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A new ultra-high pressure phase in samarium

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Structural changes in samarium under pressure were studied in a diamond-anvil cell (DAC) to 189 GPa. A number of phase transformations were observed between room pressure and 75GPa. At about 91 GPa samarium transforms to a body-centered tetragonal structure, and the unit cell parameters at 189 GPa are $a=2.402(4)$ Å and $c=4.231(17)$ Å, $V=24.40(12)$ Å^3 and $Z=2$. Identification of a body-centered tetragonal phase in Sm at about 90 GPa, which is similar to that reported in Ce, suggests that this phase could appear in other rare-earth elements too.

Jayaraman and Sherwood [1] reported a systematic behavior in the phase transformations of lanthanides as a function of pressure and their suggested structural sequence with increasing pressure is hcp–Sm-type–dhcp–fcc. Beyond the face-centered cubic (fcc) phase a six-layered structure was discovered [2,3] and at still higher pressure and orthorhombic (α-U type) phase was reported for Pr [4,2].

Studies on Ce have indicated that at about 12 GPa pressure, cerium, with an α″ body-centered monoclinic structure, transforms to a body-centered tetragonal phase [5,6]. So far no systematic search was made for the appearance of this phase in other rare-earth elements, and the pressure at which it may be stable could be very high. Recently, Sm was investigated at room temperature to 190 GPa and the data between 90 and 190 GPa are presented in this Letter. A detailed paper covering the whole pressure range from 1 atm to 190 GPa will be published at a later date.

The Sm samples were prepared from a thin foil by a sublimation process and were 99.99% pure. The sample was analyzed by optical emission spectroscopy technique, and not other rare-earth impurities could be detected. Common metal impurities present in the sample are Ca ~ 10 ppm, Cu ~ 5 ppm, Mg ~ 10 ppm and Mn ~ 10 ppm by weight. We used a diamond-anvil cell (DAC) apparatus for our studies. Type 1A diamonds were preselected for low internal strain and the anvils have a central flat of 50 μm to a culet size of 300 μm with 7° bevel angle. The Sm sample, with Pt powder as a pressure marker, was loaded into the 50 μm sample hole of a pre-indented spring steel gasket. The sample plus platinum powder acted as the pressure medium. Under the conditions of this study, the final sample size at high pressure was approximately 80 μm in diameter.

Diffraction data were obtained at the Cornell High Energy Synchroton Source (CHESS) X-ray facility. The X-ray spot from the synchroton source was collimated to ~25 μm diameter so that a small area of the sample could be X-rayed to avoid the large pressure gradient that exists across the sample [7]. We estimate the pressure gradient across 25 μm to be 1–2 GPa. A solid-state intrinsic germanium detector was used to collect energy-dispersive diffraction (EDD) spectra. The diffraction angles were calibrated by using a gold standard and a total of eleven spectra were collected for the study. A detailed description of the experimental procedure was given by Ruoff [8].

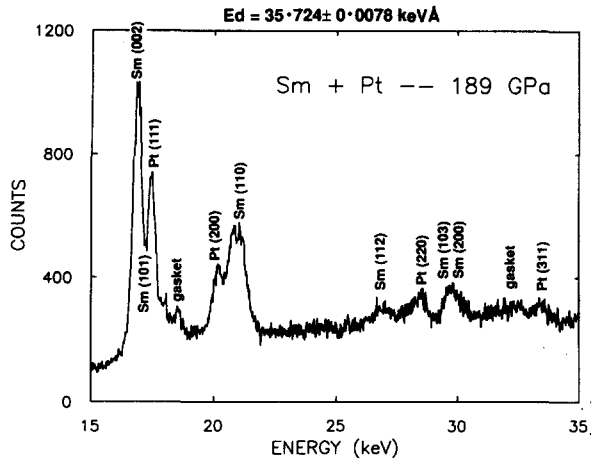

Fig. 1. Energy dispersive spectrum from the run at 189 GPa. $Ed = 35.724 \pm 0.007$ keV Å.

A number of phase transformations were observed between room pressure and 75.0 GPa and these will be discussed in detail in another paper. At about 91.0 GPa pressure, new reflections appeared in the spectrum suggesting another phase change, and the reflections (from the sample) in the 123 GPa experiment were all from the high pressure phase. These reflections persisted to the highest pressure of this study (190 GPa). There were five reflections in the higher-pressure spectra that could be attributed to the sample, while the rest were from the pressure standard, the fluorescent peaks and at times from gasket material. These reflections could be fitted to a body-centered tetragonal structure, fig. 1. A comparison was made between the observed and calculated d values for a body-centered tetragonal cell and the agreement is reasonable (table 1). However, it is evident from table 1 that one reflection at 1.099 Å could not be fitted to this structure. This is a weak reflection, but could not be ignored because of its presence in all the runs at and above 91.0 GPa pressure. At present we do not know the source for this reflection.

Table 1
Calculated and observed d values for the body-centered tetragonal phase of Sm at 189 GPA.

d (observed)	d (calculated)	hkl
2.116	2.116	0 0 2
	2.096	1 0 1
1.706	1.706	1 1 0
1.324	1.328	1 1 2
1.201	1.218	1 0 3
	1.206	2 0 0
1.099	-	NI

Volume compression data for Sm between 123.0 and 189.0 GPa were calculated on the basis of a body-centered tetragonal structure and plotted in fig. 2,

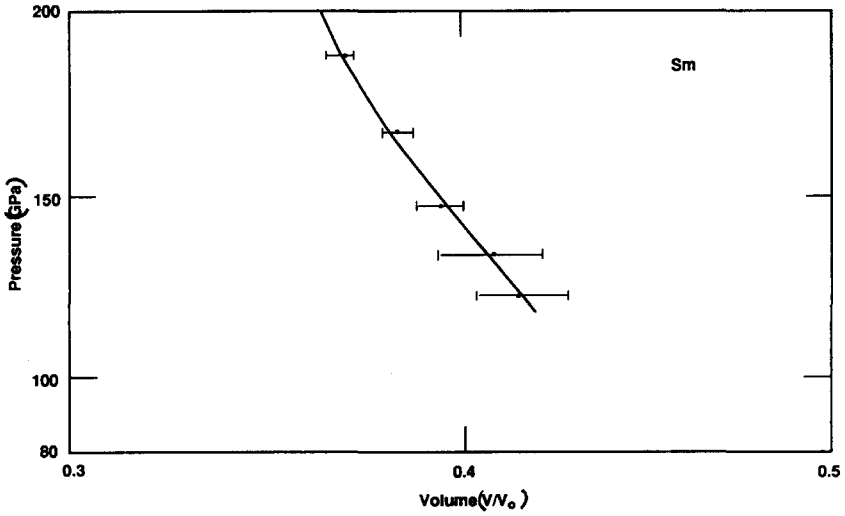

Fig. 2. Volume compression data V/V_0 for samarium between 120.0 and 190.0 GPa pressure.

and the unit cell parameters at 189.0 GPa are $a=2.402(4)$ Å and $c=4.231(17)$ Å, $V=24.40(12)$ Å^3 and $Z=2$. The c/a ratio for Sm is ~ 1.76 which compares well with the c/a ratio of 1.69 for Ce given by Olsen et al. [6]. At the highest pressure samarium is 63% compressible, $V/V_0=0{,}37$, and this compression value is within the range previously reported for other rare-earth elements (e.g. Gd at 106 GPa has $V/V_0=0.460$ [9]). Olsen et al. [10] have also reported similar compression values from their Sm equation-of-state calculations. From fig. 3 it is also evident that samarium is more compressible in the c direction relative to the a direction.

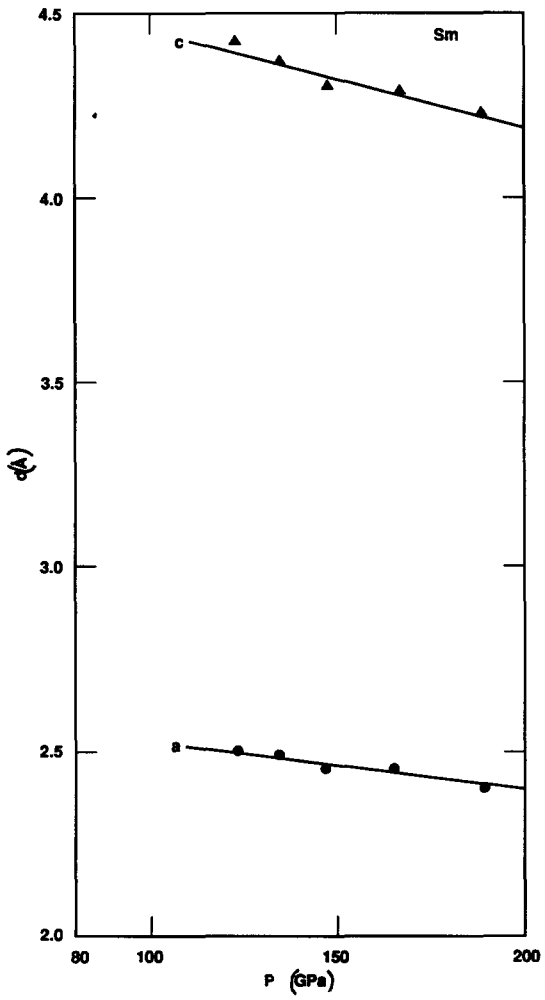

Fig. 3. Unit cell parameters a and c plotted as a function of pressure.

High pressure studies on Ce [5,6] have shown that it goes through an isostructural face-centered cubic to another face-centered cubic transformation at 0.8 GPa, at about 5 GPa it transforms from face-centered cubic to an α'' body-centered monoclinic and at about 12 GPa cerium further transforms from body-centered monoclinic to a body-centered tetragonal phase. This high pressure phase is stable to 46.0 GPa [6].

Systematics in the structural sequence of the rare-earth metals suggest that similar structures in these would appear at progressively higher pressure as the Z value increases (Ce→Lu). So far, the body-centered tetragonal phase was not encountered in other rare-earth elements, perhaps because to date the highest pressure to which a rare earth element was subjected to was 106.0 GPa (e.g. Gd [9]). Identification of the body-centered tetragonal phase in Sm at about 90.0 GPa, which is similar to that reported in Ce, suggests that this phase could appear in Gd at pressures in excess of 106 GPa and in Pr and Nd below ~ 90 GPa pressure. It would be worthwhile to study the lower Z rare earths (Ce, Pr, Nd) in order to ascertain (a) whether the body-centered tetragonal phase is present in other rare earths and (b) whether it is ultimate high pressure phase of these rare-earth metals.

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