Microsymposia

MS.35.2


**Growth of Al-based quasicrystals and other complex metallic phases**

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Quasicrystals are formed in a couple of Al-based ternary systems with decagonal AlCoNi being the best studied phase. Decagonal quasicrystals that have been successfully grown as cm$^3$-size single crystals [1] may be structurally described as periodically stacked quasiperiodic atomic planes.

Some phases in the Al-Co-Ni system as well as in related ternaries with chemical composition close to that of the parent quasicrystalline phase consist of the same type of large icosaedral clusters and the same periodicity of stacking of the planes with similar structure motifs, but are periodic in all three directions. They are called approximants to quasicrystals or complex metallic phases because sometimes they have very large lattice parameters and hundreds or even thousands of atoms per unit cell.

Comparing these two types of crystals, quasicrystals may be considered as the ultimate case of complex metallic phases with a unit cell of infinite dimensions. They allow comparative studies as to judge whether some unusual properties of quasicrystals arise from the lack of periodicity or from the clusters that are common to all these phases.

Using the Czochralski method we have grown decagonal AlCoNi and AlCoCu quasicrystals and various complex metallic phases of the Al$_7$TM$_2$ type (TM: transition metal) that are approximants to their parent quasicrystals: monoclinic Al$_7$(Co,Ni)$_2$, orthorhombic Al$_7$Co$_2$, monoclinic Al$_7$Fe$_2$, and its ternary extensions Al$_7$(Fe,Cr)$_2$ and Al$_7$(Fe,Ni)$_2$. Since all these phases cannot be crystallized from congruent melts but only at temperatures below their peritectic reaction, Czochralski growth was done from Al-rich solutions. Permanently decreasing liquids temperatures during the experiment and extremely low pulling rates in the range of 100 μm/h are some of the consequences. Nevertheless, cm$^3$-size single crystals were successfully grown [2] that are large enough for surface science studies and for a number of investigations of the physical properties of these complex phases.

Based on these approximants as well as on the decagonal AlCoNi and AlCoCu quasicrystals, some morphological features that could be observed during growth will be compared and physical properties will be presented that may help to understand the similarities and the differences between these phases. The large icosahedral clusters seem to be the dominant feature as well as the same periodicity of stacking that can be found in all these structures in individual phases. But, certainly it is too early to totally ignore some influence due to three-dimensional periodicity or quasiperiodicity.


**Keywords:** quasicrystal, approximant, crystal growth

MS.35.3


**Influence of SO$_4^{2-}$ and SeO$_4^{2-}$ on the crystallization of CaCO$_3$: structural and morphological aspects**

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Crystallization in the CaCO$_3$–H$_2$O system is a relevant topic in a wide variety of disciplines, from geology and geochemistry to biominalerization and industrial crystallization. Although calcite is its most stable polymorph under Earth’s surface conditions, CaCO$_3$ can precipitate as three different crystalline forms: vaterite, aragonite and calcite. Moreover, a number of hydrated and amorphous phases with different water contents can also precipitate. The nucleation and growth of metastable CaCO$_3$ polymorphs is commonly related to the predominance of kinetic factors over thermodynamic properties.

It is well known that the presence of different foreign ions in the fluid during CaCO$_3$ crystallization can promote the formation of metastable phases. The role played by these ions can be a consequence of different factors, ranging from their incorporation in the structure of the crystal during the growth process to their adsorption onto specific sites and to modifications of the solvent structure. The possible incorporation of foreign ions into the structure of the different polymorphs would change their energetic properties. Since the free energies of the different CaCO$_3$ polymorphs are originally close, these changes might lead to stability crossovers, with consequences regarding the polymorph selectivity at nucleation and the development of transformations between polymorphs. Therefore, when foreign ions are present in the crystallization medium, both kinetic and thermodynamic factors have to be considered to understand the formation of CaCO$_3$. Recent studies have shown that tetraedral anions like sulfate and selenate, are among the most influential in the crystallization of CaCO$_3$, contributing to the stabilization of amorphous calcium carbonate in biogenic systems [1] or vaterite [2] in inorganic systems.

We present here experimental results that illustrate the influence of the presence of SO$_4^{2-}$, and SeO$_4^{2-}$ anions in the nucleation and crystal growth of CaCO$_3$ in aqueous solutions at room temperature. In both cases, this influence involves the formation of unexpected polymorphs and affects the energy downhill transformation sequence. Furthermore, the size and the habits of the obtained calcium carbonate crystals are also modified by the presence of these anions.


**Keywords:** calcium carbonate polymorphism

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**Biomimetic calcite crystal nucleation and growth from ACC and PILP amorphous precursors**

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Biologically formed hard tissues are highly valued prototypes for the synthesis of new materials because of their remarkable structures and evolved mechanical properties. By now it is well established that biologically mediated crystallization is formed via an amorphous precursor [2], [3], [4]. Gover [1] proposed an additional step in