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Phase equilibria modelling in Bi–Sr–Co–O system—Towards crystal growth and melt-assisted material processing

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ABSTRACT

In this contribution, high-temperature phase equilibria of the partly open Bi–Sr–Co–(O) system with oxygen content given by its activity in the surrounding atmosphere, were modelled based on the experimental phase diagram determined previously. For the assessment, we also used the previously reported thermodynamic data and phase equilibria for the quasibinary Bi–Co–(O), Sr–Co–(O) and Bi–Sr–(O) subsystems as well as the thermodynamic data of quaternary phases obtained from calorimetry and simultaneous thermal analysis. Namely, the oxide melt was described based on the Redlich-Kister parameters of the corresponding quasibinary systems and the solid oxides were considered as stoichiometric. Their heat capacity and entropy were determined from calorimetry and the enthalpy of formation was refined to reproduce their melting behaviour. The constructed phase diagram focused on solid-liquid equilibria is particularly important for designing the experiments of single crystal growth and melt assisted material processing of these highly significant cobaltites.

1. Introduction

Enormous population growth and a deteriorating environment invoked an intensive search for alternative sources of energy production in the recent decade. Apart from novel sources, energy saving is extremely important. Thermoelectric energy recovery from waste-heat sources such as exhaust pipes represents one of the promising ways towards sustainable development. High temperature thermoelectrics with positive thermopower exhibiting high figure of merit (efficiency of thermoelectric conversion) have been found in the Ca–Co–O [1–3], Li–Co–O [4–6], Na–Co–O [7], Bi–Sr–Co–O [8–13] and Bi–Ca–Co–O[14] systems. The highest figure of merit has been reported for so-called misfit layered cobaltites. These materials are also very auspicious for other energy applications such as for ORR (oxygen reduction reaction) and for HER (hydrogen evolution reaction by means of electrolytic water splitting generating the elemental hydrogen on the cathode) [15]. One of these misfit layered mixed oxides, $[Bi_{2-x}Sr_2O_4][CoO_2]_{1.85}$, is belonging to the Bi-Sr-Co-O system[8]. The figure of merit can be improved by various substitutions or by additives [16–20]. Setting the appropriate phase composition can also significantly improve thermoelectric properties, hence it is highly desirable to study phase relations in Bi-Sr-Co-O system.

Several other bismuth strontium cobalt mixed oxides have been reported in this system in addition to the misfit phase. Although the pure perovskite $SrCoO_3$ is not stable at normal pressure and moderate oxygen activities, a heterovalent substitution of Bi for Sr stabilizes the perovskite structure $Sr_{1-x}Bi_xCoO_{3-\delta}$ in a narrow homogeneity range, $x = 0.1$–0.2, by lowering the Co valency [9]. Another phase, $Bi_2Sr_2CoO_{6+\delta}$, is a non-superconducting analogue of 2201 cuprate [10]. The structure of $Bi_2Sr_2CoO_{6+\delta}$ is composed of sub-layers stacked in a sequence –BiO–SrO–CoO_2–SrO–BiO– and it is modulated due to ordering of excess oxygen atoms in $Bi_2O_{2+\delta}$ double layers [21,22]. A related perovskite based structure (121-type) with a single mixed (Sr,Bi)O layer instead of $Bi_2O_{2+\delta}$ double layers has been discovered by Masset et al. who identified its composition as $(Bi_{0.4}Sr_{0.45}Co_{0.15})Sr_2CoO_{5-\delta}$ [23]. Later on, we refined this phase as $(Bi_{0.4}Sr_{0.6})Sr_2CoO_{5-\delta}$ [24]. The $Bi_{3.7}Sr_{11.4}Co_8O_{29-\delta}$ phase, reported by Pelloquin et al., represents n = 2 member of the $[Bi_2Sr_2CoO_6]_n[Sr_8Co_6O_{16-\delta}]$ homologue series and has been referred to as a tubular phase [11,25]. A re-entrant phase transition (decomposition followed by re-formation on heating) has been reported for this phase and attributed to its metastability at lower temperatures [25]. Moreover, all three quasibinary systems, Bi–Co–O [12,13], Sr–Co–O [26–28] and Bi–Sr–O [29], involve a number of stoichiometric phases as well as solid solutions. The knowledge of phase equilibria in these systems is indeed essential for the assessment of the whole Bi-Sr-Co-O system. Such phase diagram will be helpful for identifying suitable conditions for crystal growth and melt-assisted material processing. This kind of material optimization can lead to the enhancement of thermoelectric power and other properties in layered single crystal cobaltite or glass-ceramics [30,31].

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Moreover, the knowledge of suitable temperatures for annealing is essential for microstructure optimization, which would be the key to produce high-quality thermoelectrics with high figure of merit *ZT* [32,33].

In this work, we present a thermodynamic assessment of oxide phases occurring in the Bi-Sr-Co-O system, calculation of phase equilibria and construction of selected sections of the corresponding phase diagram with a focus on solid-liquid equilibria. Neglecting the volatility of bismuth, the system must be still regarded as open for oxygen as this component is shared with the surrounding atmosphere and its activity can be adjusted by fixing its partial pressure (experiments performed in a dynamic atmosphere with a given p_{O2}), while the oxygen content in the condensed subsystem is variable depending on temperature and p_{O2}. The presented diagrams thus represent isoactivity (and isothermal) sections of the entire phase diagram and the respective phase relations and topology are quite identical to conventional ternary phase diagrams. Hence for a fixed oxygen activity the system under study can be referred to as quasiternary, Bi-Sr-Co-(O), and the corresponding subsystems Bi-Co-(O), Sr-Co-(O) and Bi-Sr-(O) as quasibinary. In general, we are dealing with a partly open system with a single free (shared) component (O) and three stable (conservative) components (Bi, Sr, Co).

2. Thermodynamic model and data

FactSage program was used for the calculation of phase equilibria and phase diagram mapping. The thermodynamic models of stoichiometric phases, liquid components as well as gaseous O_2 (considered as a standard state for free component shared between the studied system and the surrounding atmosphere) are based on standard enthalpies of formation and entropies referred to ambient temperature, $T = 298$ K, and on the temperature dependence of heat capacity in a polynomial form. The data are stored in FactSage Compound database format and serve as source data for evaluation of Gibbs energies used in the calculations of phase equilibria. Values from SGTE pure substances database were used for binary oxides in solid and liquid state.

The heat capacity and the standard entropy for quasibinary and quasiternary oxide phases stable in the sub-solidus region, namely the misfit cobaltite $Bi_{1.85}Sr_2Co_{1.85}O_{7.7\text{-}\delta}$ [8], $Bi_2Sr_2CoO_{6.5\text{-}\delta}$ [10], $(Bi_{0.4}Sr_{0.6})Sr_2Co_{1.85}O_{7.7\text{-}\delta}$ [24] and the tubular phase $Bi_{3.7}Sr_{11.4}Co_8O_{29\text{-}\delta}$ [25], were adopted from our previously published papers, while their standard enthalpies of formation were assessed to reproduce the experimentally observed phase transition temperatures. Although some of them exhibit certain miscibility within the metal components as well as variable oxygen stoichiometry, all phases were considered as stoichiometric (with simplified stoichiometric coefficients) as indicated in Table 1. The oxygen stoichiometry was fixed to a value close to that observed by thermogravimetry in the interval 50–100 K below the melting/decomposition temperature. This might seem as a crude approximation; however, we believe it is reasonable with regard to the overall accuracy of the experimental data used for the optimization as well as the description of the liquid phase, which was modelled based on the respective quasibinary subsystems as shown below.

The temperature dependence of heat capacity of the perovskite phase, $Bi_{0.1}Sr_{0.9}CoO_{2.9}$, and the phase with a rough composition $BiSr_{2.5}CoO_{7.7\text{-}\delta}$, whose structure has not been determined as yet, was approximated using Neumann-Kopp rule (NKR) from the constituent binary oxides (SrO, SrO_2, CoO and Bi_2O_3). For this purpose, the mixer utility as implemented in FactSage was used, which has a disadvantage that the temperature dependence of heat capacity is described in several temperature ranges (Table 2). The standard enthalpies of formation and entropies of these two compounds were again adjusted to comply with the experimental points in the phase diagram [34]. All used thermodynamic data of the stoichiometric quasiternary phases (standard enthalpies of formation, entropies referred to ambient temperature and temperature dependence of heat capacity) are presented in Table 1 and Table 2 including the considered stoichiometries.

Table 1
Bi–Sr–Co–O system: Thermodynamic values for solid stoichiometric compounds: Enthalpies of formation $\Delta_f H^\circ_{298}$ (kJ.mol^{-1}) and entropies S°_{298} (J.mol^{-1}.K^{-1}).

Phase	Considered stoichiometry	$\Delta_f H^\circ_{298}$	S°_{298}
$Sr_{1\text{-}x}Bi_xCoO_{3\text{-}\delta}$	$Bi_{0.1}Sr_{0.9}Co_1O_{2.9}$	−918.5	120
$BiSr_{2.35}CoO_{6\text{-}\delta}$	$BiSr_{2.5}CoO_{5.5}$	−2140	275
$(Bi_{0.4}Sr_{0.6})Sr_2CoO_{5-\delta}$	$Bi_{0.4}Sr_{2.6}CoO_{4.8}$	−2054	200
$Bi_{3.7}Sr_{11.4}Co_8O_{29\text{-}\delta}$	$Bi_4Sr_{12}Co_8O_{29}$	−11060	1318
$Bi_2Sr_2CoO_{6+\delta}$	$Bi_2Sr_2CoO_{6.25}$	−2158	296
$[Bi_{2\text{-}x}Sr_2O_4][CoO_2]_{1.85}$	$Bi_{1.9}Sr_2Co_{1.9}O_{7.7}$	−2470	317

The Gibbs energy of solution phases was expressed in a standard way

$$G^{\Phi} = \sum_i (y_i G_i^\circ + RT\cdot y_i \cdot \ln y_i) + \Delta G^{ex} \tag{1}$$

as a sum of Gibbs energies of the involved species $G^0{}_i$, the ideal entropy term and the excess Gibbs energy. The latter term was considered only for high temperature liquid in the polynomial form

$$\Delta G^{ex} = \sum_{M,N} y_M y_N \sum_j L_{j(M,N)}(y_M - y_N)^j + y_{Bi} y_{Sr} y_{Co} L_{i,j,k} \tag{2}$$

where the first term on the right-hand side represents the Redlich-Kister (RK) contributions reflecting the binary interactions between the considered species (Bi_2O_3, SrO, CoO) adopted from the previously assessed phase diagrams Bi-Co-O, Bi-Sr-O and Sr-Co-O [12,26,29] while a small temperature dependent ternary contribution is involved in the second term. All parameters used to model the oxide liquid are compiled in Table 3.

By contrast, an ideal mixing on the respective sublattices and the compound energy formalism were supposed in the case of non-stoichiometric solid phases. This applies to quasibinary solid solutions and phases revealing oxygen non-stoichiometry such as $Bi_{24}[Bi_{2\text{-}x}Co_x]_2O_{39\text{-}\delta}$, $Sr_9Co_6O_{19-\delta}$, $Sr_{14}Co_{11}O_{33-\delta}$, δ-$Bi_{2\text{-}x}Sr_xO_{3\text{-}\delta}$, β-$Bi_{2\text{-}x}Sr_xO_{3\text{-}\delta}$ and γ-$Bi_{2\text{-}x}Sr_xO_{3\text{-}\delta}$. The details of their thermodynamic description are again given in the respective phase diagram assessments [12,26,29].

In summary, a quasiternary liquid phase, six solid solutions mentioned above and sixteen stoichiometric solid phases (six quasiternary phases from Table 1 + Bi_2O_3, SrO, CoO, Co_3O_4, $Sr_2Co_2O_5$, $Sr_6Co_5O_{15}$, Bi_2SrO_4, $Bi_2Sr_2O_5$, $Bi_2Sr_3O_6$ and $Bi_2Sr_6O_{11}$) were considered for the phase diagram construction.

3. Results and discussion

In order to reproduce the previously obtained experimental results all parameters were optimized for the calculation of the phase diagram using FactSage program. These optimized parameters are shown in Table 1, Table 2 and Table 3. Using these data, we constructed the isoactivity ($p_{O2}/p^0 = 0.21$) and isothermal sections at 1100 K, 1175 K, 1250 K and 1325 K (after each 75 K) of the Bi-Sr-Co-O phase diagram.

In Fig. 1a the phase equilibria at 1100 K are depicted. Except of the melt, the following phases were found to be thermodynamically stable: Co_3O_4, SrO, $Sr_6Co_5O_{15}$, $Sr_{14}Co_{11}O_{33-\delta}$, β-$Bi_{2\text{-}x}Sr_xO_{3\text{-}\delta}$, γ-$Bi_{2\text{-}x}Sr_xO_{3\text{-}\delta}$, Bi_2SrO_4, $Bi_2Sr_2O_5$, $Bi_2Sr_3O_6$, $Bi_2Sr_6O_{11}$, $Sr_{1\text{-}x}Bi_xCoO_{3\text{-}\delta}$, $BiSr_{2.35}CoO_{6\text{-}\delta}$, $(Bi_{0.4}Sr_{0.6})Sr_2CoO_{5-\delta}$, $Bi_2Sr_2CoO_{6+\delta}$ and misfit cobaltite $[Bi_{2\text{-}x}Sr_2O_4][CoO_2]_{1.85}$. These results are in good agreement with the previously obtained experimental data (XRD diffraction confirming the individual fields of stability) [34]. It can be supposed that 1100 K is the minimum temperature for the phase diagram construction, since kinetic aspects can play a significant role bellow this temperature and the calculated phase diagram cannot thus be experimentally confirmed.

At 1175 K (see Fig. 1b), it is obvious that a higher amount of liquid is present in the Bi-rich part of the phase diagram. In addition, Co_3O_4 decomposed to CoO and two new phases unstable at low temperatures, the brownmillerite-type $Sr_2Co_2O_5$ and the tubular phase