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Anand, G., Wynn, A.P., Handley, C.M. et al. (1 more author) (2018) Phase stability and distortion in high-entropy oxides. Acta Materialia, 146. pp. 119-125. ISSN 1359-6454

https://doi.org/10.1016/j.actamat.2017.12.037

Phase Stability and Distortion in High-Entropy Oxides

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Abstract

The present investigation demonstrates how configurational entropy stabilises rock-salt type single phase multi-component solid solution oxides. Classical simulations have been used to extensively sample the configurational landscape of such oxides using both random and genetic algorithm sampling strategies. The thermodynamic properties including the enthalpy and free energy of various oxide mixes have been calculated to show the influence of the chemical identity of the oxides on the phase stability. Additionally, a distance analysis between all the cation-cation and cation-anion pairs has been carried out in order to quantify the distortion in the lattice. The correlation between the multiplicity of cations in such systems with consequent enthalpy and configurational entropy has been enumerated and its relation with emergent distortion has been analysed.

(The modifications and additions have been marked in red)

Keywords

High-Entropy Solid Solution; Thermodynamics; Distortion; Functional properties; Oxides.

Introduction

As we strive to find future materials that have properties beyond those we currently, there has been an increased interest in materials design methodology based on multiple components for example in Li batteries [1] and Thermoelectrics [2]. By increasing our number of components we massively increase the configurational space for exploration of new materials. Early attention in this field has on metallic systems, also known as "High-Entropy Alloys" [3–5]. These systems tend to exhibit single-phase solid solutions with simple crystal structures, mostly as face-centred cubic or body-centred cubic crystal structures. Inspired by the above-stated strategy, multiple component oxides of Mg, Co, Cu, Ni and Zn, exhibiting a rocksalt-type simple crystal structures with uniform distributions of ions in the crystal have been synthesised [6,7]. This was particularly surprising given that none of the constituent binary oxides show solid solubility within each other. Hence, the high configurational entropy of mixing has been attributed to explain the formation of the single phase solid solution. This has subsequently been further supported by the formation of a multicomponent rare-earth based oxide (Ce,La,Pr,Sm,Y)O [8] and more recently, class of high-entropy perovskite oxides have been reported [9]. This raises the clear question of how the entropy within these systems is able to overcome the presumed enthalpic penalty associated with mixing these oxides. Manipulating and controlling this entropy factor may facilitate the production of a whole new class of materials.

Although a simple rocksalt structure has been reported for the binary oxide mixes recent studies have begun to examine the structural displacements. Berardan *et. al.* [10] demonstrated that no severe lattice distortion in the case of multiple-component oxide when no CuO is present, i.e., $(\mathrm{MgCoNiZn})_{0.8}(\mathrm{LiGa})_{0.2}$. CuO containing solid solutions are particularly interesting, as Cu^{2+} ions in an octahedral coordination are expected to express Jahn-Teller type distortion of the O^{2-} sublattice around it resulting in four short and two long Cu-O separations. Density functional theory calculations have shown that the Jahn-Teller distortion due to Cu^{2+} ions can be attributed to the splitting of Cu-d bands near the Fermi level [11]. Further Extended X-ray Absorption Fine Structure (EXAFS) studies have supported this distortion around the Cu^{2+} cation [12]. None of the other cations in these multicomponent oxides show such behaviour. The simple crystal structure, however, suggests there cannot be a cooperative distortion of all octahedra in similar direction [10]. The structural displacement of ions in the unit cell of complex oxide solid solution will potentially influence the functional properties of such materials in general [13]. Current exciting results reported for these ceramics include large dielectric constants over a range of frequencies [14] and room temperature fast ion conductivity [15]. Jahn-Teller effects in transition metal oxides can possibly lead to the anisotropic transport properties [16] and it has been shown that functional properties such as resistivity and dielectric constant can be tuned by varying the degree of distortion [10]. Therefore there is a strong interest to understand the structural behaviour in these materials. The DFT studies [11, 12] are limited to a few configurations of relatively small sizes which makes it difficult to cover the whole range of structures available to this complex mix. Classical potentials are much less expensive and therefore we can analyse a huge number of configurations and explore the different variation in structural relaxations around the cations.

Thus, in the present investigation we enumerate the thermodynamic properties of multicomponent oxides by explicit calculations of the enthalpy and entropy of the solid solution. We also perform a detailed structural analysis to determine how regular the rock-salt structure is, if any clustering or ordering occurs within the solid solution and whether particular distortions are observed around particular cations.

Simulation details

Cells were constructed from a rocksalt lattice with 1000 cations and 1000 oxide anions. All cells were fully geometry optimised (relaxing both cell and ionic positions) using the GULP code [17] before collecting any structural or energetic data. The classical Born model is assumed for oxides, where they are considered to be fully ionic and hence formal charge can be assigned to them while developing interatomic potentials for them (i.e. cations and oxides had a charge of $+2e$ and $-2e$, respectively) [18]. The Buckingham interatomic potential depicting ionic interaction between ion i and j may be expressed as [19]:

$$V_{ij}(r_{ij}) = A_{ij} \exp\left(\frac{-r_{ij}}{\rho}\right) - \frac{C_{ij}}{r_{ij}^6} \tag{1}$$

where, the values of A_{ij}, ρ_{ij}, and C_{ij} are dependent upon the identity of ionic species, while r_{ij} depicts the distance between species i and j. The values of A, ρ, and C were taken from literature [19, 20] using cutoffs of 10 Å. It should be noted that potential employed here has been originally fitted for binary system and were used for ternary systems by Lewis and Catlow themselves with consideration that effect of coordination on short-range potential is considered [19]. Now, in present investigation, we do not expect such variation in coordination, as we are simulating simple rock-salt structure and also O^{2-} have constant charge on it. The quintinery [(Co,Cu,Mg,Ni,Zn)O], quaternary [(Cu,Mg,Ni,Zn)O, (Co,Mg,Ni,Zn)O, (Co,Cu,Ni,Zn)O, (Co,Cu,Mg,Zn)O and (Co,Cu,Mg,Ni)O], ternary [(Co,Cu,Mg)O, (Co,Cu,Ni)O, (Co,Cu,Zn)O, (Co,Ni,Zn)O, (Co,Mg,Zn)O, (Cu,Mg,Zn)O, (Cu,Ni,Zn)O, (Co,Mg,Ni)O, (Cu,Mg,Ni)O, (Mg,Ni,Zn)O] and binary [(Cu,Co)O, (Co,Mg)O, (Co,Ni)O, (Co,Zn)O, (Cu,Ni)O, (Cu,Mg)O, (Cu,Zn)O, (Mg,Ni)O, (Mg,Zn)O and (Ni,Zn)O] oxide-mixes were simulated in present investigation. Molecular dynamics simulations were run using DL_POLY classic code [21]. Simulations were run with an NPT ensemble using the Nosé-Hoover thermostat and barostat with relaxation times of 0.01 ps and 0.02 ps respectively. Simulations were run at a temperature of 300K and pressure of 1 atm. Timesteps were set at 0.1 fs. Modifications made to the DL_POLY code as described by Darkins *et al.* [22] coupled with a Voronoi tessellation based approach to calculate appropriate atomic volumes, discussed by Branicio *et. al.* [23] allow for the extraction of a local stress field for a given system.

Sampling methodology

The configurational sampling of systems with positional disorder presents a formidable challenge, but extensive sampling of the potential energy landscape is essential in order to calculate the thermodynamic quantities from a statistical mechanics based framework. It is not computationally possible to consider modelling the whole ensemble of configurations available and therefore it is important that the sampling methodology employed generates a good representation of the whole ensemble. To ensure this we employed several different sampling procedures for the generation of configurations.

1. *Random*: Cations were randomly assigned to the 1000 lattice points in the cells.
2. *Systematic*: Twenty different cation arrangements were initially assigned to the lattice. After each optimisation the cations were moved to the next lattice point in the structure (i.e. a Mg

at lattice point 1 was moved to lattice point 2). As the lattice sites were listed randomly this procedure effectively randomly sampled configurations.

3. *Ordered*: Particular arrangements representing ordering of the cations into layers/clusters were specifically sampled to examine potential segregation of the cations.

4. *Genetic Algorithm*: In the genetic algorithm 100 configurations were randomly generated and optimised. These were then ranked based on their lattice energy with the lowest energy configuration at the top of the list. The algorithm systematically counted through the list from the top and had a 5% chance of selecting a configuration as a parent. Once two parents were selected a new configuration (child) was generated by merging the cation arrangements of the two configurations. Therefore configurations higher in the list (with lower lattice energies) were more likely to be selected for breeding. Each cation site was then given a 2% chance of mutation via swapping with another cation. 100 children were generated for each cycle and optimised to become the parents of the next generation. A total of 10 generational loops were carried out for each initial set of 100 configurations.

5. *Swapping*: From the previous sampling methods it was possible to identify low energy configurations. We generated a range of configurations by performing a small number of swaps between cations in the lattice from these low energy configurations with the aim of generating further low energy configurations.

In total the above-listed sampling procedures generated 23536 unique configurations for the 5-component (Mg,Co,Cu,Ni,Zn)O system. Smaller numbers of configurations were generated for the other mixes described in the paper as indicated in Table 1.

Analysis Methods

An order parameter was used to analyse the effect of potential preferential segregation/ordering of the cations within the cells with its configurational energy and quantify the potential energy landscape being sampled by various sampling schemes employed in the present work, as explained in above section. Within the rocksalt lattice, each cation has 12 and 6 first and second nearest neighbour

(NN) cations, respectively. Therefore, in a perfectly mixed five component system, it can be expected that each cation would be surrounded by 2.4 first NN of each cation type and 1.2 second NN of each cation type. For our cells of 1000 cations with 5 components, we would therefore expect 480 first NN interaction (m_{ij} where i and j are the different cations present) for each cation type (2.4 × 1000 × 2 (due to double counting of every pair by counting over all cations)). For each configuration we compare the actual recorded number of cation types around each cation to this ideal value via equation 2.

$$\text{order parameter} = \sqrt{\frac{\sum(1 - \frac{\sum m_{ij}}{n_{ij}})^2}{K^2}} \tag{2}$$

where, m_{ij} is the number of first NNs of cation type i to j, n_{ij} is expected number of NN of cation i to j (i.e. 480) and K is the number of different cations present. Therefore a perfect mix would produce a value of ∼0.

The thermodynamic properties of the oxide solid solution were determined using a statistical mechanics based framework. The macrostate in such a framework can be understood as bulk solid, while microstates represent the possible atomic configurations of cations and anions on the lattice sites. The thermodynamic property of the macrostate can be determined, if the configurational energy of the microstate is known. In this context, the partition function (Q) is important, as it contains all the thermodynamic information about the system [24]. The partition function can be mathematically represented as,

$$Q = \sum_{i=1}^{N} e^{\frac{-E_i}{k_B T}} \tag{3}$$

where, N is the number of microstates, E_i is configurational energy of the i^{th} microstate, k_B is Boltzmann's constant, and T is temperature. The value of Q gives the information about the accessible states at any given temperature. As it can be seen from equation 3 that, at higher temperature, the value of Q will be higher, as more energy states are available, while the lower bound of Q would be 1 at absolute zero, as only one state, *i.e.,* the ground state is accessible. Additionally, the value of Q provides the information about the spacing between energy levels in the system. The enthalpy (H)

and free energy (G) can be expressed as,

$$H = \frac{\sum_{i=1}^{N} \left(E_i \cdot e^{\frac{-E_i}{k_B T}} \right)}{Q} \tag{4}$$

$$G = k_B T \cdot \ln \left(Q \right) \tag{5}$$

As we cannot determine the properties of all the microstates we instead perform our average over those states collected and ensure we are seeing convergence with the thermodynamic properties which suggests we are sampling a representative sample of the population. For the free energy we can rewrite this as

$$G = k_B T \cdot \ln \left(I \right) - k_B T \cdot \ln \left(\frac{\sum_{i=1}^{I'} e^{\frac{-E_i}{k_B T}}}{I'} \right) \tag{6}$$

where I is the total number of configurations possible in the system and I' is the number of microstates (configurations) sampled. This equation effectively divides the free energy into an ideal component (the first term) and a deviation from ideality (the second term) caused by the variation in energy between the microstates.

Results and discussions

Figure 1(a) shows the variation of enthalpy of mixing for the oxide mixes. It can be seen that all the oxide mixes have a positive enthalpy of mixing with the lowest values found for (Co,Cu,Mg,Ni)O and (Co,Mg,Ni,Zn)O. But the variation in the enthalpy for five-component and all four-component oxides composed of CoO, CuO, MgO, NiO, and ZnO is small. In the case of (Ca,Co,Cu,Ni,Zn)O, however, a greater enthalpy of mixing is observed implying possible segregation tendency in such a system, as reported in ref. [25]. We therefore agree with the findings of Rost *et al.* [6] that these ceramics are not enthalpically stabilised.

The addition of configurational entropy lowers the free energy as was calculated at a range of temperatures using equation 6. From this, the temperature at which the free energy of mixing becomes zero is calculated *i.e.* when the entropy contribution equals that of the enthalpy and the system becomes entropically stabilised (see supplementary information for regression curves and equations). This data is plotted in Fig. 1(b) and it shows that for all the systems composed of CoO, CuO, MgO, and ZnO, entropy stabilises the phase at temperatures less than 1120 K. For the (Co,Cu,Mg,Ni,Zn)O, we observe entropy stabilisation at ∼800 K which is in good agreement with the experimental results [6] which identified a temperature range of 850 ^{o}C - 900 ^{o}C. As we remove a cation and make a four cation oxide-mix, the total entropy is decreased and we can see that for the (Co,Cu,Ni,Zn)O, (Co,Cu,Mg,Zn)O and (Cu,Mg,Ni,Zn)O systems the necessary temperature is increased to ∼1000 K in line with the larger enthalpy of mixing and the lower entropy. For the (Co,Mg,Ni,Zn)O and (Co,Cu,Mg,Ni)O systems the temperature is lower despite the reduced entropy which is due to the lower enthalpies of mixing for these systems (Fig. 1 (a)). Rost *et al*'s [6] observations suggested that the loss of the entropy in the 4 component mixes made formation of these phases impossible which we agree with for three of the cases. In the two cases that disagree with the trend; the system do not have either Cu^{2+} or Zn^{2+} in comparison to five-component oxide-mix. These two ceramics do not naturally form the rock-salt structure and this may explain the much lower enthalpy of mixing when either is removed from the mix and may represent a slight limitation of the forcefields as these are primarily fitted for the ideal oxide phases of each cation (würtzite for ZnO and tenorite for CuO).

In the case of Ca substitution into the lattice the enthalpy of mixing is massively increased which leads to an extremely high temperature being required to stabilise the phase. This agrees well with experiment which has been unable to form the ceramic phase with Ca present [6].

These results agree with the fact that entropy is the stabilising influence on these ceramic phases and that in general the loss of components will reduce the entropy and therefore reduce the stability of the phase.

Figure 2 shows the order parameter variation with the energy of the configurations. This shows that there is no clear link between the ordering or segregation of the materials in general and the energetics of the configuration. This implies that we are forming a disordered solid solution mix and particular low energy configurations are not dominating the population. Note that two regions of order were formed due to the different sampling strategies employed.

We can extend this analysis further by examining the frequency of particular first NN cation pairs in the lattice to determine if particular cation types will preferentially segregate. For nearly all the cation pairs we see no energy dependence on the number of pairs and they display similar plots to that of Ni-Ni as shown in Fig. 3, where the number of Ni^{2+}-Ni^{2+} pairs has no correlation to the energy of the confoguration. The only pairs where a correlation is observed is for Cu^{2+}-Cu^{2+}, where the energy lowers as the number of these pairs increases and Cu^{2+}-Zn^{2+}, where there is a weak correlation suggesting that more Cu^{2+}-Zn^{2+} pairs increases the energy of a configuration. The behaviour of the Cu^{2+} and Zn^{2+} matches our analysis of the thermodynamic properties that found the absence of the Cu and Zn lowered the enthalpy of mixing. The variation of number of cation-cation pairs and their corresponding configurational energy for all other cation-cation combinations can be seen in supplementary information.

Figures 4(a) and 4(b) show the average cation-cation and cation-oxygen separations in the lattices respectively. For the five-cation ceramic, we get an average separation of 2.08 Å for the cation-oxygen and 2.94 Å for the cation-cation which are both in excellent agreement with the experimentally reported values [12]. As can be seen in Fig. 4(a) the cation-cation separations are generally similar for all the cation pairs with the exception of those involving Cu^{2+} which are significantly shorter. When we examine the separations in the 4-cation systems the values are very similar to the 5-cation case except when Cu^{2+} is absent, *i.e.* (Co,Mg,Zn,Ni)O, where we observe all the separations increase by ~0.02 Å. A similar effect can be seen for the cation-oxygen separations where the Cu-O separation is much shorter than the other cation-oxygen separations. The cation-anion separation also increases when Cu is removed from the mix to make (Co,Mg,Zn,Ni)O.

Berardan et. al. [10] have reported that a Jahn-Teller effect may be present for the Cu^{2+} cation which leads to the shorter Cu-O separations and causes a bi-modal distribution of separations. More detailed examination of our data in the five cation systems for Cu^{2+}-O^{2-} does show a possible two hump distribution with the first peak around 2.02 Å and the second at 2.07 Å (see supplementary information). The distribution is more concentrated at shorter distance, which again agrees with experiment. The classical nature of our simulations where our ions are treated as hard spheres means that no explicit electronic effects are included and thus the Jahn-Teller effect cannot be directly modelled. This means the effect we are observing here is caused by a distortion of the local structure around the Cu, simply due to the smaller size of the Cu^{2+} cation compared to the other cations. This implies the experimentally reported effect may be a combination of both Jahn-Teller and/or simple size arguments.

The standard deviation of the cation-oxygen and cation-cation separations are shown in Figure 5(a) and 5(b) respectively. It can be clearly seen that, in the case of the oxide mix which does not contain CuO, *i.e.,* (Co,Mg,Ni,Zn)O the average standard deviation for the same oxide mix is smallest. The cation-anion and cation-cation separations become longer and far more regular when no Cu^{2+} is present. The presence of Cu with its shorter separations clearly causes larger disruptions to the surrounding lattice leading the more variability in other separations. When Cu is removed the separations all become more regular with less local variation.

We carried out a series of molecular dynamics simulations on some of the five and four-component systems to examine the local stress field on each atom. Figure 6 shows the average stress from the xx component of the stress matrix on each cation type in the five-component system. We can see that all the cations with the exception of Cu^{2+} are under compressive stress in the simulation while Cu is under a tensile stress. Similar trend is exhibited for all of the normal stress components in each system. This agrees well with variation of cation-cation and cation-anion separations, as seen in Fig. 4, which showed that the Cu^{2+}-O^{2+} and Cu^{2+}-cation separations generally wanted to be significantly shorter than the average cation-O^{2+} and cation-cation separations, respectively. Therefore, the Cu is under a tensile stress as it is being stretched by the lattice.

When we go to the 4-component system, we examine how the stress around each cation type is varied as shown in Fig. 6. It can be seen that removal of Co, Mg, Ni or Zn creates changes in stress but with no clear pattern. Some cations reduce their local stress while others increase. Removal of Cu, however, leads to a decrease in absolute stress of all the other cations in the system. This again supports the concept that Cu is unfavourable within the lattice.

The results for the 4 and 5 component ceramic systems suggest that as the number of cation components in the system is increased we drive the system towards becoming a better solid solution where all the atoms sit in similar environments and therefore the disorder in the system is encouraging further disorder. To pursue this concept further we performed a small set of random sampling on all the 2 and 3 component systems that can be formed from the Mg, Co, Zn, Cu and Ni oxides. These small runs produced between 50-1000 configurations which were used to produce values.

Figure 7 shows the average enthalpy of mixing and ideal entropy of mixing for 2, 3, 4 and 5 component systems. As expected the enthalpy of mixing increases as more cations are added to the system. The enthalpy of mixing, however, increases by smaller and smaller amounts as each cation is added to the system. There is a large enthalpy penalty of ∼0.08 kJmol^{-1} associated with the mixing of only two cations but the addition of a third cation to this mix generates an average enthalpy increase of only 0.01 kJmol^{-1}, adding a fourth cation creates a enthalpy penalty of 0.005 kJmol^{-1} and the fifth cation a penalty of 0.001 kJmol^{-1}. At the same time the associated configurational entropy increases and we can see these two terms overlap between 4 and 5 cations (at a temperature of 1000 K) explaining the general features seen experimentally. Therefore the shape of the enthalpy penalty associated with the mixing (i.e. its gradual increase) of additional cations is the crucial feature of forming these high entropy ceramics.

We can understand the shape of the enthalpy of mixing, if we examine the structure of cations in the 2, 3, 4 and 5 cation oxide-mixes. Figure 8(a) shows the average separations between each cation pair in the configurations with the total number of different cations. As might be expected there is a gradual convergence of the separations as the number of different cation types increases. As we add a new cation into a solid solution, that particular cation is forced into the local environment of the solid solution. So in the case of adding Ni^{2+} to CoO, the Ni^{2+} enters a environment with cation-cation separations of 2.99 Å where it would want 2.94 Å, which leads to a substantial enthalpy penalty as the Ni^{2+} causes substantial disruption to the surrounding lattice. If we were to add Ni^{2+} to (Co,Mg)O the separations are now 2.98 Å. Ni^{2+} into (Co,Mg,Cu)O is entering an environment with separations at 2.92 Å. (Co,Mg,Cu,Zn)O has separations of 2.94 Å. We can see that the mixing creates an average environment that matches better to that of new cations, therefore the disruption caused by the of addition of new cations is far smaller and the enthalpy penalty is smaller. Coupled to this, the diversity of cation sites increases as more cation types are added as can be evidenced by the increase of the standard deviation of separations as the number of cation types is increased (Table 2). Therefore we are generating more different local environments that can accommodate new cation types e.g., the addition of Ni^{2+} to the (Co,Mg,Cu)O solid solution might seek out sites with more surrounding Cu^{2+} since the Cu^{2+} cation wants shorter cation-oxygen separations and can therefore accommodate the longer Ni-O separations more readily (Fig. 8(b)). Effectively as we increase the number of components our system becomes more disordered and therefore the penalty of further disorder from further additions is reduced. A similar effect will occur in other multi-component solid solutions that are observed in ceramic systems.

Conclusions

The following conclusions can be drawn from the present investigation:

1. The configurational entropy of mixing stabilises the ceramic phases and lowers the free energy of mixing towards negative values in all the studied oxide mixes, with lowest temperature required for free energy to be zero was seen in the case of oxide mixes not containing CuO and ZnO.
2. The addition of CaO, instead of MgO in (Co,Cu,Ni,Zn)O oxide mix lead to large positive value of enthalpy and hence the entropic contribution cannot possibly lead to negative free energy (temperature of 3265 K is required to bring the free energy to zero value).
3. The solid solution does not show any particular ordering order segregation except in the case of Cu^{2+}-Cu^{2+} and Cu^{2+}-Zn^{2+} pairs. Lower Cu^{2+}-Cu^{2+} pairs were seen in higher energy configurations, while larger numbers of Cu^{2+}-Zn^{2+} bonds were present in high energy cases.
4. Nearest-neighbour distance analysis showed that lowest cation-cation and cation-anion bond length with minimum variation was seen in the case of Cu^{2+}-Cu^{2+} and Cu^{2+}-O^{2-}, respectively.
5. It has been shown that the enthalpy penalty from mixing additional cations into the system

reduces as the number of cations is increased, while configurational entropy increases. Hence, the stability of single phase oxide solutions for multiple-component oxide solid solutions is increasingly determined by configurational entropy as the number of cations increases.

Acknowledgements

We would like to thank C.M. Rost, D.C. Sinclair and I.M. Reaney for useful discussions in the production of this paper and GA is thankful of University of Sheffield for PhD funding..

References

[1] K. Luo, M.R. Roberts, N. Guerrini, N. Tapia-Ruiz, R. Hao, F. Massel, D.M. Pickup, S. Ramos, Y.S. Liu, J. Guo, A.V. Chadwick, L.C. Duda, P.G. Bruce, J. Am. Chem. Soc. 138 (1989) 11211-11218.

[2] Z. Lu, H. Zhang, W. Lei, D.C. Sinclair, I.M. Reaney, Chem. Mater. 28 (2016) 925-935.

[3] B.Cantor, I.T.H. Chang, P. Kinight, A.J.B. Vincent, Mater. Sci. Eng. A 375 (2004) 213-218.

[4] J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C.H. Tsau, S.Y. Chang, Adv. Eng. Mater. 6 (2004) 299-303.

[5] D.B. Miracle, O.N. Senkov, Acta Mater. 122 (2017) 448-511.

[6] C.M. Rost, E. Sachet, T. Borman, A. Moballegh, E.C. Dickey, D. Hou, J.L. Jones, S. Curtarolo, J.P. Maria, Nat. Commun. 6 (2015).

[7] A. Moballegh, C.M. Rost, J.P. Maria, E.C. Dickey, Microsc. Microanal. 21 (2015) 1349-1350.

[8] R. Djenadic, A. Sarkar, O. Clemens, C. Loho, M. Botros, V.S.K. Chakravadhanula, C. Kübel, S.S. Bhattacharya, A.S. Gandhi, H. Hahn, Mater. Res. Lett. 5 (2017) 102-109.

[9] S. Jiang, T. Hu, J. Gild, N. Zhou, J. Nie, M. Qin, T. Harrington, K. Vecchio, J. Luo, Scr. Mater. 142 (2018) 116-120.

[10] D. Berardan, A.K. Meena, S. Franger,C. Herrero, N. Dragoe, J. Alloys Compd. 704 (2017) 693-700.

[11] Zs. Rak, C.M. Rost, M. Lim, P. Sarkar, C. Toher, S. Curtarolo, J.P. Maria, D.W. Brenner, J. Appl. Phys. 120 (2016) 095105.

[12] C.M. Rost, Zs. Rak, D.W. Brenner, J.P. Maria, J. Am. Ceram. Soc. 100 (2017) 2732-2738.

[13] X. Sang, Everett D. Grimley, Changning Niu, Douglas L. Irving, James L. LeBeau, Appl. Phys. Lett. 106 (2015) 061913.

[14] D. Bérardan, S. Franger, D. Dragoe, A.K. Meena, N. Dragoe, physica status solidi (RRL)-Rapid Research Letters 4 (2016) 1-6.

[15] D. Berardan, S. Franger, A.K. Meena, N. Dragoe, J. Mater. Chem. A 4 (2016) 9536-9541.

[16] B. Raveau, J. Mater. Chem. A 704 (2005) 1965-1969.

[17] J.D. Gale, A.L. Rohl, Mol. Simul. 29 (2003) 291-341.

[18] C. R. A. Catlow, A. M. Stoneham, J. Phys. C: Solid State Phys. 16 (1983) 4321-4338.

[19] G.V. Lewis, C.R.A. Catlow, J. Phys. C: Solid State Phys. 18 (1985) 1149-1161.

[20] M. S. Islam, L. J. Winch, Physical Review B 52 (1995) 10510.

[21] W. Smith, T.R. Forester, J. Mol. Graphics 14 (1996) 136-141.

[22] R. Darkins, M.L. Sushko, J. Liu, D.M. Duffy, Phys. Chem. Chem. Phys. 16 (2014) 9441-9447.

[23] P.S. Branicio, D.J. Srolovitz, J. Comput. Phys. 228 (2009) 8467-8479.

[24] M. Glazer, J. Wark, Statistical mechanics: a survival guide Oxford University Press, 2002.

[25] C.M. Rost, Entropy-Stabilized Oxides: Explorations of a Novel Class of Multicomponent Materials PhD Thesis, North Carolina State University, USA, 2016.