Thermochimica Acta, 93 (1985) 465-468
Elsevier Science Publishers B.V., Amsterdam

PHYSICOCHEMICAL INVESTIGATION OF $Bi_{0,75}Y_{0,25}O_{1,5}$-CuO SYSTEM OF 0-25 MOL.% CuO COMPOSITION.

ALEXEY F.POLUYAN[x], VICTOR V.SAMOKHVAL, ALEXANDR A.SAVITSKY.
Byelorussian State University, Minsk, USSR.

ABSTRACT

A solid solution of $Bi_{0,75}Y_{0,25}O_{1,5}$ compound having a face-centered cubic lattice of fluorite-type is known as high conductivity oxide-ionic solid electrolyte. We found out that introduction of CuO addition into $Bi_{0,75}Y_{0,25}O_{1,5}$ leads to appearance of electronic conductivity and an insignificant increase of an ionic one. It is characteristic that the electronic conductivity increases in proportion to CuO addition. These properties alcow to apply the materials with the above compositions as electrode ones in electrochemical devices.

In order to determine a phase composition samples of system $Bi_{0,75}Y_{0,25}O_{1,5}$-CuO /0-25 mol.% CuO/ were studied by means of TA, DTA, and X-ray phase analysis methods. Losses of the samples mass were not obserwed. The X-ray phase analysis data and the presence of an endothermal effect /830-840°C/ in all heated samples allowed to find out that this system in 0-25 mol.% CuO is a mixture of Bi_2CuO_4 compound /melting temperature 850°C, black policrystals/ and Bi_2O_3-Y_2O_3 solid solution of CaF_2-type.

INTRODUCTION

A solid solution of $Bi_{0,75}Y_{0,25}O_{1,5}$ compound having a face-centered cubic lattice of fluorite type is known as a high conductivity oxygen-ionic solid electrolyte. Not taking into account the higher pressure of dissociation in comparison with solid electrolytes based on ZrO_2 / 8×10^{-9}Pa at 600°C/[1] $Bi_{0,75}Y_{0,25}O_{1,5}$ it may have an application for different electrical-chemical devices, operating at a temperature range of 400-700°C. Alloing of solid electrolytes based on bismuth oxide by some oxides leads to apperance of considerable part of electronic component at the conservation of a high ionic conductivity. Similar compositions may serve as electrode materials being in contact with solid electrolytes based on bismuth oxide. With a view to the search for such compounded conductors an investigation was carried out on system $Bi_{0,75}Y_{0,25}O_{1,5}$-CuO with admixtures of 0-25 mol.% cuprum oxide.

MEASURING METHODS

Indicated components were obtained by sintering in the air

Proceedings of ICTA 85, Bratislava

$Bi_{0,75}Y_{0,25}O_{1,5}$ which had been previously synthesised according to the method pointed out in [2] with the corresponding admixture of CuO at the temperature of ~730°C for 5 hours. Bismuth oxide and cuprum oxide of PFA type /pure for analysis/, yttrium oxide of 99,99 % purity were used as initial oxides. Prepared samples were analysed by means of RFA, DTA, TEK methods also by measuring the carry numbers and electrical conductivity at the alternating current. X-ray phase analysis was carried out the help of the DRON-1,5 diffractometr using CuK_{α} radiation. Measurements were done at heating and cooling with the speed of 5°/min. in the quartz cells. An interaction of sample materials and the cell was not observed. Determination of the mean thermal expansion coefficients obtained in the form of sample rods /0,005×0,005×0,020m^3/ was carried out by means of a quartz dilatometer with an accuracy not less 5%. A total electrical conductivity was measured at the alternoting current with the frequency of 1000 Hz. No frequency relation of electrical conductivity was observed at values higher 500 Hz. With a view to determine the nature of conductivity the transfer numbers were measured on a galvanic cell:

$$Ag,O_2/P'_{O_2}/ \mid Bi_{0,75}Y_{0,25}O_{1,5}\text{-}CuO \mid O_2/P''_{O_2}/,Ag \quad (1)$$

where $P'_{O_2} = 0,21 \times 10^5$ Pa, $P''_{O_2} = 1 \times 10^5$ Pa. A calculation was carried out according to the expression: $t_{ion.} = \frac{E\ exp.}{E\ theor.}$, where E exp. - e.m.f. of the first cell and E theor. - e.m.f. the second cell:

$$Pt,O_2/P'_{O_2}/ \mid ZrO_2 \text{ stable} \mid O_2/P''_{O_2}/,Pt . \quad (2)$$

After going through the first cell cleaned air and oxygen were received by the control sensor (2).

RESULTS AND DISCUSSION

Unlike the yellow-orange $Bi_{0,75}Y_{0,25}O_{1,5}$ the sinthesised samples had the black colour. The results of the x-ray analysis showed that the main phase in the studied intervals of CuO concentration /0-25 mol.%/ of $Bi_{0,75}Y_{0,25}O_{1,5}$-CuO system was Bi_2O_3-Y_2O_3 solid solution with the face-centered cubic lattice. The presence of additional peaks have been also found that indicates the existance of the second phase.

Measurement results of electrical conductivity and transferance numbers point out the presence of a conductive electronic component in all of the studied samples (fig. 1). It is characteristic that electronic character of conductivity dominates at lower temperatures /<500°C/ and that of ionic at higher temperatures />500°C/.

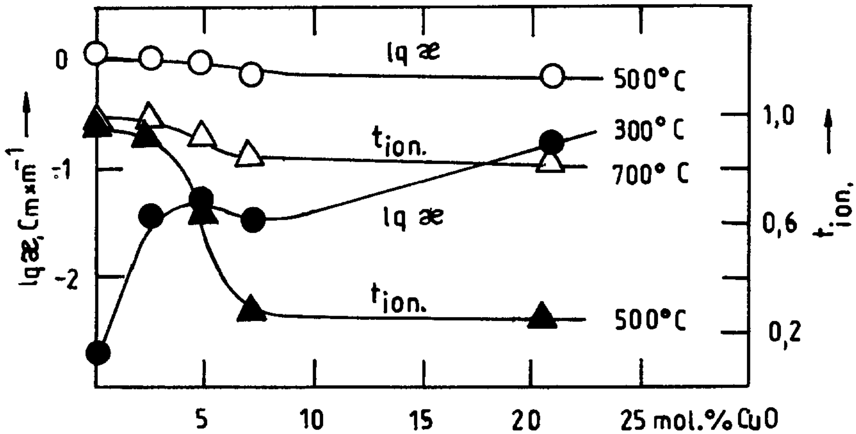

Fig. 1. Dependence of electrical conductivity upon cuprum oxide content in $Bi_{0,75}Y_{0,25}O_{1,5}$-CuO.

Investigation made according to TEK method showed that the raising of cuprum oxide contain leads at first to thermal expansion coefficients increasing for 0-7 mol.% of CuO and then to their decreasing /for concentrations >7 mol.% of CuO/. Initial increasing may be explained by improving the sintering of $Bi_{0,75}Y_{0,25}O_{1,5}$ at alloying it by cuprum oxide.

It is known that Bi_2CuO_4 compound /black policristals, $t_{mel.}$ - 850°C/[3] can be formed in Bi_2O_3-CuO binary system, this compound has a tetragonal structure and a conductivity mainly of electron character which is equal to $2{\times}10^{-12}Cm{\times}m^{-1}$ at a room temperature. Obtained information along with literature data allous to draw a conclusion that Bi_2CuO_4 compound is the second phase in the studied composition system.

The presence of the endothermal effect which is typical for a melting in the all of the samples at heating in the range of 830-840°C and exothermal effect at a cooling for 770-830°C values of which are proportional to cuprum oxide content, confirms this assumption.

According to literature data [2] Bi_2O_3-Y_2O_3 binary system the solid solution having a face-centered cubic lattice are existed in the composition system of 25-43,5 mol.% Y_2O_3. It is obvious that the doping of cuprum oxide alloying agent leads to the formation of Bi_2CuO_4 compound and to decreasing the content of bismuth oxide in $Bi_{0,75}Y_{0,25}O_{1,5}$ solid solution as a consequence of that in the latter a shift takes place to the region with the higher content of Y_2O_3, Bi_2CuO_4 at heating to a temperature higher than the melting point /850°C/ Bi_2CuO_4 decomposes partly into Bi_2O_3 and CuO [3]. The same effect was found in case of composition with >21 mol.% CuO after prolonged ageing /for ~100 hours/ at the temperature of 800°C. Such phenomenon was not observed for compositions <21 mol.% CuO.

CONCLUSIONS

The effect of cuprum oxide admixture upon the properties of $Bi_{0,75}Y_{0,25}O_{1,5}$ solid electrolyte of 0-25 mol.% CuO composition was stadied. It was found that cuprum oxide admixture leaded to the formation of Bi_2CuO_4 composition having a tetragonal lattice and to the shift of $Bi_{0,75}Y_{0,25}O_{1,5}$ solid solution with a face--centered cubic lattice to the region of composition with a higher content of Y_2O_3.

It was established that alloing $Bi_{0.75}Y_{0,25}O_{1,5}$ solid solution by cuprum oxide leaded to appearance of electron conductivity. Increasing CuO concentration raised the part of electron component and did not involve considarable decreasing of ionic conductivity.

REFERENCES

1 T. Takahashi, T. Esaka, H. Iwahara, J. Appl. Electrochem. 7 (1977) 303

2 T. Takahashi, T. Esaka, H. Iwahara, J. Appl. Electrochem. 5 (1975) 187

3 B. G. Kakhan, W.B. Lazarev, I.S. Shaplygin, Zh. Neorg. Khim. (rus.) 24 (1979) 1663