Yun Yao*, Gang Xie, Ning Song, Yanqing Hou, Xiaohua Yu and Rongxing Li

Thermodynamics of $CuInO_2$ Preparation by Cation Exchange Reaction

Abstract: To investigate the optimum conditions of the $CuInO_2$ (CIO) preparation by cation exchange reaction method, the standard entropy, thermal capacity at constant pressure, standard enthalpy and standard Gibbs free energy of formation were estimated. The relations of temperature (T) and thermodynamic equilibrium constants (K), the conditions for three independent reactions were analyzed in $CuInO_2$ preparation. The curves of Gibbs free energy-T, $K-T$ and $P_{CuCl}-T$ for those reactions have been plotted. The results showed that the CIO powder could be synthesized by cation exchange reaction. There were two main reactions through the way of $NaInO_2$ reacting with CuCl. One was $NaInO_{2(s)}$ reacting with $CuCl_{(s)}$ at $T \geq 1698$ K. The cost was higher in the way. The other was $NaInO_{2(s)}$ reacting with $CuCl_{(g)}$ at $T < 1698$ K. However, the yield of CIO would be decreased because $CuInO_2$ powder decomposed into $Cu_2O_{(s)}$ and $In_2O_{3(s)}$ with the temperature reduced, especially when $T \leq 573$ K. And the higher vapor pressure of $CuCl_{(g)}$ was necessary for the process, which needs the higher temperature since the vapor pressure of $CuCl_{(g)}$ increases with increasing temperature, especially when $T > 973$ K. It was recommended that $NaInO_{2(s)}$ react with $CuCl_{(g)}$ for preparing CIO under conditions of $973 < T \leq 1698$ K and the vacuum in the reactor.

Keywords: $CuInO_2$ powder preparation, cation exchange reaction method, thermodynamics, standard entropy, thermal capacity at constant pressure, standard enthalpy, standard Gibbs free energy of formation

1 Introduction

Copper Indium Oxide (CIO), $CuInO_2$, is a very significant transparent conductive oxide (TCO) material with crystal structure of delafossite-type oxide [1–3]. The CIO can be applied extensively in industry, for example, pinned items, electro optical device, etc. Presently, it is employed primarily in electronics and photovoltaic industry as a consequential green material. Since the middle 19th century, the solid-phase reaction method was applied by Hahn [4] and Wofgang [5] in synthesis $CuInO_2$ but failed. Then after, Liu [6, 7] proved that $CuInO_2$ powder could not be synthesized by solid-phase reaction based on first-principle calculation. However, Kawazoe et al. [8] proposed Chemical Modulation of the Valence Ban (CMVB) theory, prepared p-type TCO and found its light and electronic properties at 1997. After that, Shimode [9] prepared CIO powder by cation exchange reaction. Cation exchange reaction is also named ion exchange reaction or substitution reaction. The mechanisms of cation exchange reaction is the procedure that cation or ion of the solid reactants can exchange directly to produce other two compounds but no resin catalyst used during this reaction at a given temperature. For example: $CuCl + NaInO_2 = CuInO_2 + NaCl$, the Cu^+ can directly exchange Na^+ at solid state. Yanagi [10] prepared thin films of Ca-doped and/or Sn-doped CIO on α-Al_2O_3 (001) single crystal substrates by PLD method, and discovered bipolar electrical conductivity of the CIO. The band gap (E_g) of CIO was very large, up to about 3.9 eV, and the average visible transmittance was 70%. The Calculated results get great academic interests because of its excellent photo-electric properties and unique bipolar properties. Then, the preparation theory, preparation method, doping performance, thin film deposition of CIO, etc. have been developed quickly [3, 10–15]. The CIO has been prepared in the experimental scale in present. But the productivity of CIO was very low. Therefore, the thermodynamic of CIO preparation should be study in order to expose the reasons of low yield, find way to improve the yield and determine the optimum reaction conditions. However, the open literature rarely report the thermodynamic study on preparation of CIO powder. The main reasons for that were lack of the thermodynamic data on CIO preparation. Therefore, the thermodynamics for preparation of CIO powder have been studied in the paper with the goal of providing theoretical base for the CIO preparation process.

***Corresponding author: Yun Yao:** Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China. E-mail: yyaoun1982Happy@yahoo.com.cn
Gang Xie, Ning Song, Yanqing Hou, Xiaohua Yu, Rongxing Li: Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China

2 Thermodynamic parameters

According to cation exchange reaction, CuInO$_2$ was prepared in the air isolation condition [9, 16]. When the reactions reach equilibrium in the process, there were many species, such as CuInO$_2$, NaInO$_2$, CuCl$_{(s)}$, CuCl$_{(g)}$, In$_2$O$_3$, Cu$_2$O and NaCl in the system. Many thermodynamic calculations were involved, for example, multi-elements, multiple-phase chemical equilibrium, thermodynamic equilibrium, chemical and thermal equilibrium in these systems. So an accurate knowledge of property data was important for thermodynamic investigation. A large number of thermophysical property data related pure simple oxides have been reported, but the data for complex oxide was rarely reported in various thermodynamic handbooks. As we known, the accurate experimental thermophysical property data for complex oxide is hard to obtain though experiment because of the high cost [17]. Therefore, estimation of thermodynamic data based on theory analysis with somewhat accuracy was popular. In the present work, a large number of mathematical models have been developed to estimate thermodynamic data of complex oxide. The formulas and/or methods of estimating thermodynamic data of silicate were developed by some researchers [18–23]. These works were very good and useful, but the model parameters, which were necessary in the model, were lack in the open literature. Therefore, these models were very hard to be used in the system. However, the Two-Parameter Model developed by Guo and Zhao [24–26], which could calculate the thermodynamic data of complex oxide with good accuracy, could be employed to predicate the thermodynamic data in the system. The calculated results were efficient with the relation error within 10% by comparing with experimental data in the open literature [17]. Thus the thermodynamic data of CuInO$_2$, NaInO$_2$, etc. were calculated by application of Two-Parameter Model in this paper. The model had also been employed to investigate the thermodynamics of CuInO$_2$ preparation by solid reaction method [14].

The complex oxide of $a\mathrm{M}_m\mathrm{O}_x \cdot b\mathrm{N}_n\mathrm{O}_y$ was consisted of $\mathrm{M}_m\mathrm{O}_x$ and $\mathrm{N}_n\mathrm{O}_y$ based on the Two-Parameter Model [24–26], here a and b were the corresponding coefficients. Wen [22] proposed that the oxygen-containing compounds could be regarded as composite oxide, such as sulfate, carbonate, etc., as shown in Eq. (1). Therefore, NaInO$_2$ and CuInO$_2$ could be considered as complex oxide analogically. And the NaInO$_2$ and CuInO$_2$ could be expressed as Eqs. (2) and (3):

$$a\mathrm{M_mO_x} + b\mathrm{N_nO_y} = a\mathrm{M_mO_x} \cdot b\mathrm{N_nO_y} \tag{1}$$

$$\mathrm{Na_2O + In_2O_3 = 2NaInO_2} \tag{2}$$

$$\mathrm{Cu_2O + In_2O_3 = 2CuInO_2} \tag{3}$$

The standard enthalpy change $\Delta_f H_m^\theta$ of formation of $a\mathrm{M_mO_x} \cdot b\mathrm{N_nO_y}$ could be expressed as follows:

$$\Delta_f H_m^\theta = a\Delta_f H^\theta_{M_mO_x} + b\Delta_f H^\theta_{N_nO_y} + \Delta_r H^\theta \tag{4}$$

where $\Delta_f H^\theta_{M_mO_x}$ was the standard enthalpy change of formation of $\mathrm{M_mO_x}$. $\Delta_f H^\theta_{N_nO_y}$ was the standard enthalpy change of formation of $\mathrm{N_nO_y}$. $\Delta_r H^\theta$ was reaction change of enthalpy.

The standard reaction enthalpy changes $\Delta_r H^\theta$ for reaction (1) could be expressed as:

$$\Delta_r H^\theta = aA_H + bB_H + \frac{ab}{a+b}(A'_H + B'_H) \tag{5}$$

Here, A_H, A'_H were parameters of $\mathrm{M_mO_x}$, B_H, B'_H were parameters of $\mathrm{N_nO_y}$.

And standard entropy S_m^θ of reaction (1) could be expressed as:

$$S_m^\theta = aA_S + bB_S + \frac{ab}{a+b}(A'_S + B'_S) + D \tag{6}$$

Here, A_s, A'_S were parameters of $\mathrm{M_mO_x}$, B_s, B'_S were parameters of $\mathrm{N_nO_y}$, D was constant: $D = -8.923$ J/(mol·K).

The standard thermal capacity at a constant pressure (C_p) could be expressed as:

$$C_p = aA_{C_p} + bB_{C_p} + \frac{ab}{a+b}(A'_{C_p} + B'_{C_p}) \tag{7}$$

where A_{C_p} *and* A'_{C_p} were parameters of $\mathrm{M_mO_x}$, B_{C_p} *and* B'_{C_p} were parameters of $\mathrm{N_nO_y}$.

Here is an example about In$_2$O$_3$ with unknown value of A and A' to introduce the way in which the related parameters are calculated. The A and A' of As$_2$O$_5$ can be obtained first from Eqs. (8) and (9). Then the A and A' of In$_2$O$_3$ can be obtained from Eqs. (10) and (11) with the value obtained above. By the same way, all the A and A' of simple oxides in Tables 1–3 can be reckoned.

$$\mathrm{3FeO + As_2O_5 = Fe_3(AsO_4)_2} \tag{8}$$

$$\mathrm{Fe_2O_3 + As_2O_5 = 2FeAsO_4} \tag{9}$$

$$\mathrm{In_2O_3 + As_2O_5 = 2InAsO_4} \tag{10}$$

$$\mathrm{In_2O_3 + 3SO_3 = In_2(SO_4)_3} \tag{11}$$

Based on the reported data of simple oxide in Tables 1–3 [24–27], the parameters could be calculated with

Table 1: A_H, A'_H and ΔH_f^θ of oxides at 298.15 K

Simple oxide	A_H (kJ/mol)	A'_H (kJ/mol)	ΔH_f^θ (kJ/mol)
FeO	47.68	−94.86	−272.044
Fe_2O_3	−51.91	175.52	−824.248
Na_2O	−122.55	−115.66	−417.982
$FeSO_4$	–	–	−928.848
$Fe_2(SO_4)_3$	–	–	−2582.992
SO_3	–	–	−395.765
$Fe_3(AsO_4)_2$	–	–	−1954.974
$FeAsO_4$	–	–	−865.335
As_2O_5	–	–	−942.869
$InAsO_4$	–	–	−978.303
$In_2(SO_4)_3$	–	–	−2767.000
CuO	–	–	−156.063
In_2O_3	–	–	−925.789
Cu_2SO_4	–	–	−751.400
Cu_3AsO_4	–	–	−710.360
Cu_2O	–	–	−170.707
$CuFe_2O_4$	–	–	–
$Cu_3(AsO_4)_2$	–	–	–
$NaInO_2$	–	–	–
$CuInO_2$	–	–	–

Table 2: A_S, A'_S and S_m^θ of oxides at 298.15 K

Simple oxide	A_S (J/(mol·K))	A'_S (J/(mol·K))	(J/(mol·K))
FeO	66.106	−22.446	60.752
Fe_2O_3	68.036	69.989	87.404
Na_2O	25.756	35.944	75.040
SO_3	54.678	33.288	256.773
CuO	28.36	49.29	42.593
$Fe_3(AsO_4)_2$			339.908
$FeAsO_4$			161.54
As_2O_5			105.399
$InAsO_4$			154.850
$In_2(SO_4)_3$			272.002
In_2O_3			104.198
Cu_2SO_4			182.422
Cu_3AsO_4			255.977
Cu_2O			92.341
$NaInO_2$			
$CuInO_2$			

Table 3: A_{C_p}, A'_{C_p} and C_p of oxides at 298.15 K

Substance	A_{C_p} J/(mol·K)	A'_{C_p} J/(mol·K)	C_p J/(mol·K)
FeO	49.481	−10.704	49.942
Fe_2O_3	104.688	0.794	103.866
Na_2O	73.178	−8.774	68.892
SO_3	52.970	14.460	50.701
CuO	42.755	0	42.244
$Fe_3(AsO_4)_2$			264.642
$FeAsO_4$			117.054
As_2O_5			116.536
$InAsO_4$			119.320
$In_2(SO_4)_3$			280.002
In_2O_3			100.416
Cu_2SO_4			120.287
Cu_3AsO_4			176.361
Cu_2O			62.544
$NaInO_2$			
$CuInO_2$			

Eqs. (1)–(7), as shown in Table 4. Then, the thermodynamic data of $NaInO_2$ and $CuInO_2$ could be calculated with the Eqs. (4)–(7) as shown in Table 5.

3 Reaction condition investigation

In the $CuInO_2$ preparation process by cation exchange reaction, there were the following seven substance, $CuInO_2$, $NaInO_2$, $CuCl_{(s)}$, $CuCl_{(g)}$, In_2O_3, Cu_2O and NaCl. Based on Brinklev method, there were three independent reactions during this process as shown in Table 6. When the reactions reach equilibrium at constant temperatures (T) and standard atmospheric pressure, the standard enthalpy change, molar entropy and $\lg K - T$ equations for three independent reactions were calculated based on the standard thermodynamic data listed in Table 6. Figures 1 and 2 showed the relation of $\Delta_r G_m^\theta - T$ and $K - T$ for reactions 1–3. Based on the thermodynamic data for the related pure complex oxides, respectively. It was noted that the curve of K_3 was the relation between $\lg K_3$ and T in Figure 2.

Table 4: The parameter value of A and A'

Substance	A_H (kJ/mol)	A'_H (kJ/mol)	A_S (J/mol·K)	A'_S (J/mol·K)	A_{C_p} (J/mol·K)	A'_{C_p} (J/mol·K)
In_2O_3	5126.991	−10431.072	85.082	9.136	108.357	2.52
Cu_2O	125.065	−97.401	115.654	8.756	576.729	−1233.284
CuO	127.752	−302.519	28.36	49.29	42.755	0
Na_2O	−122.55	−115.66	25.756	35.944	73.178	−8.774

Table 5: Standard thermodynamic data of formation at 298 K

Substance	**$\Delta_f H_m^\theta$ (KJ/mol)**	**S_m^θ (J/mol·K)**	**C_p (J/mol·K)**	**$\Delta_f G_m^\theta$ (KJ/mol)**
$CuInO_2$	–554.32	104.841	34.713	–585.578
$NaInO_2$	–806.348	66.689	89.204	–826.232

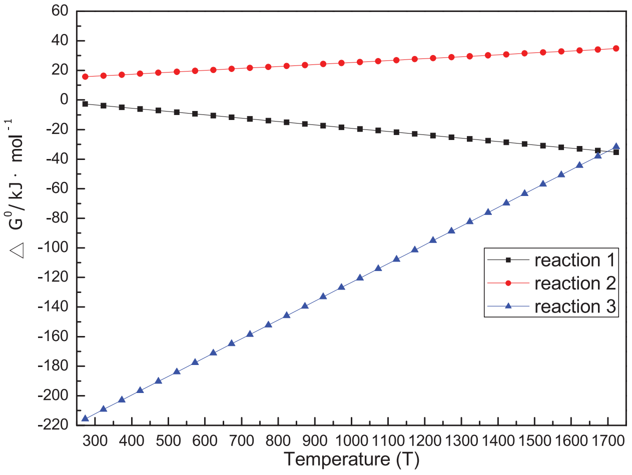

Fig. 1: The curves of $\Delta_r G_m^\theta - T$ for reactions 1–3

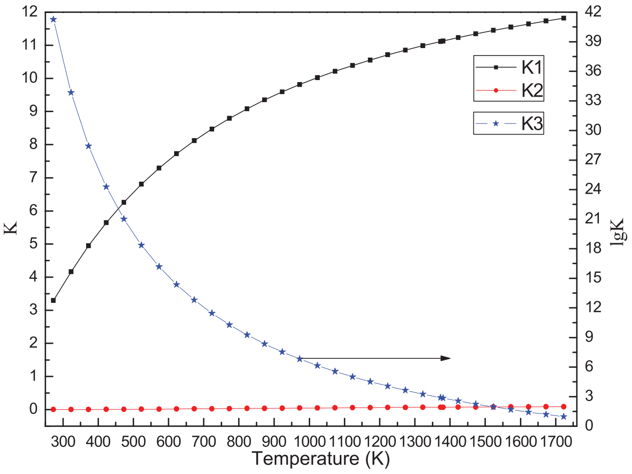

Fig. 2: The curves of $K - T$ for reactions 1–3

4 Results and discussion

4.1 The relation of Gibbs free energy and temperature

According to the Fig. 1, the $\Delta_r G_m^\theta$ for reaction 1 is smaller than zero in the range of 273 K to 1723 K, which indicate that the value of the equilibrium constant (K) is large. Under the air isolation condition, reaction 1 is solid-solid reaction in the temperature range from 273 K to 1723 K. The results indicate that reaction 1 will happen in the temperature range from 273 K to 1723 K. However, the degree of the reaction is small because of $\Delta_r G_{m,1}^\theta > -40$ kJ/mol.

In the Fig. 1, the $\Delta_r G_m^\theta$ for reaction 2 is in the range of 15.732 to 34.789 kJ/mol when the temperature increases from 273 K to 1723 K. The results indicate that change of exterior condition may possibly promote reaction 2 moves towards positive direction in the temperature range from 273 K to 1723 K because of $\Delta_r G_{m,1}^\theta < 40$ kJ/mol. However, the value of the K_2 is very small.

According to the Fig. 1, the $\Delta_r G_m^\theta$ for reaction 3 is much smaller than 0 at the temperature range from 273 K to 1723 K, which indicates that the value of the K_3 is very great. Figure 1 also indicate that the degree for reaction 3 is a very big, which indicate that the reaction is the main one in the progress. Therefore, the reaction 3 should be investigated specially, which will be addressed in detail in the following section. The $\Delta_r G_m^\theta$ for reaction 3 gradually increases with increasing temperature and the presence of CuCl in the state of gas phase from the Fig. 1, but the $\Delta_r G_{m,3}^\theta$ of reaction 3 is less than –40 kJ·mol⁻¹ when the temperature is lower than 1698 K, namely $NaInO_{2(s)}$ reacted with $CuCl_{(g)}$ and produced $CuInO_2$ thoroughly. So, the condition of reaction 3 should be controlled under the following conditions: $T < 1698$ K and with the presence of CuCl in the state of the gas phase.

4.2 The relation of equilibrium constants and temperature

Figure 2 gives the dependence of K on temperature. The value of K_1 increases slowly from 3.293 to 11.817 with tem-

Table 6: Reaction formulas, standard thermodynamic data at 298 K and lg $K - 1/T$

Eq. No.	**Reaction**	**$\Delta_r H_m^\theta$ (kJ/mol)**	**$\Delta_r S_m^\theta$ (J/mol·K)**	**Function**
1	$NaInO_{2(s)} + CuCl_{(s)} = CuInO_{2(s)} + NaCl_{(s)}$	3.447	22.541	$\lg K_1 = 1.177 - 180.027\ (1/T)$
2	$2CuInO_{2(s)} = Cu_2O_{(s)} + In_2O_{3(s)}$	12.144	–13.143	$\lg K_2 = -0.686 - 634.246\ (1/T)$
3	$NaInO_{2(s)} + CuCl_{(g)} = CuInO_{2(s)} + NaCl_{(s)}$	–250.303	–126.908	$\lg K_3 = -6.628 + 13072.604\ (1/T)$

perature increase. This indicates that K_1 was not a strong function of temperature. In other words, $CuInO_2$ may decompose which caused the yield of CIO decrease in the temperature range mentioned above. Table 6 shows that reaction 1 takes a great degree of the reaction progress when the temperature is higher than 1900 K. Nevertheless, operating problems presents at temperature higher than 1900 K including difficult design and challenge for equipment. In addition, the motives in the reaction system might become complex with temperature increase. This eventually led to difficulty in theoretical research. This is also the reason that the reaction thermodynamic condition is not proposed.

In Fig. 2, the value of K_2 is range from 9.789×10^{-4} to 8.829×10^{-2} with the temperature increase from 273 K to 1723 K. Similarly, K_2 is also a weak function of temperature. So, change of exterior condition may possibly promote reaction 2 moves toward positive direction, especially when T is smaller than 573 K. It gives the evidence that there Cu_2O, In_2O_3 and other impurities in CIO powder preparation by ion exchange reaction under the following conditions: air isolation, heated at 573 K–873 K for 6–144 h in the previous experimental [2, 9, 10, 28]. This reaction is adverse during the CIO preparation process. Reversely, increasing temperature may possibly promote reaction 2 moves toward negative direction ($Cu_2O + In_2O_3 = 2CuInO_2$, $\Delta_r H_m^\theta = -12.144$ kJ/mol and $0 > \Delta_r G_m^\theta = -16.063$ kJ/mol $>$ -40 kJ/mol [14]). This demonstrates that it is difficult to prepare CIO powder by solid reaction and/or cation exchange reaction method.

The calculated K_3 for reaction 3 decreases rapidly when the temperature increase from 273 K to 673 K, then the tendency of decrease become slow. The increased temperature can have a negative effect on the positive reaction. However, the K_3 is $1.807 \times 10^{41} - 10$ when the temperature is lower than 1698 K, namely $NaInO_{2(s)}$ reacts with $CuCl_{(g)}$ and produce $CuInO_2$ thoroughly. So, the condition of reaction 3 should be controlled under the following condition: $T < 1698$ K and with the presence of CuCl in the state of gas phase. The interesting results are aspiring in comparison with the difficult process for preparing CIO [2, 9, 10, 27]. However, it should be noted that the decomposition of $CuInO_2$ can be accelerated with temperature decrease (reaction 2), especially when $T < 573$ K. So the temperature should be controlled at an appropriate value, which is suggested that the temperature is controlled at 573–1698 K. Under the temperature, the vapor pressure of $CuCl_{(g)}$ is $6.6 \times 10^{-12} - 8623.83$ Pa correspondingly base on Fig. 2. The results indicate that the process controlled under vacuum condition is better.

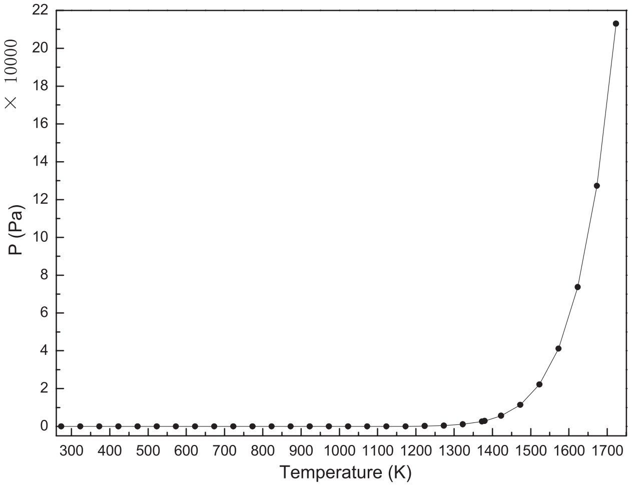

Fig. 3: The curves of lg P – lg $1/T$ for Eq. (8)

From the reaction 3 in Table 6 and analysis mentioned above, it is noted that K_3 ($K_3 = P^\theta / P_{CuCl}$) is a function of the temperature and vapor pressure of $CuCl_{(g)}$. So, the relationship of $P_{CuCl} - T$ for Eq. (12) ($CuCl_{(s)} = CuCl_{(g)}$) [27] is plotted, as shows in Figure 3.

$$\lg P_{CuCl} = 12.811 - 12892.472\,(1/T) \qquad (12)$$

Fig. 3 shows that the P_{CuCl} increases slightly when temperature $<$ 973 K, then, the P_{CuCl} is booming with T (when temperature $>$ 973 K). High temperature have a positive effect on the vaporization of $CuCl_{(g)}$. So, to assure a very high value vapor pressure of $CuCl_{(g)}$, the reaction temperature should be controlled at $\geq$ 973 K before the reaction 3 reach equilibrium. And the vapor pressure of $CuCl_{(g)}$ is $\geq$ 0.364 Pa when the T $\geq$ 973 K correspondingly base on Fig. 3. The results indicate that the process should be controlled under vacuum condition. Under these conditions, reaction 3 can occur almost completely, the decomposition of $CuInO_2$ can be restricted, and the theoretical yield of $CuInO_2$ could be near 100% if the dynamic condition permits.

From the analysis mentioned above, it can be anticipated that the processes for preparing CIO, can be divided into two conditions. In the first condition, the reaction 3 is the main part when the temperature at 973–1698 K and the vacuum in the reactor. In the second condition, the reaction 1 is the main reaction when the temperature higher than 1698 K. But, operating problems present at temperature higher than 1698 K involving difficult design and challenges for the equipment, and reaction system would become complex. And the cost must be considered. Therefore, the optimum condition of CIO preparation process should be theoretically controlled under the following conditions: the temperature at 973–1698 K, the vacuum in the reactor. So, the future work including CIO powder preparation by the cation exchange method in a vacuum reactor and kinetic investigation will be carried on based on above investigation.

5 Conclusions

The standard entropy, heat capacity at constant pressure, standard enthalpy and standard Gibbs's free energy for formation of $NaInO_2$ and $CuInO_2$ have been estimated by application of the two-parameter model. The methods of graph, qualitative and quantitative were used to analyze three independent chemical reactions for preparing $CuInO_2$ by the cation reaction method. It was certified by Thermodynamic Investigation that CIO could be prepared by cation exchange with $NaInO_{2(s)}$ and CuCl.

The CIO preparation process could be divided into two conditions. In the first condition, $NaInO_{2(s)}$ was preferred to react with $CuCl_{(g)}$ for producing $CuInO_{2(s)}$ and $NaCl_{(s)}$ thoroughly when the temperature was at 973–1698 K. In the second condition, $NaInO_{2(s)}$ was preferred to react with $CuCl_{(s)}$ for producing $CuInO_{2(s)}$ and $NaCl_{(s)}$ when reaction temperature was higher than 1698 K. It was suggested that the CIO preparing process by ion exchange reaction controlled under the following conditions: temperature at 973–1698 K and the vacuum in the reactor. Under these conditions, the theoretical yield of CIO was near 100% by thermodynamic study.

This paper is supported by the National Natural Science Foundation of China (50574045). The author wishes to thank the Government of China for financial assistance.

Received: July 17, 2013. Accepted: October 6, 2013.

References

[1] Chadwick A V, Blacklocks A N, Rougier A, Yaicle C. A Structural Study of Delafossite-type $CuInO_2$ Thin Films. Journal of Physics: Conference Series, 2010, 249: 012.

[2] Li J, Sleight A W, Jones C Y, Toby B H. Trends in negative thermal expansion behavior for AMO_2 (A = Cu or Ag; M = Al, Sc, In, or La) compounds with the delafossite structure. Journal of Solid State Chemistry, 2005, 178(1): 285.

[3] Prabhu E, Gnanasekar K I, Jayaraman V, Gnanasekaran T. Preparation, characterization and NO_x sensing characteristics of sensor grade $CuInO_2$ thin films. Mater. Sci. Forum, 2012, 710: 727.

[4] Hahn H, Loren C D. Ternary chalcogenides. VII. Synthesis of ternary oxides of aluminum, gallium, and indium with univalent copper and silver. Zeitschrift für Anorganische Chemie, 1955, 279: 281.

[5] Gessner W, Chem I A, Wiss D A, Fed R G. Ternary oxide $M^IM^{III}O_2$ with M^I = silver, copper, thallium and M^{III} = gallium, indium, thallium. Silikattechnik, 1970, 21(2): 45.

[6] Liu L, Bai K, Gong H, Wu P. First-Principles Study of Bipolar Dopability in the $CuInO_2$ Transparent Semiconductor. Chem. Mater., 2005, 17(22): 5529.

[7] Liu L, Bai K, Gong H, Wu P. First-principles study of Sn and Ca doping in $CuInO_2$. Physical Review B, 2005, 72(12): 125204/125201.

[8] Kawazoe H, Yasukawa M, Hyodo H, Kurita M, Yanagi H, Hosono H. P-type electrical conduction in transparent thin films of $CuAlO_2$. Letters to Nature, 1997, 389(6654): 939.

[9] Shimode M, Hayashi Y, Sasaki M, Mukaida K. Ion exchange synthesis and structure of new delafossite-type $CuInO_2$. Materials Transactions, 2000, 41(9): 1111.

[10] Yanagi H, Ueda K, Ohta H, Hiirano M, Hosono H. Bipolar electrical conductive transparent oxide, $CuInO_2$. Mat. Res. Soc. Symp. Proc., 2001, 666: F3.14/11.

[11] Yaicle C, Blacklocks A, Chadwick A V, Perrière J, Rougier A. Relationship between structure and deposition conditions for $CuInO_2$ thin films. Applied Surface Science, 2007, 254(4): 1343.

[12] Yang B, He Y, Polity A, Meyer B K. Structural, optical and electrical properties of transparent conducting $CuInO_2$ thin films prepared by RF sputtering. Mater. Res. Soc. Symp. Proc., 2005, 865: F14.17.11.

[13] Yanagi H, Hase T, Ibuki S, Ueda K, Hosono H. Bipolarity in electrical conduction of transparent oxide semiconductor $CuInO_2$ with delafossite structure. Applied Physics Letters, 2001, 78(11): 1583.

[14] Yao Y, Xie G, Song N, Yu X H, Li R X. Thermodynamic study on $CuInO_2$ preparation by solid reaction method. 2011 International Conference on Chemical, Material and Metallurgical Engineering. Beihai, China. 2012.

[15] Ye F X, Cai M, Fan P, Zhang D P, Liu L J. The effect of annealing on the electrical and optical properties of Cu-In-O thin films. Applications of Engineering Materials, Pts 1–4, 2011, 287–290: 2125.

[16] Shimode M. Synthesis of the Delafossite-Type $CulnO_2$. Journal of Solid State Chemistry, 2000, 151(1): 16.

[17] Qian H L, Liu C, Ji Y H, Yao W J, Feng X, Lu X H. Simple estimation method for thermodynamic data of complex oxysalt minerals. CIESC Journal, 2010, 61(3): 544.

[18] Karpov I K, Kashik S A. Computer calculation of standard isobaric isothermal potentials of silicates by multiple regression from a crystallochemical classification. Geochem. Internat., 1968, 5(4): 706.

[19] Nriagu J O. Thermochemical approximation for clay minerals. Amer. Mineral, 1975, 60: 834.

[20] Chen C H. A method of estimation of standard free energy of formation of silicate minerals at 298.15 K. Am. J. Sci., 1975, 275: 801.

[21] Tardy Y, Garrels R M. A method of estimating the Gibbs energies of formation of layer silicates. Geochim. Cosmochim. Acta, 1974, 38: 1101.

[22] Wen Y K, Shao J, Chen D W. Calculation of standard free energies of formation of oxyacid salt minerals. Scientia Geologica Sinica, 1978 (4).

[23] Li X B, Li Y F, Liu X M, Zhai Y C. A simple method of estimation of Gibbs free energy and enthalpy of complicate silicates. Journal of The Chinese Ceramic Society, 2001, 29(3): 232.

[24] Guo P M, Zhao P. Estimation of Standard Enthalpies of Formation of Complex Oxide Using Two-Parameter Model. Journal of Iron and Steel Research, 2007, 19(5): 25.

[25] Guo P M, Zhao P. Estimation of Heat Capacity of Complex Oxide Using Two-Parameter Model. Journal of Iron and Steel Research, 2006, 18(9): 17.

[26] Guo P M, Zhao P. Estimation of Standard Entropy of Complex Oxide Using Two-Parameter Model. Journal of Iron and Steel Research, 2008, 20(8): 5.

[27] Brain I. Thermochemical Data of Pure Substances. Science Press. 2003.

[28] Park S, Keszler D A. Synthesis of 3R-$CuMO_{2+\delta}$ (M = Ga, Sc, In). Journal of Solid State Chemistry, 2003, 173(2): 355.