

PRESSURE INDUCED ELECTRONIC AND NaCl TO CsCl TYPE TRANSITIONS
IN SOME RARE EARTH MONOTELLURIDES

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High pressure X-ray diffraction study reveals that PrTe, SmTe and EuTe which possess NaCl type structure transform to CsCl type at 90 ± 10 , 110 ± 10 , 100 ± 10 kbar respectively. Prior to this transformation SmTe shows an anomalous decrease in volume with pressure, which is attributed to the 4f–5d electronic transition.

RARE earth monochalcogenides crystallize in NaCl-type structure¹ and are either metallic or semiconducting depending on the valence state of the rare earth ion; metallic if trivalent and semiconducting if divalent.^{2,3} Sm, Eu and Yb have a stable divalent state and hence their compounds are semiconducting. Also Tm in TmTe is divalent and the compound is semiconducting. They have anomalously large lattice constants, in the series of rare earth chalcogenides; these exhibit a systematic decrease in the lattice constant with increasing atomic number of the rare earth ion. Recent high pressure studies on EuTe,⁴ SmTe,⁵ TmTe,⁶ SmSe⁷ and SmS⁷ have revealed that under pressure the rare earth ion undergoes an electronic transition from the divalent to the trivalent state. Resistivity measurements under pressure have indicated that such a transition takes place continuously in TmTe, SmTe and SmSe and discontinuously in SmS at about 6.5 kbar. In these transformations the NaCl-type structure is retained but the lattice parameter contracts by about 4 per cent.

In the present study we have investigated by high pressure X-ray diffraction. PrTe, SmTe and EuTe and find a pressure induced phase transformation from NaCl to CsCl-type structure near

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about 100 kbar. In SmTe, prior to this transformation, the lattice parameter undergoes an anomalous decrease with pressure, due to continuous 4f–5d electron promotion. We believe that a pressure induced transition from NaCl type structure should be a common feature among the rare earth monochalcogenides.

Samples were prepared by reacting in a quartz tube stoichiometric amounts of high purity Te and the rare earth metal at 700°C and subsequent melting of the product in a sealed tantalum container kept in vacuum. The material thus obtained was polycrystalline with large single crystal regions. The NaCl-type structure and the lattice constant were verified from X-ray powder diffraction data. SmTe and EuTe had conductivities in the range $1000 \Omega \text{ cm}$, while PrTe with Pr in the trivalent state, exhibited metallic conductivity.

High pressure X-ray studies were carried out using a diamond anvil camera of the type described by Bassett, Takahashi and Stook.⁸ Molybdenum radiation was used to record the powder patterns. The pressure generated was estimated using Ag as internal standard. Powder pattern of the sample was recorded at zero applied pressure and then at several increasing pressures up to 150 kbar. In the lower pressure ranges data were collected using McWhan–Bond⁹ camera with NaCl

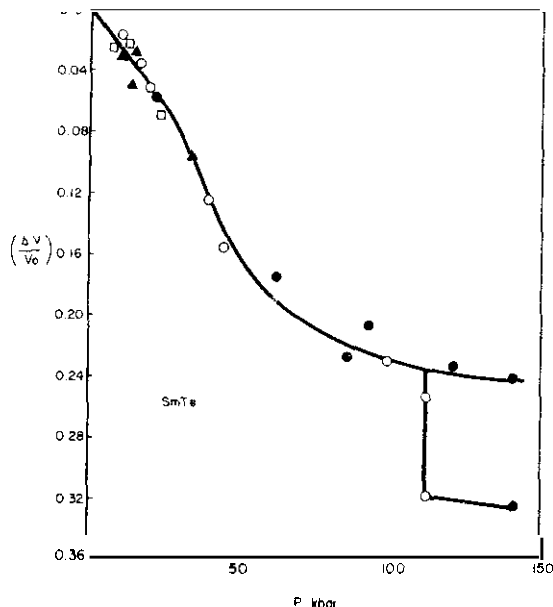


FIG. 1. The compression curve for SmTe obtained from high pressure X-ray diffraction data. ■ and ○ — data points from diamond anvil camera with a silver marker; □ — with NaCl marker. ▲ — McWhan-Bond camera with NaCl marker.

marker. A pattern recorded after the release of the pressure indicated that the changes observed were reversible.

In Fig. 1 the $\Delta V/V_0$ obtained from X-ray data is plotted against pressure for SmTe. In the pressure range 1–100kbar, the volume shows an anomalous decrease with pressure. No change in the structure is observed in this pressure range, it continues to retain the NaCl-type structure. The lattice parameter however, undergoes an anomalous decrease with pressure and the volume decrease at 100kbar is about 24 per cent. We attribute the observed abnormal compression to a change in the valence state of the Sm^{2+} to Sm^{3+} with pressure, due to $4f-5d$ electron promotion. Our pressure volume data indicate that this electronic transition is spread over a broad pressure range. In this respect the pressure–volume behaviour is consistent with earlier resistance measurements^{5,7} which indicated a continuous $4f-5d$ electron promotion.

A new set of lines are observed in the X-ray photographs at pressures above 110kbar. These

are the diffraction lines from a high pressure phase, which is identified as having the CsCl-type structure. The diffraction lines, from both NaCl and CsCl phases co-exist over a small pressure range. At about 150 kbar, only the lines from the CsCl phase are observed. In Fig. 1 the discontinuity in volume at about 110kbar is due to the phase transition from NaCl to the CsCl-type structure. The volume change associated with this transition is about 9 per cent.

Europium telluride undergoes NaCl to CsCl type phase transition at about 100 kbar. The form of the compression curve seems to be different from that observed in SmTe and does not suggest any appreciable conversion of Eu^{2+} to Eu^{3+} before NaCl–CsCl type transition takes place. The $\Delta V/V_0$ at 80 kbar is about 14 per cent. Our initial compressibility is in fair agreement with the compressibility measured by Levy and Wachter.¹⁰

In the case of PrTe, wherein Pr is in the divalent state, the NaCl-type phase has a much smaller compressibility compared to the NaCl phase of SmTe and EuTe. For instance, $\Delta V/V_0$ at 90 kbar is 4.5 per cent. The NaCl-type phase of PrTe exhibits a volume discontinuity at 90 ± 10 kbar due to a phase transition to the CsCl-type structure. The volume change associated with this transition is about 11.5 per cent.

Rooymans^{4, 11} has investigated EuTe as well as SmTe at high pressures and has reported an isostructural transition in both. The transition was attributed to a change in the valence state of Eu and Sm to the trivalent state. Further, Rooymans^{4, 11} has suggested that the above transition

occurs discontinuously near 30 and 40 kbar in EuTe and SmTe respectively. In the case of SmTe, both with regard to the mode of occurrence of this transition and the pressure ranges, our data are in variance with Rooymans. Our X-ray data suggest that the electronic transition in SmTe takes place over a broad pressure range. With regard to EuTe, our high pressure X-ray data suggest that no appreciable conversion of Eu^{2+} to Eu^{3+} takes place in the NaCl phase.

The main results of our work are summarised in Table 1.

Table I. High pressure data for PTe, SmtE and Eute.

	PtE	SmtE	Eute
Lattice constant of NaCl-phase at atmospheric pressure.	6.315 ± 0.002 Å	6.595 ± 0.002 Å	6.591 ± 0.002 Å
* Lattice constant (a_1) of the NaCl-phase at the pressure of NaCl-CsCl transition.	6.218 ± 0.02 Å	5.992 ± 0.02 Å	6.212 ± 0.02 Å
* Lattice constant (a_2) of CsCl phase at the pressure of NaCl-CsCl transition	3.761 ± 0.01 Å	3.656 ± 0.01 Å	3.755 ± 0.01 Å
* AV/V associated with the NaCl-CsCl transition	- 11.5%	9.1%	- 11.6%
$(4a_2^3/a_1^3)$	96 ± 10	110 ± 10	100 ± 10
The pressure of NaCl-CsCl			

* These values were obtained from X-ray photographs which showed diffraction lines from both the NaCl and CsCl phases.

Although we have studied only the mono-tellurides, we believe that a pressure-induced NaCl to CsCl-type transition would be commonly encountered in the rare earth monochalcogenides. However, in analogy with alkali halides,¹² one may expect the transition pressure to go up with a decrease in lattice constant.

We have also examined YbTe up to 300 kbar.¹³ In an earlier study⁶ the lattice constant of YbTe was measured up to 50 kbar. A continuous electronic transition is observed in the 1-150 kbar range, but there is no indication of NaCl to CsCl-type transition up to 300 kbar. Further studies on

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13. Results obtained by us – to be published.

Hochdruck-Röntgenbeugung untersuchungen ergeben. daß PrTe, SmTe and EuTe, die eine NaCl-artige Struktur besitzen, verwandeln sich bei 90 ± 10 , 110 ± 10 bzw. 100 ± 10 kbar in eine CsCl-artige Struktur. Vor dieser Verwandlung zeigt SmTe mit zunehmendem Dmck eine anomale Volumenverminderung auf, die auf den 4f-5d Elektronen- dbergang zurdckgeföhrt wird.