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# PHYSICOCHEMICAL ANALYSIS OF BISMUTH OXIDE-TERBIUM OXIDE OR PRASEODYMIUM OXIDE SYSTEM

Pavel P.Shuk[x], Alim A.Vecher, Victor V.Samochval
Byelorussian State University, Minsk, U.S.S.R.

## ABSTRACT

In oder to obtain electrode layers stable at high temperatures in electrochemical devices with solid electrolytes, layers of materials with mixed electron-ionic conductivity possessing good polarization properties were suggested. X-ray and derivatographical investigations of $Bi_{1-x}Tb_xO_{1,5}$ and $Bi_{1-x}Pr_xO_{1,5}$ systems showed that solid phase reaction of simple oxides beging' only at temperature higher 950 K. In $Bi_{1-x}Tb_xO_{1,5}$ system beginning from x=0,15 me found a formation of cubic fluorite phase withing the whole investigated temperature range 298÷1100 K. In $Bi_{1-x}Pr_xO_{1,5}$ system in the whole range of compositions we found a phase transition at 1000÷1040 K from low temperature rhombohedral to high temperature cubic structure. TG and DTG diagrams show a weight loss with temperature rise. Which is due to $Tb^{4+} \rightarrow Tb^{3+}$ transitions. Measurements by e.m.f. method confirmed the presence of a considerable electronic conductivity in all systems investigated.

## INTRODUCTION

Oxygen ion conducting solid electrolytes are perspective materials for producing high-temperature fuel elements, oxygen sensors and pumps. Stabilized zirconium oxide used in most of the practical devices has a very low dissociation pressure ($< 10^{-25}$ Pa at 1000K) and can be used up to high temperatures ($>$ 1600 K). However, its condustivity does not exceed 1 $ohm^{-1}m^{-1}$ at temperatures lower 900 K and a sintering temperature is rather high ($>$ 2000 K). Besides that, for electrolytes based on zirconium oxide an againg effect is observed and as a consequence its conductivity decreases at long-term operation [1]. All that caused an interest in other oxygen ion conducting solid electrolytes. In the last decade the physico-chemical properties of both pure bismuth oxide and solid solutions on its basis being sysZetically and completely investigated [2]. Solid electrolytes based on bismuth oxide are characterized by a high oxygen ion conductivity which is almost two orders higher then a conductivity of stabilized zirconium oxide so that they can be produced in the form of dense ceramics. Practical field of use of solid electrolytes based on

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$BiO_{1,5}$ is limited by oxygen partial pressure $> 10^{-4}$ Pa at 1173 K and $> 10^{-11}$ Pa at 773 K because of their easy reduction[4]

Using compound conductors based on $BiO_{1,5}$ as electrode materials in electrochemical devices with solid elecrolytes is rather perspective. If bismuth oxide high temperature phase is stabilized by adding metal oxides with a variable valency then a compound ion and electronic conductor can be produced. A high oxygen ion and electronic conductivity was found in $BiO_{1,5}$ - $TbO_{1,75}$ and $BiO_{1,5}$ - $PrO_{1,833}$ systems [4-5]. Using oxide compositions with a compound conductivity as an electrode material makes possible to reduce considerably its polarization resistance and thus to extend application range of electrochemical devices with solid electrolytes.

The purpose of this paper consisted in investigating the production conditions of materials with a compound electron-ion conductivity in bismuth oxide - praseodymium oxide and bismuth oxide - terbium oxide systems and in physicochemical analysis of produced solid solutions of given systems.

## MEASURING METHODS

Investigated samples of the following compositions : $Bi_{1-x}Tb_xO_{1,5}(x=0,025+0,375)$ and $Bi_{1-x}Pr_xO_{1,5}(x=0,075+0,310)$ were obtained by means of solid phase reaction in air at 1100+1200 K for 20-25 hours. Compound phase formations in investigated systems were observed by means of Q-derivatograph(F - MOM,Hungary). Physico-chemical analysis of samples obtained was done by means of Q-derivatograph in air and in temperature range of 300+1100 K at heating and cooling speed of 5 K/min.

An indication of x-ray patterns obtained with the help of the goniometer HZG(Freiberg GDR) was conducted by using special tables for cubic and tetragonal plattice indication.

## RESULTS AND DISCUSSION

Investigations have showed that solid phase reaction of $Bi_{1-x}Tb_xO_{1,5}$ and $Bi_{1-x}Pr_xO_{1,5}$ formation begins only at temperatures higher 950 K. For $x=0,025$ homogeneous phase formation was not observed in $Bi_{1-x}Tb_xO_{1,5}$ system. $\delta$-phase formation of $BiO_{1,5}$ at 993 K and its melting at 1097 K were found, so as the melting of Bi - Tb - phase was observed at 1123 K. Beginning with $x=0,075$ phase transitions were not observed in $Bi_{1-x}Tb_xO_{1,5}$ system in all temperature ranges investigated. According to x-ray structural analysis a cubic fluorite phase formation was determined in this case. Lattice constant does not decrease unifomly that is determined by a different ion ratio of $Tb^{+3}/Tb^{+4}$ in samples. Phase transition from low temperature rhombohedral to high temperature cubic structure of fluorite type was found in $Bi_{1-x}Pr_xO_{1,5}$ system at 1000÷1040 K and for all composition range investigated. At temperature of 973 K and higher 1093 K negligible peaks were observed on DTA curves which disappear with increasing of x. They are caused by a fine structural change at 973 K which demands a detail study, and by melting of the secondary phase consisted chiefly of bismuth oxide at temperature higher 1093 K. Determined rhombohedral phase in $Bi_{1-x}Pr_xO_{1,5}$ system is in accordance with Esaka et al. data [5]. TG and DTG diagrams indicate weight loss with temperature rise, which is due to $Tb^{+3} \rightarrow Tb^{+4}$ and $Pr^{+3} \rightarrow Pr^{+4}$ transitions.

Investigations by e.m.f method showed a considerable electron conductivity in studied $Bi_{1-x}Tb_xO_{1,5}$ system and in a less degree in $Bi_{1-x}Pr_xO_{1,5}$ , which was caused by the presense of $Tb^{+4}$(or $Pr^{+4}$) ions in the structure and by electron transitions between $Tb^{+4}$($Pr^{+4}$) and $Tb^{+3}$($Pr^{+3}$).

## REFERENCES

1. M.V.Perfiljev, M.V.Inozemcev, A.N.Vlasov, Electrochemia(rus.) 18(1982)1230
2. T.Takahashi,H.Iwahara, Mat. Res. Bull. 13(1978)1447
3. P.Shuk,A.Vecher,V.Samochval, Vestn. BGU(rus.) (1984)8
4. P.Shuk,S.Jakobs,H.-H.Möbius, Hauptjahrestag. Chem. Ges. DDR 2.-4.12.80(1980)100
5. T.Esaka,H.Iwahara,H.Kunieda, J. Appl. Electrochem. 12(1982)235