

INVESTIGATION OF SOME PHYSICO-CHEMICAL PROPERTIES OF COMPOSITE LEAD ANTIMONY OXIDE DOPED BY RHENIUM

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Some properties of rhenium-doped complex lead antimony oxide, PbSb_2O_6 , have been studied using the methods of chemical, physico-chemical and electrophysical analyses. Essential influence of the doping on dielectric properties of the samples has been shown. A new method of extraction-photometric determination of rhenium in alloys has been proposed.

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1. Introduction

The scientific and technological progress is associated with the progress in materials science the main task of which is to obtain new materials with desired physical, physico-chemical and chemical properties. Among all modern materials, semiconductors form one of the most important groups of substances.

Nowadays the task of new semiconducting materials became appreciable of the rapid progress in technology and engineering. Materials possessing special dielectric properties are particularly valuable, and many of these materials are oxides of metals. Results of investigations of physico-chemical interaction in complex systems form the scientific base for obtaining new oxide materials. It is important to note that the results from different authors are sometimes contradictory, and this fact can be explained by the strong dependence of properties of oxide ceramics upon the obtaining conditions (starting materials, methods of synthesis *etc*).

It was shown earlier that certain valuable physical parameters can be achieved by doping of some oxide materials, and lead antimonates belong to the group of such oxide materials [1].

The main purposes of this work were the synthesis of rhenium-doped (0.5-0.9 mol. %) complex lead antimony oxide, PbSb_2O_6 , and the studies of some physico-chemical properties of the obtained samples.

2. Experimental

The samples were synthesised from lead (II) oxide, antimony (V) oxide (molar 1:1 ratio) and 0.5-0.9 mol. % of rhenium [2]. Phase analyses were carried out using X-ray powder diffraction technique (powder diffractometer DRON-3, Ni-filtered Cu K_α radiation, $\lambda=1.5418 \text{ \AA}$, $10 \leq 2Q \leq 60^\circ$) [3]. Density measurements were performed by pycnometry using toluene as a working liquid (accuracy of 3-5 %). Each mean density value was obtained from five independent runs [4].

In order to carry out chemical analyses, specimens (0.2-1.0 g of the synthesised products) were thoroughly mixed with 0.5 g of NaOH and 0.5 g of Na_2O_2 and then put into nickel crucibles.

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These crucibles were heated in a muffle and kept at the temperature of 550-600 K for 2-2.5 hours. After the cooling of the crucibles, samples were put into the Erlenmeyer flasks (capacity of 100 ml). Additionally, the crucibles were flushed by distilled water, and the washing waters were collected in the same flasks. Further, the flasks with the water solutions of the samples were covered with funnels and boiled during 20-30 minutes. The obtained solutions were filtered and collected in volumetric flasks.

0.5 ml of 1×10^{-3} M solution of 5-nitro-indo-styryl, aliquot parts of the sample solutions (up to 5 μg of Re), acetate buffer solution (giving pH=8), and distilled water (to fill the volume of 5 ml) were collected in graded test tubes. Then 5 ml of the mixture toluene-ethylene dichloride (2:3 ratio) were injected into the test tubes, and extraction procedures were performed out during 30-60 s. The rhenium extracts were separated, centrifuged, and dried using waterless sodium sulphate; and then the optical densities of the obtained samples were measured (against the extract of the blank run) using spectrophotometer SF-18 at $\lambda=595$ nm.

The values of dielectric constant (ϵ) and tangent of dielectric losses ($\text{tg } \delta$) were measured at the frequency of 1 MHz using a digital device LCR E7-12 that allows determination of electric capacitance with the accuracy of $\pm 1 \times 10^{-3}$ pF and determination of $\text{tg } \delta$ with the accuracy of $\pm 1 \times 10^{-4}$. Dielectric constants of the samples were calculated from the experimental measurements of electric capacitance using the formula for parallel capacitor.

3. Results and discussion

Dependence of density of the synthesised samples upon the rhenium concentration was studied, and the results of this study are collected in Table 1 and illustrated in Fig. 1.

Table 1. Dependence of density of the samples upon the rhenium concentration in PbSb_2O_6 .

Compound		PbSb_2O_6				
mol. % Re		0.5	0.6	0.7	0.8	0.9
Density, g/cm^3	exper.	5.98 7	6.03 6	6.09 5	6.15 2	6.20 1
	calc.	7.00 4	6.99 9	6.99 5	6.99 0	6.98 6

The obtained products (powders of the different brown shades) are practically insoluble in water and alcohol.

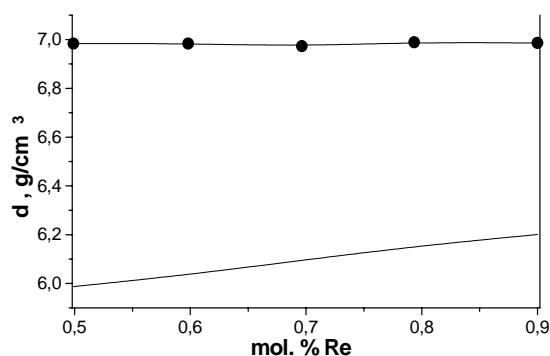


Fig. 1. Graphical presentation of dependence of density of the samples upon the rhenium concentration in PbSb_2O_6 (■ - experiment values; ● - calculated values).

On can see from Table 1 and Fig. 1 that increasing concentration of Re leads to increasing of the experimental density of the samples, and this fact can be explained by inserting of Re into the anion sublattice with the formation ReO_4^- . The dependence $d=f(x)$ (reliability factor $r=0,9994$) was obtained using the method of mathematical modeling 1.

$$d = 5.725 \cdot e^{0.0893x} \quad (1)$$

d - density

x - mol. % Re

e - exponent constant.

General composition of the samples was examined using chemical analyses. Concentration of rhenium in the samples was obtained by the method of calibrating plot, and the results of these chemical analyses are collected in Table 2.

Table 2. Concentration of Re in the samples of PbSb_2O_6 .

Sampl e	Calculate d mol. %	Found mol. %	S_r^a
1	0.50	0.51	9×10^{-3}
2	0.60	0.59	5×10^{-3}
3	0.70	0.68	1×10^{-3}
4	0.80	0.82	2.9×10^{-3}
5	0.90	0.89	5.4×10^{-3}

^a S_r – standard deviation of the experimental results.

Electrophysical studies of the samples shown that increasing concentration of Re leads to decreasing the value of dielectric constant (ϵ) from 0.18 (0.5 mol. % Re) to 15.4 (0.9 mol. % Re). The results of electrophysical studies are shown in Fig. 2 for the samples $\text{PbSb}_2\text{O}_6 + 0.5$ mol. % Re and $\text{PbSb}_2\text{O}_6 + 0.9$ mol. % Re.

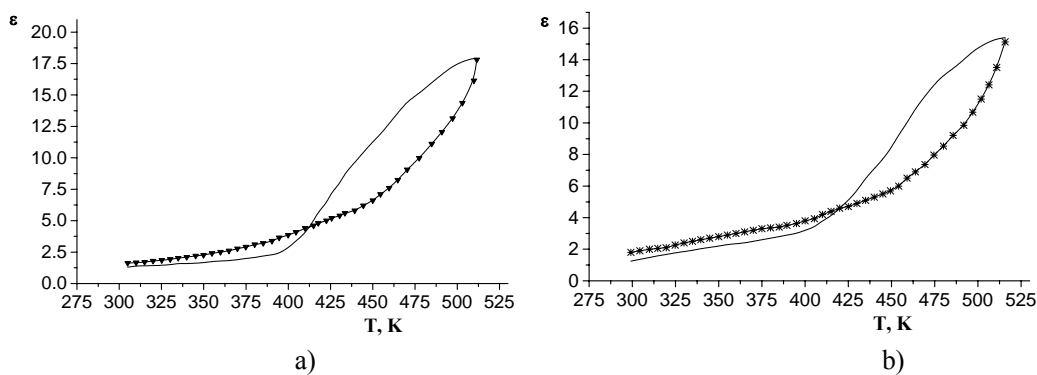


Fig. 2. Dependence of ϵ on temperature for the samples a - $\text{PbSb}_2\text{O}_6 + 0,5$ mol. % Re;
b- $\text{PbSb}_2\text{O}_6 + 0,9$ mol. % Re.

The results of our experiments indicate that the samples with smaller concentration of Re are more important for practical applications, and the sample $\text{PbSb}_2\text{O}_6 + 0.5$ mol. % Re has the highest value of ϵ . Comparison of value of ϵ for pure PbSb_2O_6 and the doped sample $\text{PbSb}_2\text{O}_6 + 0.5$ mol. % Re (Fig. 3) shown that the dielectric constant of the doped sample is almost twice higher than of pure lead antimony oxide PbSb_2O_6 .

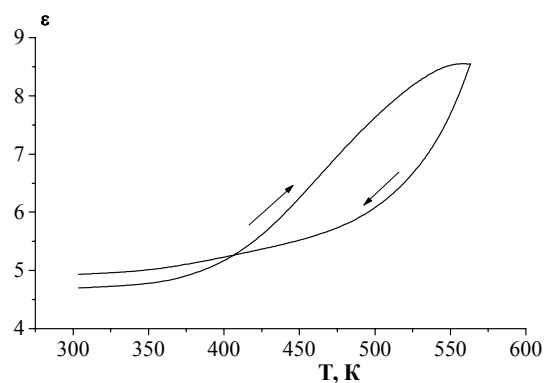


Fig. 3. Dependence of ϵ on temperature for the pure PbSb_2O_6 .

4. Conclusions

Five samples of the lead antimony oxide PbSb_2O_6 doped by rhenium were synthesised and identified by X-ray powder diffraction technique. Some properties of the samples were studied. A new method of analytical determination of rhenium in alloys has been developed.

References

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