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A MODEL FOR THE COMPOSITION MODIFICATIONS IN THE Cu-Sb-O SYSTEM

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ABSTRACT . The Sn-Sb-Cu-O system has been extensively studied [1-3] but systematic phase equilibrium studies have not been approached. The system contains useful ceramics with specific electrical and magnetic properties, employed as sensors, electrodes and catalysts.

As a preliminary step to the phase diagram calculation, the paper aims to present a model for the composition modifications in the Cu-Sb-O system, which is the most complex of all subsystems.

Exothermic effects along with mass increases can be observed in DTA/TGA curves [3], were assigned, for all samples, to Sb₂O₃ and Sb₂O₄ oxidation and to CuSb₂O₆ formation:

\[ \approx 500 \, ^\circ C \quad Sb_2O_3 + 1/2 \, O_2 \Rightarrow Sb_2O_4 \]  \hspace{1cm} (1)
\[ > 750 \, ^\circ C \quad Sb_2O_4 + CuO + 1/2 \, O_2 \Rightarrow CuSb_2O_6 \]  \hspace{1cm} (2)

For the samples having CuO in excess, the reduction of CuO to Cu₂O and the formation of the Cu₄SbO₄.₅ compound simultaneously occur:

\[ > 950 \, ^\circ C \quad CuSb_2O_6 + 7CuO \Rightarrow (1-r) \, CuSb_2O_6 + 7(1-r)CuO + 2rCu_4SbO_{4.5} + 2rO_2 \]  \hspace{1cm} (3)

where \( r \in (0,1) \) is the fraction of CuSb₂O₆ that transforms into Cu₄SbO₄.₅.

All the experimental evidences show that the Equations (1), (2) and (3) are good descriptions of the transformations that occurs in the CuO-Sb₂O₃ system along with the temperature. If the reactions are considered as completed, including \( r=1 \) in Eq. (3), then the quantity of oxygen that is gained or lost can be calculated for each sample. It is important to note that Equations (2) and (3) should be carefully solved because of the excess quantities of CuO or Sb₂O₄ that can be found in some samples. The calculated values of mass variation are in a good agreement with those obtained from the experimental TG diagrams [3]. The atomic fractions of Cu, Sb and O content change in the system and they can be also calculated.

The model assumes that at room temperature the compositions lay on the CuO-Sb₂O₃ line as shown in Fig.1. The composition line moves to CuO-Sb₂O₄ at 500°C and changes to CuO-CuSb₂O₆-Sb₂O₄ over 750°C. Finally, if reaction (3) is completed at 1000°C, the compositions can be found on CuO-Cu₄SbO₄.₅-CuSb₂O₆-Sb₂O₄ line.

Fig.1. Atomic compositions after the thermal treatment of a starting \( S_n=(10-n)CuO-nSb_2O_3 \) system.

Introduction

The Sn-Sb-Cu-O system has been extensively studied [1-3], but systematic phase equilibrium studies have not been approached. The system contains useful ceramics with specific electrical and magnetic properties, employed as sensors, electrodes and catalysts.

This paper aims to present a model for the composition modifications in the Cu-Sb-O system, which is the most complex of all subsystems. This is a preliminary step to the phase diagram calculation.

The thermal effects, along with mass modifications observed in DTA/TGA curves [3], were assigned to Sb$_2$O$_3$ and Sb$_2$O$_4$ oxidation and CuSb$_2$O$_6$ formation:

\[ \text{Sb}_2\text{O}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{Sb}_2\text{O}_4 \quad (1) \]

\[ \text{Sb}_2\text{O}_4 + \text{CuO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CuSb}_2\text{O}_6 \quad (2) \]

For the samples having excess CuO, the reduction of CuO to Cu$_2$O and the formation of the Cu$_4$Sb$_{0.5}$ compound simultaneously occur above 1273 K:

\[ \text{CuSb}_2\text{O}_6 + 7\text{CuO} \rightarrow (1-r) \text{CuSb}_2\text{O}_6 + 7(1-r)\text{CuO} + 2r\text{Cu}_4\text{Sb}_0.5 \text{O}_4 + 2r\text{O}_2 \quad (3) \]

where \( r \in (0,1) \) is the fraction of CuSb$_2$O$_6$ that transforms into Cu$_4$Sb$_{0.5}$.

All the experimental evidences show that the Equations (1), (2) and (3) are good descriptions of the transformations that occur in the CuO-Sb$_2$O$_3$ system along with the temperature at which they occur. If the reactions are considered complete, including \( r=1 \) in Eq. (3), then the quantity of oxygen that is gained or lost can be calculated for each sample. It is important to note that Equations (2) and (3) should be carefully solved because of the excess quantities of CuO or Sb$_2$O$_4$ that can be found in some samples. The atomic fractions of Cu, Sb and O change in the system and have been also calculated.

Hypothetical samples of composition \( S_n=(10-n)\text{CuO}+n\text{Sb}_2\text{O}_3 \), \( n=0;1;\ldots;10 \) were considered for performing comparisons with experimental information.
At $773\,\text{K}$ the equation is:

$$x_1\text{CuO} + y_1\text{Sb}_2\text{O}_3 + z_1\text{O}_2 = x_2\text{CuO} + y_2\text{Sb}_2\text{O}_3 + u_2\text{Sb}_2\text{O}_4$$

(4)

If we assume that only a $p$ mole fraction of $\text{Sb}_2\text{O}_3$ oxidizes to $\text{Sb}_2\text{O}_4$ then the solution is:

$$z_1 = \frac{py}{2} \quad x_2 = x - y \quad y_2 = (1 - p)y \quad u_2 = py$$

(5)

Fig. 1 The mole fraction distribution in the CuO-Sb$_2$O$_3$ system at 773 K for a completed reaction ($r=1$).
At 1023 K the equation is:

\[ x_2CuO + u_2Sb_2O_4 + z_2O_2 = x_3CuO + u_3Sb_2O_4 + v_3CuSb_2O_6 \]  \hspace{1cm} (6)

If only a \( q \) fraction of \( Sb_2O_4 \) participates in \( CuSb_2O_6 \) formation, then the solution is:

\[ z_2 = q \frac{y}{2} \quad x_3 = 1 - (1 + q)y \quad u_3 = (1 - q)y \quad v_3 = qy \]  \hspace{1cm} (7)

One can notice that both \( y \) and \( q \) must be nonnegative and less than unity so:

\[ x_3 \geq 0 \Rightarrow q \leq \frac{1 - y}{y} \quad \text{but} \quad q \leq 1 \Rightarrow q \in \left[ 0, \min\left(1, \frac{1 - y}{y}\right) \right] \]  \hspace{1cm} (8)

Fig. 2 The mole fraction distribution in the CuO-Sb\(_2\)O\(_3\) system at 1073 K for a completed reaction (\( q=q_{\text{max}} \)).
At 1273 K the equation is:

\[ x_1CuO + u_2Sb_2O_3 + v_1CuSb_2O_6 + z_3O_2 = x_1CuO + u_2Sb_2O_3 + v_1CuSb_2O_6 + w_2Cu_8Sb_2O_{16} \quad (9) \]

a) For \( y \leq 0.5 \), we can assume that a fraction \( r \) of \( CuSb_2O_6 \) participates in the \( Cu_8Sb_2O_{16} \) formation so the solution is:

\[ z_3 = -2ry \quad x_4 = 1 - (2 + 7r)y \quad v_4 = (1 - r)y \quad w_4 = ry \quad (10) \]

But for \( x_4 > 0 \Rightarrow r \leq \frac{1 - 2y}{7y} \),

\[ r \in \left[ 0, \min \left( 1, \frac{1 - 2y}{7y} \right) \right] \]

The maximum of \( f(y) = \frac{1 - 2y}{7y} \) is 1 for \( y = \frac{1}{9} = 0.11 \). So two other intervals should be considered:

a1) For \( y \in \left[ 0, \frac{1}{9} \right] \), \( r_{max} = 1 \) and

a2) For \( y \in \left[ \frac{1}{9}, \frac{1}{2} \right] \), \( r_{max} = \frac{1 - 2y}{7y} \)

b) For \( y > 0.5 \) there are no other reactions in the system

Fig. 3 The mole fraction distribution in the \( CuO-Sb_2O_3 \) system at 1273 K for a completed reaction (\( r = r_{max} \) and \( q = q_{max} \)).
At 773 K, if we denote:

\[ N_2 = 2x_2 + 5y_2 + 6u_2 = 2 + (3 + p)y \]  

then the atomic fractions of the components are:

\[ x_{ca} = \frac{x_2}{N_2} = \frac{1 - y}{2 + (3 + p)y} \]
\[ x_{sb} = \frac{2y_2 + 2u_2}{N_2} = \frac{2y}{2 + (3 + p)y} \]
\[ x_o = \frac{x_2 + 3y_2 + 4u_2}{N_2} = \frac{1 + (2 + p)y}{2 + (3 + p)y} \]  

Fig. 4 The atomic composition of the starting \( S_n=(10-n)CuO-nSb_2O_3 \) samples as calculated at 723 K. The compositions points move from the \( CuO-Sb_2O_3 \) line to the \( CuO-Sb_2O_4 \) line.
At 1023 K, if we denote:

\[ N_3 = 2x_1 + 6u_3 + 9v_3 = 2 + 4y + qy = 2 + (4 + q)y \]  \hspace{1cm} (13)

then the atomic fractions of the components are:

\[ x_{Cu} = \frac{x_1 + v_3}{N_3} = \frac{1-y}{2+(4+q)y} \]
\[ x_{Sb} = \frac{2u_3 + 2v_3}{N_3} = \frac{2y}{2+(4+q)y} \]
\[ x_{O} = \frac{x_3 + 4u_3 + 6v_3}{N_3} = \frac{1+(3+q)y}{2+(4+q)y} \]  \hspace{1cm} (14)

Fig. 5 The atomic composition of the starting \( S_n=(10-n)CuO-nSb_2O_3 \) samples as calculated at 1023 K. The compositions points move from the CuO-Sb\(_2\)O\(_4\) line to the CuO-CuSb\(_2\)O\(_6\)-Sb\(_2\)O\(_4\) line.
At 1273 K, if we denote:

\[ N_4 = 2x_4 + 9y_4 + 19w_4 = 2 + 5y - 4ry \]  \hspace{1cm} (15)

then the atomic fractions of the components are:

\[ x_{Cu} = \frac{1 - y}{2 + 5y - 4ry} \]
\[ x_{Sb} = \frac{2y}{2 + 5y - 4ry} \]
\[ x_{O} = \frac{1 + 4y - 4ry}{2 + 5y - 4ry} \]  \hspace{1cm} (16)

Fig. 6 The atomic composition of the starting \( S_n = (10-n)CuO-nSb_2O_3 \) samples as calculated at 1273 K. The compositions points move from the \( CuO-CuSb_2O_6-Sb_2O_4 \) line to the \( CuO-Cu_4SbO_{4.5}-CuSb_2O_6-Sb_2O_4 \) line.
The weight variation of the system

At 1273 K the weight variation of the system can be calculated as:

\[ VM_1 = \frac{z_1 M_0}{x_1 M_1 + y_1 M_2} = \frac{-2\gamma M_0}{(1-2\gamma)M_1 + \gamma M_2} \]  \hspace{1cm} (17)

![Graph showing weight variation at 1273 K](image)

Fig. 7 The calculated and experimental (+, ref.3) weight variation of the system at 1273 K.

At 1023 K the weight variation of the system can be calculated as:

\[ VM_2 = \frac{z_2 M_0}{x_2 M_1 + y_2 M_4} = \frac{\frac{q \gamma M_0}{2}}{(1-\gamma)M_1 + \gamma M_4} \]  \hspace{1cm} (18)

![Graph showing weight variation at 1023 K](image)

Fig. 8 The calculated and experimental (+, ref.3) weight variation of the system at 1023 K.

At 773 K the weight variation of the system is:

\[ VM_3 = \frac{Z_3 M_0}{x_3 M_1 + y_3 M_5} = \frac{0.5\pi y M_6}{(1-\gamma)M_1 + \gamma M_5} \]  \hspace{1cm} (19)

![Graph showing weight variation at 773 K](image)

Fig. 9 The calculated and experimental (+, ref.3) weight variation of the system at 773 K.
Phase equilibrium information

If we consider CuSb₂O₆ as CuO-Sb₂O₃ and 2(Cu₄SbO₄₅) as 4Cu₂O-Sb₂O₅, then Fig. 10 can be a representation of domains of phase equilibrium for the system. The presence of these phases was confirmed by x-ray studies (3).

Fig. 10. Domains of phase equilibrium in the CuO-Sb₂O₃ starting system.

The shadowed areas denote X-ray confirmations of phase compositions (ref.3).
Conclusions

Modeling composition modifications is a preliminary step to the phase diagram assessment of the Cu-Sb-Sn-O system.

For the Cu-Sb-O system, which is the most complex of all sub-systems, the model assumes that at room temperature the compositions lie on the CuO-Sb$_2$O$_3$ line. The composition points move to CuO-Sb$_2$O$_4$ at 723 K and change to CuO-CuSb$_2$O$_6$-Sb$_2$O$_4$ above 1023 K. Finally, if reaction (3) is completed at 1273 K the compositions can be found on the CuO-Cu$_4$Sb$_{0.5}$-CuSb$_2$O$_6$-Sb$_2$O$_4$ line.

The calculated values of mass variation are in good agreement with those obtained from the experimental TG diagrams. The domains of phase equilibrium are confirmed by X-ray diffraction as predicted by the model.

References