974).
 12. B.T.M. Willis, Acta Cryst., A34, 88-90(1978).
 13. D.J.M. Bevan, I.E. Grey and B.T.M. Willis, J. Solid State Chem., 61, 1-7(1986).
 14. B.O. Loopstra, J. Appl. Cryst., 3, 94-96(1970).
 15. S. Bera, S.K. Sali, S. Sampath, S.V. Narasimhan and V. Venygopal, J. Nuclear Mat., 255, 26-33(1998).
 16. G.C. Allen and P.A. Tempest, Proc. R. Soc. London Ser., A406, 325(1986).