

Chemical Homogeneity in Entropy-Stabilized Complex Metal Oxides

Ali Moballeg, Christina M. Rost, Jon-Paul Maria, Elizabeth C. Dickey

Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC, USA

Innovation in new mixtures of constituents can lead to discover exciting new materials with unexpected properties and revolutionary applications [1,2]. It is known, the Gibbs energy needs to be minimized, as the main requirement, to achieve a stable single phase compound. Conventional approach to minimize the total energy of system is searching for a large and negative enthalpy. However, in this work, we show that the phase stability can be reached where the configurational entropy is maximized with mixing as many diverse elements as possible.

In this work, five binary metal oxides, MgO, CaO, NiO, CuO, and ZnO, were chosen considering favored coordination, ionic radii, and diversity in crystal structures. An equimolar mixture of the constituent metal-oxide powders were mixed and pressed into ceramic pellets. The pellets were subsequently annealed in an air until equilibrium was achieved and then quenched to the room temperature. A series of samples was prepared and annealed at temperatures ranging from 700°C to 1100°C to monitor the phase evolution. In Figure 1, X-ray diffraction (XRD) patterns show two distinguishable phases, rocksalt and wurtzite, are present up to 700°C, but are fully converted to single-phase rocksalt between 850°C and 900°C. The multiphase state reappears when the fully uniform single-phase sample was reannealed at 700°C for 2 hours, which is consistent with an entropy-driven mechanism.

Microstructure and microchemistry of the phase-pure sample was studied by using a variety of electron microscopy and spectroscopy techniques. An Allied Multiprep polishing system was utilized to prepare a cross-sectional electron microscopy sample by wedge polishing technique [3]. An aberration corrected FEI Titan G2 60-300 kV S/TEM equipped with an X-FEG source and an advanced Super-XTM EDS detector system was used to analyze the structure and chemistry of the sample. The microscope was operated at 200 kV for high-angle annular dark-field (HAADF) scanning transmission electron microscope (STEM) imaging and energy dispersive x-ray spectroscopy (EDS) mapping with a convergence semi-angle of 15 mrad. STEM and EDS maps obtained at a variety of length scales reveal chemical and structural homogeneity of the cation mixture within the sample.

To further understand the phase stability and decomposition, the XRD studies (Fig. 1) are reproduced via in-situ heating experiments performed in Protochips AdoroTM heating holder in a JEOL 2010F operated at 200kV. The phase evolution mechanisms and kinetics are studied by a combination of energy-filtered TEM, HAADF imaging and electron diffraction

References:

- [1] Gludovatz, B. et al. *Science* 345, 1153–1158 (2014).
 [2] Gali, A. & George, E. P. *Intermetallics* 39, 74–78 (2013).
 [3] P. Voyles, J. Grazul, and D. Muller, *Ultramicroscopy* 96, 251 (2003).
 [4] This work is supported by ARO under contract W911NF-14-0285

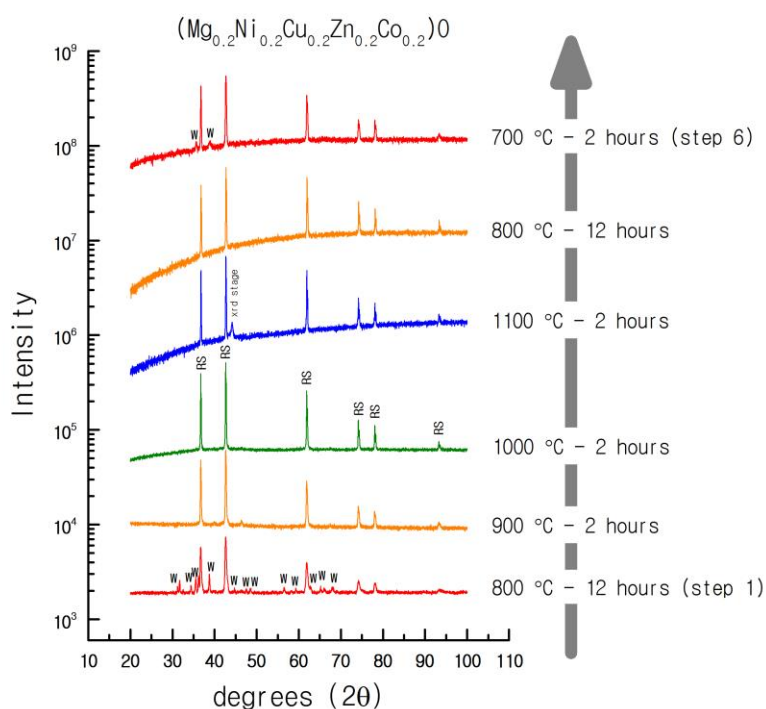


Figure 1. X-ray diffraction patterns of a single pellet during the annealing process. The temperature spanned a range from 700°C to 1100°C, in 50 °C increments.

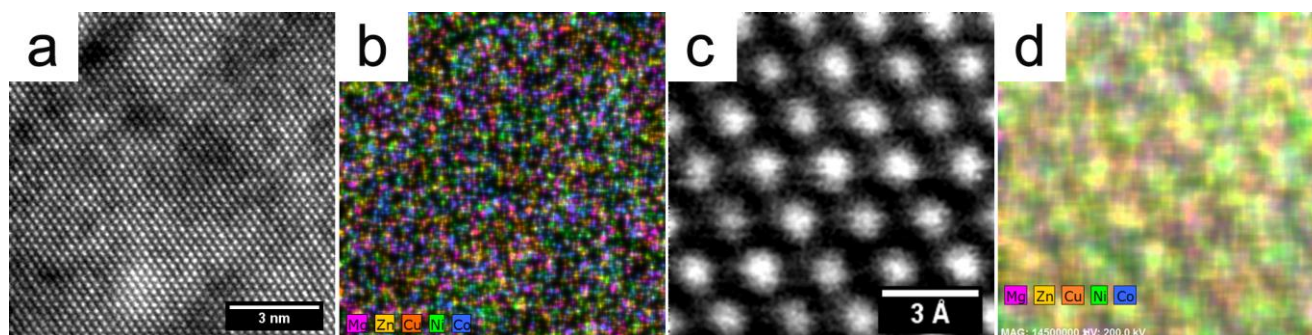


Figure 2. (a) Low magnification HAADF image of single phase rocksalt. (b) EDS map indicates uniform distribution of Zn, Ni, Cu, Mg and Co. (c) HAADF image at higher magnification taken along $\langle 110 \rangle$ direction and (d) EDS map at higher magnification shows distribution of Zn, Ni, Cu, Mg and Co at cation sublattice.