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To cite this version:
Laurent Lermusiaux, Antoine Mazel, Adrian Carretero-Genevrier, Clément Sanchez, Glenna Drisko. Metal-Induced Crystallization in Metal Oxides. Accounts of Chemical Research, American Chemical Society, 2022, 55 (2), pp.171-185. 10.1021/acs.accounts.1c00592. hal-03511965

HAL Id: hal-03511965
https://hal.sorbonne-universite.fr/hal-03511965
Submitted on 5 Jan 2022

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Metal-Induced Crystallization in Metal Oxides

Laurent Lermusiaux, Antoine Mazel, Adrian Carretero-Genevrier, Clément Sanchez,* and Glenna L. Drisko*

CONSPECTUS: The properties of a material depend upon its physical characteristics, one of these being its crystalline state. Next generation solid-state technologies will integrate crystalline oxides into thermal sensitive processes and composite materials. Crystallization of amorphous phases of metal oxides in the solid state typically requires substantial energy input to induce the amorphous to crystalline phase transformation. In the case of silica, the transformation to \( \alpha \)-quartz in a furnace occurs above 1300 °C and that of titania, above 400 °C. These calcination processes are costly in energy but also often degrade complex material architectures or compositions. Thus, low temperature crystallization techniques are required that preserve macro- and mesostructures and complex elemental composition (e.g., organic-, metal-, and semiconductor-metal oxide hybrids/composites). Some solution-based techniques exist to directly fabricate crystalline metal oxides. However, these are not always compatible with the specificities of the system or industrial constraints. A postsynthetic, solid-state approach that reduces crystallization temperature in metal oxides is metal-induced crystallization (MIC).

MIC is the introduction of catalytic amounts of a cation, which can be an s-block, p-block, or d-block cation, that migrates through the solid metal oxide lattice. The cation is thought to temporarily break metal oxide bonds, allowing \([\text{MO}_x]\) polyhedra to rotate and reform bonds with neighboring \([\text{MO}_x]\) groups in a lower energy crystalline phase. Depending on the system, the cation can favor or defavor the formation of a particular crystalline phase, providing a means to tune the purity and crystalline phase ratios. An advantage of MIC is that, although the crystallization occurs in the solid state, the crystallization process can be accomplished for particle suspensions in liquid media. In this case, the energy required to induce the crystallization can come from, for example, a microwave or an ultrasound bath. The crystallization of particles in suspension avoids aggregation from particle–particle sintering. In the case of thin films, the energy for crystallization typically comes from a laser or calcination.

MIC is only recently being used as a low temperature metal oxide crystallization technique, despite being widely used in the semiconductor industry. Here, the mechanism and previous studies in MIC are presented for titania, silica, and other oxides. The beauty of this technique is that it is extremely easy to employ: cations can be incorporated into the system postsynthetically and then are often expelled from the lattice upon phase conversion. We expect MIC to enrich materials for photochromic, optoelectronic, catalyst, biological, and other applications.

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Received: September 23, 2021
1. INTRODUCTION

The physical properties of a material are highly dependent on its crystalline phase, and many crystalline materials have significantly different properties from their amorphous counterpart and other crystal allotropes. The classic example is that of carbon, which can exist as charcoal (amorphous state), diamond (face centered cubic structure), or graphite (either hexagonal or rhombohedral structure), each allotrope exhibiting vastly different physical properties. In the example of silicon particles, the intensity and the frequency of their optical resonances are highly influenced by the crystalline state. Turning to a metal oxide, the photocatalytic activity and the toxicity of titania are both highly dependent on crystalline phase. Piezoelectricity is well-known in α-quartz but absent in amorphous silica.

Crystallization is most often achieved via calcination, where a sample is heated to high temperatures to initiate the amorphous to crystalline transition. Calcination can pose several problems; principally, it can lead to particle–particle sintering and is highly energy consuming. In the case of SiO2, the oxide typically remains amorphous until at least 1300 °C, making it hard to preserve mesostructured materials upon crystallization. One way to decrease crystallization temperature, conserve energy, retain the mesostructure, and ensure crystalline phase purity or produce hybrid crystalline materials is to use a technique called metal-induced crystallization (MIC) (Figure 1). MIC is a fully solid-state process, whereupon one material crystallizes at a lower temperature via contact with a metal that does not form part of the lattice. Soon after, amorphous silicon was also devitrified of amorphous germanium by noble metals, aluminum, and tin. Soon after, amorphous silicon was also devitrified at a lowered temperature by metals. The terminology “metal-induced crystallization” is not used often with regard to silica crystallization, but the concept of devitrification using lattice modifiers has been known since the early 1900s. The effect of dopants on titania crystallization via laser irradiation was first noticed in 1996. Ten years later, the first MIC of titania was reported in 1996.
during classical calcination via metal contamination was reported. However, despite the past 25 years of research into the MIC of oxides, this Account is the first overview on this topic. Here, we present the advances in titania, silica, and other metal oxides crystallized using MIC.

2. TITANIA

2.1. Crystalline Phase Control

Crystalline titania appears in a wide variety of applications, as photocatalysts and photovoltaics, and in a number of food and agricultural products, its crystalline phase is one of the factors impacting its properties. There are three common phases in titania: anatase, brookite, and rutile with anatase and rutile being the most commonly obtainable forms and anatase requiring the least energy to be achieved. Not only do metal cations impact the amorphous to anatase transition, but also they can promote or retard the transformation to either brookite or rutile. In these sections, we will briefly discuss the impact of metal cations on crystalline phase transition; see refs 20–24 for a deeper discussion of this topic. A summary of titania materials produced to date via MIC is presented in Table 1.

2.2. Mechanism of Metal-Induced Crystallization in Titania

Several studies on the mechanism of MIC reported that the metal diffuses throughout the titania structure, whether or not it was originally in the gel.24–28 The cations, typically acting as crystallization catalysts, do not systematically dope the final oxide. Yang et al. proposed that the metals help to rearrange the Ti−O bonds into an energetically more favorable crystalline arrangement.25 The Ti−O bond weakens when a metal cation partially transfers valence electrons to the antibonding orbitals of the Ti−O bond. Heat, coming from an external source, breaks the weakened Ti−O bonds as well as the metal−oxygen bond. Crystalline TiO₂, having free energy lower than that of its amorphous counterpart,29 results in the cation remaining mobile in the gel. By studying the effect of cation dopants on the phase transition of anatase to rutile,29 Nair et al. proposed that cations having a radius comparable to Ti⁴⁺ (60.5 pm) and a charge of less than +4 can occupy a lattice point and thus increase the oxygen vacancy concentration. However, larger cations find themselves in interstitial positions and thus decrease oxygen vacancies. They correlated increased oxygen vacancy concentration with a lower onset of crystal nucleation,29 which is complementary to the mechanism proposed by Yang et al.25 Electron paramagnetic resonance studies of the local metals’ environment within titania gels and crystals have indicated that the cation does not diffuse alone but with some of its ligands.30

2.3. Crystallization Coupling Metal-Induced Crystallization to Different Annealing Techniques

2.3.1. Laser Annealing. Raman lasers can be used to anneal doped and nondoped titania samples to produce thin films containing crystalline anatase and/or rutile phases.17 Camacho-López et al. demonstrated that the required power density to induce phase transformation is 20 times lower in the presence of 2 mol % Co²⁺ than without the metal additive.31 Moreover, the quantity of crystalline material increased with time, and the type of crystalline phase depended on the quantity of cobalt in the titania film.31

2.3.2. Ultrasound Treatment. Sonochemistry, combined with MIC, was first reported as a means to crystallize titania in 2006.19 For example, in ethylene glycol, sonicating amorphous titania led to its crystallization when in the presence of HAuCl₄.32

2.3.3. Convective Heating. Convective heating has been combined with the MIC of titania in two main ways, via incorporation of a cation prior to the sol−gel transition and by postsynthetic diffusion of a metal from a metallic contact layer. Both methods have similar crystallization temperatures.

Rodríguez-Talavera et al. observed the MIC of titania using La, Zn, Al, K, Na, Ca, Ba, and Co.33 The onset crystallization temperature did not depend on the nature of the cation employed, but there was a good correlation between the
temperature of the phase transition from anatase to rutile. The authors attributed the stabilization of the anatase phase to the cation size and oxidation state.

Garciá-Serrano et al. studied the addition of AgNO₃ to the precursor mixture before the sol−gel reaction and found that crystallite size decreased with increasing AgNO₃ concentration. Small crystallite size is commonly observed in MIC because, according to Amarjargal et al., the cation lowers the crystallization temperature, leading to widespread nucleation and a high density of grain boundaries. However, the cation is then typically ejected from the lattice, as its size is incompatible with insertion/substitution. As the cation moves to the crystallite surface, the impetus for grain boundary migration decreases.

The MIC of titania is achievable by conductive heating of TiO₂ in contact with a metallic layer. The mechanism of crystallization of thin films using a gold layer was studied via Raman imaging and showed that very small and sparse

Figure 3. SEM images of amorphous titania (a) before and (b) after MIC under microwave irradiation. (c) X-ray diffractograms of titania before treatment (red), after calcination of Mn²⁺ doped titania at 150 °C (blue), after microwave treatment of TiO₂ at 150 °C (green), and after of Mn²⁺-containing titania at 150 °C (black). Reproduced from ref 1. Copyright 2020 American Chemical Society.

Figure 4. Bright field TEM images of ultramicrotomed sections of beads (a) prior to contact and after (b) 5, (c) 10, and (d) 90 min of exposure to the cation and microwaves. The scale bars represent 1 μm. The inset represents the SAED pattern of a large collection of particles from each sample. (e) The XRD diffraction pattern, ranging from no treatment (gray) to 90 min of irradiation time (dark blue). (f–h) The EDX analysis for Mn (red) for the corresponding micrographs of (b–d). (i) SEM image and scanning Auger mapping of a single particle treated with microwaves for 10 min containing (j) titanium, (k) manganese, and (l) oxygen. Adapted from ref 1. Copyright 2020 American Chemical Society.
Table 2. Metal-Induced Crystallization Conditions for Amorphous Silica

| devitrification agent | onset temperature (°C) | phase | comments | reference |
|-----------------------|------------------------|-------|----------|-----------|
| CaCO₃                 | 975                    | α-quartz | peak intensity increases with calcination temperature | 41 |
| CaCO₃                 | 1100                   | α-cristobalite | | 41 |
| AgNO₃                 | 500                    | cristobalite | | 16 |
| H₂A₄Cl₂               | 950                    | β-cristobalite | | 19 |
| Au⁺⁺ or Na⁺           | 900                    | cristobalite | 2.2 wt % Au with 0.6−1.3% Na contained in the SiO₂ | 42 |
| CaCl₂, Sr(NO₃)₂ or BaCl₂ | 800          | α-quartz | 0.01−0.03 mol % devitrification agent/Si | 2, 4 |
| MgCl₂, CaCl₂, SrCl₂ or BaCl₂ | α-quartz | 0.1 mol % Mg⁴⁺, 0.025 mol % Ca²⁺, 0.02 mol % Sr²⁺, and 0.01 mol % Ba⁴⁺ in SiO₂ | 2 |
| LiNO₃                 | 870                    | α-quartz | infiltrated with a 0.5 M solution | 43 |
| MgCl₂                 | 1100                   | α-quartz | 0.1 mol % Mg²⁺ | 44 |
| SrCl₂                 | 1000                   | α-quartz | 0.03−0.10 ratio of Sr/SiO₂ | 45 |
| Na₂O flux             | 750                    | cristobalite | SiO₂ spheres contained in a carbon matrix containing the flux | 6 |

2.4. Applications

One of the major advantages of the MIC of titania is the ability to get relatively pure phases of rutile at relatively low temperature,⁴⁴ which show better wettability and increased optical absorption in the red, needed for photocatalytic antimicrobial coatings. Many electronic and optoelectronic devices are fabricated on substrates that are thermally unstable.⁴⁷ Titania can be used in resistive switching for use in memory devices; however, its crystalline form must be obtained, preferably on a glass substrate. These metal-containing titania films produced photoluminescent films with tailorable switching properties.⁴⁴

Further research efforts should also examine the role of the metal’s chemical nature, concentration, and oxidation state. For instance, it was observed that AuCl₃ and clusters of Au₁₁³⁺ incorporated into TiO₂ influenced both phase purity and catalytic activity.⁵⁸ The reasons why different phases are observed when a different devitrification agent is observed remain obscure.

3. SILICA

3.1. Crystalline Phase Control

There are three common polymorphs of crystalline SiO₂: α-quartz, cristobalite, and tridymite, where α-quartz is the most stable.¹⁶ MIC commonly yields either α-quartz or cristobalite with many aspects impacting the MIC of silica, including the morphology of the vitreous material, the type and quantity of cation used, and the presence of a crystalline interface with the silica gel (leading to epitaxial crystal growth). SiO₂ materials produced using MIC are presented in Table 2. Silicates can also occur for certain cations, particularly if cation concentration in the SiO₂ lattice is too high.² Just as in classical crystallization techniques, the degree of crystallinity will increase by increasing the time and temperature of the crystallization.¹⁹ The obtained crystalline phase and the ratio of quartz to cristobalite are also dependent on the calcination time and temperature.

MIC in silica is thought to occur via the reorganization of [SiO₄]₄ tetrahedra, as is the case for TiO₂. In both the amorphous and crystalline states, the oxygen atoms forming the vertices are shared by two adjacent tetrahedra.⁵⁹ Network modifiers, which are typically mobile cation species, break the connections between these [SiO₄]₄ tetrahedra, allowing them to freely move to reorganize into a lower energy, crystalline phase.⁴⁷
3.2. Impact of Amorphous Silica Morphology on Crystallization

The morphology of silica can impact the capacity of MIC in two ways. The first is the distribution of devitrification agents throughout the material; the second is related to the ability of the SiO₂ to shrink as it crystallizes. Although the ions move through solid-state silica, mesoporosity allows a homogeneous distribution of these ions throughout the material before heat treatment begins. Mesoporosity additionally accommodates volume changes, permitting the lattice to shrink during crystallization.

Garnica-Romo et al. studied the impact of the amorphous silica structure on crystallization by changing the H₂O/TEOS molar ratio during synthesis. The authors concluded that crystallization must begin at the particle surface. Authors with Ca placed in the core did not crystallize. The crystal phases other than α-quartz densification is correlated to the quality and orientation of the silica top-layer and, then, propagated into the silicon substrate as the substrate oxidized, creating a quartz layer of tunable thickness. The macropores and the larger mesopores of ~30 nm maintained their structure upon crystallization, whereas the smaller mesopores produced crystal domains with a trapezoidal habit.

3.3. Nature and Quantity of the Devitrification Agent

We previously showed that, among many different cations, only Sr²⁺, Ba²⁺, and Ca²⁺ demonstrated epitaxial growth of macroporous α-quartz films on (100) silicon substrates. To understand the mechanism, the ratio of Sr²⁺ to SiO₂ was varied and correlated to the quality and orientation of α-quartz films. For ratios larger than 0.05, the microstructure is dominated by α-quartz densification that significantly decreases the mosaicity of the films.

In our work in thin films, we reported testing Li⁺, Na⁺, Sr²⁺, Mn²⁺, Fe²⁺ /Fe³⁺, Ca²⁺, Ce³⁺, and La³⁺, where only some of these led to SiO₂ crystallization. Of the series of cations that did not induce silica crystallization, it is likely that at least some of these are able to crystallize silica but that the conditions were not suitable. We showed that, in the crystallization of hollow silica particles using alkali earth metals, the minimum salt concentration needed to induce crystallization decreases as the cation radius increases (Figure 7). When the concentration was suboptimal, residual amorphous silica was present. Higher quantities of devitrification agent are needed for smaller cations than for larger ions, as the ratio of nonbridging oxygens/Si in glass increases as a function of cation size. Venezia et al. found differing results: for larger atoms, namely, potassium and cesium, crystallization only occurred with high concentrations of alkali ions. Moreover, the concentration of sodium impacted the transition temperature of silica to cristobalite: the higher the concentration of devitrification agent, the lower was the temperature of the transition.

Matsuno et al. infiltrated a colloidal crystal of silica with Li⁺ and, then, encased the silica spheres in a matrix of poly(furfuryl alcohol). Li⁺ melted the silica completely, followed by crystallization within a carbon scaffold, producing a monocrystalline quartz superlattice with grains several micrometers in size (Figure 8). This same group has recently adapted their synthesis method using NaNO₂ dissolved into a phenolic resin to serve as the carbon scaffold to achieve mesoporous cristobalite.

3.4. Epitaxial Relationships

Silica films in contact with Si-(100) demonstrate mono-oriented α-quartz upon MIC (Figure 9). The crystalline substrate may suppress the formation of silicates and crystal phases other than α-quartz, which are otherwise observed. The crystallization is not induced by the epitaxial relationship, but the crystal phase and orientation are selected by the substrate.

3.5. Maintaining Structure during Crystallization

Thanks to MIC, we were able to produce the first quartz-based nanomaterials on a substrate via a bottom-up synthesis (Figure 10). Silica with three different pore morphologies spanning from mesopores to macropores were prepared and then crystallized on a silicon substrate using either Sr²⁺ or Ba²⁺ to induce crystallization. Crystallization started in the silica top-layer and, then, propagated into the silicon substrate as the substrate oxidized, creating a quartz layer of tunable thickness. The macropores and the larger mesopores of ~30 nm maintained their structure upon crystallization, whereas the smaller mesopores produced crystal domains with a trapezoidal habit.

To probe the range of mesopores that could be retained, we used several PB−PEO diblock copolymers as templating agents to make amorphous silica films with varying wall thicknesses and mesopore diameters (Figure 11). These were then crystallized by infiltrating the mesopores with an alkaline earth metal salt and heating in a furnace. Pores larger than 25 nm were retained upon crystallization. In samples where the mesoporosity was preserved upon crystallization, the d-spacing of the original silica film was maintained (Figure 11). Typically, mesopore structures are lost during the crystallization of silica due to the relatively slow nucleation rate followed by the extremely fast growth rate of quartz, which generates crystallites much larger than the original pore structures. However, we have observed that the MIC method...
often generates smaller crystallite sizes than those produced via high temperature calcination. In addition to curvature, wall thickness also likely affects the ability to conserve the mesopore structure during crystallization. Thus, we studied whether or not very thin walls (10 nm) permitted structural preservation during MIC. In the absence of mesoporosity, the heat treatment time needed to be tripled to achieve crystallization. However, even with SiO₂ wall thicknesses below 10 nm, the macropore structure remained upon transformation into a crystalline phase.

We further studied morphological preservation in structured nanoparticles here, exploring the impact of the metal ion radius on crystallization behavior (Figure 12). During the crystallization process, the mesopores in the silica wall, having a diameter of several nanometers, lost their structure to produce a densified 20 nm shell around a hollow center (∼80 nm). The progressive collapse of the mesoporosity with increasing treatment temperature can be observed in the SEM micrographs and in the disappearance of a hysteresis loop in the nitrogen adsorption–desorption experiments (Figure 12). The shell was polycrystalline with the average crystallite size depending on the treatment temperature.

### 3.6. Material Fabrication

The major advantage of MIC is the ability to retain a complex and delicate morphology upon crystallization. Putz et al. were able to 3D print hierarchically porous silica into a lattice-like scaffold structure. The mesoporosity was then infiltrated using a MgCl₂ solution and then calcined, crystallizing to α-quartz (Figure 13).

The MIC of silica films leads to epitaxial crystallization of the silica phase thanks to the small mismatch with the crystalline silicon substrate. Patterned substrates are no different. Zhang et al. have shown that silica xerogels containing a small amount of SrCl₂ can be patterned using soft imprint lithography (Figure 14). All of the pillars produced on the substrate contained the same crystallographic phase. There are other methods to micropattern quartz surfaces, and of these, the thinnest quartz crystals are about...
However, when a patterned silica film is crystallized using MIC, α-quartz films as thin as 200 nm are possible, allowing the operating frequency of the material to be 50 times higher than previously fabricated devices.

The ability to retain the mesostructure and use epitaxy to select for a particular phase orientation is interesting in terms of the piezoelectric properties of silica. The piezoelectric response in α-quartz films can be measured using piezoelectric force microscopy and direct piezoelectric force microscopy. When direct piezoelectric force microscopy was used, the first direct measurement of the $d_{33}$ piezoelectric coefficient in these epitaxial quartz thin films was made. The piezoelectric response was similar to bulk crystals and homogeneous irrespective of the macrostructuration, demonstrating structural and functional homogeneity within films grown by MIC.

3.7. Applications

The integration of piezoelectric quartz onto silicon in the single crystalline form can trigger development in sensors. Quartz finds a place in many application areas, ranging from biology to electronics. Its nanostructuration receives attention due to its piezoelectricity and biocompatibility. However, the current techniques for quartz-based devices on silicon substrates are limited in terms of device thickness and their integration, which directly affects the overall performance and increases the integration cost. Thanks to the MIC of sol–gel silica films combined with nanoimprint lithography and microfabrication techniques, the first α-quartz (100)-based microcantilever device was fabricated on a silicon–insulator–silicon (SOI) (100) substrate (Figure 15). The parameters that directly affect the device performance, such as the crystal
quality, piezoelectric functionality, and quality factor of the quartz, were preserved during the microfabrication process. These ultrasensitive quartz devices are capable of measuring tiny masses (<10 pg) or forces through a variation in the resonant frequency.

4. OTHER OXIDES

4.1. Alumina

Alumina is an important material possessing several crystalline phases of different chemical, electrical, and mechanical properties. Among them, α-alumina is stable at high temperatures and therefore widely used in modern industries. It is usually prepared by the first dehydration of amorphous alumina at 500 °C to form γ-alumina, followed by an annealing step at 1100 °C. The temperature of the γ-to-α transition can be influenced by some cation additives. Although some cations were found to accelerate the transition (Fe²⁺, Cu²⁺, Mn²⁺, Cr³⁺, or Ti⁴⁺), 54–57 most cations, such as the monovalent (Li⁺, Na⁺, Ag⁺, K⁺, Rb⁺, and Cs⁺) 58,59 or divalent cations (Co²⁺, Ni²⁺, Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺), had no effect or retarded the transition. 56

It has been reported that the addition of small amounts of specific fluoride salts can decrease the polymorphous transformation temperature of the α-Al₂O₃ phase. Živkovic et al. showed that the addition of 2% fluoride using AlF₃, MgF₂, and CaF₂ decreased the crystallization temperature by up to 400 °C, whereas alkali fluoride salts (NaF, LiF, and Na₃AlF₆) did not impact the phase transition of aluminum oxide. 60 Whereas Wu et al. found AlF₃ and ZnF₂ to be effective accelerating agents for the gamma to alpha phase transformation, 57 Li et al. found contradictory results: LiF and AlF₃ were capable of inducing Al₂O₃ crystallization at a much lower temperature than the pure oxide, but ZnF₂ did not. 61 Choi et al. later expanded the study of fluoride salts, adding chloride salts to

![Figure 10](image1.png)

Figure 10. (A, D, G) SEM images of amorphous silica films and (B, E, H) AFM images of crystalline α-quartz structured thin films after the MIC. (C, F, I) Diagram of the morphology of the crystalline thin film. Reproduced with permission from ref 3. Copyright 2013 AAAS.

![Figure 11](image2.png)

Figure 11. Large mesopores remain intact upon MIC using either Ba²⁺ or Sr²⁺ of structured silica films. Reproduced with permission from ref 47. Copyright 2014 The Royal Society of Chemistry.
the devitrification agent mixture. In the case of sodium ions, the chloride salts promoted larger and more homogeneous crystal growth.

4.2. Semiconductor Oxides

Amorphous semiconductor oxides, such as ZnSnO₃ (ZTO), InGaZnO (IGZO), and InGaO (IGO), have attracted considerable attention as an alternative to current silicon-based semiconductors due to their superior properties, such as high mobility, low-temperature fabrication, good transparency, and a low leakage current. They have been widely used as key elements of versatile optoelectronics and are promising candidates for active materials for high-performance thin-film transistors. However, crystalline oxide semiconductors are more performant and more likely to meet the requirements of next-generation optoelectronics, such as higher field effect mobility. Recently, Jeong’s group demonstrated that the MIC processes of vacuum-deposited amorphous semiconductors yield high-quality crystalline ZnSnO₃ semiconductors at low temperatures (Figure 16a). This achievement was obtained by applying a tantalum metal capping layer to the back surface of the metal oxide. During the annealing process, the Ta film oxidizes to form TaOₓ and releases electrons to the underlying layer. These electrons weaken the metal oxide bonds. The bonds eventually break and reform into a crystalline phase (Figure 16b). The approach was successfully extended to other oxide semiconductors, such as InGaZnO, ZnON, and IGO. They all exhibit improved performances and long-term stability, thanks to the tantalum oxide layer encapsulation, for applications in the display industry and flash memory application.

4.3. NiₓO, TiOₓ, and SnOₓ

During an attempt to incorporate a NiₓO hole-transporting layer into hybrid organic−inorganic perovskite solar cells, Hou et al. discovered that the sintering temperature of a NiₓO layer could be lowered by 100 °C by embedding it in a Au phase. The metal not only induces amorphous-to-crystalline physical transformation but also catalyzes the condensation of the sol−gel precursors. MIC was shown to occur in a variety of sol−gel materials, including NiₓO using either Au or Ag; TiOₓ using Ni, Au, or Pt; SnOₓ using Ni.

4.4. LiCoO₂

LiCoO₂ is the most widely used cathode material in thin film batteries, which is usually fabricated as amorphous thin films requiring heat treatment to crystallize and function optimally. Complete crystallization is achieved at 700 °C, which is too high for microelectronics. Cho et al. prepared LiCoO₂ thin...
Figure 14. (a, b) Crystallized, epitaxial $\alpha$-quartz pillars organized on a silicon substrate produced using soft imprint lithography. (c) TEM image and electron diffraction of a monocrystalline pillar. (d) X-ray diffractogram showing the (100) $\alpha$-quartz crystallographic orientation. (e) Synthetic protocol. Reproduced with permission from ref 45. Copyright 2019. Accessible via the Royal Society of Chemistry Creative Commons Attribution 4.0.

Figure 15. General schematic of the microfabrication steps of piezoelectric nanostructured epitaxial quartz-based micro- and nanoelectromechanical devices. Reproduced with permission from ref 53. Copyright 2021. Accessible via Wiley/VCH Creative Commons Attribution 4.0.
films by deposition using magnetron sputtering. They demonstrated that the Al-induced crystallization of LiCoO$_2$ was achieved at 600 °C and showed better structural and electrochemical properties than the reference.

4.5. MoO$_3$

Cheyns et al. demonstrated that MoO$_3$ thin films could be used as thickness-tunable transport layers in organic photovoltaics if doped with small amounts of metal. The samples were prepared by thermal evaporation and deposition on a substrate without annealing. The improved crystallinity enhanced the conductivity with the onset crystallization temperature being reduced from 450 °C to approximately room temperature.

Seeing the diversity of systems that respond to MIC, we can conclude that this is a very generalizable phenomenon. It is worth doing further research to optimize the crystallization temperature, the degree of crystallinity, and the phase control to better increase material performance and to produce crystalline temperature-sensitive hybrid and composite materials.

5. CONCLUSIONS AND PERSPECTIVES

MIC is a powerful tool to crystallize amorphous materials at low temperature and tackle industrial challenges. It is still a growing domain in metal oxides, despite its large spread usage in silicon and germanium crystallization. The basis of the MIC method is that metal cations result in the recombination of oxide bonds and a large variety of cations can be used as devitrification agents; however, the optimum concentration varies as a function of cation size and oxidation state and the metal oxide. Different cations affect the temperature of crystallization, the size of crystal domains, and the crystalline phase(s) obtained. Mixtures of cations can provide fine control over the mix of different crystal phases. However, the mechanisms involved in MIC are not yet well enough understood to have a model that predicts the effects of a given cation on the crystallization temperature of a given oxide. Many different techniques can be used to provide the energy needed for the phase transformation, including microwaves, sonochemistry, lasers, and classical calcination methods. It is possible that, in some of these techniques, a mixture of crystallization mechanisms occurs simultaneously, for instance, dissolution–reprecipitation of crystalline phases in tandem with MIC.

One aspect that still needs to be examined is crystal nucleation and growth during MIC. There are some instances where a film or a nanosized object is either perfectly crystalline or completely amorphous. We have observed this occurrence in thin films where a certain percentage does not crystallize upon heat treatment, while others are completely crystalline across the entire thin film. The same is visible in batches of particles where some are crystalline while others remain amorphous.

Future research will certainly focus on hybrid and composite materials. For instance, a metal oxide could be crystallized on heat sensitive plastic substrates, or crystallization could be induced at low temperature in the presence of metals, circumventing metal melting and dewetting.

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Figure 16. (a) Representation of the IGZO crystallization mechanism induced by a Ta layer. (b) Cross-sectional TEM images of the IGZO layer with the Ta layer after thermal annealing at (top) 200 °C and (bottom) 300 °C under an O$_2$ atmosphere. Selected area electron diffraction patterns near the top and bottom interface are shown in the insets. Adapted with permission from ref 64. Copyright 2017. Accessible via Springer Creative Commons Attribution 4.0.
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Notes
The authors declare no competing financial interest.

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Adrian Carretero-Genevrier has been a CNRS Researcher at the IES since 2016, where he leads the nanochemistry group (www.nanochemlab.com). He obtained his Ph.D. in 2010 in Materials Science from the Université Autònoma de Barcelona and then conducted a postdoc at the LCMCP. His research aims to understand the growth mechanisms of functional oxide nanostructures synthesized by soft chemistry and to integrate sensing and harvesting energy functionalities into MEMS and other resonant systems. He has been awarded a Starting Grant from the European Research Council, the young researcher award (ANR JCJC), and the outstanding Award for a Ph.D. in Materials Science.

Clément Sanchez is an Emeritus Professor at the Collège de France and chair of Chemistry of Hybrid Materials. He was the director of The Laboratoire de Chimie de la Matière Condensée de Paris from 1999 to 2013. He received a Ph.D. in physical chemistry from the University of Paris VI in 1981. He has a chair position at the Institut of Advanced Study of the University of Strasbourg (Chair of chemistry of ultradivided matter, 2020–2021, USIAS) and at the ICMCB. He specializes in the field of nanochemistry and physical properties of nanostructured porous and nonporous transition metal oxide-based gels and hybrid organic–inorganic materials in the form of monoliths, microspheres, and films.

Glenna L. Drisko pursued her doctorate at The University of Melbourne, studying the control of pore structures in metal oxides. She performed a postdoctorate at the LCMCP, where she first learned about MIC. Upon becoming a CNRS research scientist in the ICMCB in 2017, she continued studying sol–gel synthetic processes, crystallization, and fabrication of optical metamaterials from crystalline dielectric particles. She has been awarded the L’Oreal/Unesco award for Women in Science. She launched her independent career via a Junior Chair, which was followed by funding from an ERC starting grant entitled Scatter (https://glennadrisko.com/).

ACKNOWLEDGMENTS
G.L.D. received funding for this work from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (Grant agreement No. 948319). A.M. and G.L.D. were supported by the LabEx AMADEus (ANR-10-LABX-42) in the framework of IdEx Bordeaux (ANR-10-IDEX-03-02), i.e., the Investissements d’Avenir program of the French government managed by the Agence Nationale de la Recherche. A.C.-G. acknowledges the European Research Council (ERC) under the European Union’s Horizon 2020 Research and Innovation Programme (project SENSISOFT No. 803004) for financial support. C.S. thanks Université de Bordeaux and Laboratories and its Labex for support.

ABBREVIATIONS
EDX, energy-dispersive X-ray spectroscopy; SAED, selected area electron diffraction; PB−PEO, poly(butadiene−ethylene oxide); TEM, transmission electron microscopy; SEM, scanning electron microscopy; XRD, X-ray diffraction

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