PRESSURE INDUCED STRUCTURAL TRANSFORMATION IN THULIUM MONOTELLURIDE

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Thulium monotelluride undergoes a structural transformation at 15 GPa from NaCl-type structure to a hexagonal structure with unit cell dimensions: $a = 4.07 \text{ \AA}$ and $c = 6.84 \text{ \AA}$. The high pressure diffraction pattern is explained reasonably well by anti-NiAs-type structure. The volume change associated with the transformation is 3.8 per cent.

Thulium monotelluride, at one atmosphere and room temperature, has NaCl-type structure. The studies on magnetic susceptibility and lattice parameter indicate that the Tm-ion is in a divalent state $\{\}$. The pressure dependences of electrical resistivity $\{2\}$ and the unit cell volume $\{3,4\}$ suggest that the Tm-ion changes continuously to a trivalent state as the pressure is increased. The earlier work on the equation of state of TmTe was limited to a pressure up to 13 GPa. At 15 GPa TmTe undergoes a structural transformation. The analysis of the crystal structure of the high pressure phase is reported here.

The specimens used in the present experiments were same as those used in the earlier studies $\{3,4\}$. A preliminary characterization of the specimen was done by x-ray analysis. The sharpness of the diffraction patterns taken with $\text{CuK}\alpha$ radiation indicated that the specimen was highly crystalline, and all the observed diffraction lines could be explained on the basis of a cubic phase (NaCl-type). The lattice parameter ($a = 6.354 \pm 0.002 \text{ \AA}$) was obtained from the Nelson-Riley plot using the high angle reflections. The present value of lattice parameter agrees well with the value ($a = 6.364 \text{ \AA}$) reported by Bucher et al $\{5\}$, and also with the value ($a = 6.35 \text{ \AA}$) reported recently by Aldis and Fritzler $\{6\}$.

The x-ray experiments at elevated pressures were done with a diamond-anvil camera $\{7\}$. The specimen was finely powdered and placed between the anvils without gasket. The diffraction patterns were recorded with a cylindrical film cassette

using $\text{MoK}\alpha$ radiation. To avoid the complication arising from the presence of the diffraction lines from the pressure marker TmTe specimen alone (without pressure marker) was used. The x-ray patterns taken at about 15 GPa showed a new set of lines, indicating a change in the crystal structure. The new set of lines could be indexed in the hexagonal system with the following lattice parameters: $a = 4.07 \pm 0.04 \text{ \AA}$ and $c = 6.84 \pm 0.07 \text{ \AA}$. The diffraction pattern also contained lines from the untransformed NaCl-phase. The pressure on the specimen was estimated from the cell volume of the coexisting NaCl-phase of TmTe and the equation of state determined earlier $\{3,4\}$.

The intensities of the diffraction lines were estimated visually using an intensity scale containing diffraction spots of graded optical densities. The measured intensities were corrected for Lorentz-polarization and multiplicity factors. The correction factor for the absorption in the anvil and the specimen (with an assumed thickness of 25 microns) did not vary significantly over the observed range of reflections. The absorption correction factor was therefore treated as a scale factor. The maximum error in the intensities arising from the neglect of the absorption correction factor was about 10 percent. The overall uncertainty in the estimation of intensities is rather large (nearly 25 percent) because of the presence of slight preferred orientation in the high pressure diffraction patterns. The intensity of the strongest observed reflection was taken as 100 and the intensities of the other reflections scaled

accordingly. The observed d-values and the intensities are listed in Table 1.

of the reflections with large calculated intensities were not observed experimentally. Further, even for

Table 1. Crystallographic data on the high pressure phase of TmTe (hexagonal, $a = 4.07$ Å and $c = 6.84$ Å) at 15 GPa.

d_{obs} (Å)	d_{cal} (Å)	hkl	I_{obs}	I_{cal}
■	3.525	100	0 ⁺	5
-	3.419	002	0	2
3.054	3.133	101	100	100
2.926	2.945*	200*		
2.454	2.454	102	95	110
2.093	2.035 2.082*	110 220*	71	64
1.901	1.914	103	16	27
-	1.762	200	0	0.8
-	1.749	112	0	2
1.715	1.707, 710 1.700*	201,004 222*	42	20,13
1.563	1.567	202	29	30
-	1.538	104	0	0.9
1.420	1.394	203	35	10
-	1.332	210	0	0.6
1.306	1.309, 308 1.317*	114,211 420*	37	34,17

* - NaCl phase

⁺ The lowest measurable intensity is 10.

The number, n , of the molecules in the unit cell is taken as 2, because it gives a reasonable value (-3.8%) for the volume change, $\Delta V(t)$, associated with the transformation. The choice of any other value of n leads to inadmissible value of $\Delta V(t)$. A search was made in the literature for the possible hexagonal structures for compounds of type RX, containing two molecules in the unit cell. The possible structures are ZnO-type, NiAs-type and anti-NiAs-type. First, the ZnO-type structure was tried. With the Tm-ions in Zn-positions and Te-ions in the O-positions, the intensities of the possible reflections with the interplanar spacings up to 1.3 Å were calculated. The calculated intensity corresponding to the strongest observed reflection was taken as 100 and the intensities of the other reflections were scaled accordingly. A comparison of the calculated intensities with the observed values indicated that some

the observed reflections the discrepancies between the observed and calculated intensities were serious. The NiAs-type Structure was tried next, and was also discarded in view of the serious discrepancies between the observed and the calculated intensities. The anti-NiAs-type structure with Tm-ions (R-ions) at (1/3, 2/3, 1/4) and (2/3, 1/3, 3/4), and Te-ions (X-ions) at (0, 0, 0) and (0, 0, 1/2) was tried next. The observed and the calculated intensities are listed in Table 1. Out of the three structures tried, the anti-NiAs structure explains the high pressure intensity data best. Rather large discrepancies in the case of 103 and 203 reflections seem to arise from the preferred orientation effects.

The atomic arrangement in the high pressure phase of TmTe is shown in Fig.1. Each Tm-ion, marked 7 in Fig.1, is surrounded by six Te-ions (1-6) forming a trigonal prism.

Fig.1. The atomic arrangement in high pressure phase of TmTe at 15 GPa.

the distance between the Tm- and Te-ion being 2.91 Å at 15 GPa. Each Te-ion (1) has six Tm-ions (9-13 and 7) at a distance of 2.91 Å at 15 GPa; the six Tm-ions occupy octahedral positions. The environment

of the Te-ion in the high pressure phase is the same as in the low pressure phase (NaCl-type structure). However, in the high pressure phase of TmTe, each Te-ion (1) has also two Te-ions (2 and 8) at a distance of 3.42 Å. Since the nearest Te-Te distance is nearly 18 percent larger than the nearest Te-Tm distance, only a weak bonding can exist between the nearest Te-ions. Thus, the transformation results in a rearrangement of the surroundings of the Tm-ions, leaving the arrangement of ions around the Te-ions practically unaltered.

The other compounds, in the group of rare earth monochalcogenides, which exhibit structural transformations [3,4,8] under pressure are PrTe, SmTe, EuTe, EuSe and EuO. At one atmosphere these compounds, like TmTe, have NaCl-type structure and are found to transform under pressure to CsCl-type structure. The high pressure phase of TmTe however is hexagonal. In this respect TmTe differs from the other rare earth monochalcogenides. The possibility that TmTe transforms to CsCl-type structure, in conformity with the behaviour of other rare earth monochalcogenides, at still higher pressures is not ruled out.

REFERENCES

1. E.Bucher, A.C.Gossard, K.Andres, J.P.Maita & A.S.Cooper, Proc. Eighth Rare Earth Research Conference, Editors: T.H.Henrie & R.E.Lindstrom, Vol.1, p74 (1970).
2. A.Jayaraman, E.Bucher & D.B.McWhan, Proc. Eighth Rare Earth Research Conference, Editors: T.H.Henrie and R.E.Lindstrom Vol.1, p 333 (1970).
3. A.Chatterjee, A.K.Singh & A.Jayaraman, Phys. Rev. B6, 2285 (1972).
4. A.Jayaraman, A.K.Singh & A.Chatterjee & S.Usha Devi, Phys. Rev. B9, 2514 (1974).
5. E.Bucher, K.Andres, F.J.DiSalvo, J.P.Maita, A.C.Gossard, S.Cooper & G.W.Hull Jr. Phys. Rev. B11, 500 (1975).
6. E.Kaldis & B.Fritzlner, Progress. Solid State Chem. 14, 95 (1982).
7. W.A.Bassett, T.Takahashi & P.W.Stoock, Rev. Sci. Instrum. 38, 37 (1967).
8. A.K.Singh, A.Jayaraman & A.Chatterjee, Solid State. Commun. 9, 1459 (1971).