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Tl–Ba–V–O CONDUCTORS

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Abstract. The Tl-Ba-V-O system was studied extensively. It was found that the resistivity has a drop at about 50 K, but the a.c. susceptibility does not demonstrate the presence of superconductivity. We have failed to obtain compounds with layered structure.

Резюме. Изучалась интенсивно система Tl–Ba–V–O. Был найден спад сопротивления при около 50 K, но восприимчивость на переменном токе не показала наличие сверхпроводимости.
Мы не успели получить соединения со слоистой структурой.

1. Introduction

Recently, the Tl–Sr–V–O was suggested as possible high-temperature superconductor [1]. In some of the observations, the zeroresistence state was found at 130 K, while others were around 50 K. Since January the group in Hitachi has not succeeded in selecting a superconducting phase and determining its structure and properties. The measured magnetic susceptibility also was not found to demonstrate a diamagnetic behaviour.

It is worth mentioning that there are many Tl-V-O compounds with determined structure and parameters like $TlVO_3$, $TlVO_4$, $Tl_2V_6O_{16}$, $Tl_2V_5O_{14}$, Tl_3VO_4 or $Tl_3Gd(VO_4)_2$. Rare earth vanadates conductivity was also studied e.g. in the La–(Sr,Ba)–V–O system [2]. The latter appeared to be perovskite type of structure,

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showing hopping conductivity at low temperatures. It could be supposed that layered structures in the Tl-vanadates family can also appear.

We have attempted to obtain different Tl-vanadates and we studied them in respect to superconductivity. Unlucky coincidences, raised some optimism, but when carefully checked it appeared that we have not found conclusive evidence for superconductivity in these compounds. Here we report our results in selecting of some Tl–Ba–V–O phases and their conductivity temperature dependence. We should mention that we have studied more than 50 samples with different compositions and different technological history and we have failed to find transition to superconductivity in them.

We obtained first Tl–Sr–V–O pellets from nitrates firing them in H_2 atmosphere for 10 hours at 980° C with subsequent furnace cooling. The samples appeared to be multiphase with resistivity drop at around 70 K. In the X-ray spectrum we observed low angle peaks, which later turned to be false. We do not display here results for the Tl–Sr–V–O system, because we concentrated our efforts on Tl–Ba–V–O. This system turned to be more suitable because of the lower melting temperatures it had. We measured the melting temperature of the $Tl_1Ba_1V_6O_x$ starting composition obtained from nitrates to be 489°±5°C. During the subsequent annealing in vacuum we reached the boiling temperature in the range of 930–970°C. Cooling the melt in H_2 atmoshere we found it to freeze at 450° C. It can be concluded that the melting temperatures of the Tl–Ba–V–O are in the range of 400–700°C. For this reason low temperature H_2 annealing can be also effective, as well as crystallization in H_2 atmosphere. The rapid cooling of the melt produces also quite nice looking Tl-vanadate glass with conductivity at room temperatures in the range of 10 kΩ to 100 mΩ.

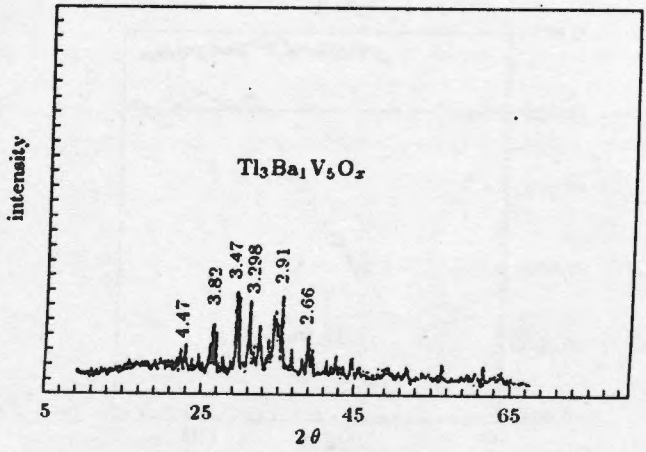

Fig. 1. X-ray powder diffraction spectrum of the 135 phase of Ba-Tl-V-O

The $Tl_3Ba_1V_5O_x$ X-ray powder diffraction spectrum is shown in Fig. 1. This and other phases spectra which we do not demonstrate are similar. The characteristic for layered structures low angle peaks are absent. Therefore, we conclude that we have not succeeded to obtain layered structures. The SEM analysis of the

same sample shows grains with a composition of Ba-16.4, Tl-30.2 and V-53.4 at.%. We have not yet determined the cell parameters because of the presence of other impurity phases like Ba-V-O type and Tl-V-O type.

The resistivity temperature dependence of a sample of the $Tl_1Ba_1V_6$ starting composition is shown in Fig. 2. Its behaviour is similar to the one observed in [1].

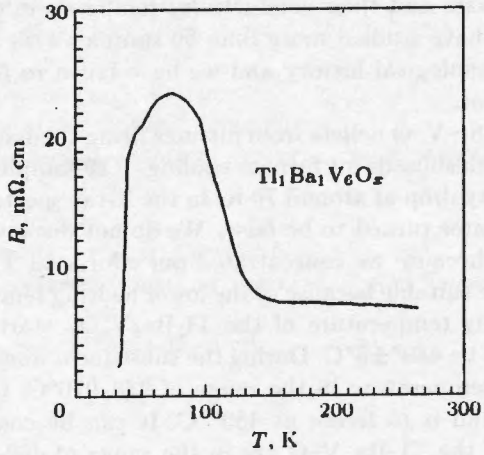

Fig. 2. Resivity temperature dependence of Tl-Ba-V-O

The a.c. susceptibility of a rectangular sample with the $Tl_1Ba_1V_6O_x$ composition was measured down to about 30 K (Fig. 3). The real part χ' has some very small

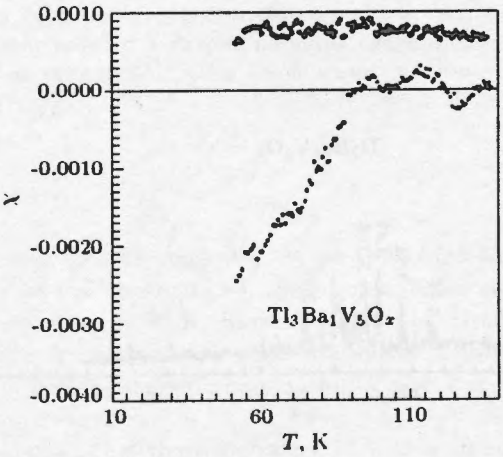

Fig. 3. The real and imaginary parts of AC susceptibility

deviation at about 90 K, while the imaginary part χ'' is insensitive to the transition. It cannot be taken as an evidence for a transition.

Annealing some of the samples at higher temperatures (1100°C) in H_2, we observed decomposition of the material and an appearance of droplets of metallic

Thallium with a different size, as confirmed by SEM analysis.

We suggest the possibility of a percolative type metal-to-metal transition, with a temperature range determined maily by the contacts of the oxidized surfaces of grains of a different composition. The relatively large thermopower observed frequently in our measurements may be related to the hydrogen diffusion.

In conclusion we briefly list the results of the present paper.

(*i*) We found two phases $Tl_1Ba_1V_6O_x$, $Tl_1Ba_3V_5O_x$ exibiting resistivity anomalies at about 50 K.

(*ii*) We have not detected a transition to superconducting state measuring the a.c. susceptibility down to about 25 K.

(*iii*) The X-ray spectra studied do not show layered structures.

(*iv*) The resistivity anomaly is possibly due to the metal to metal percolative transition the Tl droplets, being the second metal.

The insulating state conductivity is probably due to hopping transport.

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