INTRODUCTION
Solid oxides have come to prominence with applications such as window coatings due to their durability and optical properties. Oxides with the rock salt structure are considered ideal systems for mixing to give new solid oxide solutions with interesting properties and potential new applications. The unfavourable thermodynamics of mixing mean theoretical studies are a useful way of quickly calculating the properties of these oxides. In this study we have used computational methods based on interatomic potentials to investigate the thermodynamic and structural properties of solid mixed solutions of oxides with magnesium, strontium and barium.

Figure 1. Visualisation of most stable configurations of Ca₀.₃SrO (left to right: x = 0.25, 0.5, 0.75) at 300K. Materials studio was used; oxygen is red, calcium is blue, and strontium is green.

THERMODYNAMIC PROPERTIES

GIBBS ENERGY
- The process is unfavourable for mixing of CaO with BaO/MgO at all temperatures tested (ΔGmix is positive), but is only unfavourable for mixing of CaO with SrO at low temperatures (shown in Figures 2 and 3).
- At high temperatures, mixing CaO with SrO is favourable (ΔGmix is negative).
- As temperature increases, ΔGmix decreases due to increased entropic contributions, following the equation:

\[ \Delta S_{\text{mix}} = \Delta H_{\text{mix}} / T \]

ENTHALPY
- Figure 4 shows that the mixing of group two metal oxides are all endothermic processes at the temperatures tested.
- As temperature increases, the enthalpy becomes more positive, as expected from Kirchhoff's law:

\[ C_v = \Delta H / \Delta T \]

- As composition (x) tends to 0.5, the enthalpy of mixing increases due to increased differences in product and reactant.
- Ba has the largest ΔHmix, which is expected due to the large difference in lattice parameter with CaO (~0.7 Å); with SrO, the lattice parameter difference is ~0.3 Å compared to a difference of ~0.5 Å for MgO which explains why the enthalpy change is the smallest.

CONCLUSION
- Structural and thermodynamic properties of Caₓ₋ₓMₓO (M = Mg, Sr, Ba) have been calculated using interatomic potentials with SOD.
- Mixing was found to be endothermic for all the cases and conditions studied.
- The Gibbs energy change showed that the process is unfavourable for all solid oxide solutions at all temperatures tested except for Caₓ₋ₓSrₓO at high temperatures.
- Vegard’s law was obeyed at all temperatures.

FUTURE WORK
- This work could be taken further by adding pressure as an independent variable, to study the pressure-dependence of thermodynamic and structural characteristics of solid metal oxide solutions.
- Furthermore, the accuracy of the calculations can be improved through the use of larger supercells.
- Additionally, more values of x could be studied, especially around the anomaly (at x = 0.625 for magnesium).
- More data could be taken at low temperatures and around x = 0.5 in order to increase understanding of the apparent metastable state at x = 0.5 for lower temperatures.

REFERENCES