

Is Configurational Entropy the Main Stabilizing Term in Rock-Salt $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$ High-Entropy Oxide?

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In their paper “Entropy-Stabilized Oxides,” Rost *et al.* [1] reported the synthesis of a new $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$ phase (E1) with rock-salt structure as a test case for the concept of high entropy in oxides. Their claim is that “entropy predominates the thermodynamic landscape and drives a reversible solid-state transformation between a multiphase and single-phase state.” In the present study, we demonstrated that configurational entropy does not dominate the thermodynamic stability of the phase E1, using thermodynamic considerations and replicating the experiments in [1], but reducing appropriately the configurational entropy.

We showed that most of the experimental evidence supporting the entropic stabilization of E1 applies even when the configurational term was considerably reduced. In this respect, it should be noted that the five cations are not equivalent: Mg, Co and Ni form rock-salt oxides, whereas Cu and Zn oxides exhibit different crystal structures. The first cations are soluble among each other, with their relative stoichiometry being adjustable without altering significantly the behavior of the mixture. Conversely, CuO and ZnO present limited solubility in rock-salt oxides. Hence, when modifying the stoichiometry in order to adjust the configurational entropy, particular care must be taken to keep constant the stoichiometric ratio of CuO and ZnO, to avoid modification in the phase composition produced by the solubility equilibria.

To demonstrate the relevance of these considerations, we synthesized various solid solutions with different numbers of cations, but under the constraint that Cu and Zn molar fractions were kept equal to 0.2, the same as in the E1 phase. Fig. 1 reports the results for binary $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}$, three-cation $\text{Ni}_{0.6}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$ and four-cation $\text{Ni}_{0.4}\text{Co}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$, compared to E1. The syntheses were performed by solid-state reaction of stoichiometric mixtures of the parent oxides (Aldrich, >99.9%), firing in air at 1000 °C for 6 days, with intermediate grinding and final quenching to room temperature (RT). All these solid solutions – not only E1 – were obtained as single-phase rock salt with homogeneous cation distribution down to the nanometer scale. This applied even to binary $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}$.

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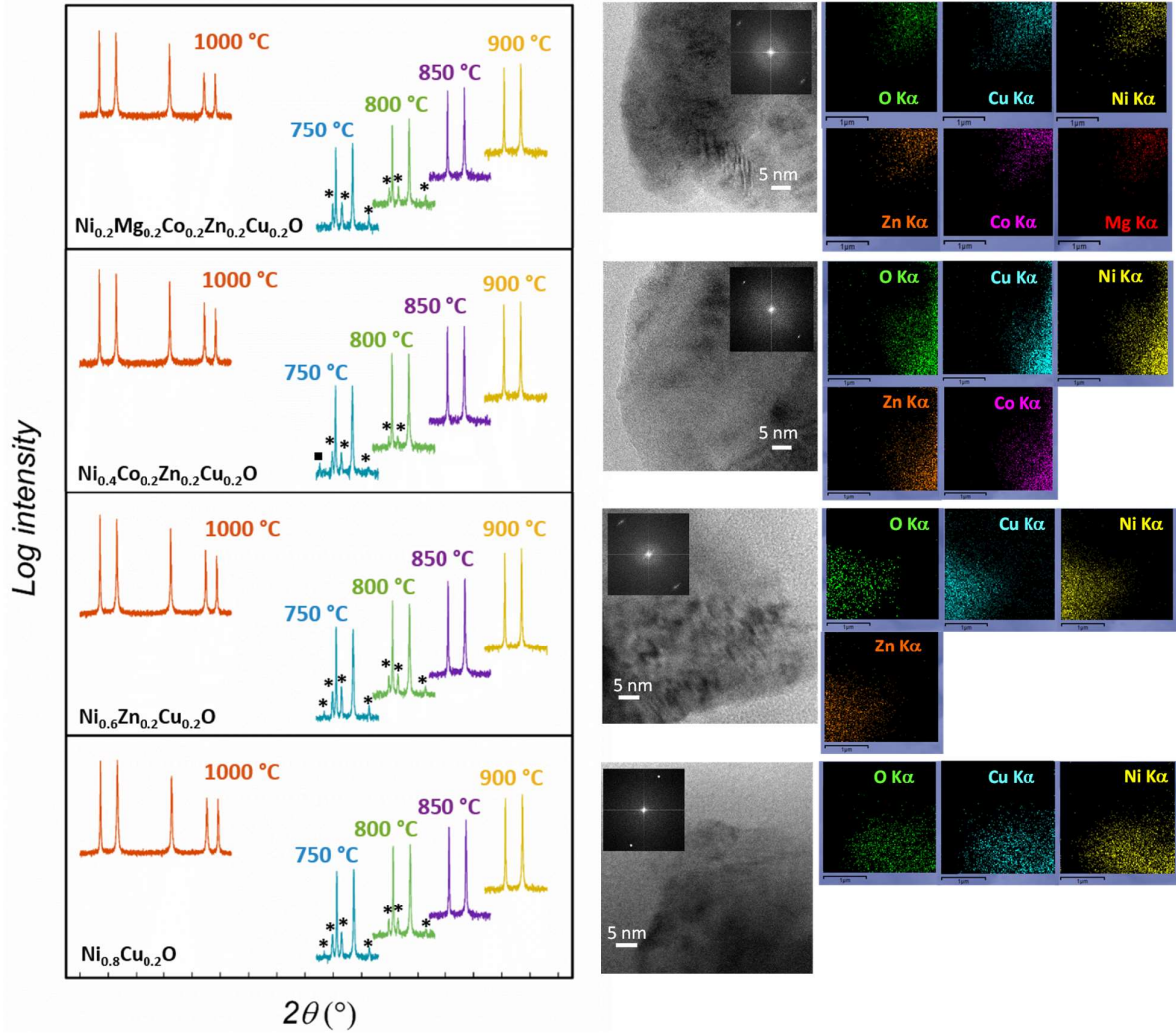


Figure 1. Left: powder diffraction patterns for the five-, four-, three- and two-component solid solutions quenched from 1000 °C to RT (red lines). The solid solutions were heated to 900, 850, 800 and 750 °C, and quenched to RT. The corresponding powder diffraction patterns are shown as yellow, violet, green and cyan lines, respectively. * and ■ mark the diffraction peaks of CuO tenorite and spinel phases, respectively. The right panel shows high-resolution transmission electron microscopy (TEM) with corresponding fast Fourier Transform (FFT) and energy-dispersive spectroscopy (EDS) maps for all the elements present. Instrumental magnification: 400 000 \times .

This result is in contrast with the conclusions drawn by Rost *et al.*, who suggested that only the composition E1 can produce a homogeneous solid solution down to 875 °C. This contradiction must be discussed on the basis of thermodynamic considerations.

Following the same argument presented by Rost *et al.* [1], for 1 mole of E1 solid solution containing 0.2 moles of CuO and ZnO, the destabilizing term is $0.2\Delta G_{\text{ZnO}}^{\text{wurtzite} \rightarrow \text{HEO}} + 0.2\Delta G_{\text{CuO}}^{\text{tenorite} \rightarrow \text{HEO}} = 9.4 \text{ kJ mol}^{-1}$, as the transition free energies of CuO and ZnO from their regular tenorite and wurtzite forms to rock salt are the following [2, 3]:

$$\Delta G_{\text{CuO}}^{\text{tenorite} \rightarrow \text{halite}} = 25 \text{ kJ mol}^{-1}$$

$$\Delta G_{\text{ZnO}}^{\text{wurtzite} \rightarrow \text{halite}} = 22 \text{ kJ mol}^{-1}$$

The configurational entropy is given by $S_{\text{Config}} = -R \sum_{i=1}^n \chi_i \ln \chi_i$, where χ_i is the molar fraction of the i -th component. The values of configurational entropy of the compositions that we investigated are reported in Table 1. At the temperature of synthesis, i.e., 1000 °C, TS_{Config} nearly doubled the value required to transform these oxides into rock salt. This implies that, at 1000 °C, the E1 composition is as stable as that of a single-phase solid solution, and the three- and four-component compounds with fraction of Cu and Zn equal to 0.2 should be stable as well. Even the binary $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}$ at 1000 °C showed a TS_{Config} equal to 5.3 kJ mol⁻¹, which is greater than $0.2\Delta G_{\text{CuO}}^{\text{tenorite} \rightarrow \text{HEO}} = 5.0$ kJ mol⁻¹. In fact, all these solid solutions do form at this temperature.

N	χ_{CuO}	χ_2	χ_3	χ_4	χ_5	S_{Config}	TS_{Config} (kJ mol ⁻¹) at 1000 °C	TS_{Config} (kJ mol ⁻¹) at 850 °C	TS_{Config} (kJ mol ⁻¹) at 800 °C	$\Delta G_{\text{CuO, ZnO}}^{\text{phase transition}}$ (kJ mol ⁻¹)
2	0.2	0.8				0.5R	5.3	4.7	4.5	5.0
3	0.2	0.2	0.6			0.95R	10.1	8.9	8.5	9.4
4	0.2	0.2	0.2	0.4		1.33R	14.1	12.4	11.9	9.4
5	0.2	0.2	0.2	0.2	0.2	1.61R	17.1	15.1	14.4	9.4

Table 1. Thermodynamic properties of the solid solutions reported in this work. χ_i is the molar fraction of the i -th component, N is the total number of components, and S_{Config} is the corresponding configurational entropy. Values of the product TS_{Config} are given at some selected temperatures and the overall $\Delta G_{\text{CuO, ZnO}}^{\text{phase transition}}$ of the structural transitions from tenorite and wurtzite to rock salt is reported in the last column.

To test the stability of these solid solutions at lower temperatures, we annealed them at 750, 800, 850 and 900 °C for 2 h and then quenched them (Fig. 1). All compositions showed segregation of tenorite CuO at $T < 850$ °C, while for $T \geq 850$ °C a single phase was retained. The TS_{Config} terms at 800 and 850 °C for all the compositions are reported in Table 1. At both temperatures, for the two- and three-component oxides, these terms were lower than $\Delta G_{\text{CuO, ZnO}}^{\text{phase transition}}$, while for the four- and five-component oxides, they were higher than $\Delta G_{\text{CuO, ZnO}}^{\text{phase transition}}$. Thus, based on configurational entropy only, the solid solutions with two or three cations should not exist at 800 and 850 °C, while they should exist at both temperatures for the phases containing four or five cations. The presence of an additional impurity phase with the spinel structure (probably Co_3O_4) which is found for the 4 component system at 750 °C is irrelevant for the above discussion as this phase disappears at $T = 800$ °C. It is therefore concluded that the stability of these solid solutions cannot be discussed only in term of configurational entropy, and that additional terms must contribute.

Let us now consider the role of solubility equilibria, starting from the simplest case, the binary $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}$. The equilibrium phase diagram for this system shows that, at 1000 °C, this composition corresponds to a stable solid solution. The solubility of CuO in NiO drops rapidly with temperature [4]. However, Fig. 1 shows that a homogeneous solid solution in a metastable form, could be obtained at room temperature upon quenching. When this solid solution was annealed at 750 °C, CuO segregated. Further heating at 1000 °C restored the solid solution. This reversible behavior, similar to that reported by Rost *et al.* for E1 composition, can easily be explained in this case as a reversible transition between monophasic and biphasic regions of the phase diagram. The solubility limit for this composition is indeed around 800 °C [4]. We suggest that a similar argument can explain the behavior of the other, more complex, compositions, although the details of the phase equilibria in multicomponent systems are largely unknown. It is known, however, that all binaries within the MgCoNiCuZn/O system exhibit at 1000 °C a reciprocal solubility above 20%. A stable rock-salt solid solution for a molar fraction of CuO and NiO below 0.2 at 1000 °C in the system CuO-MgO-NiO has also been reported [5].

Further indications on the stability of the rock-salt solid solutions were obtained by cooling all the compositions from 1000 °C to room temperature at a rate of 30 °C/min. This rate was fast enough to inhibit CuO segregation, but slow enough to allow structural relaxations. The diffraction patterns at the end of the cooling procedure are shown in Fig. 2. E1 shows a considerable broadening of all the reflections, except for the 111 family. This broadening is consistent with a tetragonal distortion of the rock-salt structure [6, 7]. The broadening decreases significantly by decreasing the number of components, and therefore the configurational entropy. In other words, decreasing the configurational entropy decreases the tendency of the rock-salt structure to distort from the perfect cubic symmetry. This is a clear indication that the configurational entropy does not play the simple role of stabilizing the cubic rock-salt structure.

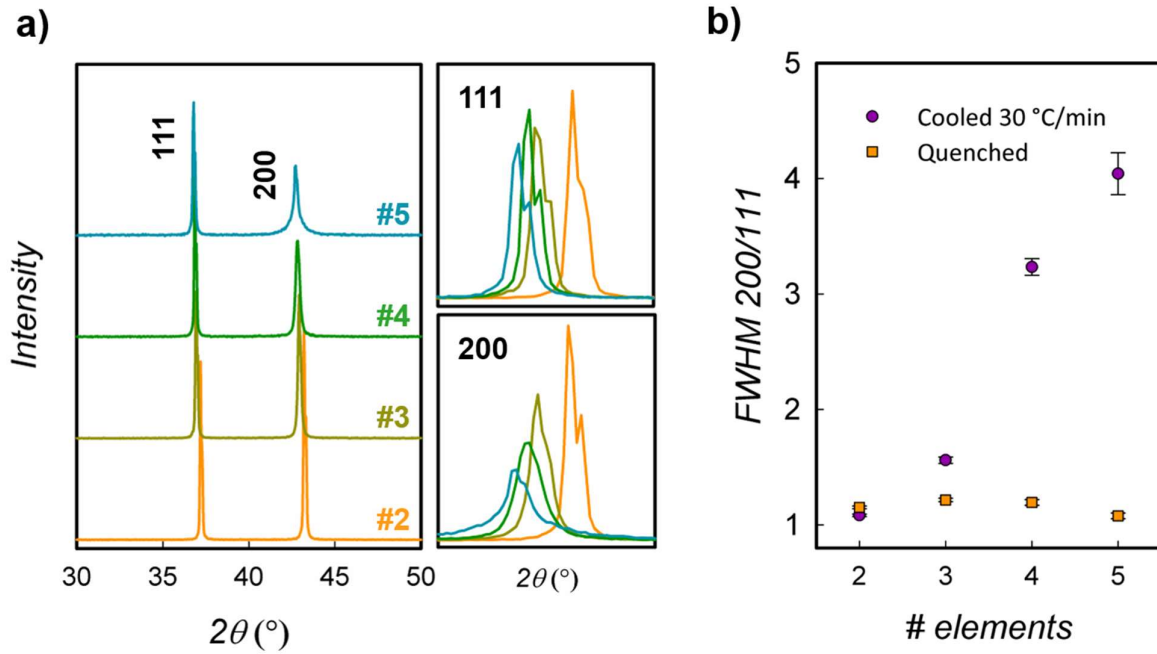


Figure 2. a) Powder diffraction patterns for the five- (cyan), four- (green), three- (dark yellow) and two- (orange) component solid solutions rapidly cooled (30 °C/min) from 1000 °C to RT. The 111 and 200 reflections are magnified to illustrate better the different broadenings. This is demonstrated in b), where the ratio of the full widths at half maximum (FWHM) for the two reflections are plotted as a function of the number of components for the quenched (orange squares) and rapidly cooled (violet circles) samples.

In summary, we have shown that the synthesis of homogeneous rock-salt solid solutions is possible in the MgCoNiCuZn/O system with two, three or four components, provided that the molar fractions of CuO and ZnO are kept below a limiting value close to 0.2, which is dictated by the high-temperature solubility equilibria. These solid solutions behave in a quasi-identical way to E1 $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$ phase when quenched at room temperature and then annealed at intermediate temperatures. Also, the tendency of the rock-salt structure to distort from the cubic symmetry decreases with the configurational entropy. All this evidence points toward the fact that, although the contribution of configurational entropy is undoubtedly present and significant, its role towards the stability of $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$ is limited. Configurational entropy is surely a robust and fruitful approach for controlling the stability of complex oxides, but its role must be carefully analyzed in view of the solubility equilibria in the system under consideration.

References

- [1] Rost, C., Sachet, E., Borman, T. Moballegh, A. Elizabeth C. Dickey, E. C., Hou, Dong, Jones, J. L., Curtarolo, S. & Maria, J.-P. Entropy-stabilized Oxides *Nat. Commun.* **6**, 8485 (2015).
- [2] Davies, P. & Navrotsky, A. Thermodynamics of solid solution formation in NiO-MgO and NiO-ZnO. *J. Solid State Chem.* **38**, 264–276 (1981).
- [3] Bularzik, J., Davies, P. & Navrotsky, A. Thermodynamics of solid-solution formation in NiO-CuO. *J. Am. Ceram. Soc.* **69**, 453–457 (1986).
- [4] Eric, H. and Timucin, M. Equilibrium Relations in the System Nickel Oxide-Copper Oxide *Metall. Trans. B* **10**, 561-563 (1979).
- [5] Davies, P. K. An X-Ray Powder Diffraction Study of Phases in the System CuO-NiO-MgO at 1000 °C *J. Electrochem. Soc.* **129**, 31C (1982).
- [6] Fracchia, M., Ghigna, P., Pozzi, T., Anselmi Tamburini, U., Colombo, V., Braglia, L. & Torelli, P. Stabilization by Configurational Entropy of the Cu(II) Active Site during CO Oxidation on $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}$ *J. Phys. Chem. Lett.* **11**, 3589-3593 (2020).
- [7] Berardan, D., Meena, A. K., Franger, S., Herrero, C. & Dragoe, N. Controlled Jahn-Teller distortion in (MgCoNiCuZn)O-based high entropy oxides. *J. Alloys Compd.* **704**, 693– 700 (2017).