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Journal of Alloys and Compounds 226 (1995) 143–145

Journal of
ALLOYS
AND COMPOUNDS

Phase transformation of the monochalcogenides SmX ($X \equiv S$, Se, Te) under high pressure

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Received 24 February 1995

Abstract

The high-pressure behaviour of the monochalcogenides of samarium (SmS, SmSe and SmTe) was investigated up to pressures of 55 GPa using the energy dispersive X-ray diffraction technique and synchrotron radiation. SmTe and SmSe show abnormal volume changes around 5 and 7 GPa respectively. SmS shows a phase transformation at low pressure (less than 1.8 GPa), retaining the same cubic structure, but undergoing a considerable volume collapse and a change of colour. SmS and SmSe both exhibit a phase transition from NaCl- to CsCl-type structure at high pressure, which has not been observed previously.

Keywords: High pressure; Structure; Diamond anvil cell; Chalcogenides; Samarium

1. Introduction

Compounds of divalent lanthanides have been reported to undergo isostructural phase transitions under pressure, which indicate an increase in the lanthanide valence towards trivalency. This has, for instance, been observed for SmS, SmSe and SmTe [1]. The present study extends these measurements to higher pressure using recent techniques which have become available in high-pressure research. In particular, the use of the ruby fluorescence method for pressure determination is, in general, more precise than the results obtained from an NaCl pressure marker due to the difference in compressibilities between marker and sample. Also, the use of synchrotron radiation and modern high- pressure cells enables the 50–60 GPa pressure region to be reached easily.

2. Experimental details

2.1. Materials

The three compounds SmS, SmSe and SmTe were synthesized using the same method. Samarium turnings and the desired chalcogen were heated in an evacuated and sealed quartz tube up to 700 °C resulting in a fine black powder. Afterwards, this powder was pressed into a pellet and sealed under vacuum in a tungsten crucible which was kept about 50 °C below the melting temperature of the respective chalcogenide. Within several weeks, single crystals (cubic space group *Fm*3*m*) were grown by recrystallization up to 1–5 mm.

Table 1
Lattice parameters of SmX ($X \equiv S$, Se, Te) at ambient pressure

Compound	Lattice parameter *a* (pm)	Literature values (pm)
SmS	597.02(23)	596.2(2) [2]
SmSe	619.89(7)	620.0 [3]
SmTe	660.08(5)	659.4 [4]

The samples employed in our high-pressure work were obtained by grinding these crystals to a fine powder. The room temperature–pressure lattice parameters of these materials are reported in Table 1 and are in good agreement with literature values.

2.2. High-pressure studies

The energy dispersive X-ray high-pressure studies of the monochalcogenides were performed at room temperature using a Syassen–Holzapfel-type diamond anvil cell. The samples were loaded into a 200 μm hole drilled into a pre-indented Inconel gasket together with a ruby chip for pressure determination by the ruby fluorescence method [5]. Silicone oil was used as the pressure transmitting medium.

0925-8388/95/$09.50
SSDI 0925-8388(95)01629-5

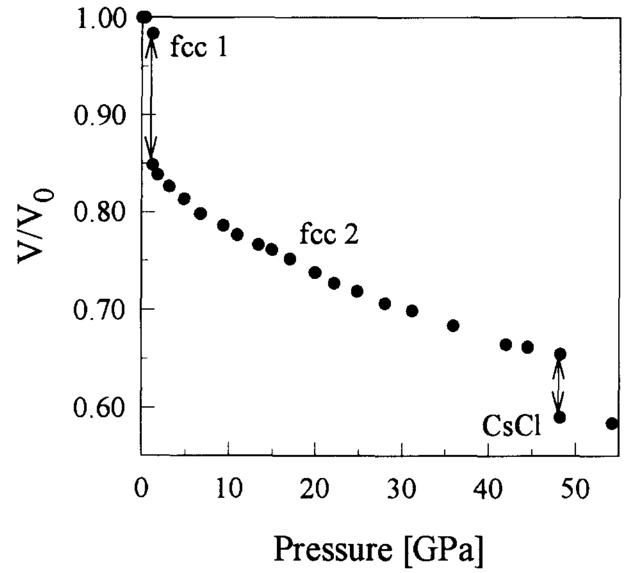

Fig. 1. Pressure–volume data for SmS.

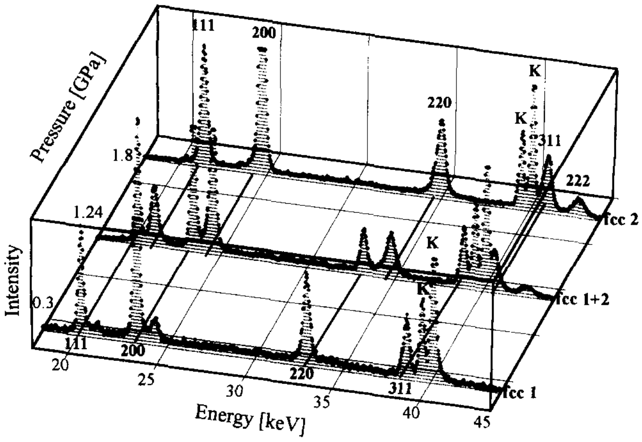

Fig. 2. F.c.c. 1 to f.c.c. 2 transition in SmS, showing region of coexistence (fluorescence lines are marked with K).

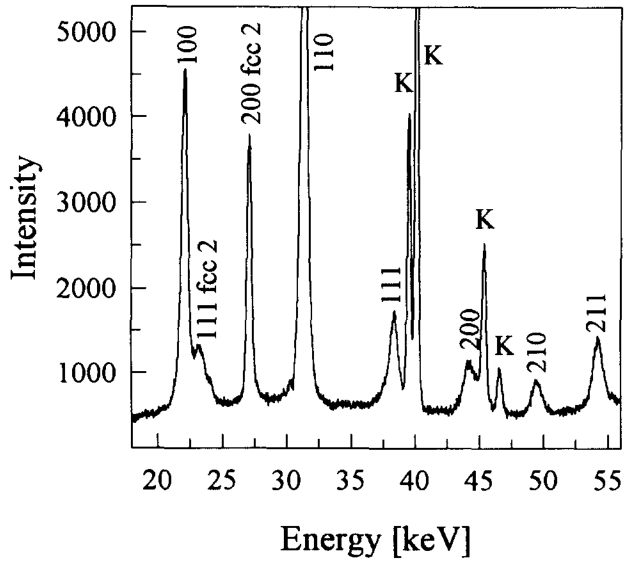

Fig. 3. Diffraction spectrum of SmS CsCl phase at 54 GPa (fluorescence lines are marked with K).

Experiments were carried out at the EDS facility of the electron storage ring DORIS III of Hasylab, DESY, Hamburg (Germany). The exact value of the Bragg angle was determined using a UC standard in the exact configuration as employed for the chalcogenide samples. This value was found to be equal to 5.116°. The lattice spacings were calculated as a function of the applied pressure for each sample using these calibrations and the energy dispersive diffraction data.

For each pressure step, the lattice parameters and the relative volume V/V_0 were calculated. The $V(P)$ data were fitted to the Birch and Murnaghan equations of state [6–8] to obtain the bulk modulus B_0 and its pressure derivative B'_0 (the subscript zero indicates ambient pressure).

3. Results and discussion

3.1. SmS

The relative volume–pressure behaviour of SmS was studied up to 54 GPa in 23 steps of increasing pressure. A plot of the results of the measurements is shown in Fig. 1. It can be observed that the sample undergoes a phase transformation (f.c.c. 1 to f.c.c. 2) at 1.24 GPa, retaining the initial NaCl-type structure, but undergoing a considerable volume collapse (13.8%). At 1.8 GPa, this transformation is completed (Fig. 2), and the sample changes from blue/black to a golden colour. This phenomenon can be attributed to a valence transition of the Sm^{2+} ion to the trivalent state. A relatively normal compression curve is obtained from this point until 42 GPa, when a previously unobserved phase transition to a CsCl-type structure starts to occur. This transformation, accompanied by a 10% change in the relative volume, is almost complete at the highest pressure obtained, i.e. 54 GPa (Fig. 3). At this pressure, the sample has undergone an unusually large 42% change in volume compared with its initial value. All these transformations are reversible on release of pressure.

The bulk modulus B_0 and its pressure derivative B'_0 were determined by fitting the pressure–volume data of SmS (golden phase) to the Birch and Murnaghan equations of state; values of $B_0 = 89.8$ GPa and $B'_0 = 4.9$ (Birch) and $B_0 = 92$ GPa and $B'_0 = 4.3$ (Murnaghan) were obtained.

3.2. SmSe

The high-pressure behaviour of SmSe was studied up to 50 GPa in 33 increments of increasing pressure and in six steps of decreasing pressure. At ambient pressure, the initial sample of SmSe exists in the NaCl-type structure. Applying pressure to the sample gives rise to an extremely anomalous compression curve as can be seen in Fig. 4, which is attributed to a 4f–5d electronic collapse. This transition is completed by 9 GPa and, like SmS, a change in colour (from black to gold) is observed. Afterwards, a normal compression curve

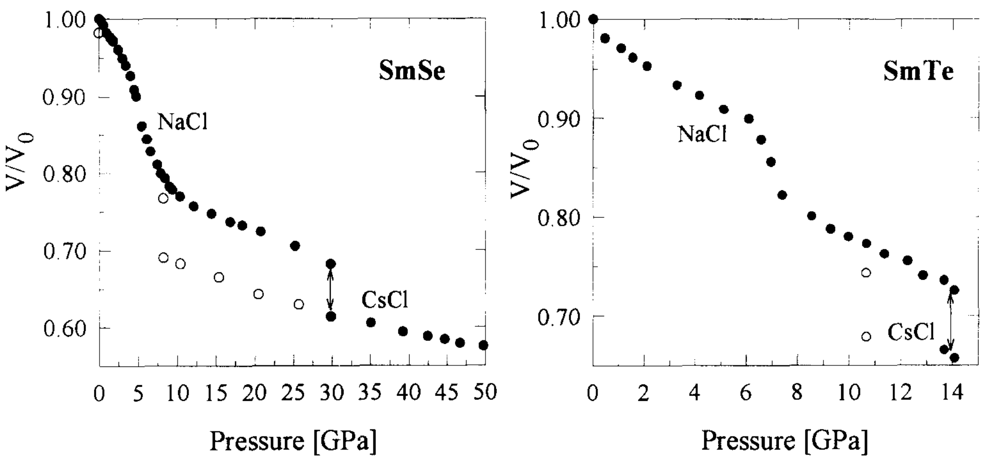

Fig. 4. Relative volume of SmSe and SmTe as a function of pressure (open circles denote decreasing pressure).

is obtained until another change from the NaCl- to CsCl-type structure occurs at 25 GPa being completed at 35 GPa. The phase change is accompanied by a 6.8% volume collapse and, afterwards, the CsCl-type structure remains stable until the highest pressure of 50 GPa is reached. On release of pressure the CsCl phase is observed down to about 8 GPa before changing completely back to the NaCl- type structure. This represents a significant hysteresis effect. Like SmS, this sample undergoes a 45% change in volume over the pressure range studied.

3.3. SmTe

The relative volume V/V_0 as a function of pressure is shown in Fig. 4 for SmTe. This compound was studied up to 14 GPa in 20 increasing and three decreasing pressure steps. As with SmSe, the sample shows an extremely anomalous compression curve similar to those of the UX_3-type compounds [9]. Again this transformation is believed to be owing to the promotion of a 4f electron of the rare earth ion into the 5d conduction band states. This transformation occurs between 6 and 8 GPa and is followed at 12.9 GPa by a further change to a CsCl- type structure and a 6.8% volume collapse which is completed by 14 GPa.

4. Conclusions

The isostructural transitions have been confirmed for SmS, SmSe and SmTe. Anomalies in the pressure–volume curves were observed and explained in the three cases by a change in the valence state of the Sm ion from divalent to trivalent owing to $4f \rightarrow 5d$ electron promotion. The NaCl to CsCl transition reported for SmTe has been confirmed and, in the case of SmS and SmSe, this transition was observed for the first time since it occurs in a pressure range that has not been investigated previously.

Acknowledgements

The authors wish to thank Hasylab-DESY for permission to use the synchrotron radiation facility. Support given to T.L.B. and S.D. within the framework of the EC-funded training programme "human capital and mobility" is also acknowledged.

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