Journal of Alloys and Compounds, 213/214 (1994) 394–397
JALCOM 4003

Phase behavior of actinide trihalides under pressure

J.R. Peterson

Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600 (USA) and Transuranium Research Laboratory (Chemistry Division), Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6375 (USA)

Abstract

Actinide trihalides exhibit in common a limited number of crystal structures. The range of existence of each structure correlates well with the cationic:anionic radius ratio. It is the efficiency of packing of the actinide cations and halide anions that determines which crystal structure is exhibited by a particular actinide trihalide. It appears that the packing efficiency and this ionic radius ratio control the high pressure phase behavior of the actinide trihalides as well. From other studies of lanthanide trihalides under pressure, the following series of crystal structures, in order of increasing packing efficiency, can be derived: $AlCl_3$-type monoclinic → BiI_3-type rhombohedral → UCl_3-type hexagonal → $PuBr_3$-type orthorhombic. Arguments based on cation coordination number (CN) changes with increasing pressure can be used to justify this series of structures and to speculate on the identity of a new, even higher pressure phase that f element trihalides may exhibit. We have used several spectroscopic techniques to monitor the phase behavior of selected f element trihalides under pressure. The results of our studies are summarized, correlated with packing efficiency, and used to propose the potential existence of a "new", higher pressure, trihalide phase with a cation CN of 6.

1. Introduction

After the oxides the trihalides of the lanthanides and actinides (lanacts) are perhaps the most studied group of compounds of the f elements [1]. As such there are data available to correlate their behaviors and to determine the systematics of their physical and chemical properties. Crystal structure data is one example, and the 4f and 5f trihalides exhibit in common six structures. Two of these pertain only to the trifluorides and will be excluded from the present discussion, because the trifluorides are not easily melted (to gain optical transparency) and their preparation is less straightforward than that of the heavier trihalides. The four remaining crystal structures are the $AlCl_3$-type monoclinic (M), BiI_3-type rhombohedral (R), UCl_3-type hexagonal (H), and the $PuBr_3$-type orthorhombic (O). Most pertinent to the present work are the results of Beck and Gladrow [2, 3], who have investigated the structural behavior of the lanthanide trihalides as a function of pressure and temperature. We have used absorption, phonon Raman, and/or luminescence spectroscopic techniques to monitor the phase behavior of selected f element trihalides under pressure [4–11]. The results of our studies are summarized here, correlated with packing efficiency, and used to propose the existence of a "new", higher pressure, trihalide phase with a cation coordination number (CN) of 6.

2. Experimental details

f element trihalides have been prepared by a variety of techniques [1, 12]. Hydrohalogenation reactions on the corresponding oxides are recommended for the synthesis of trichlorides and tribromides; triiodides are most conveniently prepared via reaction of anhydrous HI(g) with the corresponding trichloride or tribromide. Details of our trihalide syntheses, Merrill–Bassett-type diamond anvil pressure cells, pressure measuring techniques, absorption, phonon Raman, and luminescence spectroscopic analysis procedures and apparatus, data handling operations, etc. have been published previously (*e.g.* refs. 12–15). Our development and use of data bases of absorption, phonon Raman, and luminescence data to identify crystal structures have already been documented [14–18]. The transplutonium isotopes used in this work were synthesized directly, or resulted from the decay of isotopes synthesized directly, in the ORNL High Flux Isotope Reactor. They were separated and purified in the Radiochemical Engineering Development Center and made available for study as part of the US Department of Energy's national program for transplutonium element production and research.

3. Results and discussion

Some characteristics of the four relevant crystal structures are listed in Table 1. As noted in the work of

0925-8388/94/$07.00
SSDI 0925-8388(93)04003-9

TABLE 1. Some characteristics of relevant lanact trihalide crystal structures

Symbol[a]	Prototype crystal structure	Space group	ITC[b] number	Z (Z^B)[c]	Cation coordination number; atomic position[d]
M	$AlCl_3$-type monoclinic	$C^3_{2h}(C2/m)$	12	4 (2)	6; 2g
R	BiI_3-type rhombohedral	$C^2_{3i}(R\bar{3})$	148	2 (2)	6; 2c
H	UCl_3-type hexagonal	$C^2_{6h}(P6_3/m)$	176	2 (2)	9; 2d
O	$PuBr_3$-type orthorhombic	$D^{17}_{2h}(Cmcm)$	63	4 (2)	8; 2c

[a] Adopted here for conciseness.
[b] From ref. 19.
[c] Number of formula units in the crystallographic unit cell (Bravais space cell).
[d] Atomic position in Wyckoff notation.

others [2, 3], the range of existence of each of the four, trihalide crystal structures correlates well with the cationic:anionic radius ratio. At room temperature and pressure (RTP), the order of the structures with increasing M^{3+}:X^- radius ratio is R → M → O → H, with corresponding cation CNs 6 → 6 → 8 → 9. It is the efficiency of packing of the lanact cations and halide anions that determines which crystal structure is exhibited by a particular lanact trihalide. It appears that the packing efficiency and this ionic radius ratio control the high pressure phase behavior of the lanact trihalides as well. From the results of Beck and Gladrow on the behavior of lanthanide trihalides under pressure [2], one can determine that the order of the trihalide crystal structures with increasing packing efficiency ($\Sigma V_{\text{ions}}/V_{\text{cell}}$) is M → R → H → O, with corresponding cation CNs 6 → 6 → 9 → 8. It is this sequence of structures, then, that should be expected to be followed when a lanact trihalide is subjected to applied pressure.

In Fig. 1 are summarized the results of optical spectroscopic studies of lanact trihalides under pressure carried out in our laboratory (TRL) over the past nine years in comparison with the above-described sequence of crystal structures with increasing packing efficiency [4–11]. The starting material in each case is denoted by RTP followed by its formula and is listed under the structure which the sample exhibited. Observed high pressure phases are denoted by HP followed by its formula and are listed under the spectrally identified structure. Details about the phase transition are given in the reference cited. Indeed, increasing pressure does promote better packing efficiency. All of our experimental results are consistent with this sequence of crystal structures for lanact trihalides under pressure. Also, the several observations of a reversible phase transition to a potentially "new", higher pressure phase in $PrBr_3$ [9], $NdBr_3$ [9], $CfCl_3$ [10], and $CmCl_3$ [11] should be noted. Attempts to date to identify this potentially new phase have met with conflicting results. Collaborative experiments on $NdBr_3$ at 25–30 GPa carried out at the National Synchrotron Light Source (Brookhaven National Laboratory) have yielded data suggestive of a "new", higher pressure structure different from the RTP orthorhombic structure [20]. However, X-ray diffraction studies on $NdBr_3$ in collaboration with the European Institute for Transuranium Elements in Karlsruhe, Germany, have revealed only a distortion of the RTP orthorhombic structure up to 52 GPa [21]. Thus, it is still uncertain whether or not a "new", higher pressure phase exists.

Let us now focus on the behavior of the lanact cation CN with increasing pressure in these trihalide compounds. We shall consider only the simplified ion radius ratio model. When the lanact cation is large (as it is for the light lanacts) and the halide anion is small (as it is for Cl^- ion), then we have the maximum possible CN of the lanact cation (*e.g.* 9, as in the H structure). Likewise, when the lanact cation is small (heavy lanacts) and the halide anion is large (*e.g.* I^- ion), then we should have the minimum CN of the lanact cation (*e.g.* 6, as in the M and R structures). In the latter cases the corresponding crystal structure will be controlled by the closest-packed halide ions. For the intermediate sizes of cations and anions, the CN of the lanact cation in the resulting trihalide compound will be intermediate in value (*e.g.* 8, as in the O structure).

In general the crystal structure adopted by a lanact trihalide will be dominated by the balance of the coulombic attraction (M^{3+}–X^-) and anion–anion repulsion (X^-–X^-) forces. As the pressure increases, the M^{3+}–X^- distance decreases, so the coulombic attraction force increases, thus promoting an increase

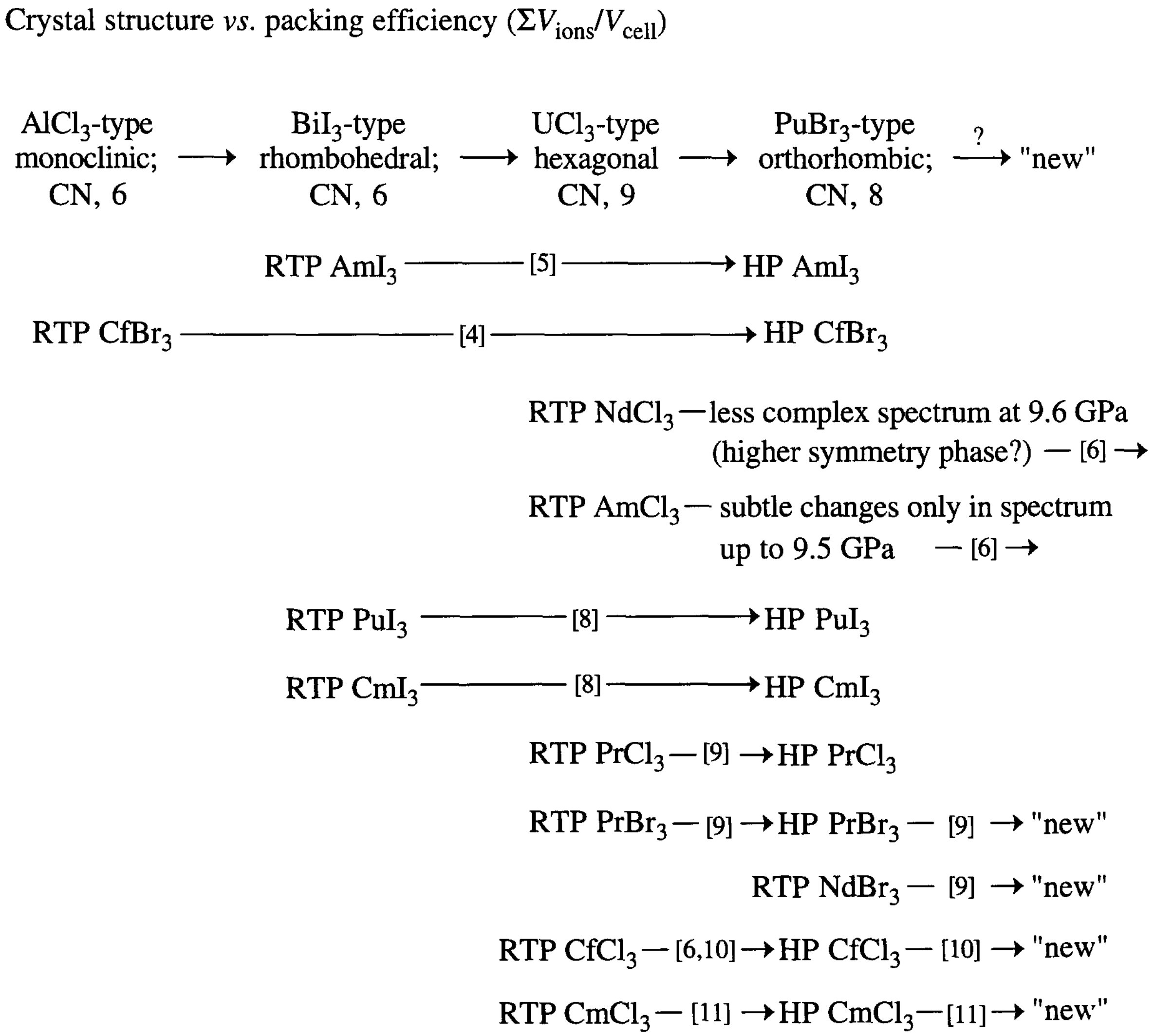

Fig. 1. TRL experimental results of studies on selected lanact trihalides under pressure correlated to the sequence of trihalide crystal structures with increasing packing efficiency.

in the CN of the lanact cation. Simultaneously, however, as the pressure increases, the X^-–X^- distance decreases, which increases the anion–anion repulsion, thus promoting a decrease in the CN of the lanact cation. Therefore, it should not be unexpected that the sequence of crystal structures with increasing pressure increases in cation CN to some maximum value and then decreases. Following this conclusion, then, the above-mentioned, "new", higher pressure phase of the lanact trihalides may be a hexacoordinated, closest-packed structure.

It is interesting to note that several of the lanact metals have been shown recently to undergo a phase transition at very high pressure from a crystal structure of lower symmetry to one of higher symmetry [22]. The present author suggests that this behavior parallels that described herein; this phase transition occurs from a structure dominated by attractive forces (maximizing the chemical bonding and packing efficiency) to one dominated by repulsive forces (minimizing the core ion M^{n+}–M^{n+} repulsion). At such a phase transition one would not expect a significant change in the relative volume of the lanact metal.

It is expected that future studies of lanact trihalides under high pressure will determine whether or not an O→"new" phase transition occurs. Of considerable interest as well is the identification of the crystal structure of this potentially common, higher pressure phase of the lanact trihalides.

Acknowledgments

The author gratefully acknowledges with appreciation and thanks the contributions of his past and present graduate and postdoctoral students and his professional colleagues who have worked with him over the years on characterizing the behavior of lanact trihalides under pressure. Their names are given in the various references cited herein. This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy, under Grant DE-FG05-88ER13865 to the University of Tennessee, Knoxville, and Contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

References

1 D. Brown, *Halides of the Lanthanides and Actinides,* Wiley, London, 1968.

2 H.P. Beck and E. Gladrow, *Z. Anorg. Allg. Chem., 453* (1979) 79.

3 H.P. Beck and E. Gladrow, *Z. Anorg. Allg. Chem., 502* (1983) 178.

4 J.R. Peterson, J.P. Young, R.G. Haire, G.M. Begun and U. Benedict, *Inorg. Chem., 24* (1985) 2466.

5 R.G. Haire, U. Benedict, J.P. Young, J.R. Peterson and G.M. Begun, *J. Phys. C, 18* (1985) 4595.

6 J.R. Peterson, J.P. Young, R.G. Haire and U. Benedict, *Physica B, 144* (1986) 85.

7 J.R. Peterson, R.G. Haire, U. Benedict and J.P. Young, *J. Less-Common Met., 133* (1987) 143.

8 R.G. Haire, J.P. Young, J.R. Peterson and U. Benedict, *J. Less-Common Met., 133* (1987) 167.

9 W.R. Wilmarth, G.M. Begun, R.G. Haire, J.P. Young and J.R. Peterson, *Appl. Spectrosc., 43* (1989) 1038.

10 J.P. Young, J.R. Peterson, R.G. Haire, W.R. Wilmarth and G.M. Begun, *High Pressure Res., 2* (1990) 391.

11 G.D. Del Cul, R.G. Haire and J.R. Peterson, *J. Alloys Comp., 181* (1992) 63.

12 J.P. Young, R.G. Haire, R.F. Fellows and J.R. Peterson, *J. Radioanal. Chem., 43* (1978) 479.

13 J.R. Peterson, U. Benedict, J.P. Young, R.G. Haire and G.M. Begun, *Microchem. J., 34* (1986) 76.

14 J.R. Peterson, J.P. Young, W.R. Wilmarth and R.G. Haire, *Appl. Spectrosc., 44* (1990) 461.

15 J.R. Peterson, *J. Alloys Comp., 193* (1993) 165.

16 W.R. Wilmarth and J.R. Peterson, in A.J. Freeman and C. Keller (eds.), *Handbook on the Physics and Chemistry of the Actinides,* Vol. 6, North-Holland, Amsterdam, 1991, p. 1.

17 N.A. Stump, G. Chen and J.R. Peterson, in Council of Scientific Research Integration (ed.), *Trends in Applied Spectroscopy,* Trivandrum, CSIR, in the press.

18 N.A. Stump, G. Chen, R.G. Haire and J.R. Peterson, *Appl. Spectrosc., 47* (1993) 1951.

19 *International Tables for X-ray Crystallography,* Vol. 1, Kynoch, Birmingham, 1969.

20 L.W. Finger, Geophysical Laboratory, Carnegie Institution, Washington, DC, personal communication, 1990.

21 J.R. Peterson, S. Heathman and U. Benedict, *J. Alloys Comp., 193* (1993) 306.

22 J. Akella, Ultrahigh-pressure studies of f-electron metals, *Joint AIRAPT–APS Conf. on High Pressure Science and Technology, Colorado Springs, CO, June 28–July 2, 1993,* Paper 06 2; *Bull. Am. Phys. Soc., 38* (1993) 1569.