Proceedings of the 48th International School and Conference on the Physics of Semiconductors "Jaszowiec 2019"

Effect of Tantalum Substitution on Dielectric Constant of $ZnSb_{2-x}Ta_xO_6$ Solid Solution ($x = 0.0, 0.1, 0.25, 0.75, 1.6$)

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The electrical measurements of $ZnSb_{2-x}Ta_xO_6$ phases with $x = 0.0, 0.1, 0.25, 0.75, 1.6$ have revealed insulating behavior with strongly decreasing electrical conductivity when tantalum x content is increased. As a consequence, high values of relative permittivity ε_r and loss tangent $\tan(\delta)$ were observed, that decreased with increase of temperature and frequencies, for samples with low Ta content, below $x = 0.75$. In turn, for samples richer in tantalum, ε_r reaches 14, and $\tan(\delta)$ becomes as low as 0.02 for $x = 1.6$. These effects have been interpreted either by the framework of the relaxation processes, or by the spatial charge polarization leading to the low energy loss of materials.

DOI: 10.12693/APhysPolA.136.633

PACS/topics: 72.80.Sk, 77.22.–d, 77.22.Gm

1. Introduction

Antimonates and tantalates of transition metals of the general formula MM'_2O_6 (M = Zn, Cd, Pb, Ni; M′ = Sb, Ta) are interesting because of their applications in structural, electrical, and optical properties [1–3]. Antimonates MSb_2O_6 (M = Zn, Mg, Ba, Cd) are n-type semiconductors [1–3]. $ZnSb_2O_6$ and $MgSb_2O_6$ make interesting electrode material for dye sensitized solar cells (DSSC) [1]. Recently, much attention has been paid to $ZnSb_2O_6$ and $ZnTa_2O_6$, because of their possible application in photocatalysis and sensors for detection of nitrogen oxides and hydrogen sulfide [4]. Other possibility is to apply them as materials for dielectric microwave devices used for satellite communication [5]. In the $ZnSb_2O_6$–$ZnTa_2O_6$ system a limited substitutional solid solution of the formula $ZnSb_{2-x}Ta_xO_6$ for $0 < x \leq 1.6$ crystallized in a tetragonal system and adopted a tri-rutile type structure. IR studies showed extension of the crystal lattice and the shift of the position of IR absorption bands towards higher wave numbers. In turn, UV–vis–NIR studies showed an increase in the energy gap in the range of 3.65–4.60 eV for $0.25 \leq x \leq 1.60$ [6]. The experimental densities d_{exp} of $ZnSb_{2-x}Ta_xO_6$ determined in argon with the help of an Ultrapyc 1200e ultrapycnometer increased with increase of tantalum content, as well as the calculated ones d_{cal} [6].

In the present work we have measured electrical conductivity, relative permittivity, and loss tangent of $ZnSb_{2-x}Ta_xO_6$ phases.

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2. Experimental details

All samples of the $ZnSb_{2-x}Ta_xO_6$ system were obtained by the solid-state method (details in [6]).

The electrical conductivity was measured by the DC method using a KEITHLEY 6517B Electrometer/High Resistance Meter. Broadband dielectric spectroscopy measurements were carried out using pellets, polished and sputtered with (≈ 80 nm) Ag electrodes in the frequency range from 200 Hz to 1 MHz with a LCR HITESTER (HIOKI 3532-50, Japan) within the temperature range of 79–400 K. For the electrical measurements, the powder samples were compacted in a disc form (10 mm in diameter and 1–2 mm thick) using a pressure of 1.5 GPa. They were then sintered for 2 h at 923 K. The electrical and thermal contacts were made by a silver lacquer mixture (Degussa Leitsilber 200).

3. Results and discussion

The samples of $ZnSb_{2-x}Ta_xO_6$ solid solution ($x = 0.0$, 0.1, 0.25, 0.75, 1.6) are insulators at low temperatures, while in higher ones they are strongly active. The electrical conductivity decreased sharply with increase of tantalum x content although in non-Arrhenius manner (Fig. 1).

Broadband dielectric spectroscopy measurements showed a strong dependence on temperature and frequency. Dielectric constant ε_r reaches a value up to 1.500 (Fig. 2) and high loss tangent $\tan(\delta) > 10$ (Fig. 3) for samples with low Ta content, below $x = 0.75$. On the contrary, a weak dependence of these quantities on temperature and frequency was observed for samples with contents of $x = 0.75$ and 1.6, which have low value of $\varepsilon_r \approx 14$ and very low losses below $\tan(\delta) = 0.01$.

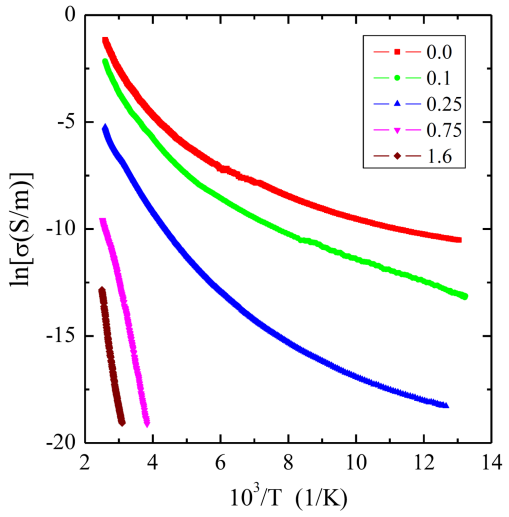

Fig. 1. Electrical conductivity ($\ln\sigma$) vs. reciprocal temperature $10^3/T$ of $ZnSb_{2-x}Ta_xO_6$.

The most spectacular result of this research is a dramatic change in ε_r and $\tan(\delta)$ due to tantalum doping between $x = 0.25$ and $x = 0.75$. The above results are interpreted as (i) part of the dipole relaxation for samples with small Ta content and as (ii) the spatial charge polarization for samples richer in tantalum, for which the freedom of electron or ion charge is limited. The polarization mechanisms described above are shown in the diagram at 300 K and at 100 kHz (Fig. 4). Interestingly, no spatial charge polarization in the $M_2FeV_3O_{11}$ (M = Mg, Zn, Pb, Co, Ni) ceramics was observed [7].

A closer look at the spectra shown in Figs. 2 and 3 suggests that high values of both dielectric and energy losses are accompanied by dipole relaxation visible as anomaly in T-dependence of ε_r and $\tan(\delta)$ that moves to lower temperatures with decreasing frequency, and high accumulation of electric charge in samples (up to $x = 0.25$) of lower density, related to lower amount of Ta in the solution (Fig. 5). When quantity of Ta, and consequently density of the material increases, then the accumulation of electric charge decreases strongly as well as intensity of dipole relaxation. Whereas it is still visible, although slightly for a sample with tantalum content $x = 0.75$ above 300 K, it completely disappears for a sample with $x = 1.6$, for which the energy loss falls below $\tan(\delta) = 0.02$. In other words, there is no dielectric relaxation, and there is no energy loss.

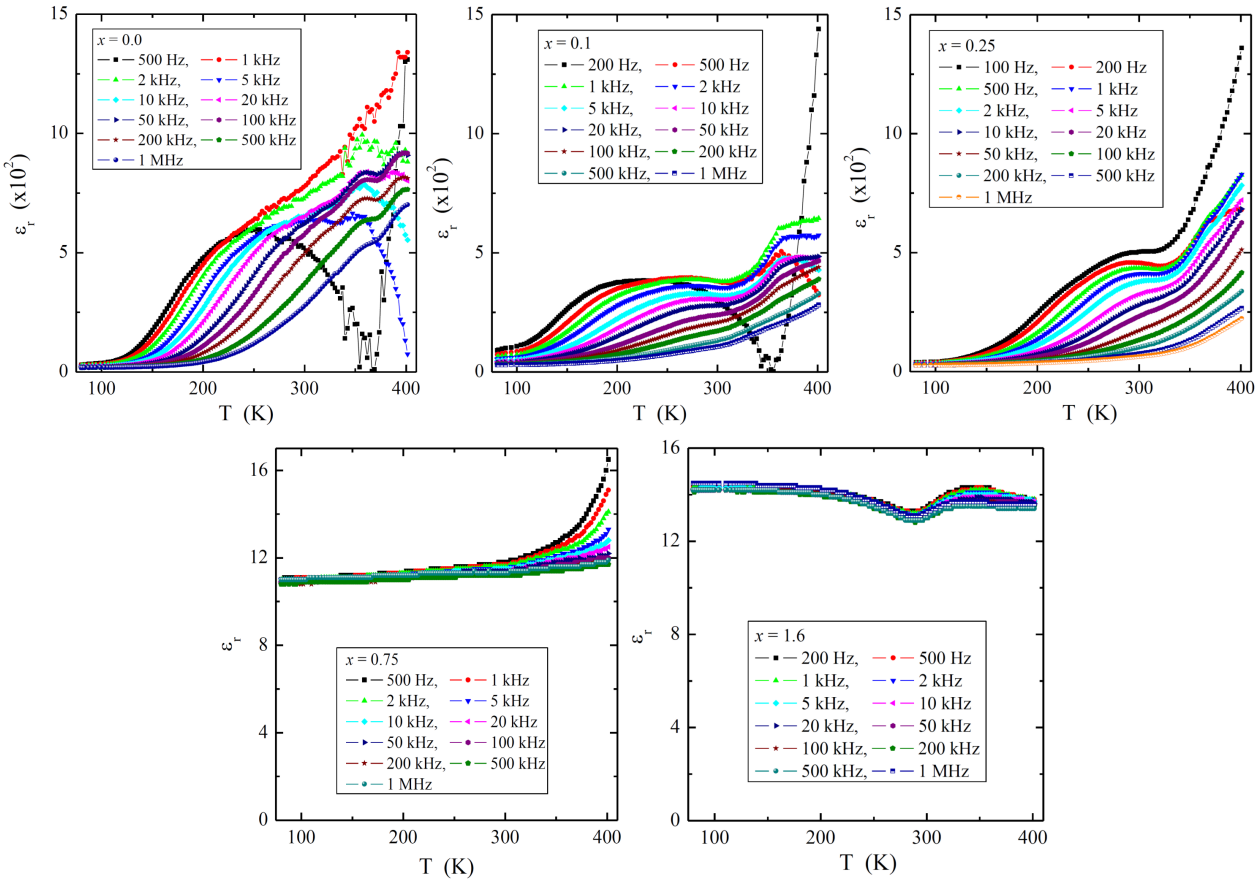

Fig. 2. Dielectric constant ε_r vs. temperature T of $ZnSb_{2-x}Ta_xO_6$ solid solution recorded in the frequency range of 200 Hz–1 MHz.

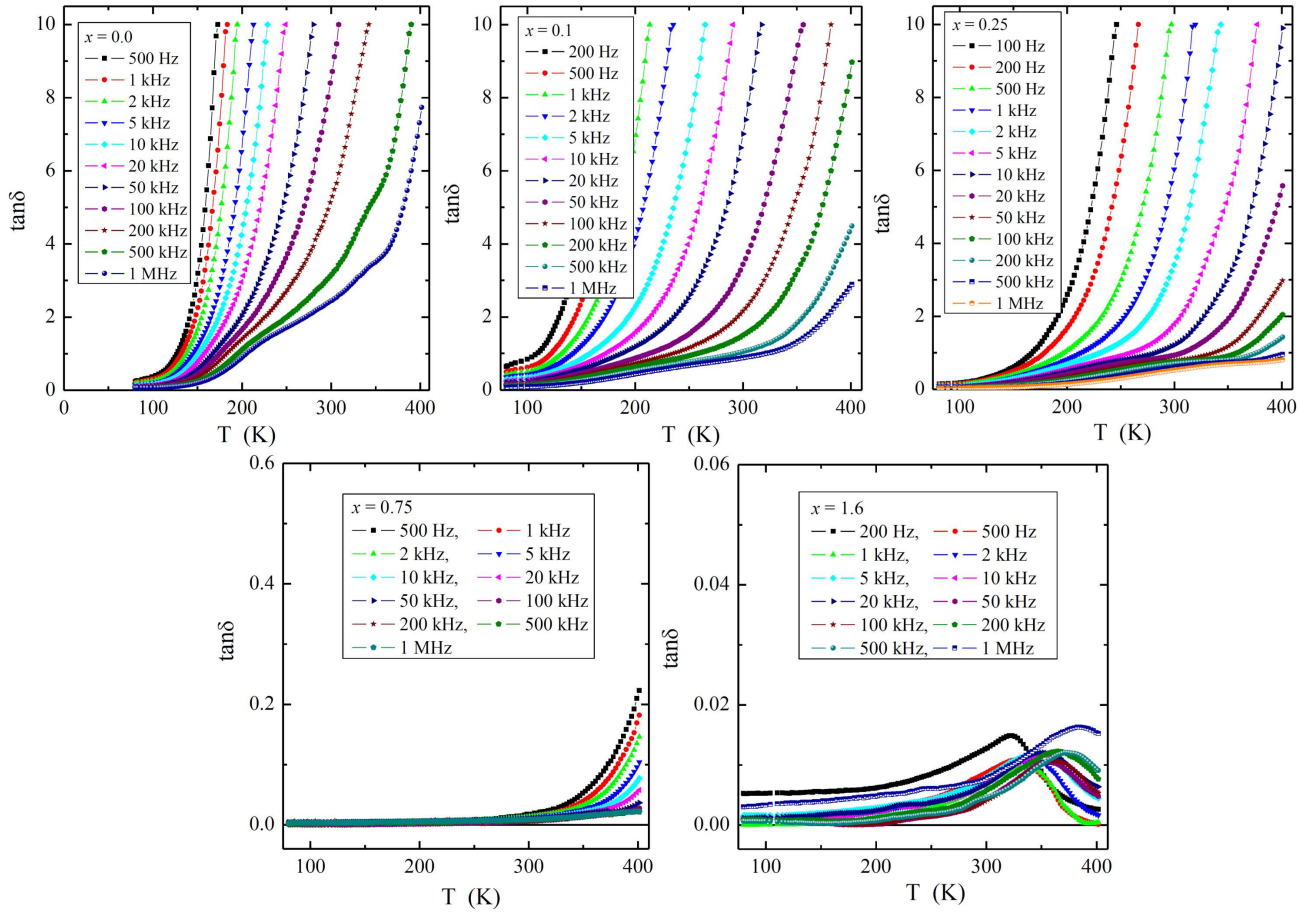

Fig. 3. Loss tangent $\tan(\delta)$ vs. temperature T of $ZnSb_{2-x}Ta_xO_6$ solid solution recorded in the frequency range of 200 Hz–1 MHz.

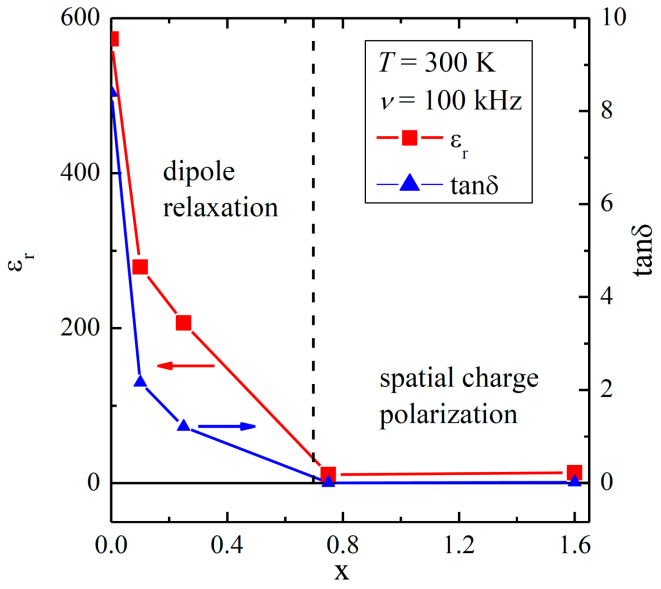

Fig. 4. Dielectric constant ε_r and loss tangent $\tan(\delta)$ vs. temperature T of $ZnSb_{2-x}Ta_xO_6$ solid solution recorded at 300 K and at 100 kHz.

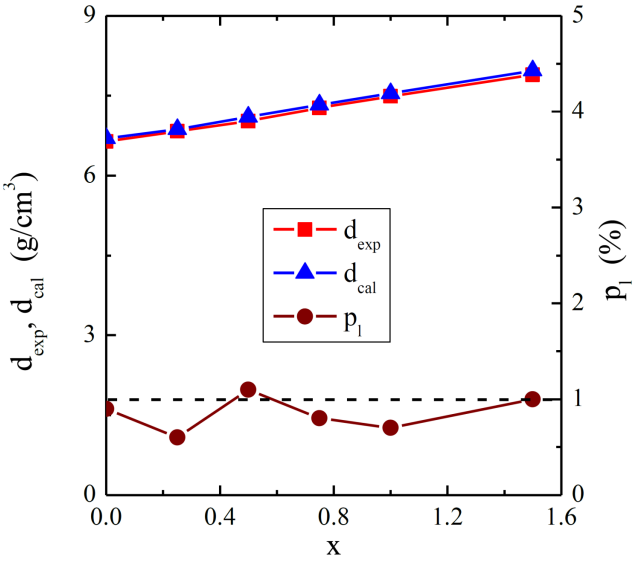

Fig. 5. Calculated (d_{cal}) and experimental (d_{exp}) densities and porosity level (p_l) vs. temperature T of $ZnSb_{2-x}Ta_xO_6$ solid solution. Data of d_{cal} and d_{exp} taken from [6].

The estimated level of porosity p_l from calculated d_{cal} and measured d_{exp} densities with an average value below one percent does not have a significant impact on the processes described above. A similar phenomenon was observed for $Pb_{1-3x}\square_x Gd_{2x}$ $(MoO_4)_{1-3x}(WO_4)_{3x}$ materials ($x = 0.0455, 0.0839, 0.1154, 0.1430, 0.1667$, and 0.1774, where $\square$ denotes vacancies) [8] and for $RE_2W_2O_9$ ceramics (RE = Pr, Sm–Gd) [9] that have a higher density. The accumulation of electric charge is also influenced by those ions that have unscreened electrons in unfilled shells. For example, a colossal dielectric effect was observed in (Co, Mn)$Pr_2W_2O_{10}$ [10] and in $CoEu_4W_3O_{16}$ [11].

4. Conclusions

The samples of $ZnSb_{2-x}Ta_xO_6$ solid solution ($x = 0.0$, 0.1, 0.25, 0.75, 1.6) were characterized by electrical conductivity and dielectric spectroscopy measurements. We have noticed insulating properties of measured samples with the residual conductivity strongly activated at higher temperatures as well as strong dependence on temperature, frequency, and tantalum content at least up to $x = 0.25$ of relative dielectric constant and loss tangent, well described by existence of the dipole relaxation mechanism. In turn, for samples richer in tantalum, and hence denser, i.e. for $x > 0.75$, the relaxation mechanism disappeared in favor of the accumulation of electric charge. Both mechanisms strongly depended on the amount of Ta directly related to the density of the sample, and the level of porosity did not have much impact on them. The materials under study with a high content of tantalum can be successfully used for the production of lossless capacitors.

Acknowledgments

This work was partly supported by Ministry of Science and Higher Education (Poland) and funded from Science Resources No. 1S-0300-500-1-05-06 and UPB-DZS 518-10-020-3101-01/18.

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