

Phase diagram and electronic properties of Ag_xTiTe_2

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Abstract

Results of phase diagram investigations and electronic properties studies are presented of TiTe_2 that was electrochemically intercalated by silver. The in plane ordering of the silver atoms is supposed as a cause of the single phase regions occurring around the $\text{Ag}_{0.5+\delta}\text{TiTe}_2$ and $\text{Ag}_{0.75-\delta}\text{TiTe}_2$ compounds. The temperature and concentration dependences of the DC conductivity and the Seebeck coefficient are explained by localization of charge carriers. © 1997 Elsevier Science S.A.

Keywords: Intercalation; Ordering; Localization of charge carriers

1. Introduction

TiTe_2 belongs to a family of layered dichalcogenides of titanium. Much experimental and theoretical interest has centred on these materials and their intercalates because of their unusual anisotropic optical, mechanical and transport properties and the observation of charge–density waves in TiSe_2 . There are potential applications as solid superionic cathodes in the new battery systems.

In contrast with both TiS_2 and TiSe_2 , which were subjects of an extensive study [1], information concerning properties of TiTe_2 and its intercalates is scarce.

TiTe_2 has the hexagonal crystal structure of the CdI_2 type, space group $P\bar{3}m1$ [2]. This structure consists of stacked composite layers, each comprising sheets of hexagonally close-packed telluride atoms sandwiching a sheet of titanium atoms in such a way that half of the octahedral intersites are filled. Adjacent layers are held together by the relatively weak van der Waals forces. The van der Waals gap between the layers is sufficiently large for the material to be able to intercalate a range of metals and other electron donors.

The band structure calculation for TiTe_2 made in agreement with spectroscopic, electronic and magnetic properties data [3] shows that TiTe_2 is a semimetal with the an overlap of ~ 0.65 eV between the p-band of Te and

d-band of Ti. The value of the carrier concentration according to the band-overlap is $n_e = n_h = 6.5 \times 10^{20} \text{ cm}^{-3}$, n_e and n_h are concentrations of electrons and holes, respectively. In this study, we investigate the intercalation of silver into TiTe_2 and its influence on the transport properties of the material.

2. Experimental details

The material for investigation was prepared by reaction of the elements in an evacuated quartz ampoule at 900°C for two weeks. A typical difficulty in the preparation of such compounds is a contamination of the obtained material by an excess of titanium which appears owing to the high pressure of the chalcogen [1,4]. For comparison we have prepared both TiTe_2 and Ag_xTiTe_2 ($x=0.2$ and 0.4). It seems that increasing the metal:chalcogen ratio leads to a decrease of the equilibrium pressure of the chalcogen above the surface of the charge. After synthesis the charges were powdered and pressed into pellets, which were annealed in an evacuated pyrex ampoule at 600°C for two weeks for homogenization.

The electrochemical cell $\text{Ag}-\text{AgI}-\text{Ag}_x\text{TiTe}_2-\text{Pt}$ was used for the intercalation of silver into TiTe_2 . Details of this technique have already been described elsewhere [5]. Characterization of the prepared material and structural investigations of powder samples were performed at room temperature using an X-ray diffractometer of the type DRON-4-13 ($\text{CuK}\beta$ -radiation, graphite monochromator).

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The variable silver content x in the samples used for the conductivity (σ) and Seebeck coefficient (α) measurements was determined by means of the electrochemical cell. In this way the concentration dependences $\sigma(x)$ and $\alpha(x)$ were obtained for every sample. Four samples were used for these measurements: two samples with the starting composition TiTe_2 and two samples with a silver content corresponding to $x=0.2$ and 0.4 . Experimental data obtained using these samples were indistinguishable. DC-conductivity was measured by the four-point technique. A differential thermal analyser (DTA) of the type Q-1500 was used for the thermal analysis. The sample was placed in an evacuated pyrex ampoule. Infrared reflectance spectra were obtained using an IKS-21 spectrometer ($5 > \lambda > 2.2 \mu\text{m}$, λ —wavelength of light) and an SF-46 spectrometer ($2.2 > \lambda > 0.5 \mu\text{m}$). Single crystals of Ag_xTiTe_2 for optical investigations were prepared by electrochemical intercalation of silver into crystals of TiTe_2 which were grown occasionally during of the synthesis.

3. Results

The dependence of $R(\omega)$, where ω is the frequency of light and R is the reflectance coefficient, for TiTe_2 (see Fig. 1) obeys quite accurately the Drude expression [6] with the following values of parameters: plasma frequency $\omega_p = (4\pi e^2 n/m)^{1/2} = 24.58 \times 10^{14} \text{ s}^{-1}$; relaxation time $\tau = 4.1 \times 10^{-15} \text{ s}$; dielectric constant $\epsilon_\infty = 14.6$. The value of the plasma frequency corresponds to a carrier concentration $n/m = 1.9 \times 10^{21} \text{ cm}^{-3}$, where m is the carrier mass. This value of carrier concentration is consistent both with the bond-overlap value [3], $n_e + n_h = 1.3 \times 10^{21} \text{ cm}^{-3}$, and with results of the conductivity measurements at room temperature, $\sigma = (e^2 n \tau)/m = 9 \times 10^3 (\text{ohm} \times \text{cm})^{-1}$, with $m = 1.5 m_0$, where m_0 is the free electron mass. This result indicates the good quality of the TiTe_2 material used.

The open-circuit voltage E of the electrochemical cell versus x at $T=473 \text{ K}$ shown in Fig. 2 indicates the existence of three single-phase regions.

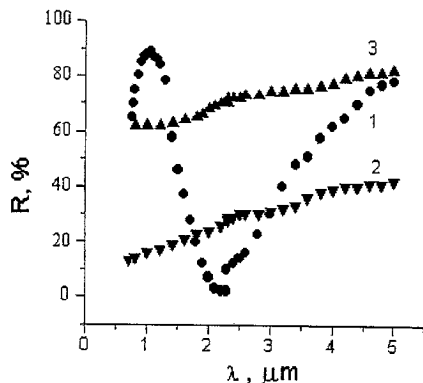


Fig. 1. Reflectivity R as the function of the wavelength of light λ for TiTe_2 (1), $\text{Ag}_{0.55}\text{TiTe}_2$ (2) and $\text{Ag}_{0.75}\text{TiTe}_2$ (3).

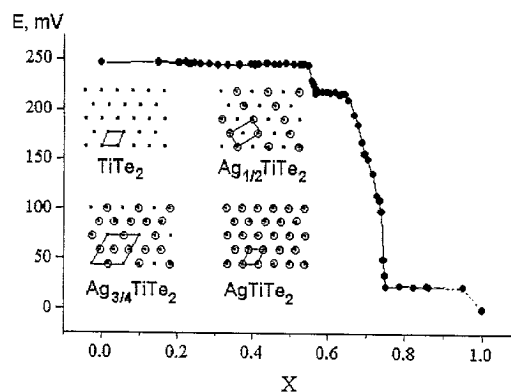


Fig. 2. The open-circuit voltage E of the electrochemical cell $\text{Ag-AgI-Ag}_x\text{TiTe}_2\text{-Pt}$ as a function of the silver content x in Ag_xTiTe_2 at 473 K, together with structural models (ab-plane) of an ordered distribution of Ag atoms for $x=1/2$ and $x=3/4$. The part of the $E(x)$ curve for $x \sim 1$ is shown as supposition.

For compounds with $0.55 < x < 0.57$ in the X-ray pattern, small additional reflections were observed in comparison with TiTe_2 . These reflections may be indexed as (141), (232) and (321), for a superlattice with orthorhombic structure: $a = a_0$; $b = a_0 \sqrt{3}$; $c = c_0$. This result allows us to suppose that the phase with $0.55 < x < 0.57$ may be characterized as a structure where half of the octahedral sites are occupied by silver (see Fig. 2). Therefore we call this phase “ $\text{Ag}_{1/2}\text{TiTe}_2$ ” (but one should note that the compounds belonging to this phase actually have the composition $\text{Ag}_{0.5+\delta}\text{TiTe}_2$).

For another single-phase region with a richer silver content $0.65 < x < 0.75$, we have observed two additional reflections which were indexed as (012) and (321) for a superlattice with hexagonal structure: $a = 2a_0$; $c = c_0$. The model of this superstructure, where every three out of four octahedral sites filled by silver, is shown in Fig. 2. As in the previous case we call this phase “ $\text{Ag}_{3/4}\text{TiTe}_2$ ”. The compounds belonging to this phase have the composition $\text{Ag}_{0.75-\delta}\text{TiTe}_2$.

The unit cell constants of the Ag_xTiTe_2 phases are listed in Table 1. It is commonly accepted, that the intercalation leads to an increase of the van der Waals gap width of the host lattice due to repulsion between the intercalated ions and the layers of the host lattice [7]. The unusual behaviour of the unit cell constant $c_0(x)$ for Ag_xTiTe_2 (see Table 1) indicates the presence of an attraction between Ag-ions and TiTe_2 -layers, that is more powerful than the usual repulsion. This attraction cannot be caused by the large width of the van der Waals gap given the size of the Ag-ion, because the intercalation of TiTe_2 even by ions as small as Li leads to the usual increase of c_0 [8].

The location of the boundaries of the single phase regions in the T - x plane is shown in Fig. 3. It was impossible to investigate the location of phase boundaries of AgTiTe_2 due to both the instability of this compound at room temperature and the very low decomposition voltage:

Table 1
Structural characteristics of single phase regions in the Ag_xTiTe_2 system

Ag_xTiTe_2 phase	Compound	Space group	Unit cell dimensions (nm)		
			<i>a</i>	<i>b</i>	<i>c</i>
$\text{Ti}_{1+x}\text{Te}_2$ [9] $0 < x < 0.33$	TiTe_2 [9]	$\text{P}\bar{3}\text{m}1$	0.3755		0.6460
	TiTe_2 [3]		0.3786		0.6491
	$\text{Ti}_{1.33}\text{Te}_2$ [9]		0.3884		0.6348
	TiTe_2		0.3792		0.6466
$\text{Ag}_{\frac{1}{2}}\text{TiTe}_2$, $0.55 < x < 0.57$	$\text{Ag}_{0.55}\text{TiTe}_2$	$\text{P}2/\text{m}$	0.3816	0.6513	0.6446
	$\text{Ag}_{0.57}\text{TiTe}_2$		0.3765	0.6576	0.6405
$\text{Ag}_{\frac{3}{4}}\text{TiTe}_2$, $0.63 < x < 0.75$	$\text{Ag}_{0.65}\text{TiTe}_2$	$\text{P}\bar{3}\text{m}1$	0.7604		0.6408
	$\text{Ag}_{0.75}\text{TiTe}_2$		0.7596		0.6402
$\text{Ag}_{1.0}\text{TiTe}_2$, $0.95 < x < 1.0$	$\text{Ag}_{0.95}\text{TiTe}_2$	$\text{P}\bar{3}\text{m}1$	0.7615		0.6399

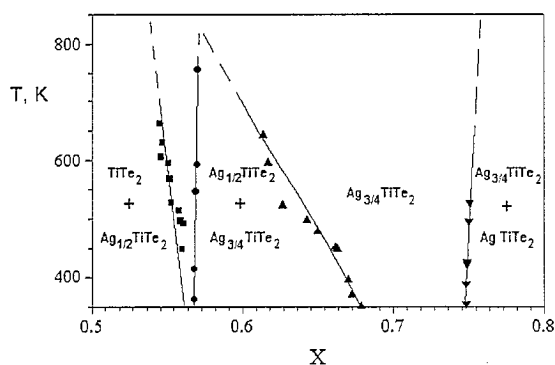


Fig. 3. Phase diagram of Ag_xTiTe_2 . The location of phase boundaries has been obtained from the temperature dependences of the electrochemical cell voltage for samples with different x . Points which falls above 600 K and below 420 K are obtained by extrapolation of the respective $E(T)$ dependences.

approximately 8 mV at 473 K. The temperature of decay of AgTiTe_2 was found from the condition $E(T)=0$, where the function $E(T)$ was taken for samples being a mixture of $\text{Ag}_{\frac{3}{4}}\text{TiTe}_2$ and AgTiTe_2 . This condition means the simultaneous equilibrium between the binary system consisting of these phases and silver metal can be reached in the ternary point. We have found that the temperature of the ternary

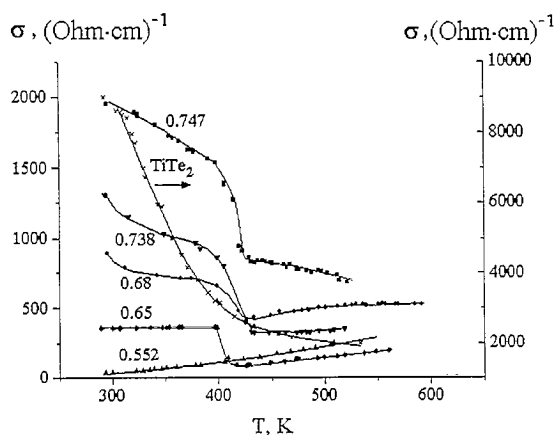


Fig. 4. The temperature dependences of the DC-conductivity σ for Ag_xTiTe_2 . For each curve the values of x are indicated.

point is equal to 360 ± 10 K. Similar estimations show that $\text{Ag}_{\frac{3}{4}}\text{TiTe}_2$ and $\text{Ag}_{\frac{1}{2}}\text{TiTe}_2$ are stable up to 0 K.

The dependences of $\sigma(T)$ and $\alpha(T)$ for the phases investigated in the $\text{Ag}-\text{TiTe}_2$ system in the temperature range 300–600 K are shown in Figs. 4 and 5.

The $\sigma(T)$ dependence for $\text{Ag}_{\frac{1}{2}}\text{TiTe}_2$ indicates a semiconductor-like behaviour with an activation energy 0.12 eV. The positive sign of α indicates p-type conductivity of this material, in spite of the large concentration of electrons $\sim 6.6 \times 10^{21} \text{ cm}^{-3}$ donated by Ag. It should be noted that a change of x within the homogeneity range of this phase does not lead to a change in value or in behaviour of σ and α .

4. Discussion

The decrease of the conductivity for Ag_xTiTe_2 in comparison with the conductivity of TiTe_2 points to a localization of charge carriers as a result of the influence of the Ag-ions. The absence of the Drude-edge in the IR-spectra of Ag_xTiTe_2 samples could be the consequence of a low value of the relaxation time τ for charge carriers in these materials, in agreement with the previous conclusion.

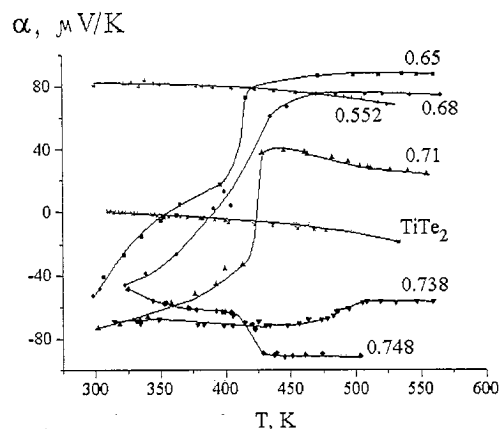


Fig. 5. The temperature dependences of the Seebeck coefficient α for Ag_xTiTe_2 . The values of x are indicated for each curve.

The absence of a disordered solid solution region for low values of x in the phase diagram of Ag_xTiTe_2 indicates a powerful interaction of the Ag-ions with the host lattice. The decrease of c_0 with increasing x could be the result of the appearance of covalent "bridges" between the host lattice layers near the Ag-ions. Such a centre may be called "Ti–Ag–Ti". A similar dependence of $c_0(x)$ was observed for Ti_xTiTe_2 in Ref. [9] where the extra atoms of Ti have been found in the same sites as Ag in Ag_xTiTe_2 . The ultraviolet spectroscopy investigation of TiTe_2 [3] shows the presence of a narrow band of localized states just below the Fermi level. One of the possible origins of the appearance this band consists in a contamination of the sample by the overstoichiometric titanium. The similarity in behaviour of $c_0(x)$ for Ag_xTiTe_2 and Ti_xTiTe_2 gives reason to suppose the presence in this system of "Ti–M–Ti" (M=Ti, Ag) centres having localized electrons. A similar conclusion was reached in Ref. [10] from the analysis of thermochemical data for Ti_xTiTe_2 .

An increasing silver content is expected to lead to a replacement of "Ti–Ag–Ti" by "Ag–Ti–Ag" centres. The concentration of each kind of these centres has been calculated in the framework of the lattice-gas approximation, and is plotted versus x in Fig. 6. This approximation seems appropriate because of the disordering of the intercalation layers in the c -direction.

The localization of electrons in Ag_xTiTe_2 allows us to interpret the conductivity in this material in the framework of the percolation theory. The value of the percolation threshold for the site problem in triangular lattices with the bond between the nearest sites is well known [11,12] and equals 0.5. Between $x=0.293$ and 0.707 one can therefore observe a "localization area", if a single kind of centres participates in the conductivity. The homogeneity range of $\text{Ag}_{1/2}\text{TiTe}_2$ falls into this area and the material displays semiconductor-like behaviour with p-type conductivity. Hence the activation energy of the conductivity in $\text{Ag}_{1/2}\text{TiTe}_2$ may be interpreted as the activation energy of

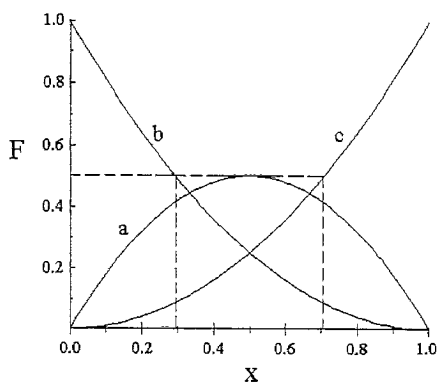


Fig. 6. Normalized concentration of centres "Ti–Ag–Ti" (a), "Ti–Ti" (b) and "Ag–Ti–Ag" (c) calculated in the lattice-gas approximation as function of silver content x in Ag_xTiTe_2 .

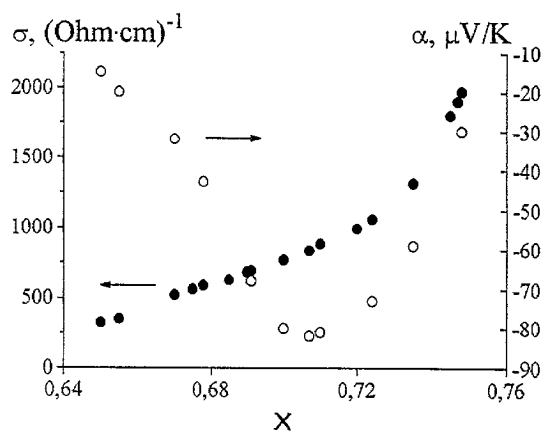


Fig. 7. The conductivity (σ) and Seebeck coefficient (α) versus x at $T=300$ K for the Ag_xTiTe_2 phase.

electrons from the valence band to the band of the localized states.

At $x=0.71$ the concentration of "Ag–Ti–Ag" centres is equal to 0.5 (see Fig. 6) and percolation over these centres should become possible. The conductivity of $\text{Ag}_{3/4}\text{TiTe}_2$ for $x<0.71$ shows nearly semiconductor-like behaviour and metal-like character for $x>0.71$, at $T<420$ K (see Fig. 4). The increase both of σ and α for compounds with $x<0.71$ (see Fig. 7) points to a hopping character of the conductivity [13] in this composition range which transfers to good metal-like conductivity for $x>0.71$. Another evidence for the validity of the presented model has been obtained from the functions $\sigma(T)$ and $\alpha(T)$ at low temperature. The results for two samples with $x=0.675<0.71$ and $x=0.735>0.71$ are shown in Fig. 8. The sharp decrease of the conductivity for the sample with $x=0.675$

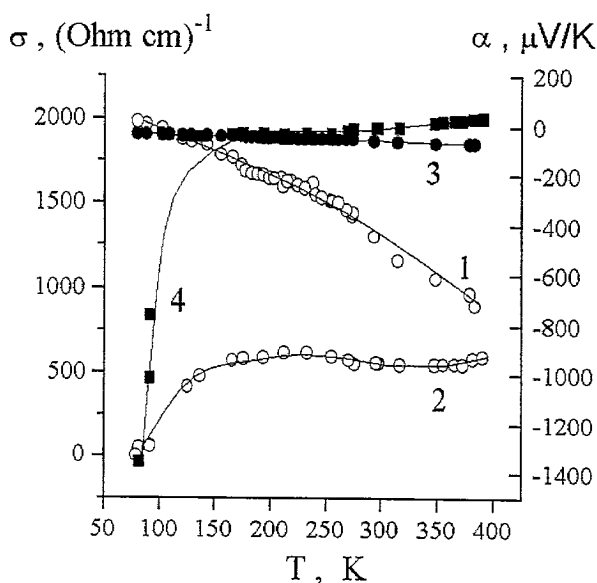


Fig. 8. The temperature dependences of the conductivity σ (2,3) and Seebeck coefficient α (1,4) for Ag_xTiTe_2 samples with $x=0.675$ (2,4) and $x=0.735$ (1,3) in temperature range 300–80 K.

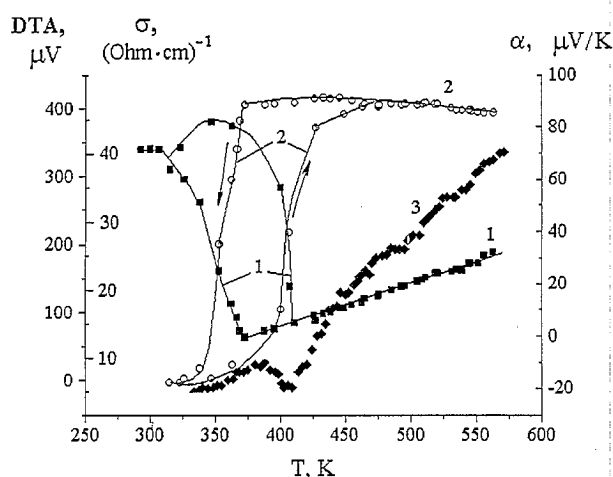


Fig. 9. The temperature dependences of the conductivity σ (1) and Seebeck coefficient α (2) for $\text{Ag}_{0.675}\text{TiTe}_2$ obtained upon heating and cooling together with a DTA trace of this sample (3).

below 80 K appears probably due to freezing of holes in the valence band. For the sample with $x=0.735$ such decreasing of the conductivity is apparently absent due to the appearance of extended states on the Fermi level.

The transformation behaviour of σ from metal to semiconductor in $\text{Ag}_{\frac{3}{4}}\text{TiTe}_2$ at 400–420 K (see Fig. 4) may be connected with some kind of disorder in the Ag-sublattice. A hysteresis in the temperature dependences of σ and α obtained upon heating and cooling together with endothermal effect on DTA trace (see Fig. 9) form strong support for such a conclusion. Although the origin of this transition is unknown, it seems to be possible to

connect it with changes of the shape of the clusters “Ag–Ti–Ag” centres due to a reconstruction of the Ag-sublattice. The dependences of $\sigma(T)$ for $\text{Ag}_{\frac{3}{4}}\text{TiTe}_2$ at $T > 420$ K (see Fig. 4), being in agreement with this supposition, show a behaviour similar to that of $\sigma(T)$ at $T < 420$ K, with a transition from the semiconductor-like character for low values of x to metal character for large x . The behaviour of $\alpha(T)$ for $\text{Ag}_{\frac{3}{4}}\text{TiTe}_2$ also may be explained as a result of changes in the mobility of the electrons in the conduction band.

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