Stability and Compressibility of Cation-Doped High-Entropy Oxide MgCoNiCuZnO$_5$

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ABSTRACT: High-entropy oxides (HEOx) are multicomponent (≥5) complex oxides that possess material properties and functions unexpected from their constituent simple oxides. Previous studies demonstrated that a cation-doped HEOx, MgCoNiCuZnO$_5$, shows good catalytic activity, excellent ionic conductivity, and high energy storage. The structural and mechanical stabilities of materials are pivotal to their applications. However, how temperature and pressure influence the structural stability of cation-doped HEOx and how doping affects the mechanical properties are yet to be understood. In this work, we investigated the structural stabilities of undoped and Li/Mn-doped MgCoNiCuZnO$_5$ in heating or under compression using in situ synchrotron X-ray diffraction (XRD), and determined their elastic moduli using high-pressure XRD. Our results show that the HEOx compounds are structurally stable at temperatures up to ~450 °C or at pressures up to ~50 GPa, and that Li/Mn doping makes the HEOx more compressible. Our molecular static (MS) calculations predicted that the formation reaction of a HEOx is endothermic, consistent with the fact that a single-phase HEOx can only be produced at high temperatures. The MS calculations also revealed that the observed doping-induced elastic softening stems from the introduction of the Li–O/Mn–O ionic bonds in the HEOx compound, which are weaker than other cation–oxygen ionic bonds in the undoped HEOx. These findings will be indispensable to engineer HEOx materials for use in ion batteries, catalysis, and other fields.

1. INTRODUCTION

High-entropy oxides (HEOx) are a new class of multi-component (usually ≥ 5) complex oxides that possess material properties different from the simple combination of their constituent simple oxides. The first HEOx, MgCoNiCuZnO$_5$, was synthesized through high-temperature (HT) solid-state reactions in 2015.‡ Later studies show that MgCoNiCuZnO$_5$ can generate high capacity in lithium battery energy storage;§ Pt-doped MgCoNiCuZnO$_5$ can produce stable and efficient catalytic oxidation of carbon monoxide;³ Li/Na-doped MgCoNiCuZnO$_5$ has very high ionic mobility and electrical conductivity;⁴ and a similar compound, (FeMgCoNi)O$_{1.2}$, exhibits high efficiency in thermochemical water splitting.⁵ Recently, other kinds of HEOx compounds with different chemical compositions and perovskites structures;⁶,⁷ fluorite structures,⁸–¹⁰ and spinel structures¹¹ have been synthesized. With these diversities in the structures and chemical compositions, HEOx compounds are promising in contributing to clean and renewable energy.

The structural stability of HEOx as a function of temperature (T) and pressure (P) is critical to their applications. For instance, in Li-doped HEOx ion batteries, in cycles of charging and discharging, the system enthalpy and volume change repeatedly, which can cause temperature and pressure fluctuations in the cell, making the battery system unstable and even malfunction. Thus, it is necessary to optimize the cell design and fabrication of the whole battery system with the knowledge of the stability and mechanical properties of the HEOx materials. However, a comprehensive understanding of how T and P affect the stability of HEOx is lacking. How doping affects the mechanical properties of HEOx is also unknown. Thus, in this work, we developed different routes to synthesize Li- and Mn-doped MgCoNiCuZnO$_5$ considering that Mn-doping can enhance the stability and performance of lithium-ion battery materials.¹² Then, using in situ synchrotron X-ray diffraction (XRD), we studied their thermal stability during heating and mechanical stability under compression. These experiments enable us to identify the effects of doping, temperature, and pressure on the structural and mechanical properties of undoped and Li/Mn-doped MgCoNiCuZnO$_5$. Further, molecular simulations were used to probe the intrinsic mechanism accounting for the
observed structure–property relationship. The findings from this work will provide essential knowledge for developing novel applications of the new materials.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Magnesium oxide (MgO, 99.9% wt), cobalt oxide (CoO, AR), nickel oxide (NiO, 99.5% wt), cupric oxide (CuO, 99.5% wt), and zinc oxide (ZnO, 99.9% wt) were purchased from Macklin Biochem. Co. Ltd. (Shanghai). Manganese monoxide (MnO, 99% wt) and lithium carbonate (Li2CO3, 99.9% wt) were purchased from Aladdin Bio-Chem. Tech. Co., Ltd. (Shanghai). All chemicals were used directly without further purification.

2.2. Sample Preparations. 2.2.1. Preparation of Undoped MgCoNiCuZnO5 (u-HEOx). Following ref 1, undoped MgCoNiCuZnO5 (that can also be written as (Mg0.92Co0.2Ni0.2Cu0.3Zn0.2)O) was prepared, which would produce a Li-doped HEOx with a nominal formula of (Mg,Co,Ni,Cu,Zn)0.95Li0.05O0.975 if there is no Li loss. The prepared values were well-mixed powders with a molar ratio of MgO/CoO/NiO/CuO/ZnO were mixed well in an agate mortar and then ground for 6 h for attaining uniform dispersion of the constituent oxides among each other. The well-mixed powders were then cold-compressed into a thin disk ~10 mm in diameter and ~1 mm in thickness under a pressure of ~300 MPa. The disk was then heated at 1100 °C in air for 3 h in a tube furnace, followed by quenching to room temperature (RT) in air.

2.2.2. Preparation of Li-Doped MgCoNiCuZnO5 (Li-HEOx). Bérard et al. doped Li+ in MgCoNiCuZnO5 using Li2CO3 as the lithium source via solid-state reaction at 1000 °C.13 When synthesizing Li-doped HEOx at such a high temperature using this one-step route, Li in the raw mixture may volatilize due to the low melting point of Li2CO3 (~723 °C).14 This might cause deviation of the lithium content from the desired stoichiometry. Therefore, in this work, we proposed a two-step synthesis route in an attempt to reduce the lithium loss. First, a stoichiometric powder mixture with a molar ratio of MgO/CoO/NiO/CuO/ZnO/Li2CO3 = 1:1:1:1:1:0.13 was prepared, which would cause deviation of the lithium content from the desired stoichiometry. Therefore, in this work, we proposed a two-step synthesis route in an attempt to reduce the lithium loss. First, a powder mixture with a molar ratio of MgO/CoO/NiO/CuO/ZnO/Li2CO3 = 1:1:1:1:1:0.13 was prepared, which would produce a Li-doped HEOx with a nominal formula of (MgCoNiCuZn)0.95Li0.05O2 if there is no Li loss. The mixture was cold-compressed and heated at 720 °C in air for 6 h to introduce partial reaction of Li2O with other oxide components, which was formed from the gradual decomposition of Li2CO3 around its melting point. Then, the sample was heated at 1100 °C in air for 3 h, followed by quenching to room temperature in air.

2.2.3. Preparation of Mn-Doped MgCoNiCuZnO5 (Mn-HEOx). In the previous work,15 ions of Sc, Cr, Sb, Ge, and Sn were successfully doped in MgCoNiCuZnO5 while maintaining a stable rocksalt structure. Doping of Mn in HEOx has not been reported so far. In this work, we used following method to dope Mn in MgCoNiCuZnO5. A powder mixture of MgO, CoO, NiO, CuO, ZnO, and MnO in the molar ratio of 1:1:1:1:1:0.26 was ground and cold-compressed to form disks, as described above. Then, three of the disks were heat-treated in air for 3 h at 1100, 1300, and 1500 °C, respectively, followed by quenching to room temperature in air. The prepared samples have a nominal formula of (Mg0.93Co0.2Ni0.2Cu0.3Zn0.15Mn0.01)O.

2.3. Characterization of Sample Structures and Elemental Distributions. XRD patterns of synthesized samples were collected using a PANalytical Empyrean X-ray diffractometer operated at 40 kV and 40 mA, with a Cu Kα radiation (X-ray wavelength 1.5406 Å). Scanning electron microscopy (SEM) image of the samples were taken using a FEI Versa 3D dual-beam FIB/SEM operated at 25 kV. Elemental mapping of the samples was carried out using the energy-dispersive X-ray spectroscopy (EDXS) of the SEM. All of the samples were characterized by XRD for phase identifications, by SEM for morphology examinations, and by EDXS for elemental mapping.6,8,16 Lattice parameters of the samples at room temperature were determined accurately from the XRD data of the samples with Si as an internal 20 calibrant. Transmission electron microscopy (TEM) analyses of the samples were conducted using a JEOL 2100 TEM instrument with a general double-tilt sample holder. As the samples were sensitive to electron beam irradiation, TEM images were taken using a medium beam spot size (no. 3) and at a small current density of 19.2 μA cm−2. These operating parameters were helpful in controlling the radiation damage of the samples. Selected area electron diffraction (SAED) patterns were collected with a SAED aperture of 15 μm.

2.4. Determination of Lithium Contents in Li-Doped HEOx Samples. Due to the possible volatilization of lithium at high temperature, the actual Li content of a Li-doped sample may deviate from the prepared value. Thus, the Li contents of Li-HEOx samples prepared from the one-step and two-step routes were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES; Optima 5300DV). A sample of ~0.1 g was dissolved in a glass beaker using a hydrochloric acid while heating on a stove and then transferred to a measuring flask. The solution was diluted using a 1% nitric acid to form a 50 mL solution. This solution was then used to perform the ICP-AES measurement for the Li concentration at an optimal AES wavelength of 670.784 nm. The needed calibration curve was generated from Li standard solutions containing 1, 5, and 10 ppm Li. The precision of the determined Li concentration is ~95%.

2.5. In Situ High-Temperature X-ray Diffraction. In situ high-temperature (HT) XRD was conducted at the micro-XRD beamline station 12.3.2 of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory. All of the HEOx samples were ground to fine powders and then pressed into thin disks ~5 mm in diameter and ~1 mm in thickness. The disks were glued to the heating surface of an Anton Paar DHS 900 heating stage mounted on the sample stage of the beamline station. Before heating, ambient XRD patterns of the samples were collected at room temperature and in air. In situ heating XRD experiments were conducted in a flowing nitrogen gas, while the heating stage was enclosed by a graphite dome lid. This maintained the thermal stability of the samples and prevented direct thermal irradiation to the X-ray detector. The samples were heated from room temperature to ~450 °C at a step of 50 °C and with a stay time of ~0.5 h at each temperature.

A focused monochromatic X-ray beam (energy 10 keV) ~10 μm in diameter was used to scan a chosen sample area of ~200 × 200 μm2. The diffracted X-ray beams were recorded using a DECTRIS Pilatus 1 M hybrid pixel array detector. The sample-to-detector distance was calibrated using an Al2O3 standard powder sample. The collected diffraction images were processed using the software XMAS,17 yielding the numerical intensity vs diffraction angle data. The XRD patterns from the whole scanning area were averaged to yield an average XRD pattern of the sample at a given temperature.
Table 1. Lattice Parameters, Bulk Moduli, and Lattice Energies of Simple and High-Entropy Oxides Obtained from Molecular Static Calculations

<table>
<thead>
<tr>
<th>oxide</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β or γ (°)</th>
<th>( B_0 ) (GPa) calc</th>
<th>( B_0 ) (GPa) exp/Lit.</th>
<th>( E_{\text{in}} ) (kJ mol(^{-1}))</th>
<th>( \Delta H ) (0 K) (kJ mol(^{-1}))</th>
<th>( \text{ref for } B_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO (cubic)</td>
<td>4.245</td>
<td></td>
<td></td>
<td></td>
<td>194.7</td>
<td>190.5</td>
<td>3859.01</td>
<td>27</td>
<td></td>
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<tr>
<td>CuO (mono.)</td>
<td>5.138</td>
<td>3.730</td>
<td>5.138</td>
<td>86.9</td>
<td>110.0</td>
<td>73.9</td>
<td>3669.18</td>
<td>28</td>
<td></td>
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<tr>
<td>CuO (cubic)</td>
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<td></td>
<td></td>
<td>148.6</td>
<td></td>
<td>3665.60</td>
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<tr>
<td>Li(_2)O (cubic)</td>
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<td>103.6</td>
<td>93.6</td>
<td>2932.00</td>
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<td></td>
<td></td>
<td>156.2</td>
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<td>158.8</td>
<td>156−178</td>
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<td>202.9</td>
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<td>ZnO (hex.)</td>
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<td>3.268</td>
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<td>143.5</td>
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<td>183</td>
<td>3842.57</td>
<td>34</td>
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<td></td>
<td></td>
<td></td>
<td>185.8</td>
<td>187.7</td>
<td>3929.83</td>
<td>0.07 this work</td>
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<tr>
<td>Li-HEOx (cubic)</td>
<td>4.235</td>
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<td>176.8</td>
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<tr>
<td>Li-HEOx (cubic; one-step)</td>
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<td></td>
<td></td>
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<td></td>
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<td>72.60 this work</td>
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<td></td>
<td>184.8</td>
<td>162.2</td>
<td>3916.26</td>
<td>3.89 this work</td>
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<tr>
<td>Mn-HEOx (cubic)</td>
<td>4.237</td>
<td></td>
<td></td>
<td></td>
<td>177.9</td>
<td></td>
<td>3929.83</td>
<td>6.21 this work</td>
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\( \text{COD (ref 35) } \#1533087. \text{ COD } \#9015924. \text{ COD } \#4121515. \text{ COD } \#9000499. \text{ COD } \#9005946. \text{ COD } \#4320487. \text{ COD } \#2107059. \text{ COD } \#1534836. \text{ Expt. from present work. } \text{ Molar fraction weighted-sum of MS-derived } B_0 \text{ of simple oxides (cubic). } \text{ΔH (0 K) from most stable simple oxides. } \text{Values for Li-HEOx were highly overestimated due to treating O vacancy as randomly distributed in the anion sublattice in the MS calculations (see text).} \)

2.6. In Situ High-Pressure X-ray Diffraction. In situ high-pressure (HP) XRD experiments were performed at the high-pressure beamline 12.2.2. of ALS. The pressure on a sample was generated using a diamond anvil cell (DAC) with an anvil culet size of ~300 μm. A T301 stainless steel gasket with a thickness of ~250 μm was preindented to ~30 μm in thickness and then drilled through its center using laser ablation, forming a hole of ~120 μm in diameter to serve as the sample chamber. A small amount of fine sample powders was loaded into the sample chamber together with 1–3 small ruby balls as the pressure calibrant for measuring the pressure using the fluorescence method. Neon or a methanol–ethanol mixture (volume ratio of 4:1) was used as the pressure-transmitting medium. The DAC loaded with the sample was then mounted on the sample stage of the beamline station for HP-XRD.

HP-XRD patterns were collected at a beam energy of 25 keV (wavelength 0.4959 Å) with a beam size of ~15 μm. A MAR345 image plate was used to record the diffraction images, which were then converted to the numerical intensity vs 2θ data using the Fit2d or Dioptas program. The sample-to-detector distance was calibrated using a CeO\(_2\) standard sample. The lattice parameters of the HEOx samples at different pressures were derived from Rietveld fitting of the XRD patterns using the GSAS + EXPGUI software.

3. COMPUTATIONAL SECTION
To explore the mechanism underlying the doping effect on the elasticity of HEOx, we used molecular static (MS) calculations to calculate the bulk moduli of u-HEOx, Li-HEOx, Mn-HEOx, and their constituent simple oxides. In the calculations, the interaction potential (\( u_{ij} \)) between atoms \( i \) and \( j \) was described by the Buckingham potential function

\[
 u_{ij} = \frac{z_i z_j}{r_{ij}} + A_{ij} \exp \left( -\frac{r_{ij}}{r_0} \right) - \frac{c_{ij}}{r_{ij}^6}
\]

The first term on the right-hand side (rhs) of eq 1 represents the electrostatic interaction between atoms \( i \) and \( j \) and the rest of the rhs represent the short-range (repulsive and van der Waals) interactions between them. In the above equation, \( z_i \) and \( z_j \) are, respectively, the electric charges of atoms \( i \) and \( j \); \( r_{ij} \) is the distance between them; and \( A_{ij}, r_0 \), and \( c_{ij} \) are the potential function parameters pertinent to the atomic pair of \( i \) and \( j \).

In our MS calculations, the cations concerned include Mg\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Mn\(^{2+}\), and Li\(^{+}\), and the only anion is \( \text{O}^{2-} \). Following previous work, all cations are modeled as simple point charges, while the oxygen anion \( \text{O}^{2-} \) is modeled using the shell model. That is, O atom is treated as a core spring, accounting for the ionic polarization induced under a
local electric field. The potential function parameters for the atomic pairs Co–O, Ni–O, Zn–O, and O–O were taken from those derived by Lewis et al. (Table 1 of ref 21), as compiled in the force field library of the General Utility Lattice Program (GULP). 23 For the atomic pairs Mg–O, Cu–O, Mn–O, and Li–O, we derived the potential function parameters using empirical fitting to available material properties using the program GULP (v.5.1) 23 (see Table S1 in the Supporting Information (SI)). GULP was again used to conduct the MS calculations. First, the crystal structure of a concerned oxide (including MgO, CoO, NiO, CuO, ZnO, MnO, Li2O, u-HEOx, Li-HEOx, and Mn-HEOx) was optimized. Then, the bulk modulus and the lattice energy (adopting definition in ref 14) of the compound were computed.

4. RESULTS AND DISCUSSION

4.1. Characterization of Undoped MgCoNiCuZnO5 (u-HEOx). XRD, SEM/EDXS, and TEM/SAED were used to characterize the synthesized sample (Figure 1). The XRD pattern of u-HEOx in Figure 1a shows that the synthesized sample is crystalline and has a rocksalt structure, consistent with a previous work. 1 The Rietveld fitting 24 of the XRD pattern (with an internal standard Si; Figure 2) using the perovskite phase of MgO (space group Fm̅3m) as the structure model gave a lattice parameter of \( a = 4.238 \pm 0.003 \) Å. The SEM image (Figure 1b) shows that the sample contains lots of grains with sizes varying from submicrons to \( \sim 25 \) μm, with a typical grain size of \( \sim 10 \) μm. The EDXS elemental mapping (Figures 1c, and S1, S2 in the SI at a relatively high resolution) shows that the constituent elements are uniformly distributed in the sample, and hence no phase segregations are present. The SAED pattern (Figure 1d) shows that the very fine particles produced by grinding are still crystalline. Since the sample is crystalline with very fine sizes (Figure 1d) to bulk sizes (Figure 1a), the SEM image in Figure 1b unveils the polycrystalline nature of the synthesized sample.

4.2. Characterization of Li-Doped MgCoNiCuZnO5 (Li-HEOx). The ICP-AES experimental results show that the lithium contents (mass percentages) in the one-step and two-step HEOx samples are, respectively, 0.43 and 0.69%. These data confirm that the two-step method indeed produced less lithium loss than the one-step one. Based on these Li contents, the nominal formula of the one-step Li-HEOx is \((Mg,Co,Ni,Cu,Zn)_{0.95}Li_{0.05}O_{0.975}\) and that of the two-step Li-HEOx is \((Mg,Co,Ni,Cu,Zn)_{0.93}Li_{0.07}O_{0.965}\). The first formula coincides with the ideal one without the lithium loss (see above) possibly due to a slight overestimation of the Li content by the ICP-AES measurements.

XRD patterns of the Li-HEOx samples synthesized from the two different routes are shown in Figure 3a. It is seen that they are similar to that of u-HEOx, indicating that Li has been doped into the cation sublattice of the rocksalt structure, in agreement with the results from previous works. 5,13 From the Rietveld fitting of the XRD patterns using Si as the internal 2θ calibrant (Figure 2), the values of lattice parameter \( a \) of the samples prepared from the one-step and two-step routes are, respectively, \(4.233 \pm 0.003 \) and \(4.218 \pm 0.007 \) Å. Both values are smaller than that of undoped HEOx (4.238 Å; see above).

The ionic radius in an octahedra coordination of Li⁺ (0.90 Å) 25 is close to those of other divalent cations: Mg²⁺ 0.86 Å, Co²⁺ 0.79 Å (low spin) or 0.885 Å (high spin), Ni²⁺ 0.83 Å, Cu²⁺ 0.87 Å, and Zn²⁺ 0.88 Å. 25 Thus, substitution of those divalent cations by Li⁺ ions is feasible. However, substitution of one divalent cation by one monovalent Li⁺ cation produces...
one negative charge around the cation site. Two of such substitutions then would require the creation of one oxygen vacancy (\( V_0 \) that carries +2 charges) in the anion sublattice to reach charge neutrality in the whole crystal. Thus, considering the requirement of charge neutrality and possible Li loss at a high temperature, the nominal formula of the synthesized Li-doped HEOx should be written as \( (\text{Mg,Co,Ni,}-\text{Cu,Zn})_{0.95}\text{Li}_{0.05}-x\text{O}_{0.975-x} \), where \( x \) represents the Li loss due to volatilization. According to ref 26, charged oxygen vacancies can cause lattice contraction of original undoped HEOx and hence the values of the lattice parameter \( a \) of Li-doped HEOx should be smaller than those of the former, explaining our above results. The value of \( a \) of the two-step Li-HEOx is smaller than that of the one-step Li-HEOx, indicating that more Li has been doped into the cation sublattice in the former than in the latter, consistent with the ICP-AES results (see above).

Figure 3b–d show, respectively, the SEM image, EDXS element mapping, and TEM image/SAED pattern of the two-step Li-HEOx sample. Additional EDXS elemental mapping at a relatively high resolution is shown in Figure S3 (SI). All these data shown that, similar to the u-HEOx, the prepared sample is polycrystalline and the constituent elements are uniformly distributed in the sample.

4.3. Characterization of Mn-Doped MgCoNiCuZnO\(_5\) (Mn-HEOx). Figure 4a shows the XRD patterns of the synthesized Mn-HEOx samples. It is seen that the samples synthesized at 1100 and 1300 °C contained secondary phases in addition to the major rocksalt phase. However, when the synthesis temperature was 1500 °C, a single rocksalt phase was formed. Thus, the single-phase formation temperature is \( \sim 400 \) °C higher than that of u-HEOx (\( \sim 1100 \) °C), suggesting that the introduction of Mn\(^{2+} \) to undoped HEOx may have synthesize Mn-HEOx samples. It is seen that the samples synthesized at 1100 and 1300 °C contained secondary phases in addition to the major rocksalt phase. However, when the synthesis temperature was 1500 °C, a single rocksalt phase was formed. Thus, the single-phase formation temperature is \( \sim 400 \) °C higher than that of u-HEOx (\( \sim 1100 \) °C), suggesting that the introduction of Mn\(^{2+} \) to undoped HEOx may have
increased the formation enthalpy; hence, it needs a higher temperature to form a single-phase Mn-HEOx. The increased formation enthalpy was confirmed by our molecular static calculations (see Table 1). From the Rietveld fitting of the XRD pattern with Si as the internal 2θ calibrant (Figure 2), the lattice parameter of the sample prepared at 1500 °C was obtained: \( a = 4.237 \pm 0.005 \) Å. The ionic radius of \( \text{Mn}^{2+} \) is 0.81 Å (low spin) or 0.97 Å (high spin),\(^{25}\) close to those of other cations (see above). As a result, there should be no significant change in the dimension of the cation sublattice of HEOx after occupation of some cation sites by \( \text{Mn}^{2+} \). Thus, the value of \( a \) of Mn-HEOx (4.237 Å) is close to that of undoped HEOx (4.238 Å).

The SEM image of the Mn-HEOx sample synthesized at 1500 °C (Figure 4b) reveals that the synthesized sample contains lots of micron-sized grains. The EDXS elemental mapping of the sample (Figure 4c; Figure S4 at a relatively high resolution in the SI) shows that there is no spatial enrichment or clustering of cations in the sample, indicating a uniform distribution of the elements in the sample. The SAED pattern (Figure 4d) shows that the very fine sample particles are crystalline. Thus, the experimental data in Figure 4a,b,d reveal the fact that the synthesized Mn-HEOx sample is polycrystalline and has a rocksalt structure.

4.4. Thermal Stability of Undoped and Doped HEOx.

The free energy of formation \( (\Delta G) \) of a high-entropy oxide from its constituent simple oxides is

\[
\Delta G = \Delta H - T \Delta S
\]

(2)

where \( \Delta H \) and \( \Delta S \) are, respectively, the enthalpy of formation and entropy of formation from the simple oxides. Previous thermal analysis experiment showed that \( \Delta H > 0 \) for MgCoNiCoZnO\(_5\).\(^1\) Our MS calculation results (Table 1) show that the formation enthalpies of undoped and doped HEOx are all above zero, i.e., \( \Delta H (0 K) > 0 \). Assuming that the experimental \( \Delta H \) is dominated by the potential energy (due to atomic interactions) rather than the kinetic energy (due to thermal vibrations), the predicted \( \Delta H (0 K) > 0 \) is consistent with the experimental \( \Delta H > 0 \) in ref 1. Moreover, Table 1 shows that the formation enthalpy of HEOx increases after doping. This can be attributed to the introduction of Li/Mn–O bonds to HEOx, as they have a weaker bond strength (characterized by the magnitude of the lattice energy of MeO; Table 1) than other cation–O bonds in the u-HEOx (except that Mn–O and Cu–O bonds have similar strengths), causing a doped HEOx to possess a higher enthalpy. Particularly, the formation energy of Li-HEOx is much higher than that of Mn-HEOx. This arose because O vacancies were treated as distributed randomly in the anion sublattice of Li-HEOx in the MS calculations. More realistically, O vacancies should be preferably distributed near Li-doping sites to reduce the total system energy, since the electrostatic repulsion between a \( \text{V}_0 \) and a nearby Li\(^+\) ion is lower than that between a \( \text{V}_0 \) and a nearby Me\(^{2+}\) ion. We will use molecular dynamics simulations to treat this scenario in a future work.

The entropy of a high-entropy oxide at high temperature comes mainly from the configurational entropy due to the random distribution of cations in the cation sublattice.\(^1\) Thus, for one molar HEOx (e.g., (Mg,Co,Ni,Cu,Zn)O for the u-HEOx), the molar entropy change \( \Delta S \approx -R \sum x_i \ln x_i \), where \( R \) represents the universal gas constant \((8.314 \text{ J mol}^{-1} \text{ K}^{-1})\) and \( x_i \) is the molar fraction of a constituent simple oxide. Using this approximation, \( \Delta S = 13.4 \) and \( 14.4 \text{ J mol}^{-1} \text{ K}^{-1} \) for u-HEOx and Li/Mn-HEOx, respectively. Then, according to eq 2, high-entropy oxides are thermodynamically stable (i.e., \( \Delta G \leq 0 \)) only at temperatures higher than the formation temperature \( T_f = (\Delta H/\Delta S) > 0 \). Our synthesis experiments show that \( T_f \geq 1100, 1100, \) and \( 1500 °C \) for u-HEOx, Li-HEOx, and Mn-HEOx, respectively (see above). Based on this, we deduced that \( \Delta H(\text{Mn-HEOx}) > \Delta H(\text{u-HEOx} \text{ or Li-HEOx}) > 0 \). This supports our MS-derived results in Table 1: \( \Delta H(\text{Mn-HEOx}, 0 K) > \Delta H(\text{u-HEOx}, 0 K) \).

As high-entropy oxides are thermodynamically stable only at temperatures higher than \( T_f \) at lower temperatures, they become thermodynamically unstable and thus may decompose into simple oxides (or fewer-component complex oxides), subject to attainable kinetics at given temperatures. With this consideration, we investigated the thermal stabilities of undoped and Li/Mn-doped HEOx using in situ XRD. The experimental results (Figure 5) show that on heating the samples from RT to 450 °C in a flowing nitrogen gas, no phase decompositions were observed. Thus, the HEOx compounds.

**Figure 5.** In situ XRD patterns of u-HEOx (a), Li-HEOx (b), and Mn-HEOx (c) on heating from RT to 450 °C in a flowing nitrogen gas (X-ray wavelength 1.2400 Å). Prefix “f” prior to a temperature value denotes cooling; “ff” symbols indicate diffraction peaks from the dome lid of the heating stage. The very bottom XRD pattern in each diagram was collected at RT without enclosing the dome lid onto the heating stage.
are thermally stable in the experimental conditions. These results suggest that the activation energies for the decompositions of the HEOx compounds to constituent simple oxides are relatively high. In a decomposition reaction of HEOx, it is necessary to break and rearrange different kinds of metal cation–O bonds via migrations of cations from a randomly distributed HEOx cation sublattice to several orderly distributed cation sublattices of the constituent simple oxides. These factors make the decomposition reaction difficult at relatively low temperatures.

4.5. Mechanical Stability and Elasticity of Undoped and Doped HEOx. High-pressure XRD patterns of undoped HEOx (in neon pressure medium) and the Li/Mn-doped HEOx (in methanol–ethanol medium) are shown in Figure 6. It is seen that no phase transitions occurred in all HEOx at pressures up to ~50 GPa at room temperature (further confirmed by repeated HP-XRD measurements of the latter two; see Figure S5 in the SI). By comparison, some constituent simple oxides undergo pressure-induced phase transitions at $P < 50$ GPa. For instance, CoO and MnO change from a cubic to a rhombohedral structure at 37 and 40 GPa, respectively, and ZnO from a hexagonal to a cubic structure at ~9 GPa. We infer that the random cation distribution in the cation sublattice of HEOx increases more the free energy of a potential high-pressure phase than that of the ambient cubic phase, which widens the phase stability of the cubic phase; hence, no phase transitions occurred in the HEOx in our experimental pressure range. Thus, all of the undoped and Li/Mn-doped HEOx compounds are quite mechanically stable at room temperature (at $P$ up to ~50 GPa). The relatively high thermal and mechanical stabilities of HEOx facilitate development of versatile applications in wide range of temperature and pressure.

Again, we used the periclase phase of MgO as the structure model to perform the Rietveld fitting of the HP-XRD data of the undoped and Li/Mn-doped HEOx (Figure 6) to obtain their pressure-dependent lattice parameters and hence the unit cell volumes. Figure S6 (SI) illustrates representative Rietveld fittings at chosen pressures. The obtained unit cell volumes as a function of pressure are shown in Figure 7.
in our fitting of the experimental data to eq 3, all compression data points in Figure 7a and those below 10 GPa in Figure 7b,c were used, as done in a previous work. Decompression data points were not included in the fittings due to their apparent deviations from the compression data, which are more apparent in the neon medium (Figure 7a) possibly due to continuous structure relaxation of HEOx while subjected to X-ray diffraction. The fit results are shown in Figure 7, and the obtained bulk moduli are $B_0$(u-HEOx) = 187.7 ± 3.5 GPa, $B_0$(two-step Li-HEOx) = 156.2 ± 2.8 GPa, and $B_0$(Mn-HEOx) = 162.2 ± 5.9 GPa.

4.6. Understanding Doping Effect on Compressibility of High-Entropy Oxides Using MS Calculations. The above experimental results show that Li/Mn doping causes decrease in the bulk modulus of HEOx, making HEOx more compressible (i.e., softer). Under compression, the Me–O bond length of a MeO compound shortens, causing increase in the internal energy. A MeO compound with stronger Me–O bonds can resist more the compression, producing a higher bulk modulus. Thus, a decrease in the bulk modulus of HEOx after doping suggests a weakening of the Me–O bond, as verified by our MS calculations (below).

For ionic crystals, the strength of ionic interactions (or ionic bond strength) can be characterized by the lattice energy. Our MS-derived bulk moduli and lattice energies of concerned simple and high-entropy oxides are listed in Table 1. It is seen that the calculated bulk moduli agree fairly well with the available literature and/or experimental data. The calculated lattice energies also agree fairly well with those derived from the Born–Fajans–Haber cycle. These illustrate that the MS calculations describe consistently and reasonably well the atomic interactions in both simple and high-entropy oxides, giving that no any level of quantum mechanical treatments were employed. Table 1 shows that, for the undoped and Li/Mn-doped HEOx, their molar fraction weighted-sum of the bulk moduli of constituent simple oxides are close to the MS-derived values (though the former underestimate the latter to some degrees), suggesting that all kinds of Me–O bonds in HEOx resist external compression cooperatively.

As seen from Table 1, both $B_0$ and the magnitude of $E_{\text{latt}}$ of Li$_{0.5}$(1/2 Li$_2$O) are smaller than those of other constituent oxides, indicating that Li–O bonds are weaker than other Me–O bonds in our concerned oxides. Thus, the experimentally observed lower bulk modulus of Li-HEOx than u-HEOx (Table 1) can be attributed to the introduction of the less strong Li–O bonds to the HEOx structure.

Although $B_0$ of MnO is close to those of cubic CuO and MgO, it is smaller than those of cubic CoO, NiO, and ZnO (Table 1). The magnitude of $E_{\text{latt}}$ of MnO is comparable to that of cubic CuO but smaller than those of cubic MgO, CoO, NiO, and ZnO (Table 1). Thus, the average strength of all of the Me–O bonds in Mn-HEOx should be smaller than that in u-HEOx due to introduction of Mn–O bonds to the HEOx structure. As a result, $B_0$ of Mn-HEOx should be smaller than that of u-HEOx, as confirmed by the experimental results (Table 1).

Because $B_0$(103.6 GPa) and the magnitude of $E_{\text{latt}}$(1466.00 kJ mol$^{-1}$) of Li$_{0.5}$O$_{0.5}$ are smaller than $B_0$ (158.8 GPa) and the magnitude of $E_{\text{latt}}$(3678.03 kJ mol$^{-1}$) of MnO, $B_0$ of Li-HEOx should be smaller than that of Mn-HEOx, as confirmed by both MS and experimental results (Table 1). Overall, the MS calculations predict $B_0$(Li-HEOx) < $B_0$(Mn-HEOx) < $B_0$(u-HEOx) as a consequence of increasing average bond strength

Figure 7. Variations of unit cell volumes (described using a Fm$\overline{3}$m space group) of u-HEOx (a), two-step Li-HEOx (b), and Mn-HEOx (c) as function of pressure. Lines are fits to the experimental data using the third-order Birch–Murnaghan equation of state.

We then used the third-order Birch–Murnaghan equations of state (EOS) to fit the unit cell volume vs pressure data shown in Figure 7

$$P(V) = 1.5B_0 \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \times \left\{ 1 + \frac{2}{3} \left( B_0' - 4 \right) \left( \frac{V_0}{V} \right)^{2/3} - 1 \right\}$$

(3)

where $P$ is the pressure, $B_0$ is the bulk modulus, $B_0'$ is the pressure derivative of the bulk modulus, and $V_0$ and $V$ are the unit cell volumes at ambient pressure and pressure $P$, respectively. In fitting the experimental data to the EOS above, $B_0'$ is commonly fixed at 4.0 GPa. Rigorously, eq 3 is applicable only to systems at hydrostatic conditions.

It has been shown that the neon pressure medium can produce hydrostatic and quasi-hydrostatic conditions at $P$ up to ~50 GPa, while methanol–ethanol medium can only produce hydrostatic conditions at $P$ up to ~10.5 GPa. Thus, it was determined in fitting the experimental data to eq 3, all compression data points in Figure 7a and those below 10 GPa in Figure 7b,c were used, as done in a previous work. Decompression data points were not included in the fittings due to their apparent deviations from the compression data, which are more apparent in the neon medium (Figure 7a) possibly due to continuous structure relaxation of HEOx while subjected to X-ray diffraction. The fit results are shown in Figure 7, and the obtained bulk moduli are $B_0$(u-HEOx) = 187.7 ± 3.5 GPa, $B_0$(two-step Li-HEOx) = 156.2 ± 2.8 GPa, and $B_0$(Mn-HEOx) = 162.2 ± 5.9 GPa. For ionic crystals, the strength of ionic interactions (or ionic bond strength) can be characterized by the lattice energy. Our MS-derived bulk moduli and lattice energies of concerned simple and high-entropy oxides are listed in Table 1. It is seen that the calculated bulk moduli agree fairly well with the available literature and/or experimental data. The calculated lattice energies also agree fairly well with those derived from the Born–Fajans–Haber cycle. These illustrate that the MS calculations describe consistently and reasonably well the atomic interactions in both simple and high-entropy oxides, giving that no any level of quantum mechanical treatments were employed. Table 1 shows that, for the undoped and Li/Mn-doped HEOx, their molar fraction weighted-sum of the bulk moduli of constituent simple oxides are close to the MS-derived values (though the former underestimate the latter to some degrees), suggesting that all kinds of Me–O bonds in HEOx resist external compression cooperatively.

As seen from Table 1, both $B_0$ and the magnitude of $E_{\text{latt}}$ of Li$_{0.5}$(1/2 Li$_2$O) are smaller than those of other constituent oxides, indicating that Li–O bonds are weaker than other Me–O bonds in our concerned oxides. Thus, the experimentally observed lower bulk modulus of Li-HEOx than u-HEOx (Table 1) can be attributed to the introduction of the less strong Li–O bonds to the HEOx structure. Although $B_0$ of MnO is close to those of cubic CuO and MgO, it is smaller than those of cubic CoO, NiO, and ZnO (Table 1). The magnitude of $E_{\text{latt}}$ of MnO is comparable to that of cubic CuO but smaller than those of cubic MgO, CoO, NiO, and ZnO (Table 1). Thus, the average strength of all of the Me–O bonds in Mn-HEOx should be smaller than that in u-HEOx due to introduction of Mn–O bonds to the HEOx structure. As a result, $B_0$ of Mn-HEOx should be smaller than that of u-HEOx, as confirmed by the experimental results (Table 1).

Because $B_0$(103.6 GPa) and the magnitude of $E_{\text{latt}}$(1466.00 kJ mol$^{-1}$) of Li$_{0.5}$O$_{0.5}$ are smaller than $B_0$ (158.8 GPa) and the magnitude of $E_{\text{latt}}$(3678.03 kJ mol$^{-1}$) of MnO, $B_0$ of Li-HEOx should be smaller than that of Mn-HEOx, as confirmed by both MS and experimental results (Table 1). Overall, the MS calculations predict $B_0$(Li-HEOx) < $B_0$(Mn-HEOx) < $B_0$(u-HEOx) as a consequence of increasing average bond strength.
of the Me–O bonds in these oxides, consistent with the HP-XRD results (Table 1). Based on above discussions, we argue that the doping-induced elastic softening of HEOx arises from introduction of weaker Li–O or Mn–O bonds in the high-entropy compound.

5. CONCLUSIONS

In this work, we have prepared undoped and Li- and Mn-doped high-entropy oxides using solid-state reactions at high temperatures. In situ heating and compression synchrotron XRD experimental results show that these HEOx compounds are thermally stable at T up to ~450 °C and mechanically stable at P up to ~50 GPa. High-pressure XRD experimental results show that doping of Li and Mn makes the HEOx more compressible because of introduction of Li–O or Mn–O ionic interactions that are weaker than other cation–O interactions, as revealed by molecular static calculations. The formation reaction of HEOx was predicted as endothermic by MS calculations, consistent with the reported experimental data. The formation reaction of HEOx was predicted as endothermic by MS calculations, consistent with the reported experimental data. The formation reaction of HEOx was predicted as endothermic by MS calculations, consistent with the reported experimental data. The formation reaction of HEOx was predicted as endothermic by MS calculations, consistent with the reported experimental data.

The authors declare no competing financial interest.

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