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Thermodynamic modeling of the chromium-yttrium-oxygen system

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Abstract

Based on the CALPHAD (CALculation of PHase Diagrams) method, a complete thermodynamic description of the Cr-Y-O ternary system is obtained in the present work. The thermodynamic properties of YCrO₃ phase are critically assessed and the experimentally determined Cr₂O₃-Y₂O₃ quasi-binary section is reproduced. The current optimization results agree well with most of the experimental data in literature. The thermodynamic description of Cr-Y-O is then used to calculate the phase relations under different temperatures or oxygen partial pressures. The stability of the YCrO₃ phase is discussed based on the calculation results.

Keywords: Phase diagram; Thermodynamic modeling; Cr₂O₃-Y₂O₃; YCrO₃; Chromium-yttrium-oxygen

1. Introduction

Metal oxides are widely used in electrical, optical, electrochemical, mechanical and magnetic devices owing to the variety of physical, chemical, and mechanical properties [1-5]. Specifically, orthochromites with a formula of RCrO_3 ($\text{R}=\text{Y}$ and rare earth) is an interesting family of compounds showing intriguing physical and chemical properties depending on the rare earth ion, complex magnetic interactions, isotropic properties and magnetic ordering [6-8]. In recent years, this group of compounds have received wider attention owing to the possibility of combining ferroelectric, ferromagnetic and possible multiferroic properties for applications in magnetoelectric coupling devices [6,9,10]. In addition, their high chemical stability attracts great interest in applications such as high temperature electrodes and thermoelectric materials [11-14].

For the orthochromite YCrO_3 phase in the Cr-Y-O system, there are already several reports characterizing its electronic conductivity, sintering behavior, crystal structure etc. [15-18]. As a high temperature electrode and thermoelectric material, it is also important to investigate the thermodynamic properties of YCrO_3 such as thermal stability, decomposition temperature and oxygen partial pressure, and so on, in order to further understand its temperature-dependent behavior. However, to the best of our knowledge, there is no systematic thermodynamic description of the YCrO_3 phase or of the Cr-Y-O system, which hampers the prediction of phase equilibria with varying conditions.

The current work is thus devoted to obtaining a comprehensive thermodynamic description of the Cr-Y-O ternary system, and provides predictions on the thermal stability of orthochromite YCrO_3 . The three binary sub-systems in the Cr-Y-O ternary system have been modeled previously [19-32]. Thus, a critical review on these assessments will firstly be done to select suitable thermodynamic modeling of the binary sub-systems for construction of the ternary thermodynamic database in this work. The experimentally determined thermodynamic properties of orthochromite YCrO_3 and phase diagram information of the Cr-Y-O ternary system are critically reviewed. Then, the thermodynamic model of each phase in the system will be determined and subjected to CALPHAD (CALculation of PHase Diagrams) method for conducting the thermodynamic modeling. Finally, the key phase diagrams of the quasi-binary Cr_2O_3 - Y_2O_3 will be computed based on the obtained thermodynamic description and compared with the experimental results. Phase relations of the Cr-Y-O ternary system, including the quasi-binary phase diagram, the isothermal PO_2 -composition phase diagrams and the isothermal sections, will be calculated. The thermal stability and decomposition conditions of YCrO_3 compound will be predicted based on the calculated phase diagrams.

2. Literature review

2.1 Thermodynamic descriptions of the binary sub-systems

The critical literature review on thermodynamic modeling of the Y-O, Cr-O and Cr-Y binary systems is firstly performed.

The Y-O binary system has been thermodynamically assessed in several studies [19-24]. Apart from the work of Chen et al. [23] and Djurovic et al. [24], all the other evaluations have used essentially the same sublattice models to describe the solid solution phases, as those originally adopted by Ran et al. [19], while they differ somehow with regard to the experimental data used. In their work, the solubility of oxygen in α - and β -yttrium polymorphs was described using an interstitial solution model. The Wager-Schottky model was used to describe the small deviation from stoichiometric α -yttria, which was also extended to the high temperature polymorph, i.e. β -yttria. Chen et al. [23] and Djurovic et al. [24] reassessed the Y-O system and changed the sublattice models of the solid solution phases, in order to account for thermochemical properties, crystal structure, defect chemistry and phase diagram of the Y-O system simultaneously. They used mainly the phase diagram data from Tucker et al. [33], with additional data at low temperature from Carlson et al. [34] and data on the nonstoichiometry of α -Y₂O₃ from Ackermann et al. [35] for the optimization. The difference between the work of Chen et al. [23] and Djurovic et al. [24] is the model for β -yttrium i.e. the bcc phase. Djurovic et al. [24] modeled the bcc phase as (Y)₁(Va, O)₁, while Chen et al. [23] modeled the bcc phase as (Y)₁(O, Va)_{1.5}. In this work, the model (Y)₁(O, Va)₃ was used for the bcc phase to keep the thermodynamic description physically reasonable and to be compatible with other databases based on traditional description of bcc. A slight adjustment of the corresponding thermodynamic parameters was performed based on the results of Chen et al. [23] and will be presented in Section 4 of this paper.

The phase diagram for the Cr-O system has been established by Banik et al. [25] based on a sub-regular solution model, Degterov and Pelton [26] by using a modified quasi-chemical model for the molten slag database, Kowalski and Spencer [27] by using an associated solution model for liquid phase and Taylor and Dinsdale [28] and Povoden et al. [29] by the two-sublattice ionic model for liquid phase and the compound energy model for Cr₂O₃ phase. The last two works [28,29] proposed a phase diagram in good agreement with the experimental data in the literature. However, Taylor and Dinsdale's [28] optimization on one of the charged endpoints in their compound energy model for eskolaite (Cr₂O₃) and the use of six interaction parameters to describe the liquid phase may lead to problems when extrapolating to higher-order systems, especially as the miscibility gap does not disappear with increasing temperature. The use of six parameters for the description of another oxide phase, Cr₃O₄ is somewhat incommensurate with the very limited experimental information of this phase. Considering the model consistency, the thermodynamic evaluation for the Cr-O binary system by Povoden et al. [29] was chosen in the present work.

The Cr-Y phase diagram was experimentally investigated by several studies [36-40]. Venkatraman et al. [30] assessed the Cr-Y phase diagram based on a model developed by Miedema and Chatel [41], which was used to calculate the enthalpy of formation in the Cr-Rare Earth metal systems to predict the type of phase diagram. Okamoto [31] calculated the Cr-Y phase diagram by using a sub-regular solution model considering the enthalpies of solution at infinite dilution given by Terekhov et al. [42], but the calculation result did not address the reaction type involving liquid, β -Y and α -Y on the Y-rich side (β -Y $\rightarrow$ Liquid + α -Y). Y has two polymorphs, α -Y is hcp while β -Y is bcc. The maximum solubility of Cr in Y is very small, less than 1 at%, according to Venkatraman et al. [30] as well as that of Y in Cr. Based on the former experimental data and assessments, Chan et al. [32]

reassessed this binary system by using the sublattice model. The calculated Cr-Y phase diagram by Chan et al. [32] was in good agreement with the experimental data. So in the present work, the thermodynamic description of the Cr-Y system by Chan et al. [32] is directly accepted without any change.

2.2 Thermodynamic and phase diagram information of the ternary system

There is only one ternary solid oxide phase existing in the Cr-Y-O ternary system, i.e. the YCrO_3 compound. In the present work, we have critically evaluated the available thermodynamic properties of the YCrO_3 phase and the phase diagram data of the Cr-Y-O ternary system. Table 1 gives an overview of the experimental data reported in the literature.

Table 1. Summary of the experimental data from literature.

Reference	Type of data	Experimental methods	Temperature, K	Remark
I: Thermodynamic data				
Stoppe et al. [43]	Heat capacity of YCrO_3	Calorimetry	5-310	5-273 K, not used 273-310 K, used
	Entropy at 298.15 K for YCrO_3	Calorimetry	298.15	Used
Satoh et al. [44]	Heat capacity of YCrO_3	Calorimetry DSC Extrapolated	77-280 150-489 298-1500	77-273 K, not used 273-489 K, used Used
Su et al. [6]	Heat capacity of YCrO_3	Calorimetry	2-300	Not used
Suponitskii [46]	Heat content (H_T-H_{298})	Calorimetry	865-1350	Used
	Enthalpy of formation for YCrO_3	EMF	298.15	Not used
Satoh et al. [44]	Heat content (H_T-H_{298})	Extrapolated	298-1500	Used
	Entropy at 298.15 K for YCrO_3	Calorimetry	298.15	Used
Dzhaoshvili et al. [47]	Heat content (H_T-H_{298})	Calorimetry	387-1524	Used
Kawamura et al. [45]	Electromotive force	EMF	1385-1470	Used
II: Phase diagram data				
Ranganathan et al. [50]	Phase diagram in air	XRD and EMF	1473, 1573, 1873	Used
Mikhailov et al. [51]	Phase diagram in air	Calculated	Up to 2773	Not used

The thermodynamic properties of the YCrO_3 compound were well studied in the literature [6,43-47]. The heat capacity of YCrO_3 below room temperature was measured by Stoppe et al. [43] using a vacuum adiabatic calorimeter from 5 K to 310 K. The entropy of YCrO_3 at 298.15 K was also reported in their work. Satoh et al. [44] measured the heat capacity of YCrO_3 by ACC (AC Calorimetric) in the range of 77-280 K and by DSC (Differential Scanning Calorimeter) in the range of 150-489 K and also the entropy at 298.15 K. By performing a multiple regression analysis to unify the heat content data (enthalpy increment, H_T-H_{298}) measured by Dzhaoshvili et al. [47] using drop calorimetry, Satoh et al. [44] then derived the thermodynamic functions of YCrO_3 in the temperature range of 298.15 K to 1500 K. Su et al. [6] measured the specific heat capacity C_p of YCrO_3 from 2 K to 300 K upon cooling by a pulse relaxation method using a commercial calorimeter in PPMS (Physical Property Measurement System) equipment. Most of these experimentally measured data of heat capacity exhibit good consistency with each other. The high

temperature enthalpy increments ($H_T - H_{298}$) of $YCrO_3$ were measured by Suponitskii [46] on an HT-1500 (Setaram) high temperature heat conducting calorimeter in the temperature range of 865-1350 K under argon atmosphere (99.98%; <0.0007 wt.% O_2). The standard enthalpy of formation for $YCrO_3$ at 298.15 K was also reported in Suponitskii's [46] work based on the Gibbs energy of formation of $YCrO_3$ ($0.5Y_2O_3 + 0.5Cr_2O_3 = YCrO_3$) measured by Wang et al. [48] and Kovba et al. [49] using the EMF (ElectroMotive Force) method. Kawamura et al. [45] measured EMF for the decomposition reaction of $YCrO_3 = 0.5Y_2O_3 + Cr + 0.75O_2$ in the temperature range of 1385-1470 K. Based on the obtained emf data and the standard Gibbs energy of formation of Cr_2O_3 and Y_2O_3 , the Gibbs energies of formation for $YCrO_3$ based on the reactions $0.5Y_2O_3 + Cr + 0.75O_2 = YCrO_3$ and $Y + Cr + 1.5O_2 = YCrO_3$ were calculated in their work in the temperature range of 1385-1470 K. The Gibbs energy of formation of $YCrO_3$ was also reported in the work of Wang et al. [48] (1182-1386 K), Kovba et al. [49] (1200 K and 1400 K), Ranganathan [50] (1473 K and 1573 K) by using the EMF method. The Gibbs energies of formation for $YCrO_3$ from oxides or from elements are listed in Table 4. In our assessments, we adopted the directly measured EMF data from literature, not the derived Gibbs energy of formation data. Table 4 is hence for comparison only.

The phase equilibria in the Cr-Y-O system has been experimentally investigated by Ranganathan [50], including the phase diagram information on the invariant reactions and the melting point of $YCrO_3$. In the work of Ranganathan [50], the chromite was prepared from a stoichiometric mixture of the yttrium oxide and chromium oxide. Formation of the $YCrO_3$ compound was confirmed by X-ray analysis and the Gibbs energy of formation for $YCrO_3$ was obtained from the EMF method. Based on the experimental data in Ranganathan [50] and the sub-regular ionic solution theory, Mikhailov et al. [51] performed a simple calculation of the quasi-binary phase diagram of the Cr_2O_3 - Y_2O_3 oxide system. The experimentally determined phase diagram information by Ranganathan [50] has been used in the present work for optimization and the calculation results from Mikhailov et al. [51] are listed for comparison. There is no report about the solubility between Cr_2O_3 and Y_2O_3 in the literature. Thus, in the present work, we considered no mutual solubility between Cr_2O_3 and Y_2O_3 .

3. Thermodynamic modeling

In the present work, the thermodynamic database of the Cr-Y-O system is constructed starting with assembling the binary systems assessed in literature, i.e. Y-O by Chen et al. [23], Cr-O by Povoden et al. [29], and Cr-Y by Chan et al. [32]. The lattice stabilities of pure elements were adopted from Dinsdale [52]. The magnetic contribution to the Gibbs energy is given by the "Hillert-Jarl-Inden" model proposed by Inden [53] and further revised by Hillert and Jarl [54]. The compound energy formalism [55], which is widely used in CALPHAD assessments, was used to model all the phases in the Cr-Y-O system.

3.1 Ionic liquid phase

The liquid phase was modeled as $(Cr^{2+}, Cr^{3+}, Y^{3+})_p(O^{2-}, Va^q)_q$ using the two-sublattice ionic model [56,57], where

$$p = 2y_{O^{2-}} + qy_{Va^{q-}} \quad (1)$$

$$q = 2y_{Cr^{2+}} + 3y_{Cr^{3+}} + 3y_{Y^{3+}} \quad (2)$$

The Gibbs energy of liquid phase is expressed as:

$$G_m^L = q \sum_i y_i y_{Va} {}^oG_{i:Va}^L + \sum_i y_i y_{O^{2-}} {}^oG_{i:O^{2-}}^L + pRT \sum_i y_i \ln y_i + qRT \sum_j y_j \ln y_j + {}^E G_m^L \quad (3)$$

where i represents the constituents in the first sublattice, and j represents the constituents in the second lattice. The excess Gibbs energy ${}^E G_m^L$ is formulated as follow:

$${}^E G_m^L = \sum_{i_m} \sum_{i_n \neq i_m} y_{i_m} y_{i_n} (y_{O^{2-}} L_{i_m, i_n: O^{2-}}^L + q y_{Va} {}^2 L_{i_m, i_n: Va}^L) + \sum_{i_m} y_{i_m} y_{O^{2-}} y_{Va} L_{i_m: O^{2-}, Va}^L \quad (4)$$

where m and n represents the constituents in the first sublattice. In the above expressions, colons were used to separate species on different sublattices and commas to separate species on the same sublattice. The Gibbs energy expressions for the 6 end-members were taken from the binary systems: ${}^oG_{Cr^{2+}:O^{2-}}^L$, ${}^oG_{Cr^{3+}:O^{2-}}^L$, ${}^oG_{Cr^{2+}:Va}^L$, ${}^oG_{Cr^{3+}:Va}^L$ from Cr-O system [29] and ${}^oG_{Y^{3+}:O^{2-}}^L$, ${}^oG_{Y^{3+}:Va}^L$ from Y-O system [23]. Interaction parameters $L_{Cr^{3+}, Y^{3+}:Va}^L$ were taken from the Cr-Y system [32], $L_{Cr^{3+}:O^{2-}, Va}^L$ and $L_{Cr^{2+}:O^{2-}, Va}^L$ were taken from the Cr-O system [29], and $L_{Cr^{3+}, Y^{3+}:O^{2-}}^L$ and $L_{Cr^{2+}, Y^{3+}:O^{2-}}^L$ were evaluated in the present work.

3.2 YCrO₃ ternary oxide

In the present work, the YCrO₃ phase was treated as a stoichiometric compound and modeled as (Y³⁺)₁(Cr³⁺)₁(O²⁻)₃. The molar Gibbs energy of YCrO₃ is described as:

$$GYCRO3 = {}^oG_{Y^{3+}, Cr^{3+}: O^{2-}}^{YCrO_3} - H_Y^{SER} - H_{Cr}^{SER} - 3H_O^{SER} = A + BT + CT \ln T + DT^2 + ET^{-1} \quad (5)$$

3.3 Binary oxides

There are 4 binary oxides in the Cr-Y-O system, i.e. Cr₂O₃, Cr₃O₄, α-Y₂O₃ and β-Y₂O₃ phases. Since there is no solubility between Cr₂O₃ and Y₂O₃, these two phases were all modeled the same as the corresponding binary sub-systems. The Cr₂O₃ phase was modeled by Povoden et al. [29] using a three-sublattice model as (Cr²⁺, Cr³⁺)₂(Cr³⁺, Va)₁(O²⁻)₃, and the Cr₃O₄ phase was treated as a stoichiometric compound as (Cr²⁺)₁(Cr³⁺)₂(O²⁻)₄. These descriptions were adopted from Povoden et al. [29] without any change in the present work. The α-Y₂O₃ and β-Y₂O₃ phase were modeled by Chen et al. [23] in the Y-Zr-O system considering the occupation of Zr in the sublattices, which is eliminated in the current work. The α-Y₂O₃ phase was then modeled with a three-sublattice model as (Y, Y³⁺)₂(O²⁻, Va)₃(O²⁻, Va)₁, while the β-Y₂O₃ phase was modeled with a two-sublattice model as (Y, Y³⁺)₁(O²⁻, Va)₂ as reported by Chen et al. [23].

3.4 Solid solution phases

Since there are no experimental data on the ternary solid solution phases in the Cr-Y-O system, the descriptions for BCC_A2 and HCP_A3 were taken from the subsystems [23,29,32] with a slight modification on the BCC_A2 parameters in the Y-O system. The models for BCC_A2 and HCP_A3 phase are $(\text{Cr}, \text{Y})_1(\text{O}, \text{Va})_3$ and $(\text{Cr}, \text{Y})_1(\text{O}, \text{Va})_{0.5}$, respectively.

3.5 Optimization procedure

The optimization of the thermodynamic parameters was performed using the PARROT module of the Thermo-Calc software [58]. In principle, PARROT can take into account all sorts of thermodynamic and phase diagram data simultaneously. The program minimizes the sum of squared errors. As the usage of all the experimental data in a simultaneous least square calculation often leads to divergence, one should selectively adjust the weight of each experimental data point and exclude data that were inconsistent with most of the data points during the optimization procedure. In the present work, we first adjust the parameters of the bcc phase in the Y-O system using the same set of experimental data as used by Chen et al. [23]. Then, the Gibbs energy functions of the YCrO_3 phase and liquid phase in the Cr-Y-O system are determined. During optimization, the parameters C, D, E in Eq. (5) were first optimized by fitting to the heat capacity data. The parameters A and B in Eq. (5) were then optimized using standard entropy, heat contents, melting point and emf data. Finally, the ternary interaction parameters of the liquid phase were optimized to achieve a good agreement with the reported phase diagram data in literature.

4. Results and discussion

A complete thermodynamic description of the Cr-Y-O ternary system is given in Table 2. The calculated thermodynamic properties and phase diagrams are presented in Figs. 1-8 and Table 3-5.

Table 2. Thermodynamic description of the Cr–Y–O system.

Element	Element reference	Mass	$H_{298}-H_0$	S_{298}
O	$\frac{1}{2}$ mol O_2	15.999	4341.0	102.52
Y	Y-HCP_A3	88.906	5966.4	44.434
Cr	Cr-BCC_A2	51.996	4050.0	23.543

BCC_A2

$(\text{Cr}, \text{Y})_1(\text{O}, \text{Va})_3$

$$^{\circ}G_{\text{Cr:O}} - H_{\text{Cr}}^{\text{SER}} - 1.5H_{\text{O}}^{\text{SER}} = \text{GHSECR} + 3\text{GHSEROO} + 243 T \text{ [29]}$$

$$^{\circ}G_{\text{Y:O}} - H_{\text{Y}}^{\text{SER}} - 1.5H_{\text{O}}^{\text{SER}} = \text{GYYBCC} + 3\text{GHSEROO} - 800000 + 360 T \text{ [This work]}$$

$$^{\circ}G_{\text{Cr:Va}} - H_{\text{Cr}}^{\text{SER}} = \text{GHSECR} \text{ [29]}$$

$$^{\circ}G_{\text{Y:Va}} - H_{\text{Y}}^{\text{SER}} = \text{GYYBCC} \text{ [23]}$$

$$^0L_{\text{Cr:O,Va}} = -709542 \text{ [29]}$$

$$^0L_{\text{Y:O,Va}} = -1681600 - 103.08 T \text{ [This work]}$$

$$^1L_{\text{Y:O,Va}} = -697000 \text{ [This work]}$$

$$^0L_{\text{Cr,Y:Va}} = 69000 \text{ [32]}$$

$$^1L_{\text{Cr,Y:Va}} = -14000 \text{ [32]}$$

$$^{\circ}T_{\text{Cr:Va}} = -311.5 \text{ [29]}$$

$$^{\circ}\beta_{\text{Cr:Va}} = -0.008 \text{ [29]}$$

Cr₂O₃

$${}^\circ G_{\text{Cr}^{2+}:\text{Cr}^{3+}:\text{O}^{2-}} - 3H_{\text{Cr}}^{\text{SER}} - 3H_{\text{O}}^{\text{SER}} = \text{GCROO} + 1/3 \text{GHSERCR} - 5.2923 \text{ T} [29]$$

$${}^\circ T_{\text{cCr}^{2+}:\text{Cr}^{3+}:\text{O}^{2-}} = 308.6 [29]$$

$${}^\circ \beta_{\text{Cr}^{2+}:\text{Cr}^{3+}:\text{O}^{2-}} = 3.0 [29]$$

$${}^\circ G_{\text{Cr}^{3+}:\text{Cr}^{3+}:\text{O}^{2-}} - 3H_{\text{Cr}}^{\text{SER}} - 3H_{\text{O}}^{\text{SER}} = \text{GCR2O3} + \text{GHSERCR} [29]$$

$${}^\circ T_{\text{cCr}^{3+}:\text{Cr}^{3+}:\text{O}^{2-}} = 308.6 [29]$$

$${}^\circ \beta_{\text{Cr}^{3+}:\text{Cr}^{3+}:\text{O}^{2-}} = 3.0 [29]$$

$${}^\circ G_{\text{Cr}^{2+}:\text{Va}:\text{O}^{2-}} - 2H_{\text{Cr}}^{\text{SER}} - 3H_{\text{O}}^{\text{SER}} = \text{GCROO} - 2/3 \text{GHSERCR} - 5.2913 \text{ T} [29]$$

$${}^\circ T_{\text{cCr}^{2+}:\text{Va}:\text{O}^{2-}} = 308.6 [29]$$

$${}^\circ \beta_{\text{Cr}^{2+}:\text{Va}:\text{O}^{2-}} = 3.0 [29]$$

$${}^\circ G_{\text{Cr}^{3+}:\text{Va}:\text{O}^{2-}} - 2H_{\text{Cr}}^{\text{SER}} - 3H_{\text{O}}^{\text{SER}} = \text{GCR2O3} [29]$$

$${}^\circ T_{\text{cCr}^{3+}:\text{Va}:\text{O}^{2-}} = 308.6 [29]$$

$${}^\circ \beta_{\text{Cr}^{3+}:\text{Va}:\text{O}^{2-}} = 3.0 [29]$$

Cr₃O₄

$${}^\circ G_{\text{Cr}^{2+}:\text{Cr}^{3+}:\text{O}^{2-}} - 3H_{\text{Cr}}^{\text{SER}} - 4H_{\text{O}}^{\text{SER}} = \text{GCR3O4} [29]$$

HCP_A3

$${}^\circ G_{\text{Cr}:\text{O}} - H_{\text{Cr}}^{\text{SER}} - 0.5H_{\text{O}}^{\text{SER}} = \text{GHSERCR} + 0.5\text{GHSEROO} + 4438 [29]$$

$${}^\circ G_{\text{Y}:\text{O}} - H_{\text{Y}}^{\text{SER}} - 0.5H_{\text{O}}^{\text{SER}} = \text{GHSEYYY} + 0.5\text{GHSEROO} - 303600 + 37.5 \text{ T} [23]$$

$${}^\circ G_{\text{Cr}:\text{Va}} - H_{\text{Cr}}^{\text{SER}} = \text{GHSERCR} + 4438 [29]$$

$${}^\circ G_{\text{Y}:\text{Va}} - H_{\text{Y}}^{\text{SER}} = \text{GHSEYYY} [23]$$

$${}^0 L_{\text{Y}:\text{O}, \text{Va}} = 3500 [23]$$

$${}^0 L_{\text{Cr}, \text{Y}:\text{Va}} = 63000 [32]$$

$${}^\circ T_{\text{cCr}:\text{Va}} = -1109 [29]$$

$${}^\circ \beta_{\text{Cr}:\text{Va}} = -2.46 [29]$$

Y₂O₃_C (α -Y₂O₃)

$${}^\circ G_{\text{Y}:\text{O}^{2-}:\text{O}^{2-}} - 2H_{\text{Y}}^{\text{SER}} - 4H_{\text{O}}^{\text{SER}} = 2\text{GHSEYYY} + 4\text{GHSEROO} + 345600 + 15.87691 \text{ T} [23]$$

$${}^\circ G_{\text{Y}^{3+}:\text{O}^{2-}:\text{O}^{2-}} - 2H_{\text{Y}}^{\text{SER}} - 4H_{\text{O}}^{\text{SER}} = 2\text{GCCYO15} + \text{GHSEROO} + 100000 + 15.87691 \text{ T} [23]$$

$${}^\circ G_{\text{Y}:\text{Va}:\text{O}^{2-}} - 2H_{\text{Y}}^{\text{SER}} - H_{\text{O}}^{\text{SER}} = 2\text{GHSEYYY} + \text{GHSEROO} + 345600 + 15.87691 \text{ T} [23]$$

$${}^\circ G_{\text{Y}^{3+}:\text{Va}:\text{O}^{2-}} - 2H_{\text{Y}}^{\text{SER}} - H_{\text{O}}^{\text{SER}} = 2\text{GCCYO15} - 2\text{GHSEROO} + 100000 + 15.87691 \text{ T} [23]$$

$${}^\circ G_{\text{Y}:\text{O}^{2-}:\text{Va}} - 2H_{\text{Y}}^{\text{SER}} - 3H_{\text{O}}^{\text{SER}} = 2\text{GHSEYYY} + 3\text{GHSEROO} + 245600 [23]$$

$${}^\circ G_{\text{Y}^{3+}:\text{O}^{2-}:\text{Va}} - 2H_{\text{Y}}^{\text{SER}} - 3H_{\text{O}}^{\text{SER}} = 2\text{GCCYO15} [23]$$

$${}^\circ G_{\text{Y}:\text{Va}:\text{Va}} - 2H_{\text{Y}}^{\text{SER}} = 2\text{GHSEYYY} + 245600 [23]$$

$${}^\circ G_{\text{Y}^{3+}:\text{Va}:\text{Va}} - 2H_{\text{Y}}^{\text{SER}} = 2\text{GCCYO15} - 3\text{GHSEROO} [23]$$

Y₂O₃_H (β -Y₂O₃)

$${}^\circ G_{\text{Y}:\text{O}^{2-}} - H_{\text{Y}}^{\text{SER}} - 2H_{\text{O}}^{\text{SER}} = \text{GHSEYYY} + 2\text{GHSEROO} + 122800 [23]$$

$${}^\circ G_{\text{Y}^{3+}:\text{O}^{2-}} - H_{\text{Y}}^{\text{SER}} - 2H_{\text{O}}^{\text{SER}} = \text{GHHYO15} + 0.5\text{GHSEROO} + 9.3511 \text{ T} [23]$$

$${}^\circ G_{\text{Y}:\text{Va}} - H_{\text{Y}}^{\text{SER}} = \text{GHSEYYY} + 122800 [23]$$

$${}^\circ G_{\text{Y}^{3+}:\text{Va}} - H_{\text{Y}}^{\text{SER}} = \text{GHHYO15} - 1.5\text{GHSEROO} + 9.3511 \text{ T} [23]$$

YCrO₃

$$^{\circ}G_{Y^{3+};Cr^{3+};O^{2-}} - H_Y^{SER} - H_{Cr}^{SER} - 3H_O^{SER} = GYCRO3 \text{ [This work]}$$

Liquid

$$p=2y_{O^{2-}}+qy_{Va^{q-}}, q=2y_{Cr^{2+}}+3y_{Cr^{3+}}+3y_{Y^{3+}}$$

$$^{\circ}G_{Cr^{2+};O^{2-}} - 2H_{Cr}^{SER} - 2H_O^{SER} = 2GCR101_L \text{ [29]}$$

$$^{\circ}G_{Cr^{3+};O^{2-}} - 2H_{Cr}^{SER} - 3H_O^{SER} = GCR203_L \text{ [29]}$$

$$^{\circ}G_{Y^{3+};O^{2-}} - 2H_Y^{SER} - 3H_O^{SER} = GY203LIQ \text{ [23]}$$

$$^{\circ}G_{Cr^{2+};Va} - H_{Cr}^{SER} = GCR_L \text{ [29]}$$

$$^{\circ}G_{Cr^{3+};Va} - H_{Cr}^{SER} = 2GCR_L + GCR203_L - 3GCR101_L \text{ [29]}$$

$$^{\circ}G_{Y^{3+};Va} - H_Y^{SER} = GYYLIQ \text{ [23]}$$

$$^0L_{Cr^{3+};Y^{3+};Va} = 32000 \text{ [32]}$$

$$^1L_{Cr^{3+};Y^{3+};Va} = 8500 \text{ [32]}$$

$$^0L_{Cr^{2+};Y^{3+};Va} = 32000 \text{ [32]}$$

$$^1L_{Cr^{2+};Y^{3+};Va} = 8500 \text{ [32]}$$

$$^0L_{Cr^{2+};Y^{3+};O^{2-}} = -124890 \text{ [This work]}$$

$$^1L_{Cr^{2+};Y^{3+};O^{2-}} = -89246 \text{ [This work]}$$

$$^2L_{Cr^{2+};Y^{3+};O^{2-}} = -205190 \text{ [This work]}$$

$$^0L_{Cr^{2+};O^{2-};Va} = 121000 \text{ [29]}$$

$$^0L_{Cr^{3+};Y^{3+};O^{2-}} = -124890 \text{ [This work]}$$

$$^1L_{Cr^{3+};Y^{3+};O^{2-}} = -89246 \text{ [This work]}$$

$$^2L_{Cr^{3+};Y^{3+};O^{2-}} = -205190 \text{ [This work]}$$

$$^0L_{Cr^{3+};O^{2-};Va} = 121000 \text{ [29]}$$

$$^0L_{Y^{3+};O^{2-};Va} = 6900 \text{ [23]}$$

$$^1L_{Y^{3+};O^{2-};Va} = -17000 \text{ [23]}$$

O₂ gas

$$^{\circ}G_{O_2} - 2H_O^{SER} = 2GHSEROO + RT \ln(1 \times 10^{-5} P) \text{ [52]}$$

Functions

GHSEROO=

$$298.15 < T < 1000.00$$

$$-3480.87 - 25.503038 T - 11.136 T \ln T - 0.005098888 T^2 + 6.61846 \times 10^{-07} T^3 - 38365 T^{-1}$$

$$1000.00 < T < 3300.00$$

$$-6568.763 + 12.65988 T - 16.8138 T \ln T - 5.95798 \times 10^{-04} T^2 + 6.781 \times 10^{-09} T^3 + 262905 T^{-1}$$

$$3300.00 < T < 6000.00$$

$$-13986.728 + 31.259625 T - 18.9536 T \ln T - 4.25243 \times 10^{-04} T^2 + 1.0721 \times 10^{-8} T^3 + 4383200 T^{-1} \text{ [52]}$$

GHSERCR=

$$298.15 < T < 2180.00$$

$$-8856.94 + 157.48 T - 26.908 T \ln T + 0.00189435 T^2 - 1.47721 \times 10^{-06} T^3 + 139250 T^{-1}$$

$$2180.00 < T < 6000.00$$

$$-34869.344 + 344.18 T - 50 T \ln T - 2.88526 \times 10^{32} T^9 \text{ [29]}$$

GCR_L=

$$298.15 < T < 2180.00$$

$$+15483.015 + 146.059775 T - 26.908 T \ln T + 0.00189435 T^2 - 1.47721 \times 10^{-06} T^3 + 139250 T^{-1} + 2.37615 \times 10^{-21} T^7$$

$$2180.00 < T < 6000.00$$

$$-16459.984+335.616317 T-50 T \ln T [29]$$

GHSEYYY=

$$100.00 < T < 1000.00$$

$$-8011.09379+128.572856 T-25.6656992 T \ln T-0.00175716414 T^2-4.17561786 \times 10^{-07} T^3+26911.509 T^{-1}$$

$$1000.00 < T < 1795.15$$

$$-7179.74574+114.497104 T-23.4941827 T \ln T-0.0038211802 T^2-8.2534534 \times 10^{-08} T^3$$

$$1795.15 < T < 3700.00$$

$$-67480.7761+382.124727 T-56.9527111 T \ln T+0.00231774379 T^2-7.22513088 \times 10^{-08} T^3+18077162.6 T^{-1} [23]$$

GYBCC=

$$100.00 < T < 1000.00$$

$$-833.658863+123.667346 T-25.5832578 T \ln T-0.00237175965 T^2+9.10372497 \times 10^{-09} T^3+27340.0687 T^{-1}$$

$$1000.00 < T < 1795.15$$

$$-1297.79829+134.528352 T-27.3038477 T \ln T-5.41757644 \times 10^{-04} T^2-3.05012175 \times 10^{-07} T^3$$

$$1795.15 < T < 3700.00$$

$$+15389.4975+.981325399 T-8.88296647 T \ln T-0.00904576576 T^2+4.02944768 \times 10^{-07} T^3-2542575.96 T^{-1} [23]$$

GYLIQ=

$$100.00 < T < 1000.00$$

$$+2098.50738+119.41873 T-24.6467508 T \ln T-0.00347023463 T^2-8.12981167 \times 10^{-07} T^3+23713.7332 T^{-1}$$

$$1000.00 < T < 1795.15$$

$$+7386.44846+19.4520171 T-9.0681627 T \ln T-0.0189533369 T^2+1.7595327 \times 10^{-06} T^3$$

$$1795.15 < T < 3700.00$$

$$-12976.5957+257.400783 T-43.0952 T \ln T [23]$$

$$\mathbf{GCR2O3= -1164542+728.56 T-119.8 T \ln T-0.00497 T^2+1050000 T^{-1} [29]}$$

$$\mathbf{GCR1O1= +0.5 GCR2O3-0.5 GHSEROO+255269-53.82 T [29]}$$

$$\mathbf{GCROO= +108305+GCR2O3+0.666666667 GHSERCR [29]}$$

$$\mathbf{GCR3O4= +1.5 GCR2O3-0.5 GHSEROO+280045-93.76 T [29]}$$

$$\mathbf{GCR1O1_L= +0.5 GCR2O3-0.5 GHSEROO+339673-121.4 T [29]}$$

$$\mathbf{GCR2O3_L= +GCR2O3+439078-169 T [29]}$$

$$\mathbf{GCCYO15= -977270+376.86 T-62.85 T \ln T-0.0028 T^2+1172000 T^{-1} -59000000 T^{-2} [23]}$$

$$\mathbf{GY2O3LIQ= +2 GYYLIQ+3 GHSEROO-1824600+246 T [23]}$$

$$\mathbf{GYCRO3= -1635130+682.7899 T-114.1586 T \ln T-0.00626760316 T^2+991861.047 T^{-1} [This work]}$$

Note: All parameters are in SI units: J, mol, K, Pa: $R= 8.31451\text{J}/(\text{mol K})$. Parameters for Y-O are from Chen et al. [23], parameters for Cr-O are from Povoden et al. [29], and parameters for Y-Cr are from Chan et al. [32].

Fig. 1 shows the calculated Y-O phase diagram when the bcc phase is modeled as $(\text{Y})_1(\text{O}, \text{Va})_3$. The parameters are listed in Table 2 and used for thermodynamic description of the Cr-Y-O system. Fig. 2 presents the calculated heat capacity of the YCrO_3 phase in comparison with the experimental data listed in Table 1. The experimental data in the temperature range above 273 K from Stoppe et al. [43] and Satoh et al. [44] were used in the present assessment, since the two sets of data represent good consistency. The experimental data from Su et al. [6] were also included for comparison, though they are not used in the present assessment. As shown in Fig. 2, the calculated heat capacity agrees well with the experimental data from Stoppe et al. [43] and Satoh et al. [44], and deviates slightly from the data from Su et al. [6].

Fig. 1. Calculated phase diagram of the Y-O binary system based on the parameters obtained in the present work.

Fig. 2. Calculated heat capacity of YCrO_3 (per mole of formula unit) as a function of temperature compared with experimental data.

Fig. 3 shows the calculated heat content of the YCrO_3 phase together with the data from Suponitskii et al. [46], Satoh et al. [44] and Dzhaoshvili et al. [47]. The currently calculated heat content can reproduce most of the experimental data well. The units in Figure 2 and Figure 3 are all per mole of formula unit.

Fig. 3. Calculated heat content of YCrO_3 (per mole of formula unit) as a function of temperature compared with experimental data.

The standard entropy and heat capacity of YCrO_3 at 298.15 K are listed in Table 5. The calculated results in this work meet with the experimental data in the literature well.

Table 5. Entropy and heat capacity of YCrO_3 at 298.15 K.

Reference	$S_{298.15}, J/(mol K)$	$C_{p298.15}, J/(mol K)$	Method
Satoh et al. [44]	96.80	97.21	Calorimetry
Stoppe et al. [43]	96.41	96.80	Calorimetry
Su et al. [6]		104.20	Calorimetry
This work	96.69	96.58	Assessed

The currently calculated and previously reported experimental data for the electromotive force of YCrO_3 are shown in Fig. 4. The reference electrode is $\text{Cr-Cr}_2\text{O}_3$, whose Gibbs energy of reaction ($2/3\text{Cr}+1/2\text{O}_2=1/3\text{Cr}_2\text{O}_3$) is $\Delta G^\circ = -367337.5+80.06 T$ (1385 K-1470 K), adopted from Povoden et al. [29]. Our calculated electromotive force values reproduce the experimental data from Kawamura et al. [45] well. The Gibbs energy of formation for YCrO_3 formed by different combination of elements and oxides are also calculated for comparison. The results are listed in Table 4 and plotted in Fig. 9 together with the values reported in the literature [45, 48-50]. Our calculation results fit most of the literature data well.

Fig. 4. Calculated electromotive force (EMF) of YCrO_3 as a function of temperature compared with experimental data.

Table 4. Gibbs energy of formation for YCrO_3 .

Reaction	$\Delta G^\circ, \text{J/mol}$	Temperature, K	Reference
$0.5\text{Cr}_2\text{O}_3+0.5\text{Y}_2\text{O}_3=\text{YCrO}_3$	$81950 - 73.15 T$	1182-1386	Wang et al. [48]
	-43600	1200	Kovba et al. [49]
	-43700	1400	Kovba et al. [49]
	$-73146 + 4.82 T$	1100-1700	This work
$\text{Cr}+0.75\text{O}_2+0.5\text{Y}_2\text{O}_3=\text{YCrO}_3$	$-630000 + 152 T$	1385-1470	Kawamura et al. [45]
	$-504800 + 40.795 T$	1182-1386	Wang et al. [48]
	$-565050+111.7 T$	1273-1673	Ranganathan et al. [50]
	$-627055 + 127.43 T$	1100-1700	This work
$\text{Cr}+\text{Y}+1.5\text{O}_2=\text{YCrO}_3$	$-1580000 + 293 T$	1385-1470	Kawamura et al. [45]
	-1236200	1200	Kovba et al. [49]
	-1183500	1400	Kovba et al. [49]
	$-1584013 + 264.87 T$	1100-1700	This work

Fig. 5 shows the calculated phase diagram of $\text{Cr}_2\text{O}_3\text{-Y}_2\text{O}_3$ in air, including mainly the reproduction of liquidus, eutectic transformation points and the melting temperature of YCrO_3 . The symbols in Fig. 5 stand for the values reported in the literature [50, 51]. A good agreement was achieved between the calculated and reported values. The eutectic temperature and compositions of the two

invariant reactions, i.e. $\text{Liquid} \rightarrow \text{Cr}_2\text{O}_3 + \text{YCrO}_3$ and $\text{Liquid} \rightarrow \text{Y}_2\text{O}_3 + \text{YCrO}_3$, are calculated to be at 2348 K (20 at.% Y_2O_3) and 2296 K (85 at.% Y_2O_3), respectively. The melting temperature of the compound YCrO_3 is calculated to be 2546 K, very close to the value reported in literature [50]. A list of the invariant reactions is presented in Table 3, where most of experimentally measured data in this quasi-binary section are well reproduced.

Table 3. Temperatures and compositions of invariant reactions.

Invariant reactions	Reaction type	$x(\text{Y}_2\text{O}_3)$			T, K		
		This work	Ranganathan et al. [50]	Mikhailov et al. [51]	This work	Ranganathan et al. [50]	Mikhailov et al. [51]
(a) $\text{L} \rightarrow \text{Cr}_2\text{O}_3 + \text{YCrO}_3$	eutectic	0.21	0.20	0.25	2348	2343 ± 30	2343
(b) $\text{L} \rightarrow \text{Y}_2\text{O}_3 + \text{YCrO}_3$	eutectic	0.85	0.72	0.77	2296	2293 ± 30	2293
(c) $\text{L} \rightarrow \text{YCrO}_3$	melting	0.5	0.5	0.5	2546	2563 ± 30	2573

Fig. 5. Calculated phase diagram of Cr_2O_3 - Y_2O_3 in air based on the parameters obtained in the present work.

So far, construction of the thermodynamic database of the chromium-yttrium-oxygen system is completed. The phase relations of the Cr-Y-O ternary system in different atmospheres, i.e. the quasi-binary phase diagram, the isothermal PO_2 -composition phase diagrams and the iso-thermal sections, can be calculated. The thermal stability and decomposition conditions of YCrO_3 can then be predicted based on the calculated phase diagrams.

Fig. 6 shows a series of calculated phase diagram of Y_2O_3 - Cr_2O_3 under different oxygen partial pressure based on the thermodynamic parameters obtained in the present work. It can be seen that with the decrement of oxygen partial pressure from 10^{-16} to 10^{-20} bar, the eutectic temperatures of the two invariant reactions, i.e. $\text{Liquid} \rightarrow \text{Cr}_2\text{O}_3 + \text{YCrO}_3$ and $\text{Liquid} \rightarrow \text{Y}_2\text{O}_3 + \text{YCrO}_3$, decrease. This is also the case for the melting point of YCrO_3 . We calculated the site fractions of Cr^{+2} , Cr^{+3} , and Y^{+3} species in the liquid phase in air and under different oxygen partial pressures (not shown in this work). We found that the site fraction of Cr^{+2} increases with increasing temperature or decreasing oxygen partial pressure. The site fraction of Cr^{+2} becomes appreciable e.g. >10 at. % at $T > 2500 \text{ K}$

in air or at $T > 2000$ K and $P(\text{O}_2) = 10^{-6}$ bar. This shall account for decreasing the melting point of YCrO_3 with decreasing oxygen partial pressure.

Fig. 6. Calculated phase diagram of Cr_2O_3 - Y_2O_3 at different P_{O_2} (a) $P_{\text{O}_2} = 10^{-16}$ bar, (b) $P_{\text{O}_2} = 10^{-18}$ bar, and (c) $P_{\text{O}_2} = 10^{-20}$ bar based on the parameters obtained in the present work.

A series of calculated isothermal P_{O_2} -composition phase diagrams at different temperatures are presented in Fig. 7. The stable phases at certain temperatures under different P_{O_2} can be read directly from the plots. It can be seen that at all temperatures, YCrO_3 decomposes into Y_2O_3 , Cr and O_2 when the oxygen pressure is under certain value. Y_2O_3 is then reduced to metallic Y when the oxygen partial pressure is further reduced. The transformation from $\beta\text{-Y}$ to $\alpha\text{-Y}$ happens above 1200 °C. With increasing temperature, the oxygen partial pressure for the decomposition of the YCrO_3 phase also increases. That is to say, the decomposition of YCrO_3 phase is easier at higher temperature.

The current work provides a complete thermodynamic description of the Cr-Y-O ternary system, which can also be used to predict the phase relations including YCrO_3 at different temperatures. In

Fig. 8, isothermal sections of the Cr-Y-O ternary system at 800 °C, 1000 °C, 1200 °C and 1500 °C are calculated and the phase relations in these regions are identified.

Fig. 7. Calculated isothermal PO_2 -composition phase diagrams at 800 °C, 1000 °C, 1200 °C, and 1500 °C based on the parameters obtained in the present work.

Fig. 8. Calculated isothermal sections of the Cr-Y-O system at 800 °C, 1000 °C, 1200 °C, and 1500 °C based on the parameters obtained in the present work.

Fig. 9. Calculated Gibbs energy of formation for YCrO₃ compared with literature data.

Conclusions

In the present work, a self-consistent thermodynamic description of the Cr-Y-O ternary system is established. The thermodynamic properties of YCrO₃ are critically assessed and an optimized set of parameters of Gibbs energy functions is obtained. The invariant reactions and the melting point of YCrO₃ presented in the quasi-binary Cr₂O₃-Y₂O₃ system can be reproduced using the current set of parameters. The current database reproduces most of the previously reported experimental data well and further provides reasonable prediction of the phase relation and the stability of YCrO₃ as a material for high-temperature electrodes and thermoelectric material. According to the present calculation results, the melting temperature of the YCrO₃ phase drops down with decreasing the oxygen pressure, while the decomposition oxygen partial pressure of YCrO₃ decreases with increasing temperature.

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