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Phase diagram of the pseudobinary system Bi–Co–O

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Abstract

Samples with different ratios of Bi_2O_3 and Co_2O_3 were prepared by ceramic route. Based on the results of differential thermal analysis, X-ray powder diffraction, SEM–EDXA and *FactSage* database the phase diagram of the Bi–Co–O diagram in air atmosphere was assessed and calculated using the *FactSage* software. The sillenite structure of $Bi_{24}Co_2O_{39}$ was identified and the single phase homogeneity range of $Bi_{24}Bi_{2-x}Co_xO_{39}$, $x = 0.9$–2.0 was determined by Rietveld analysis and SEM–EDXA. To verify the composition in the various parts of the phase diagram at elevated temperatures, a number of high-temperature annealing experiments was performed followed by rapid quenching to room temperature.

Keywords: Bi–Co–O system; Sillenite; Phase diagram; Thermodynamic properties

1. Introduction

The cobalt based mixed oxides attracted recently much attention on account of their outstanding fundamental properties (incommensurate crystal structures, spin state transitions, spin fluctuations giving rise to large thermopower, anomalous magnetism, transport properties, etc.) whose knowledge and understanding opened up a way to a development of materials with prospective application potential, for instance in the field thermoelectric power generation. Among these the misfit layered cobaltite $[Bi_2Sr_2O_3][CoO_2]_{1.82}$ discovered by Tarascon et al.[1] represents a potential candidate for p-type cells in thermoelectric batteries for high-temperature energy recovery.

Although the structure of this misfit phase has been in detail described by Leligny et al.[2] and the thermoelectric properties of BiSrCoO based ceramics have been extensively studied, see e.g. by Sotelo et al.,[3–5] there is relatively little known on the thermodynamic behavior of these materials, which is essential for both material tailoring and predicting their stability in long-term operation at elevated temperatures. Modeling of phase equilibria and construction of the corresponding phase diagrams indeed represents an effective way to assess the phase stability with respect to melting/decomposition, accommodating various types of defects and sharing some components (oxygen) with surrounding atmosphere. However, this approach requires a detailed knowledge of thermodynamic properties of the involved phases and, in the case of multicomponent systems, also thermodynamic assessments of the respective subsystems. Hence the knowledge of Sr–Co–O, Bi–Sr–O and Bi–Co–O phase diagrams is necessary for modeling the phase stability of the quaternary phases involved in the Bi–Sr–Co–O system, namely the misfit cobaltite $[Bi_2Sr_2O_3][CoO_2]_{1.82}$ and the analog to Bi-based cuprate, $Bi_2Sr_2CoO_{6+\delta}$. In the present study we focus on the relatively simple Bi–Co–O system.

There are nowadays not many studies dealing with phase equilibria in the Bi–Co–O system. This may be partly due to experimental obstacles related to highly aggressive chemical behavior of bismuth, bismuth oxides and their vapors with respect to most instruments and laboratory equipment at elevated temperatures. The properties and structure polymorphs of bismuth sesquioxide were studied by Harwig.[6] The only available phase diagram of Bi–Co–O system at room temperature has been published by Vanderah et al.,[7] however this study was mainly focused on the Bi–Co–Nb–O system. The authors assume a formation of a single stoichiometric phase $Bi_{25}CoO_{40}$ in this system. Its structure has been in fact identified as γ-Bi_2O_3 belonging to sillenite phases which were discovered by Sillen et al.[8]

Models for sillenites with a formula $Bi_{24}M_2O_{40}$ have been proposed and elaborated by Valant et al.[9] and a number of

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different cogeners from sillenite family with a general composition $Bi_{24}M_{2-x}{}^{n+}O_{40}$ have been described in this work. The substituting atom M^{n+} in these solid solutions can occur in a different valence state: aside from M^{3+} sillenites with Ga^{3+}, Fe^{3+}, Cr^{3+} and Tl^{3+} several heterovalent substitutions have been successfully carried out with divalent (Cd^{2+}, Zn^{2+}), tetravalent (Si^{4+}, Ti^{4+}, Ge^{4+} and Mn^{4+}) and even pentavalent (V^{5+}, As^{5+} and P^{5+}) cations occupying completely or partly the two fourfold coordinated sites. For instance, the sillenite structure stabilized by Zn in Bi_2O_3-rich region was described by de la Rubia et al.,[10] Bi_2O_3 doped with various amounts of SnO_2 was prepared by Kuo et al.,[11] Bi_2O_3 based oxide ion conductors doped by Fe^{3+}, Sb^{3+}/Sb^{5+} and Ta^{5+} were studied by Fruth et al.[12,13] and Ti-doped Bi_2O_3 has been reported by Kuo et al.[14] Concerning the Co substitution, crystal structure of $Bi_{12.7}Co_{0.3}O_{19.35}$ was reported by Mary et al.[15] although there is no evidence of other ternary phases being stable under normal conditions a perovskite type structure $BiCoO_3$ has been stabilized at elevated pressures applying hot pressing technique in the Belt-type apparatus.[16]

In this work we examine the prepared ceramic materials with different Bi/Co ratio by several experimental techniques – differential thermal analysis (DTA), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) combined with microprobe analysis using energy dispersive X-ray analysis (EDXA). The obtained results are subsequently used to determine the pseudobinary phase diagram of the Bi–Co–O in air atmosphere by means of *FactSage* database and phase equilibria calculation program.[17] As shown below the formation of sillenite structure is indeed confirmed and, moreover, its homogeneity range with respect to variable cobalt stoichiometry and its melting behavior is assessed.

2. Experimental

The starting materials used for powder preparations were Bi_2O_3 (*Aldrich*, ACS) and Co_2O_3 (*Riedel-de Haen*, ACS). Powders were weighted on digital balances with an accuracy of 0.1 mg and mixed in appropriate stoichiometric rates (100/0, 98/2, 95/5, 90/10, 80/20, 70/30, 60/40, 20/80 and 0/100). The corresponding samples will be denoted as BC100-0, BC98-2, ..., BC0-100 hereinafter. After homogenization in the agate mortar the powders were calcined in the platinum crucible at 973 K for 24 h. Then the sample was homogenized and calcined at 1003 K for the next 24 h. After homogenization in an achate mortar, all samples were cold pressed under the pressure of 0.5 GPa. The green pellets were sintered for 200 h in air atmosphere at 1013 K and they were slowly (3 K/min) cooled down to room temperature to guarantee the stabilization of low-temperature phase equilibria.

All samples were analyzed by XRD on Bruker AXS D8 Θ-Θ powder diffractometer with parafocusing Bragg–Brentano geometry using CoK_α radiation ($\lambda = 1.79021$ Å, $U = 34$ kV, $I = 20$ mA). To confirm the composition of the various parts of the phase diagram at elevated temperatures, a number of high-temperature annealing experiments at 973 K was performed followed by a rapid quenching to room temperature. The samples were pulled out from the furnace and thrown into a container with liquid nitrogen. We can assume that all phase transformations to low temperature equilibrium state are kinetically hindered during this short time, so the sample remained in its high temperature thermodynamic equilibrium during the XRD measurements. XRD patterns were analyzed by *HighScore Plus* software and by Rietveld analysis using *FullProff* software[18] to identify the phase composition and the ratio of the present phases.

The samples were further analyzed by SEM in BSE mode on *TESCAN Vega 3 LMU* microscope and EDXA on *Oxford instruments INCA 350* EDXA analyser to confirm the Rietveld analysis results. DTA and thermogravimetric (TG) analysis were performed from 293 K to 1350 K to determine phase transitions, temperatures of decompositions and melting temperatures of the synthetized materials. All samples were measured by DTA on device *Netzsch STA409C* with a heating rate of 10 K/min. DTA and TG curves of the sample BC95-5 were recorded simultaneously on Setaram STA apparatus, model *Setsys Evolution*, with the same heating rate.

The calculations of phase equilibria and the construction of phase diagrams were carried out by means of the *FactSage* thermo-chemical software and databases,[17] version 6.1.

3. Thermodynamic models and data

The thermodynamic models of stoichiometric phases (α, δ-Bi_2O_3(s), Co_3O_4(s), and CoO(s)), the end-members of solution phases $Bi_{26}O_{39}$(s) (γ-Bi_2O_3), $Bi_{24}Co_2O_{39}$(s) (sillenite phase), Bi_2O_3(l), CoO(l), Co(l)) (oxide liquid) as well as O_2(g) (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. All these values are stored in *FactSage Compound* database format and serve as source data for calculation of Gibbs free energies.

SGTE values from SGPS (pure substances) database were used for binary oxides in solid and liquid state, Bi_2O_3 (s,l), CoO(s,l), as well as for Co(l), whereas for cobalt spinel Co_3O_4 the recently reported data[19] were applied. The entropy and heat capacity of $Bi_{24}Co_2O_{39}$(s) was approximated by a modified Neumann–Kopp rule (NKR):

$$C_p(\mathrm{Bi_{24}Co_2O_{39}}) = 12C_p(\mathrm{Bi_2O_3}) + C_p(\mathrm{Co_3O_4}) - C_p(\mathrm{CoO}), \quad (1)$$

$$S^\circ_{298}(\mathrm{Bi_{24}Co_2O_{39}}) = 12S^\circ_{298}(\mathrm{Bi_2O_3}) + S^\circ_{298}(\mathrm{Co_3O_4}) - S^\circ_{298}(\mathrm{CoO}). \quad (2)$$

For this purpose the large peak on the heat capacity data of Co_3O_4 centered around 1000 K and attributed to a spin state