



Co₃O₄–Co₂ZnO₄ 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 Co₃O₄–Co₂ZnO₄ system, with a negligibly small mixing enthalpy. In this work we tested this prediction on bulk, large-grained specimens across the Co₃O₄–Co₂ZnO₄ 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 Co₃O₄ and Co₂ZnO₄ have essentially identical lattice parameters, this energetic destabilization must arise from factors other than the strain energy resulting from size mismatch. Changes in Co³⁺P

[20, 21, 22]. When $\Delta H_{\text{mixing}} < 0$, 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 $\text{Co}_3\text{O}_4\text{-Co}_2\text{ZnO}_4$ 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 $\text{Co}_2\text{ZnO}_4\text{-Co}_3\text{O}_4$ as a continuous solid solution in his very early phase diagram.

phase diagram (surp)-71ou37(loemperxe)-s88TD-d07mperxe)-s88TD-d07

detector (GLP-10195/07-S, EG&G ORTEC, Oak Ridge, TN), a step size of 0.02° , a dwell time of 1 s, a divergence slit of 2 mm, and a receiving slit of 0.5 mm. Lattice parameters were determined from subsequent XRD scans using Si powder (99.9995%, Sigma Aldrich) as an internal or external standard (both gave similar results) and the “whole pattern fitting” Rietveld refinement option (with fixed Si lattice parameter) in JADE 9 software. The lattice parameter of $\text{Co}_{2.3}\text{Zn}_{0.7}\text{O}_4$ was also determined by neutron diffraction as described below.

2.3. Oxide melt solution calorimetry

High temperature oxide melt solution calorimetry was performed using instruments and techniques described previously [29,30]. Sample pellets (5 mg) were dropped into a sodium molybdate ($3\text{Na}_2\text{O}-4\text{MoO}_3$) melt (20 g) at 700°C in a platinum crucible in a custom built Calvet microcalorimeter. The final state was dissolved ZnO and CoO. Calibration used the heat content of alumina.

2.4. Anomalous X-ray diffraction and neutron diffraction

The distribution of A, B, and B^0 cations in an $\text{A}_2\text{BO}_4-\text{A}_2\text{B}^0\text{O}_4$ spinel solid solution is one factor contributing to the thermodynamics of mixing. For example, the magnitude of the ideal configurational entropy resulting from cation distributions is proportional to the number of sites involved in cation exchange going from one end-member to the other. In this work, the fractions of anti-site defects (Zn on octahedral sites and Co on tetrahedral sites) in selected bulk samples (quenched from 800°C) were determined experimentally by anomalous X-ray diffraction (AXRD) on beamline 2-1 at the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory. For the spinel structure, certain diffraction peaks correspond to scattering from different sublattices of octahedrally and tetrahedrally coordinated cations. Specifically, the (2 2 2) reflection probes only octahedral sites (Oh sites), whereas the (4 2 2) reflection probes only tetrahedral sites (Td sites). The intensity of these reflections was measured as we varied the energy of the incident X-ray through the K absorption edges of Co and Zn. The shape of the intensity vs. energy plot near a given element's edge indicates how much of that element populates the relevant site. Qualitatively, a large minimum in (2 2 2) peak (or (4 2 2) peak) intensity near the edge signals a large fraction of the Oh sites (or Td sites) is occupied by this specific element. Quantitatively, by using composition as a constraint and the fraction of site occupancy as variables, we fit the energy-dependent integrated peak intensities to simulated AXRD results. This allows us to determine the fraction of Oh and Td sites occupied by Co and Zn, and therefore the complete cation arrangement for a known composition. Further details of this approach, as applied to thin films of Co_2ZnO_4 , are given in Ref. [31].

The neutron diffraction experiment was performed on the high-resolution BT-1 32 detector powder diffractometer at the NIST Center for Neutron Research (Gaithersburg, MD). A Cu (3 1 1) monochromator with a 90

3.2. Thermal analysis

In the differential scanning calorimetry measurements, shown in [Fig. 3](#), both $\text{Co}_{2.7}\text{Zn}_{0.3}\text{O}$

$\text{Co}_{2.7}\text{Zn}_{0.3}\text{O}_4$ might occur at lower temperature, with a smaller transition enthalpy (since the entropy would remain the same). If this transition is more spread out in temperature, it might not be detectable in the DSC scan. In this case the extent of spin disorder at the synthesis temperature would increase with zinc content. A lower temperature spin-unpairing transition for $\text{Co}^{3\text{P}}$ in Co_2ZnO_4 than in Co_3O_4 has previously been suggested by Cossee [12] on the basis of magnetic measurements, where high temperature deviations from Curie–Weiss behavior began at lower temperatures in Co_2ZnO_4 than in Co_3O_4 . (3) A less likely scenario, since it is at variance with previous reports [12,36], is that even at room temperature, zinc-containing spinels contain exclusively high spin $\text{Co}^{3\text{P}}$

The magnitude of the interaction parameter is much larger than that expected from consideration of strain energy arising from ionic size mismatch or lattice parameter change alone [37], since these differences are very small in the present system.² If we consider the mixing entropy of the spinel solid solution to arise from the mixing of divalent Co and Zn on tetrahedral sites, then the system would show regular solution behavior, with the free energy of mixing given by

$$\Delta G_{\text{mixing}} = Wx_1x_2 - RT[x_1 \ln x_1 + x_2 \ln x_2]$$

The critical temperature for exsolution (the top of the solvus or immiscibility dome) would be given by

$$T_c = W/2R = 1989 \pm 491\text{K} \text{ or } 1716 \pm 491\text{ }^\circ\text{C}$$

Furthermore, based on the calculated solvus for this model, a maximum of 9.4 mol% of each end-member would be soluble in the other end-member at the synthesis temperature of 800 °C (using the smallest possible value for W), which is at variance with the computational, microanalysis, and calorimetric observations.

The drop solution enthalpies could alternatively be interpreted to show a straight line segment separating two curved regions, as in the dashed curve of Fig. 5. Such an interpretation would be consistent with a small miscibility gap in the center of the Co₃O₄–Co₂ZnO₄ system, but not with the very large immiscibility implied by the regular solution model above. In contrast, the relatively high degree of homogeneity observed in the EPMA results argues in favor of complete solid solution rather than this small miscibility gap. Equilibrium electrical conductivity and thermopower measurements in the range 700–800 °C (see Table 1) also showed monotonic trends with composition, without discontinuities that might be expected to arise from phase separation at intermediate compositions. Further work is warranted to confirm the phase separation and solvus behavior at lower temperatures.

At 800 °C, the spinel phase does not extend all the way to Co₂ZnO₄ (Fig. 1); for this composition, a more cobalt-rich exists in equilibrium with a wurtzite (Co,Zn)O solid solution [23]. This retrograde solubility into the spinel does not imply any substantial destabilization in the spinel solid solution itself, but rather a more favorable free energy for the two-phase assemblage. We will analyze this equilibrium at both bulk and nano-scale in a future communication.

We conclude that the thermodynamics of mixing in this system is more complex than a simple regular solution and seek structural explanations for both the surprisingly large positive enthalpy of mixing and the observed large solid solubility.

3.5. Cation distributions, spin states, and thermodynamic complexity

The large positive heats of mixing in the present work appear to be at variance with the observed solid formation and exceed considerably the values calculated from first principles. One possible resolution would be the existence of additional

