Understanding the growth of doped MgO

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**Experimental conditions**

- Magnetron sputter deposition conditions
  - Unbalanced magnetrons
  - Metallic Mg and Al, Cr, Ti, Y and Zr targets
  - $I_d$ Mg = Cr = 0.5 A
  - $I_d$ Al = 0.7 A
  - $I_d$ Y = 0.8 A
  - $P$ = 0.8 Pa
  - Substrate tilted 45°

- Thin film characterisation
  - Profilometry
  - EPMA
  - XRD: θ-2θ and pole figures
  - TEM

Film:
- 1 µm on Si with native oxide layer

T–S distance and O₂ flow adapted according to the desired stoichiometry
Simulation framework:
- MD simulations
  - MD package DL_POLY
  - Growth simulation**

- Interatomic potential
- Mg\(^{2+}\), Mn\(^{2+}\) and O\(^{2-}\) ions
- Substrate temperature
- \(v_0\) and \(v_{\text{ions}}\)
- Cell size
- Time-step


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Influence of Adding M

- Mg(Cr)O
  - Increase in Cr content
- Mg(Y)O
  - Change in MgO orientation
  - Lack of mobility*

**Mg(M)O systems behave as a solid solution!**

\[
\frac{\text{Crystallinity (a.u.)}}{} = \frac{\text{sample} - \text{background}}{\text{MgO powder}}
\]

\[\chi = 0 - 80^\circ\]
\[\varphi = 0 - 360^\circ\]
Influence of Adding M

Crystallinity (a.u.) = \frac{\text{sample} - \text{background}}{\text{MgO powder}}

• Atomic scattering factor
Replacing $\text{Mg}^{2+}$ by $\text{M}^{3+}$ will affect the structure in two ways:

1) Change in the size of the octahedra.
2) Formation of vacancies, i.e. empty octahedral positions.

**Structure destabilisation**

How many octahedra can be removed?

A first guess*

Based on geometrical considerations, the structure collapses when half of the octahedra positions are replaced.

\[
\text{Mg}_x\text{M}_{1-x}\text{O} = \frac{2x + z(1-x)}{2} \quad \frac{z(1-x)}{2} = \frac{2x + z(1-x)}{4}
\]

\[z=2 \rightarrow \text{Mg(Zn)}\text{O}, \text{transition point at 50% Zn}^{**}\]
\[z=3 \rightarrow \text{Mg(Al,Cr,Y)}\text{O}, \text{transition point at 40% M}\]


A first guess

Based on geometrical considerations, the structure collapses when half of octahedra positions are replaced.

Did we do fine?

Transition point

Not bad but we should do better!

Amorpous

Crystalline

Decreasing packing density

By introducing M ions, we reduce the packing density of the filled octahedral positions. Hence, we should see a transition. But... can we proof this?

Z. Nussinov, Physics 1 (2008) 40
Calculating the Density

- Experimental density
- Calculated density (MD)*

![Graph showing density vs. metal ratio]

How do we use this data?


Calculating the Packing Density

Replacing Mg$^{2+}$ by M$^{3+}$ will affect the structure in two ways:

1) Change in the size of the octahedra. → Problem!
2) Formation of vacancies, i.e. empty octahedral positions.

![Hard sphere model and MD simulations diagrams]
Calculating the Packing Density

![Graph showing O-O distance vs. M metal ratio](image)

Lattice increase → anion size increase

Correction factor, \( f \), is needed!

### Experimental Conditions

- Conditions
- Simulations
- Framework
- Adding M

### Transition

- Why?
- In between?
- Conclusions

### Recognition

- Formulae:
  \[
  \phi = \frac{4 \times 4}{3} \pi R^3 \\
  \frac{a^3}{\sqrt{2}a} = 4R
  \]

- Formulae:
  \[
  \phi = \frac{4 \times 4}{3} \pi f^2 R^3 \\
  \frac{f^2 a^3}{\sqrt{2} f a} = 4 f R
  \]
Calculating the Packing Density

Packing density calculated using theoretic ion radii

Experimental Conditions
Simulations Framework
Adding M Transition
Why?
In between?
Conclusions Recognition

Calculating the Packing Density

amorphous crystalline

amorphous crystalline

What about this region?
In the transition zone, nanocrystals are noticed within an amorphous matrix.

Conclusions

- Change in MgO orientation: lack of mobility
- Change in MgO lattice parameter: Vegard’s law
- Vanishing of the crystalline MgO phase.
- Change packing density
- Transition zone: nanocrystals + amorphous
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