HIGH RESOLUTION THERMOCHEMICAL STUDY OF PHASE STABILITY AND RAPID OXYGEN INCORPORATION IN $YBaCo_{4-x}Zn_xO_{7+\delta}$ 114-COBALTITES

Dmitry Tsvetkov, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia
Dmitry.Tsvetkov@urfu.ru
Pardha Maram, Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California Davis, USA
Nadezhda Tsvetkova, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia
Andrey Zuev, Institute of Natural Sciences and Mathematics, Ural Federal University, Russia
Alexandra Navrotsky, Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California Davis, USA

Key Words: calorimetry, 114-oxides, $YBaCo_4O_7$, thermodynamic stability, oxygen sorption.

The formation enthalpies of $YBaCo_{4-x}Zn_xO_{7+\delta}$ (x = 0, 1 and 3) oxides were measured by high temperature oxide melt solution calorimetry. All the studied oxides were shown to be thermodynamically metastable at low temperature with respect to a mixture of binary oxides Y_2O_3, BaO, Co_3O_4, CoO and ZnO. The tendency of cobalt to increase oxidation state under oxidizing conditions as well as significant bond valence sum mismatch for Ba and Y in 114-oxides are the main destabilizing factors. As a result, the studied 114-oxides are thermodynamically stable in air only at relatively high temperatures (> ca. 900 °C) when CoO is stable. Oxygen absorption in $YBaCo_{4-x}Zn_xO_{7+\delta}$ (x = 0, 1 and 3) at 350-400 °C was studied by calorimetry combined with precise oxygen dosing. Complex phase evolution in $YBaCo_4O_{7+\delta}$ upon oxygen absorption was revealed. Several single and two phase fields were identified and a sketch of the phase diagram for $YBaCo_4O_{7+\delta}$ was proposed. The calorimetric results support observations using in situ XRD. At the same time, thermochemical measurements were shown to have higher resolution with respect to the amount of oxygen absorbed by $YBaCo_{4-x}Zn_xO_{7+\delta}$ sample under equilibrium conditions.

This work was supported by the Ural Federal University within the framework of Act 211 of Government of the Russian Federation, agreement № 02.A03.21.0006. The thermochemistry work at Davis was supported by US Department of Energy Grant DE-FG02-03ER46053.