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Structural Incorporation and Electrical Efficiency of Tl in PbTe

By

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PbTe with a bandgap $E_g = 0.21$ eV (77 K) is an important semiconductor for optoelectronic devices in the medium infrared region. Thallium ions Tl^+ are known as acceptors in PbTe, if they are substituting lead ions, Pb^{2+} . The electrical efficiency of Tl in PbTe should be poor /1/; nevertheless there has been found a different electrical behaviour after 'additive' and 'substitutional' incorporation, respectively /2/, and even a rather high electrical activity of Tl^+ /3/, at least at concentrations $c_{Tl} \lesssim 0.3$ at% /4/. Of course, one has to take into consideration the electrical activity of point defects due to non-stoichiometry, dependent on the kind of producing the crystal, at least at small dopant concentrations.

We were interested in the incorporation behaviour and the electrical activity of Tl in PbTe. Our crystals have been synthesized Te-rich and have been grown, after adding Tl, by the travelling heater method from Te-rich solution /5/. We investigated the lattice constant by the so-called Soller slit technique /6/, the carrier concentration by thermoprobe as well as Hall measurements, and the Tl concentration by SIMS measurements, calibrated by Tl implantation investigations.

Fig. 1 shows that the lattice constant decreases with increasing carrier concentration. Fig. 2 shows that $p_{77K} \approx \left(\frac{1}{3} \text{ to } \frac{1}{5}\right)c_{Tl}$.

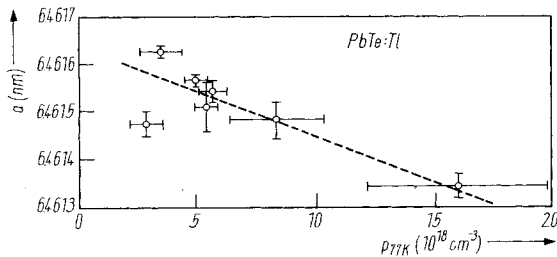


Fig. 1. Lattice constant versus carrier concentration of PbTe:Tl

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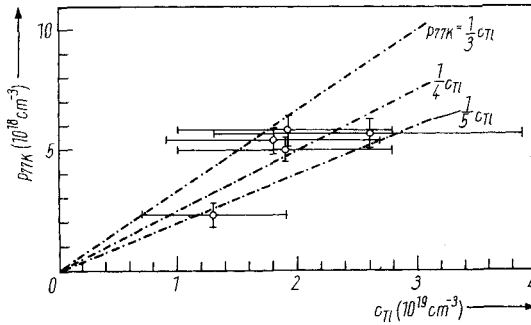


Fig. 2. Carrier concentration versus Tl concentration of PbTe:Tl. The dash-dotted lines serve only for estimation of the electrical efficiency of the Tl ions

While, for example, Bi^{3+} as a smaller ion than Pb^{2+} decreases the lattice constant of PbTe with increasing carrier concentration /7/, one should assume that Tl^+ as a bigger ion than Pb^{2+} ($r_{\text{Tl}^+} \approx 0.149$ nm, $r_{\text{Pb}^{2+}} \approx 0.132$ nm, supposing a predominantly heteropolar binding in PbTe /8/; $r_{\text{Tl}^+} \approx 0.140$ nm, $r_{\text{Pb}^{2+}} \approx 0.114$ nm, considering homopolar binding parts /1/) would increase the lattice constant of PbTe, but the contrary is the fact. Tl^+ should substitute the Pb^{2+} ions, because the predominant non-stoichiometry defects are lead vacancies, V_{Pb} (e.g. /9/); interstitial lattice sites are too small for the big Tl^+ ions or even for the still bigger neutral atoms, and Tl^{3+} ions at V_{Pb} ($r_{\text{Tl}^{3+}} \approx 0.095$ nm /1/) would act as donors.

We explain the decreasing lattice constant with growing Tl concentration on the basis of complexes formed by the dopants and point defects (vacancies). The compression fields around the big Tl^+ ions lead to an addition of vacancies, which reduce the lattice strain and may compensate the charge. Whether these complexes are created by diffusion or are incorporated directly during crystallization, cannot be decided by our experiments.

There are known some stable Tl_mTe_n complexes which are presented in Table 1 /10/. In Table 1 we have presumed: monovalent Tl^+ at Pb^{2+} sites, no Tl-containing precipitates (because of $c_{\text{Tl}} \leq 0.2$ mol%), only Schottky defects in PbTe, V_{Te} probably monovalent /11/ (possibly divalent /12/), V_{Pb} probably divalent /13/ (possibly monovalent /14/). From Table 1 and Fig. 2 as probable defect complexes result $[\text{Tl}_2\text{Te} + V_{\text{Te}}]$ and/or $[\text{Tl}_5\text{Te}_3 + 2V_{\text{Te}}]$; i. e., for the ex-

Table 1

	$[Ti_2Te]$	$[Ti_5Te_3]$	TlTe	$[Ti_2Te_3]$
structure of complex substituted PbTe units	$Ti_2Te + V_{Te}$ 2	$Ti_5Te_3 + 2V_{Te}$ 5	TlTe 1	$Ti_2Te_3 + V_{Pb}$ 3
carrier balance	$2h + e$ (2e)	$5h + 2e$ (4e)	h	$2h + 2h$ (h)
resulting charge p	$h(0)$	$3h$ (h)	h	$4h$ (3H)
p/c_{Ti}	0.5 (0)	0.6 (0.2)	1	2 (1.5)
da/dp	<0	<0	>0	<0

planation of Fig. 1 the creation of Te vacancies, V_{Te} , in the direct neighbourhood of Ti^+ dopants has to be assumed. Of course, a mixture of these defect complexes with Ti^{3+} Pb ions should also be possible.

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References

- /1/ W. WEISER, Phys. Rev. B 23, 2741 (1981).
- /2/ L.F. ALENINA, A.N. VEIS, V.I. KAIDANOV, and R.B. MELNIK, in: Legirovanniepolutprovodniki, Nauka, Moscow 1975 (p. 27).
- /3/ A.L. DAWAR, D.P. TANEJA, S. K. PARADKAR, P. KUMAR, and P.C. MATHUR, Thin Solid Films 91, 357 (1982).
- /4/ B.F. GRUZINOV, I.A. DRABKIN, YU.YA. ELISEEVA, E.YA. LEV, and I.V. NELSON, Fiz. Tekh. Poluprov. 13, 1308 (1979).
- /5/ P. GILLE, Thesis A, in preparation.
- /6/ H. BERGER, J. appl. Cryst., in the press.
- /7/ N.D. TAP, M. SCHENK, and P. SCHÄFER, Crystal Research Technol. 18, K33 (1983).
- /8/ W. KLEBER, in: Einführung in die Kristallographie, 10th ed., 1970 (p. 155).
- /9/ B.J. SEALY and A.J. CROCKER, J. Mater. Sci. 8, 1737 (1973).
- /10/ L.G. BERG and Z.M. LATYPOV, Izv. Akad. Nauk SSSR, Ser. neorg. Mater. 13, 1596 (1977).

- /11/ T.C. HARMAN, J. Nonmetals 1, 183 (1973).
- /12/ N.J. PARADA and G.W. PRATT, Phys. Rev. Letters 22, 5 (1969).
- /13/ H. HEINRICH, A. LOPEZ- OTERO, L. PALMETSHOFER, and
L.D. HAAS, Inst. Phys. Conf. Ser. 23, 264 (1975).
- /14/ T.D. GEORGE and J.B. WAGNER, J. appl. Phys. 42, 220 (1971).

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