JOURNAL OF SOLID STATE CHEMISTRY **102**, 566–569 (1993)

The Magnetic Susceptibility and Structure of $BaUO_3$

YUKIO HINATSU

Department of Chemistry, Japan Atomic Energy Research Institute,
Tokai-mura, Ibaraki 319-11, Japan

Received April 13, 1992; accepted June 2, 1992

Barium uranate, $BaUO_{3.023}$, was prepared and its magnetic susceptibility was measured in the temperature range between 4.2 K and room temperature. X-ray diffraction analysis showed it was an ideal cubic perovskite. From the magnetic susceptibility measurements, it was found that oxygen stoichiometric $BaUO_3$ shows the temperature-independent paramagnetism over the temperature range from 4.2 K to room temperature, which is in accord with the octahedral oxygen coordination around the U^{4+} ion. The susceptibility of $BaU_{1-y}Th_yO_3$ was also measured. © 1993 Academic Press, Inc.

Introduction

During fission of uranium, a variety of fission products are formed, some of which are accommodated in UO_2 fuel (*1*). Among them, barium has a quite low solubility into UO_2 (*2*), because of its large ionic radius (*3*), and forms various kinds of ternary oxides (*1*).

In the Ba–U–O compounds, we focus our attention to the perovskite-type compound $BaUO_3$. Previously many of the perovskite-type compounds were thought to be ideally cubic. Actually, most of them are distorted tetragonally, rhombohedrally, or orthorhombically (*4*). For example, even calcium titanate $CaTiO_3$, the mineral perovskite, is orthorhombically distorted (*5*). In this paper, we prepared $BaUO_3$ and studied its structure through X-ray diffraction and magnetic susceptibility measurements. We also prepared $BaU_{1-y}Th_yO_3$ compounds, in which some diamagnetic thorium ions substitute for uranium ions, and measured their magnetic susceptibilities to elucidate the electronic state of U^{4+} in the $BaUO_3$.

Experimental

1. Preparation

UO_3. Uranium precipitates were formed by adding hydrogen peroxide into nitric acid solution of $UO_2(NO_3)_2 \cdot 6H_2O$. Uranium trioxide (UO_3) was prepared by heating them in air at 400°C.

$BaUO_3$. $BaUO_3$ was prepared by the following reactions:

$$UO_3 + BaCO_3 \rightarrow BaUO_4 + CO_2, \quad (1)$$

$$BaUO_4 + H_2 \rightarrow BaUO_3 + H_2O. \quad (2)$$

The UO_3 and $BaCO_3$ were weighed, first in the metal ratio U : Ba = 1 : 1.02. Since no significant evaporation of barium was found under following experimental conditions, we then weighed the UO_3 and $BaCO_3$ in the stoichiometric metal ratio. They were intimately mixed in an agate mortar and then

0022-4596/93 $5.00

pressed into pellet. The pellet was fired in air at 850°C. After cooling to room temperature, the product was crushed, ground, and repressed into pellet followed by firing. $BaUO_4$ was obtained by repeated mixing and firing. $BaUO_3$ was prepared by the reduction of this $BaUO_4$ in a flowing hydrogen atmosphere at 1400°C for 8 hr. The purity of hydrogen gas used was more than 99.9%. Because a slight oxygen nonstoichiometry was found in this $BaUO_3$, we repeated the preparation of $BaUO_3$ five times to confirm this nonstoichiometry.

$BaU_{1-y}Th_yO_3$. We avoided the traditional synthesis method of a complex oxide from solid binary oxides, or from oxides and carbonates, because once perovskite $BaUO_3$ and $BaThO_3$ were formed, solid-state diffusion of uranium and thorium into these substances would be very slow. Instead, this type of solid solutions was prepared by evaporating dilute nitric acid solutions of mixtures of $Ba(NO_3)_2$, $UO_2(NO_3)_2 \cdot 6H_2O$, and $Th(NO_3)_4 \cdot 4H_2O$ and heating mixtures of them in a flowing hydrogen atmosphere at 1400°C for 5 hr. After cooling to room temperature, the specimen was crushed into powder, ground well, pressed into pellets, and reduced under the same conditions.

2. *Analysis*

X-ray diffraction analysis. An X-ray diffraction study was performed with Cu$K\alpha$ radiation on a Philips PW 1390 diffractometer equipped with a curved graphite monochromator. The diffraction measurements were carried out not only by the continuous scanning in the range of $10° \leq 2\theta \leq 140°$, but also by the step scanning in which the step width of the angle is 0.02°. The lattice parameter was determined by a least-squares method.

Determination of oxygen amount. The oxygen nonstoichiometry in the barium uranate was determined by the back-titration method (*6, 7*); 20 ~ 30 mg of the sample was weighed out and dissolved in excess cerium(IV) sulfate solution. The cerium(IV) sulfate solution was standardized in advance with stoichiometric UO_2. The excess cerium(IV) was titrated against a standard iron(II) ammonium sulfate solution with ferroin indicator. The oxygen amount was determined for predetermined Ba/U ratio.

3. *Magnetic Susceptibility Measurement*

The magnetic susceptibility was measured with a Faraday-type torsion balance in the 4.2–300 K temperature range. The apparatus was calibrated with a Manganese Tutton's salt ($\chi_g = 10980 \times 10^{-6}/(T + 0.7)$). The temperature of the sample was measured by an Ag vs Au-0.07 at %Fe thermocouple (4.2 K ~ 40 K) (*8*) and an Au–Co vs Cu thermocouple (10 K ~ room temperature). Details of the experimental procedure have been described elsewhere (*9*).

Results and Discussion

The barium uranate prepared in this study was a cubic single phase, i.e., all of the peaks observed by X-ray powder diffraction were indexed using a cubic cell. Special care was taken to verify the absence of small line splittings of *hkl* lines due to tetragonal, rhombohedral, or orthorhombic distortion. For example, splittings of each of (2 2 0), (2 2 2), and (4 0 0) lines into two or three lines were not found. The lattice parameter of this cubic perovskite (space group: *Pm*3*m*) is 4.4075(10) Å. From the chemical analysis of the oxygen concentration, the specimen prepared in this study was found to be nearly oxygen stoichiometric, $BaUO_{3.023}$. Recently Barrett *et al.* (*10*) reported that $BaUO_{3.30}$ was orthorhombically distorted. This distortion is probably due to the large excess oxygen. In fact, Williams *et al.* (*11*) have reported that X-ray powder diffraction Debye–Scherrer film for $BaUO_{3.06}$ was indexed as single cubic, although several weak noncubic lines were found for a film of $Ba_{0.99}UO_{3.20}$. We tried to prepare exactly oxygen-stoichiometric bar-

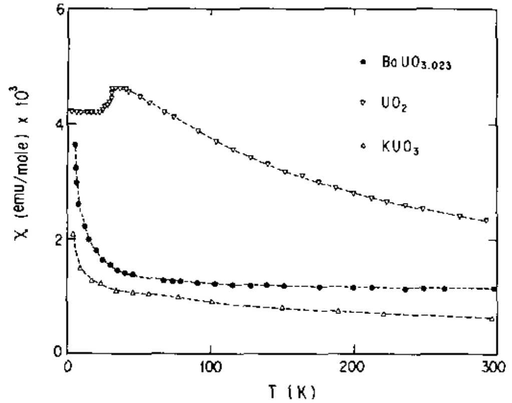

FIG. 1. Temperature dependence of magnetic susceptibility for $BaUO_{3.023}$. For comparison, susceptibilities for UO_2 and KUO_3 are also shown.

ium uranate several times. However, the specimens prepared were slightly oxygen-excess.

In $BaUO_3$, the U^{4+} ions have an octahedral arrangement of nearest-neighbor oxygens, with U–O distances of 2.204 Å. Figure 1 shows the temperature dependence of magnetic susceptibility for the $BaUO_{3.023}$ prepared in this study. With increasing temperature, the susceptibility decreases. However, the susceptibilities above 60 K are almost constant. To compare this behavior, the temperature dependence of magnetic susceptibilities for UO_2 and KUO_3 is also shown in Fig. 1. In UO_2, the central U^{4+} ion is surrounded by eight oxygen ions with cubic symmetry. An antiferromagnetic transition is found at 30.8 K (*12*). On the other hand, KUO_3 is isostructural with $BaUO_3$, i.e., cubic perovskite, and shows a paramagnetic behavior down to 4.2 K (*13*). Figure 2 shows the variation of susceptibility of $BaUO_{3.023}$ with reciprocal temperature, $1/T$. From the extrapolation of $1/T$ to 0, we get the temperature-independent paramagnetic susceptibility, $\chi_{TIP} = 1110 \times 10^{-6}$ (emu/mole). Similar temperature-independent paramagnetism has been found for the actinide ions with $[Rn]5f^2$ electronic configuration in octahedral crystal field (*14*). The ground state of U^{4+} ion is the $^3H_4$ state, the degeneracy of which is nine. In octahedral symmetry, the Γ_1 crystal field level (a singlet) is lowest with Γ_4 (a triplet) as the first excited state. The singlet Γ_1 can have no temperature-dependent (first-order) magnetism, but does interact with the Γ_4 level to give a temperature-independent term (second order). Then there will be a range of temperature for which the compound will exhibit only temperature-independent paramagnetism. This susceptibility is given by the equation

$$\chi = \frac{40Ng^2\beta^2}{3\,\Delta E} \qquad (3)$$

where ΔE is the energy gap between the Γ_1 and Γ_4 levels. By subtracting this temperature independent susceptibility from the susceptibility data measured here, the temperature-dependent susceptibility is obtained (which could be expressed by the equation $\chi = 0.0138/(T + 1.5)$). This means that due to excess oxygens, some of the U^{4+} ions are oxidized not to the U^{6+} state, but to the U^{5+} state, because the U^{6+} ions are diamagnetic. From its variation as a func-

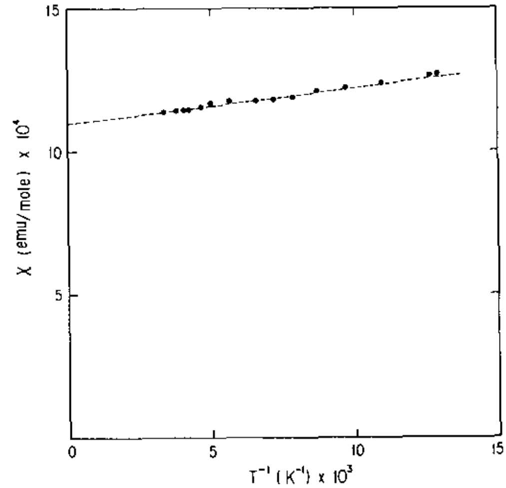

FIG. 2. Magnetic susceptibility for $BaUO_{3.023}$ versus reciprocal temperature.

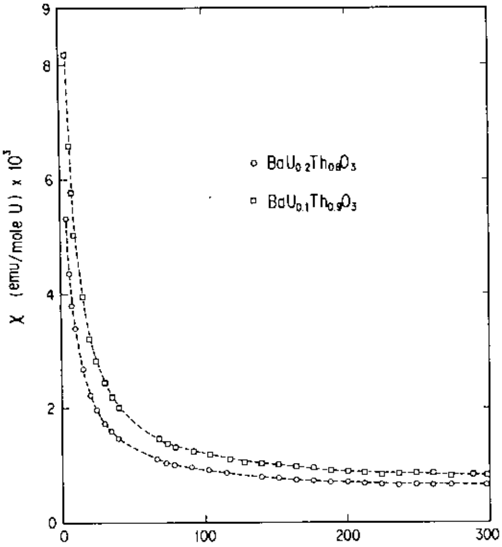

FIG. 3. Temperature dependence of magnetic susceptibility for $BaU_{1-y}Th_yO_3$.

tion of temperature, the effective magnetic moment of U^{5+} is obtained to be 2.00 μ_B. This moment is often found for the U^{5+} in octahedral crystal field (*15*).

To confirm the oxygen coordination around the U^{4+} ion in $BaUO_3$, magnetic susceptibility measurements were carried out for $BaU_{1-y}Th_yO_3$ solid solutions (y = 0.8, 0.9) in which diamagnetic Th^{4+} ions substitute for the U^{4+} ions. The temperature dependence of their magnetic susceptibilities is shown in Fig. 3. They show normal paramagnetic behavior, i.e., the susceptibility increases with decreasing temperature. With increasing thorium concentration (y value), the temperature dependence of magnetic susceptibility becomes greater. The results of X-ray diffraction analysis show that these solid solutions are no longer simple cubic, i.e., not all the peaks observed by the X-ray powder diffraction were indexed using a cubic cell. This means the coordination symmetry of oxygens around uranium ion is no longer octahedral. From these, it is concluded that the large temperature-independent paramagnetic susceptibility found for $BaUO_3$ is the result of the octahedral coordination around U^{4+}. The magnitude of the temperature-independent paramagnetism for $BaUO_3$ is about half of that for $(NH_4)_2UCl_6$, for example (*16*). This means that the crystal field strength for $BaUO_3$ is larger than that for $(NH_4)_2UCl_6$, which results in the energy gap between the ground and the first excited energy levels being larger in the former compound than in the latter compound (see Eq. (3)).

References

1. "Gmelin's Handbuch der Anorganischen Chemie," System-Nr55, U, Teil C3, Springer-Verlag, New York/Berlin (1975).

2. H. KLEYKAMP, *J. Nucl. Mater.* **131,** 221 (1985).

3. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32,** 751 (1976).

4. R. W. G. WYCKOFF, "Crystal Structures (II)," Interscience, New York (1964).

5. H. D. MEGAW, *Proc. Phys. Soc.* **58,** 133 (1946).

6. S. R. DHARWADKAR AND M. S. CHANDRASEKHARAIAH, *Anal. Chim. Acta* **45,** 545 (1969).

7. T. FUJINO AND T. YAMASHITA, *Fresenius' Z. Anal. Chem.* **314,** 156 (1983).

8. L. L. SPARKS AND R. L. POWELL, *J. Res. Nat. Bur. Stand. (U.S.) Sect. A* **76,** 263 (1972).

9. Y. HINATSU AND T. FUJINO, *J. Solid State Chem.* **60,** 195 (1985).

10. S. A. BARRETT, A. J. JACOBSON, B. C. TOFIELD, AND B. E. F. FENDER, *Acta Crystallogr. Sect. B* **38,** 2775 (1982).

11. C. W. WILLIAMS, L. R. MORSS, I.-K. CHOI, *in* "Geochemical Behavior of Disposed Radioactive Waste (G. S. Barney, J. P. Navratil, and W. W. Schultz, Eds.) ACS Symposium Series, No. 246, p. 323, Washington, DC (1984).

12. B. C. FRAZER, G. SHIRANE, D. E. COX, AND C. E. OLSEN, *Phys. Rev. A* **140,** 1148 (1965).

13. B. KANELLAKOPULOS, E. HENRICH, C. KELLER, F. BAUMGÄRTNER, E. KÖNIG, AND V. P. DESAI, *Chem. Phys.* **53,** 197 (1980).

14. N. M. EDELSTEIN AND J. GOFFART, *in* "The Chemistry of the Actinide Elements" (J. J. Katz, G. T. Seaborg, and L. R. Morss, Eds.), 2nd ed., Chap. 18, Chapman and Hall, London/New York (1986).

15. B. KANELLAKOPULOS, *in* "Gmelin Handbuch der Anorgannischen Chemie," Uranium Supplement Volume A6, p. 1, Springer-Verlag, Berlin (1983).

16. C. A. HUTCHISON, JR., AND G. A. CANDELA, *J. Chem. Phys.* **27,** 707 (1957).