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Co_3O_4–Co_2ZnO_4 spinels: The case for a solid solution

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ABSTRACT

In prior first-principles theoretical work we predicted a complete solid solution in the Co_3O_4–Co_2ZnO_4 system, with a negligibly small mixing enthalpy. In this work we tested this prediction on bulk, large-grained specimens across the Co_3O_4–Co_2ZnO_4 join, combining oxide melt solution calorimetry, differential scanning calorimetry, precise lattice parameter measurements, anomalous X-ray and neutron diffraction, and in situ electrical measurements. The calorimetric results confirm the presence of a solid solution at high temperatures, but with a large enthalpy of mixing that exceeds the predicted value. Because Co_3O_4 and Co_2ZnO_4 have essentially identical lattice parameters, this energetic destabilization must arise from factors other than the strain energy resulting from size mismatch. Changes in Co^{3+} spin states vs. temperature and zinc content are proposed to account for the positive excess enthalpy, and may also provide additional entropy to stabilize the solid solution at high temperature.

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1. Introduction

Cobalt-based spinels have been widely investigated for their electrical, optical, and magnetic properties, with application in catalysts [1–3], batteries [4–6], sensors [7], pigments [8], and electrochromic [9] devices. While both Co_3O_4 and Co_2ZnO_4[1] have been studied for decades, interest in Co_2ZnO_4 has increased recently, owing to its relationship to the new p-type transparent semiconductor Ir_2ZnO_4 [10] and its application as a hole transport layer in organic photovoltaics [11]. The electrical, optical, and magnetic properties enabling these applications are related to the underlying thermodynamics governing the temperature-dependence of phase stability, cation arrangement, and spin states in these compounds. For example, the low temperature anti-ferromagnetism of Co_3O_4 (at $T < \sim 40$ K) has been attributed to the tetrahedral Co^{2+} ions, since octahedral Co^{3+} in the low spin state has no unpaired electrons or magnetic moment [12,13]. Changes in cation distributions and spin states (e.g., with temperature or composition) could potentially change the magnetic properties, since, for example, high spin Co^{3+} does have a magnetic moment. The site occupancy and spin state of Co is also relevant in the context of understanding the behavior of a related material, Co-substituted ZnO, which is considered a ferromagnetic "dilute magnetic semiconductor" [14], though the origins of such behavior remain under discussion. Also from an electrical perspective, cation distributions play a vital role, because the intrinsic p-type behavior of Co_2ZnO_4 is caused by the presence of anti-site Zn on Co acceptor defects [15]. Of particular importance in the Co_3O_4–Co_2ZnO_4 system is the question of whether a solid solution exists between the two end-member spinels, permitting tailoring of properties, in-depth studies of the roles of constituent cations and defects, and explanations for composition-dependent properties.

In general, solid solutions (alloys) of isovalent and isostructural compounds have positive enthalpies of mixing (ΔH_{mixing}). Examples include (III–V)–(III–V) or (II–VI)–(II–VI) alloys [16,17], oxide and halide solid solutions [18], and ternary chalcopyrites [19]. The mixing enthalpy generally scales with the size-mismatch between the constituents [18,19]. A few systems, usually with small size-mismatch, show zero or slightly negative heats of mixing

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[1] Another widely used way of writing the spinel chemical formula is AB_2O_4 (e.g., $ZnCo_2O_4$). We, however, write A_2BO_4 (e.g., Co_2ZnO_4), which is common for spinels with formal cation valencies $Z_A=2$ and $Z_B=4$ such as Mg_2TiO_4. For a normal 3–2 spinel, A here refers to the octahedral sites and *B* to the tetrahedral sites. The main reason for our choice is the fact that the work presented here is part of a larger project that treats all A_2BX_4 compounds (not only spinels) in different structure-types including olivine Fe_2SiO_4, β-K_2SO_4 or La_2CuO_4 for which A_2BX_4 is the generally used notation.

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[20, 21, 22]. When $\Delta H_{mixing} > 0$, the phase diagram exhibits a miscibility gap below some critical temperature (T_c), and complete solid solution above. Thus, a positive heat of mixing is an indication of possible exsolution at low temperature, whereas a negative heat of mixing is suggestive of ordering.

The isovalent and isostructural system Co_3O_4–Co_2ZnO_4 is likely to show a small positive mixing enthalpy and the consequent existence of solid solution above a moderately low temperature and phase separation below. Both end-member spinels are nominally normal in cation distribution, with Co^{3+} on octahedral sites and Zn^{2+} and Co^{2+} on tetrahedral sites [23]. The ionic radii of Zn^{2+} and Co^{2+} in tetrahedral coordination are very similar (0.74 Å and 0.72 Å, respectively [24]), and the lattice parameters of the two end-members are virtually identical (e.g., 8.0837 Å at 23 °C for Co_3O_4 from PDF card 01–080-1541 [25] and 8.0946 Å at 25 °C for Co_2ZnO_4 from PDF card 00–23-1390 [26]). Thus one expects the mixing enthalpy to be small-positive. Not surprisingly, Robin [27] described Co_2ZnO_4–Co_3O_4 as a continuous solid solution in his very early phase diagram (though without extensive substantiation).

In spite of these observations, there is no conclusive experimental evidence to date for the existence of a solid solution. One of the challenges is related to the aforementioned similarity of the Zn and Co ionic radii. For example, Robin [27] noted the difficulty of quantitative measurements of composition from lattice parameters of equilibrated samples because the parameters varied so little across the supposed solid solution. In the present work we confirm that the lattice parameters of equilibrated compositions in the Co_3O_4–Co_2ZnO_4 join are virtually indistinguishable. It should be pointed out that our work is in contrast to that of Petrov et al. [28] on samples prepared at low temperature in potentially metastable structural states (see below). Thus the question of whether a complete solid solution exists under equilibrium conditions remains open.

In our recent theoretical efforts on the Co_3O_4–Co_2ZnO_4 system [23] we have calculated the energy needed to substitute a single Co-on-Zn (tetrahedral) anti-site defect in the 56 atom supercell of Co_2ZnO_4 and a single Zn-on-Co (octahedral) anti-site defect in the same size supercell of Co_2CoO_4 (Co_3O_4), using first principles approaches. The calculated anti-site enthalpies of formation are $< 0.05 \pm 0.1$ eV in either case, indicating a very small enthalpy of mixing in thermodynamic equilibrium. Straightforward calculation of the enthalpy of mixing ($\Delta H_{mixing} = E((Co_2CoO_4)_{0.125}(Co_2ZnO_4)_{0.875}) - 0.125E(Co_2CoO_4) - 0.875E(Co_2ZnO_4)$) yields a negligibly small value, consistent with the small anti-site formation energies. Accounting for entropy (owing to configurational contributions of arranging Co-on-Zn sites in Co_2ZnO_4 and Zn-on-Co sites in Co_2CoO_4) at higher temperatures resulted in the calculated phase diagram of Fig. 1, showing continuous solid solution at high temperature, as evidenced by the overlap of the Zn-substituted Co_3O_4 and Co-subsituted Co_2ZnO_4 boundaries.

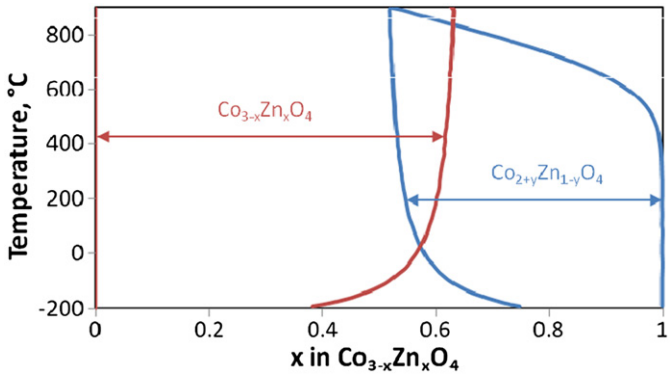

Fig. 1. Theoretical prediction of spinel ($Co_{2+y}Zn_{1-y}O_4$ and $Co_{3-x}Zn_xO_4$) stability regions (modified from Ref. [23]). The two regions overlap at high temperatures indicating the prediction of a complete solid solution.

The present work was undertaken to test our first-principles predictions regarding the Co_3O_4–Co_2ZnO_4 solid solution, in particular to provide experimental evidence for high temperature solid solution and to probe the thermodynamics of mixing in this system. To accomplish these tasks, we combined high temperature oxide melt solution calorimetric methods, differential scanning calorimetry, precise lattice parameter measurements (on quenched specimens), in situ electrical property measurements (conductivity, thermopower), and neutron and anomalous X-ray diffraction (on quenched specimens).

2. Experimental approach

2.1. Synthesis

The spinel phase(s) of the ZnO–Co_3O_4 system require synthesis at relatively low temperatures [27], so a low temperature aqueous processing route (decomposition of mixed nitrates) was chosen. This approach mixes cations at the atomic level in a much faster time frame than conventional solid state processing at low temperatures. The exact water contents of cobalt nitrate hexahydrate, 99.999%, and zinc nitrate hexahydrate, 99.998%, (both Alfa Aesar, Ward Hill, MA) were determined by measuring the weight loss of the nitrates upon heating to oxides in pre-dried crucibles. Then stoichiometric amounts of the Co and Zn nitrate hydrates were added to de-ionized water to yield nominal compositions $Co_{3-x}Zn_xO_4$ in the range $0 \le x \le 0.9$. The nitrate solutions were stirred for approximately 8 h at 40–50 °C to mix the cations and evaporate most of the water. Then the concentrated solutions/gels were heated to 390 °C in a box furnace in a fume hood to remove residual water and nitrogen oxides, resulting in the formation of cobalt zinc oxide powders. Powders were ground with an agate mortar and pestle, pressed uniaxially at 125 MPa into pellets, sintered in air and quenched in air. Three sintering options were employed to fabricate samples with different phase compositions and cation ratios: 60 h at 800 °C (spinel phase(s) for $0 \le x \le 0.72$ and spinel + wurtzite for $x > 0.72$ [23]), 134 h at 600 °C followed by 96 h at 570 °C (spinel phase(s) for $x = 0.9$), and 134 h at 650 °C followed by 96 h at 570 °C (spinel phase(s) for $x = 0.75$). During sintering, the pellets were nested inside three crucibles within a bed of sacrificial powder of the same composition, to minimize both contamination and cation volatilization.

2.2. Sample characterization: Composition, microstructure, lattice parameters

Wavelength-dispersive X-ray fluorescence (XRF) with a Bruker S4 Pioneer spectrometer (Bruker AXS Inc, Madison, WI) was employed to verify the compositions of selected samples. To further analyze compositions as well as compositional homogeneity, electron probe microanalysis (EPMA) was also performed on every sample (15 points per sample) with a Cameca SX-100 electron microprobe (Cameca Instruments, Inc., Madison, WI). Sample densities were determined from measured masses and geometries and were found to be approximately 50% of the theoretical density. To determine average grain sizes, fracture surfaces were observed using a S4800 FE-SEM (Hitachi High-Technologies, Schaumburg, IL), and the resulting micrographs were analyzed with the program ImageJ to measure and determine the average of the apparent grain diameters. Phase verification was performed by X-ray diffraction (XRD) with Cu K_α radiation over the 2θ range of 25–80° using a Scintag XDS2000 diffractometer (Scintag Inc, Cupertino, CA), a liquid N_2-cooled Ge

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