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STABILITY OF TETRAVALENT ACTINIDES IN PEROVSKITES

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A HERD OF SMALL WHITE DEER (A RARE MUTATION OF THE FALLOW DEER, DAMA DAMA) ROAM THE ARGONNE GROUNDS.
THE DRAWING ON THE COVER SHOWS THREE OF THESE UNUSUAL ANIMALS.

STABILITY OF TETRAVALENT ACTINIDES IN PEROVSKITES

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This paper reports the first determination of the enthalpy of formation of a complex actinide(IV) oxide: ΔH_f° ($\text{BaUO}_3, s, 298 \text{ K}$) = $-1690 \pm 10 \text{ kJ mol}^{-1}$. The preparation and properties of this and other actinide(IV) complex oxides are described and are compared with other perovskites BaMO_3 . The relative stabilities of tetravalent and hexavalent uranium in various environments are compared in terms of the oxidation-reduction behavior of uranium in geological nuclear waste storage media; in perovskite, uranium(IV) is very unstable in comparison with uranium(VI).

Introduction

In simple oxides, the actinides are most stable in the +4 oxidation state; the dioxides, AnO_2 , are known for all elements thorium through californium. Although the properties of ThO_2 , UO_2 , and PuO_2 are especially important in nuclear technology, complex actinide oxides (oxides with one or more metal ions in addition to an actinide) are also important since they may be found as fission products in nuclear fuels and they are models for possible matrices in which nuclear wastes will be stored. It is surprising that so much effort has been devoted to complex actinide oxides that contain actinides in the +6 rather than the +4 oxidation state (1).

Because the preparative conditions of complex actinide oxides indicate that they favor higher actinide oxidation states, we have selected a model system in which both +4 and +6 actinides are easily prepared in similar oxide coordination. In the dioxides each actinide is surrounded by 8 equidistant oxygens at the corners of a cube, but in complex oxides the actinide ion is usually surrounded by 6 oxygens at the apices

of a regular or distorted octahedron (2). Our model system is perovskite, the mineral CaTiO_3 , in which structure type many complex actinide(IV), (V), (VI), and even (VII) oxides crystallize (1,2) (Figure 1).

We have previously determined the enthalpies of formation of several perovskite +4 and +6 oxides (3,4,7). Our objective in this study was to determine the enthalpy of formation of BaUO_3 and to evaluate the relative stability of uranium(IV) and (VI) in comparable complex oxides, especially in comparison with binary oxides, halides, and aqueous ions.

From a practical point of view, these compounds are models of crystalline matrices for nuclear waste disposal. One such storage material is SYNROC, a synthetic mineral whose major constituents are the complex oxides hollandite, zirconolite, and perovskite. We have chosen perovskite as a model structural family because of its efficient packing and its accommodation of a wide range of cations, both in size and oxidation state (5).

Previous Work. The best-known set of actinide(IV) perovskites is BaMO_3 (M=Th through Cf) (1,6). The corresponding lanthanide(IV) oxides BaCeO_3 , BaPrO_3 , and BaTbO_3 are also known and have been well characterized (7). A few compounds SrMO_3 (M=Pa, U, Np, Pu) are also known (1). Recently, EuUO_3 and EuNpO_3 were prepared and characterized as $(\text{Eu}^{2+})(\text{U}^{4+})(\text{O}^{2-})_3$ (8,9).

By far the greatest body of literature exists for BaUO_3 (10). Very thorough studies of the BaO-UO_2 system revealed a pseudo-cubic BaUO_3 phase with $a_0 = 4.387 \text{ \AA}$ (12), or $a_0 = 4.410 \text{ \AA}$ (13). In general, it was found that BaUO_3 could only be prepared by heating BaO with UO_2 at 1200-1900°C in inert gas or hydrogen. Partial oxidation and loss of Ba have been noted, as has the fact that BaUO_3 can take up more than 1 mol of BaO in solid solution (10,13).

While our work was in progress, a new report on BaUO_{3+x} appeared (14). Hydrogen reduction of BaUO_4 was incomplete even at 1100°C, yielding $\text{BaUO}_{3.23}$ or $\text{BaUO}_{3.3}$, $a_0 = 4.40 \text{ \AA}$. Reaction of Ba_3UO_6 with UO_2 in hydrogen at 1150-1200°C yielded $\text{BaUO}_{2.83}$ or $\text{Ba}_{0.98}\text{UO}_3$, $a_0 = 4.39 \text{ \AA}$. These pseudocubic x-ray lattice parameters were resolved by powder neutron diffraction into the orthorhombic space group Pnma with refined vacancy structures of $\text{Ba}_{0.911}\text{U}_{0.909}\text{O}_3$ and $\text{Ba}_{0.976}\text{U}_{1.001}\text{O}_3$.

The two other most important actinide(IV) complex oxides are BaThO_3 and BaPuO_3 . The former has been prepared many times (15); however, there are disputes concerning its properties. Fava et al. (16) prepared BaThO_3 from stoichiometric amounts of BaO and ThO_2 and observed an ideal perovskite, whereas Nakamura (17) found that an excess of BaO is necessary and identified a distorted perovskite structure. It is also not obvious why BaO is not taken up in solid solution with BaThO_3 (15); BaUO_3 is

reported to form a solid solution with up to 2 moles of BaO (10). Some doubt remains concerning the Ba/Th ratio in these samples, since no analyses were reported and loss of Ba is possible by volatilization during heating or during methanol extraction. BaPuO₃ was thoroughly studied by Keller (18) who found it necessary to use a BaO:PuO₂ ratio of 3:1 to react all of the PuO₂; excess BaO was then extracted with methanol.

Experimental

We prepared BaUO₃ twice, each time beginning with high-purity BaO (CERAC, assay 99.3% by acidimetric titration, found free of Ba(OH)₂ or BaCO₃ by x-ray powder diffraction) and UO_{2.00} (reduced from high-purity U₃O₈ in H₂ at 1000°C; composition verified gravimetrically by ignition to U₃O₈ at 800°C). The stoichiometric amount of each oxide was weighed in a dry box (<5 ppm H₂O and O₂), mixed thoroughly in an agate mortar, and heated to 1000°C for 24 hours in 99.998% H₂. After repeating the grinding in the dry box and heating in H₂, each sample was handled only in the dry box.

The first sample was analyzed as Ba_{0.99}UO_{3.20} (referred to subsequently as BaUO_{3.20}) by separating the cations by ion exchange followed by gravimetric analysis of Ba as BaSO₄ and analysis of U using weight-buret modified Davies and Gray titration (19). The oxygen content was determined gravimetrically by ignition of a sample to BaUO₄ at 1000°C. The second sample was analyzed similarly as BaUO_{3.06}. X-ray powder diffraction Debye-Scherrer films were indexed as simple cubic with $a_0 = 4.4155 \pm 0.0005$ Å for Ba_{0.99}UO_{3.20} and $a_0 = 4.4007 \pm 0.0020$ Å for BaUO_{3.06}. Several weak non-cubic lines were found on the Ba_{0.99}UO_{3.20} film.

Attempted preparation of BaThO₃ and BaPuO₃ by similar procedures were not as successful. As recommended by Scholder et al. (20), BaThO₃ was prepared from a 10% excess of BaCO₃ mixed with ThO₂ and fired in nitrogen at 900°C. Although the product dissolved completely in 1M HCl(aq) and was extracted with absolute methanol in a dry box to remove excess BaO, its analysis still revealed excess BaO. Although the X-ray powder diffraction film (cubic, $a_0 = 4.4960 \pm 0.0010$ Å) showed no BaO, BaCO₃, or ThO₂ lines, the sample was not considered suitable for calorimetry.

The preparation of BaPuO₃ paralleled that of BaUO₃, beginning with ²⁴²PuO₂ ignited at 800°C, a sufficiently low temperature that it would not be refractory. Although the x-ray powder diffraction film (cubic $a_0 = 4.3839 \pm 0.0004$ Å) showed no PuO₂ lines, the sample dissolved slowly in 1M HCl(aq) or HClO₄(aq). Radiometric (alpha assay) and spectrophotometric analyses indicated only 90% of theoretical plutonium in solution after 30 minutes in dilute acid, with some insoluble resi-

due (perhaps amorphous PuO_2) remaining after several days. These results were consistent with those of Keller (18).

Part of the BaPuO_3 was oxidized in flowing O_2 in a Mettler TGA-2 apparatus. Weight gain was complete at 700°C but corresponded only to $\text{BaPuO}_{3.5}$. The product showed an x-ray diffraction pattern of a mixture of BaPuO_3 , PuO_2 , and Ba_3PuO_6 .

Solution calorimetry of BaUO_{3+x} was carried in an 880 cm^3 isoperibol calorimeter described by Nocera *et al.* (21). Samples of BaUO_{3+x} were weighed on a Cahn GRAM electrobalance in the dry box and reacted sequentially in the calorimeter in 1M HCl(aq) .

Results

Enthalpies of solution were measured separately for $\text{BaUO}_{3.20}$ and $\text{BaUO}_{3.06}$ samples. The data are shown in Table I. The thermochemical cycles that lead to the enthalpies of formation of these nonstoichiometric compounds are shown in Table II.

In view of the difficulty in approaching the stoichiometric composition of BaUO_3 , it is necessary to estimate its enthalpy of formation by extrapolation. It is well known that the partial molal thermodynamic properties of solid solutions vary smoothly as function of nonstoichiometric parameters (22), so that, by integration, the integral thermodynamic properties of corresponding nonstoichiometric compounds also vary smoothly. It is not as obvious that the enthalpies of formation of a series of compounds such as AB_x and ABC_x also vary smoothly as a function of x , even when the compounds pass through structure changes. Such a series of compounds, which is relevant to this study, is UO_{2+x} , shown at the top of Figure 2. Similar smooth variation of $\Delta H_f^\circ(\text{BaUO}_{3+x})$ is seen in the lower curve of Figure 2; two of the data points are from Table II and that for BaUO_4 ($\Delta H_f^\circ = -1997.1 \pm 2.1 \text{ kJ mol}^{-1}$) is from O'Hare *et al.* (23). By extrapolating the lower curve of Figure 2 to $x = 0$, we estimate $\Delta H_f^\circ(\text{BaUO}_{3.00}) = -1690 \pm 10 \text{ kJ mol}^{-1}$.

Discussion

It is interesting to note the differences in slopes of the two curves of Figure 2. The slope of the BaUO_{3+x} data is approximately twice that of the UO_{2+x} data; this fact reflects the enhanced stability of hexavalent compared to that of tetravalent uranium in complex oxides versus simple oxides. Ackermann and Chandrasekharaiah (24) calculated similar data for UO_{2-x} , which plot on a steeper curve than the $\Delta H_f^\circ(\text{UO}_{2+x})$ because UO_{2-x} is a cation-vacancy U(IV) compound rather than a mixed-valence U(IV)-U(VI) oxide.

In Table III are shown ΔG° data for several U(IV)-U(VI) reactions, each of which is normalized by including $1/2 \text{O}_2(\text{g})$ as the oxidant. The first reaction is useful as a reference, paralleling the two extremes on the oxygen ΔH curve of Figure 2. The next three reactions are oxyhalides and are slightly more favorable. The fifth reaction is that of standard-state aqueous ions, and includes acid-base effects [weak acid $\text{U}^{4+}(\text{aq})$ on left and strong acid $\text{H}^+(\text{aq})$ on right]. Nevertheless, it is more favorable for the oxidation U(IV)-U(VI) than the reactions above, presumably because of the formation of the strongly covalently bonded UO_2^{2+} ion. Parallel stabilizations are found for NpO_2^{2+} , PuO_2^{2+} , and $^{242}\text{AmO}_2^{2+}$, where the M(VI) dioxo cations are relatively stable. The last two reactions show the stability of U(VI) in complex oxides. Each of these reactions takes U(IV) in octahedral (sixfold) coordination to U(VI) in sixfold coordination; the very favorable free energy changes illustrate how strongly hexavalent actinides are stabilized in complex oxides.

It is easy to show that BaUO_3 is a very strong reductant; using estimated $S^\circ(\text{BaUO}_3)$, we calculate $\Delta G^\circ(298 \text{ K}) = -50 \text{ kJ}$ for the reaction



so that BaUO_3 is a significantly stronger reductant than hydrogen. This calculation confirms the experimental observation (14) that hydrogen will not reduce BaUO_4 to BaUO_3 .

A useful parameter by which the stability of perovskites can be judged is the Goldschmidt tolerance factor t (25). In a study of the thermochemistry of the lanthanide(IV) perovskites $\text{Ba}(\text{Ce}, \text{Pr}, \text{Tb})\text{O}_3$, Morss and Mensi (7) showed that the tolerance factor correlates roughly with $\Delta H(\text{complex})$, i.e., ΔH for the reaction



Table III is an expanded table of the sort used by Morss and Mensi, showing that BaUO_3 behaves, as expected, like BaCeO_3 with respect to reaction (2). Because of the importance of other actinide(IV) ions in sixfold coordination, we have included estimates of $\Delta H(\text{complex})$ for BaThO_3 and BaPuO_3 . BaThO_3 is clearly a compound of marginal stability; BaPuO_3 is much more stable but difficult to synthesize free of PuO_2 unless excess BaO is used. The estimates in Table IV are useful because it may be very difficult to prepare BaThO_3 and BaPuO_3 in sufficiently high purity for thermochemical measurements.

Finally, we wish to point out that our results are significant in the context of geochemical behavior of uranium in

oxide hosts. For example, Schreiber et al. (26) found that U(IV), U(V), and U(VI) coexist in Ca-Mg-Al-silicate glasses, with high-calcium glass favoring the higher oxidation states. Pepin et al. (27) argue that U(VI) and interstitial oxygen are favored in fluorite solid solutions such as $(U,Th)O_{2+x}$ with unit cells larger than that of UO_2 . It is well known that UO_2^{2+} is much more readily leached than U^{4+} ; Wang and Katayama (28) showed that the dissolution of UO_2 and spent nuclear fuel in water, bicarbonate, and brine is initiated by oxidation of U^{4+} in the solids to $UO_2^{2+}(aq)$. Our study shows that perovskite is a weak stabilizing agent for U(IV) and a very strong stabilizing agent for U(VI); we have presented quantitative data to show how much more stable is U(VI) than U(IV) in perovskite (29).

Most kinetic studies (e.g., 30) and a thermodynamic study (31) of nuclear waste host dissolution focus on heterogeneous reactions with major concern for temperature, pH, and complexation. We believe that strongly reducing conditions are necessary to inhibit the undesirable U(IV)-U(VI) oxidation in nuclear waste matrices. Therefore, nuclear waste matrices should incorporate reductants or oxidation-reduction Eh buffers to maintain very low oxygen partial pressure, and leach studies should be conducted under oxidation-reduction conditions that nearly match repository conditions.

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Table I. Enthalpy of Solution of BaUO_{3+x} in 880 cm^3
of 1M HCl(aq) at 298.15 K

Composition	Mass/mg	$\frac{\Delta H^a}{\text{J}}$	$\frac{\Delta H_{\text{soln}}}{\text{kJ mol}^{-1}}$
$\text{BaUO}_{3.20}$	92.46	-51.62	-238.2
$\text{BaUO}_{3.20}$	73.97	-41.37	-238.6
$\text{BaUO}_{3.06}$	74.32	-48.70	-274.3
$\text{BaUO}_{3.06}$	69.10	-45.45	-278.5
$\text{BaUO}_{3.06}$	83.48	-55.39	-280.9
$\text{BaUO}_{3.06}$	68.04	-44.36	-276.0
	Ave. ΔH_{soln} ($\text{BaUO}_{3.20}$)		-238.4 ± 5.0^b
	Ave. ΔH_{soln} ($\text{BaUO}_{3.06}$)		-278.8 ± 2.9^b

- a. Corrected for bulb breaking and evaporation of solvent into bulb gas.
b. 95% confidence.

Table II. Thermochemical Cycles for $\Delta H_f^\circ(\text{BaUO}_{3+x})$.

<u>Reaction</u>	<u>ΔH_f° (kJ mol⁻¹)</u>
$\text{BaUO}_{3+x}(\text{c}) + (6-2x)\text{HCl}(1\text{M}) = \text{BaCl}_2(\text{in } 1\text{M HCl})$ $+ (1-x)\text{UCl}_4(\text{in } 1\text{M HCl}) + x\text{UO}_2\text{Cl}_2(\text{in } 1\text{M HCl})$ $+ (3-x)\text{H}_2\text{O}(\text{in } 1\text{M HCl})$	$\Delta H(\text{soln, BaUO}_{3+x})^a$
$\text{Ba}(\text{c}) + \text{Cl}_2(\text{g}) = \text{BaCl}_2(\text{in } 1\text{M HCl})$	$\Delta H_1 = -864.1 \pm 1.7^b$
$(1-x)[\text{U}(\text{c}) + 2\text{Cl}_2(\text{g}) = \text{UCl}_4(\text{in } 1\text{M HCl})]$	$\Delta H_2 = (1-x)(-1247.3 \pm 2.5)^c$
$x[\text{U}(\text{c}) + \text{O}_2(\text{g}) + \text{Cl}_2(\text{g}) = \text{UO}_2\text{Cl}_2(\text{in } 1\text{M HCl})]$	$\Delta H_3 = x(-1345.2 \pm 1.3)^c$
$(3-x)[\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{in } 1\text{M HCl})]$	$\Delta H_4 = (3-x)(-285.85 \pm 0.04)^d$
$(6-2x)[1/2 \text{H}_2(\text{g}) + 1/2 \text{Cl}_2(\text{g}) = \text{HCl}(1\text{M})]$	$\Delta H_5 = (6-2x)(-164.36 \pm 0.04)^d$

For $\text{BaUO}_{3.06}$:

$$\begin{aligned} \Delta H_f^\circ &= -(-278.8 \pm 2.9) + (-864.1 \pm 1.7) + 0.94(-1247.3 \pm 2.5) \\ &+ 0.06(-1345.2 \pm 1.3) + 2.94(-285.85 \pm 0.04) - 5.88(-164.36 \pm 0.04) \\ &= (-1712.4 \pm 4.1) \text{ kJ mol}^{-1} \end{aligned}$$

For $\text{BaUO}_{3.20}$:

$$\begin{aligned} \Delta H_f^\circ &= -(-238.4 \pm 5.0) + (-864.1 \pm 1.7) + 0.8(-1247.3 \pm 2.5) \\ &+ 0.2(-1345.2 \pm 1.3) + 2.8(-285.85 \pm 0.04) - 5.6(-164.36 \pm 0.04) \\ &= (-1772.5 \pm 5.7) \text{ kJ mol}^{-1} \end{aligned}$$

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Table III. ΔG_{298K}° for U(IV)-U(VI) Reactions^a

Reaction	$\Delta G^\circ(298K)/(kJ\ mol^{-1})$
$UO_2(c) + 1/2\ O_2(g) \rightarrow UO_3(c)$	-114
$UOF_2(c) + 1/2\ O_2(g) = UO_2F_2(c)$	-123
$UOCl_2(c) + 1/2\ O_2(g) = UO_2Cl_2(c)$	-150
$UOBr_2(c) + 1/2\ O_2(g) = UO_2Br_2(c)$	-137
$H_2O(l) + U^{4+}(aq) + 1/2\ O_2(g) = UO_2^{2+}(aq) + 2H^+(aq)$	-185
$BaUO_3(c) + 1/2\ O_2(g) = BaUO_4(c)$	-278
$BaUO_3(c) + 2\ BaO(s) + 1/2\ O_2(g) = Ba_3UO_6(c)$	-400

Thermodynamic data from Wagman, D. D. *et al.*, "Selected Values of Chemical Thermodynamic Properties," NBS Technical Notes 270-3, 270-6, and 270-8, U. S. Government Printing Office, Washington, D.C., 1981. Entropies of $BaUO_3$ and Ba_3UO_6 estimated as sums of corresponding binary oxide enthalpies.

TABLE IV. Perovskites: Structural and Thermodynamic Parameters

Compound	IR(B^{4+}) Å	t	$MO_2(s) + BaO(s) = BaMO_3(s)$	
			$\Delta(\text{Molar Vol.})$ cm^3/mol	$\Delta H(\text{complex})$ kJ/mol
BaTiO ₃	0.605	0.97	-5.8	-163
BaMoO ₃	0.650	0.95	-5.4	-92 ^a
BaHfO ₃	0.71	0.92	-3.5	-134
BaZrO ₃	0.72	0.92	-2.4	-126
BaTbO ₃	0.76	0.90	+0.5	-88
BaPrO ₃	0.85	0.864	+0.5	-147
BaPuO ₃	0.86	0.860	+0.5	(-80) ^b
BaCeO ₃	0.87	0.856	+1.7	-52
BaUO ₃	0.89	0.849	+0.7	-57
BaThO ₃	0.94	0.831	+2.3	(-20) ^b

a. Unusually small $\Delta H(\text{complex})$ since MoO_2 is stabilized by Mo-Mo bonds.

b. Estimated.

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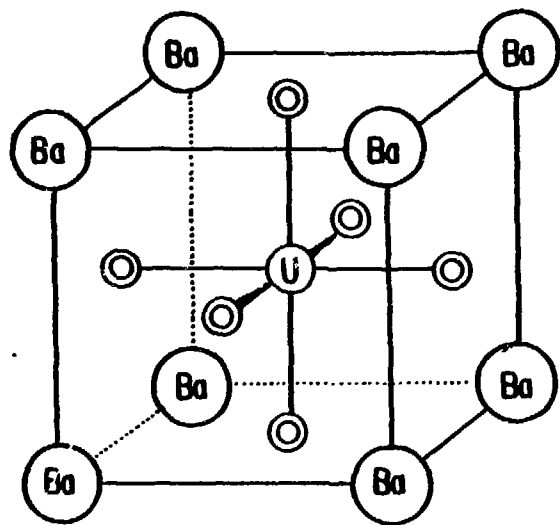
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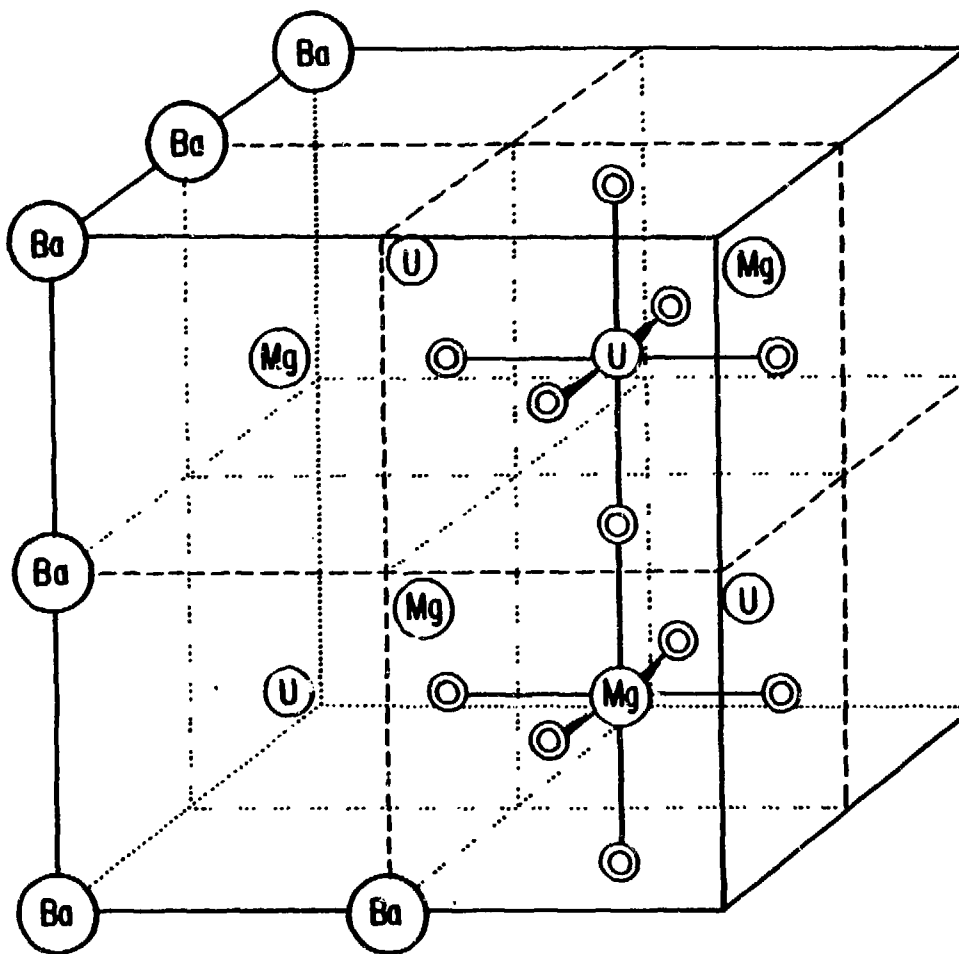
Figure Captions

Figure 1. Perovskite structures: (a) simple perovskite, shown as idealized cubic BaUO_3 . (b) ordered perovskite Ba_2MgUO_6 ($\text{BaMg}_{0.5}\text{U}_{0.5}\text{O}_3$).

Figure 2. Enthalpies of formation of UO_{2+x} and BaUO_{3+x} .



(a) Idealized BaUO_3



(b) Ba_2MgUO_6

