1. Introduction
The requirement of nanomaterials with novel properties is prevalent in current society [1]. In general metal oxides are utilized for a multitude of purposes, from waste water treatment to self-cleaning glasses [2]. Hence, the utilization of rational modelling to determine properties and behaviour of such systems is critical in finding new materials with unique, utilisable properties. Modelling of ionic systems has seen widespread use in many fields in the last decade, and is increasing with the significant progression of computational processing power [3]. The aim of this study is to explore how doping CaO with different proportions of MgO, SrO and BaO affects their observed thermodynamic properties. Fig. 1 illustrates how the supercell changes when varying the composition.

![Figure 1: Visualisation of the changing composition within the 2x2x1 supercell. The green atoms represent Calcium ions, while the blue represents the dopant cations.](image)

2. Methodology

**SOD (GULP v3.4)**
Site-occupancy Disorder (SOD) software was used to generate the 2x2x1 supercell of the solid solution of Ca$_x$M$_{1-x}$O where (M= Mg$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) [4]. SOD generates the many input files for the corresponding number of microstates which arise from doping the system. From this the configurational average of the entropy; enthalpy; Gibbs free energy and cell volume is obtained.

**Mean field Theory**
An alternative approach to using SOD for the calculation of thermodynamic properties with varying composition is to use mean field theory (MFT). When using SOD in tandem with GULP, multiple input files are generated corresponding to each microstate for a given value of composition. The coulombic interactions are calculated via a Ewald summation for each microstate and then the interactions are averaged. However when using MFT the coulombic interactions are averaged directly from the GULP calculation by tuning the occupation at each site within the lattice. (i.e.) for x=0.5 we represent the occupation at each site as $\frac{1}{2}$Ca and $\frac{1}{2}$M, where M = Mg$^{2+}$, Ba$^{2+}$, Sr$^{2+}$. While MFT may be seen as less accurate, thermodynamic parameters of compositions that may be difficult/inaccessible to obtain using SOD can be calculated (i.e. x=0.0001).

**Thermodynamic Data**
The Gibbs and enthalpy mixing energies were calculated via the extracted data from the SOD calculations, at 300K and 20000K. Cell parameters were determined via the calculated cell volumes at each composition. The data for the MFT calculations were calculated directly using GULP for each composition.

3. Vegard’s Law
Vegard’s law states that the variation of the cell parameter with composition is linear. Fig. 2 shows the results for each composition, and are in compliance with Vegard’s law. In comparing the different cations, Ba$^{2+}$ and Sr$^{2+}$ substitutions have a positive gradient and follow the same trend. The cell parameter increases with x. However, for Mg$^{2+}$ this is not the case, the gradient is negative. This can be attributed to variation in the ionic radii of the cations. The metals vary in ionic radii in the order Mg$^{2+}$<Ca$^{2+}$<Sr$^{2+}$<Ba$^{2+}$, in the case of Mg$^{2+}$ a smaller metal cation is being substituted; hence a decrease in the cell parameter is observed. Literature data of Ca$^{2+}$ substitutions in SrO show a similar trend, a negative slope is the result of a smaller cation being substituted [5].

![Figure 2: Plots of the lattice parameter vs changing composition. The plot on the right represents the calculation of the lattice parameter using MFT.](image)

4. Enthalpy & Gibbs of mixing
The data shows that at higher temperatures the Gibbs energy of mixing decreases, implying mixing is more favourable at higher temperatures. The trend was observed regardless of the substituted cation, this trend can be attributed to the relationship shown in eqn. (1). Mixing energies were calculated using eqns. (3) and (4)

$$\Delta G = \Delta H - T \Delta S \quad \text{(1)}$$

As the composition changes from x = 0.000 - 0.5 the $\Delta G$ is increasing as mixing is an unfavourable process, though a slight decrease in $\Delta G$ is observed at x=0.5 probably due to the symmetry of the system at this composition. This trend is observed for all the solid solutions. At higher temperature the magnitude of $\Delta S$ also increases in turn causing mixing to be more favourable at higher temperatures. The mixing phenomenon was observed to be endothermic in all cases, as can be seen from Fig 3, the data regarding the other solid solutions has been omitted.

$$\Delta G_{mix} = \sum \left[ x \left[H(M, Ca_{1-x}, O) \right] - x[H(M, Ca_{1-x}, O)] - (1-x)[H(Ca_{2-x}, O)] \right] \quad \text{(3)}$$

$$\Delta H_{mix} = \sum \left[ x[H(M, Ca_{1-x}, O)] - x[H(M, Ca_{1-x}, O)] - (1-x)[H(Ca_{2-x}, O)] \right] \quad \text{(4)}$$

![Figure 3: Plots of the lattice energy vs varying composition. The plots on the left and right represent the calculation of the lattice energy using SOD and MFT respectively.](image)

5. Lattice energetics using Mean Field Theory
As mentioned in the methodology, when using MFT we take the average of all the coulombic interactions of a system, rather than summing all the interactions and then averaging using SOD. As can be seen from the tabulated data the differences in the MFT lattice energies and SOD energies are in the range of -0.1-0.03 eV, which translates to differences of about 1-10 kJmol$^{-1}$. As expected accuracy is compromised, however it must be considered that MFT is a great way to simplify and reduce time taken for calculations involving varying composition.

![Figure 4: The Gibbs free energy of mixing for the solid solution Ca$_x$M$_{1-x}$O (A=Mg$^{2+}$ (B) = Sr$^{2+}$ (C) = Ba$^{2+}$).](image)

6. Conclusion
- Various thermodynamic and structural properties have been computed using SOD (configurational averaging) as well as MFT.
- Vegard’s Law holds for the three oxides studied at 300K and 20000K. The MFT calculation of the lattice parameters show only slight deviation from the SOD values. Suggesting, when calculating structural parameters MFT is a sufficient approximation.
- An anomalous value for the mixture Ca$_x$Mg$_{1-x}$O$_2$ is obtained when averaging using SOD, but not when using MFT. Suggesting there may be an issue with SOD’s generation of the GULP inputs, as this anomaly was not observed when calculating energies using MFT.
- Gibbs energy of mixing was observed to be unfavourable for all the oxides at 300K and 20000K. In the case of Ca$_x$Sr$_{1-x}$O mixing was observed to be favourable at 20000K.
- Lattice energetics calculated using MFT and SOD show differences within the range of 10kJmol$^{-1}$. MFT is less accurate, but much quicker to run and can be useful for when large amounts of computing power aren’t available.

References:
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