

Synthesis and Phase Relations of Binary Quasicrystalline and Approximant Phases

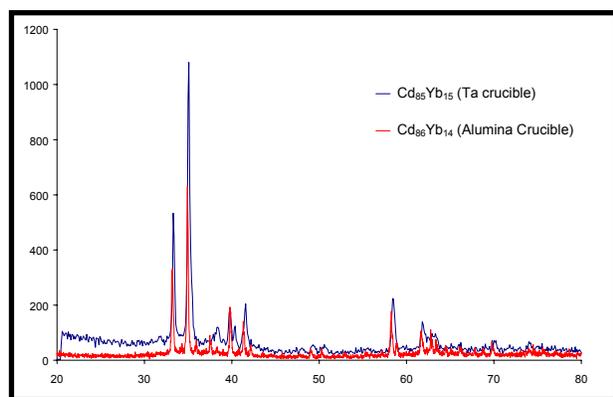
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Abstract:

This project is directed towards the determination of phase stability differences between aperiodic and crystalline materials. Thermodynamically stable quasicrystalline phases were long held to exist only in ternary systems, but the recent discovery of stable binary alloys provides the intriguing opportunity to gain better insight between the structural versus chemical stabilities that has been elusive in ternary and higher order systems. The simplicity of a binary system presents numerous advantages in both computational and experimental investigations of structure.

Recent Results:

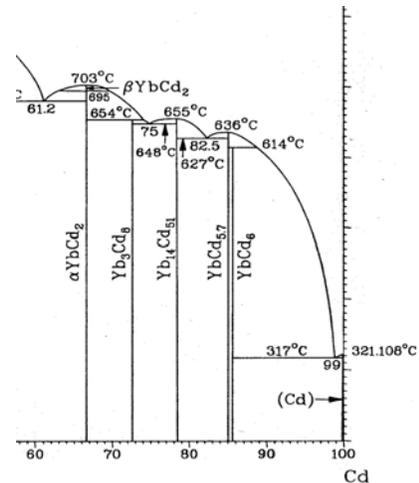
We report, for the first time, the synthesis of a bulk single grain of icosahedral $\text{Cd}_{84}\text{Yb}_{16}$ quasicrystalline phase. Synthesis was accomplished using both Ta and alumina crucibles, by controlled solidification in a Bridgman configuration. Single grains on the order of 0.75 cm^3 have been characterized using scanning electron microscopy, powder X-ray diffraction and transmission electron microscopy. The as-grown samples are single phase with little compositional differences as present along their length. Furthermore, no evidence of the formation of porosity, common to almost all ternary quasicrystalline phases, was found in the as-grown or annealed Cd-Yb. X-ray diffraction spectra (below) of powdered single grains from both crucibles are consistent with published patterns, verifying that the icosahedral structure solidified directly from the liquid.



The primitive nature of the icosahedral order was verified by selected area diffraction in the TEM. Work will continue to investigate the solidification of Cd-Yb alloys, with emphasis on single crystal growth of both the aperiodic and neighboring crystalline phases. Microstructural development will be characterized over a range of growth rate/temperature gradient regimes for stoichiometric and off stoichiometric quasicrystalline and crystalline approximant compositions. These results are currently being augmented with thermal analysis, X-ray diffraction and compositional analysis to characterize the phase relations and solidification behavior. Additional X-ray diffraction and electron microscopy studies will characterize the type of structural defects and correlate their origin and density to the synthesis route. These results will provide a firm basis to begin detailed studies of crystal chemistry of the quasicrystalline structure as well as discerning differences between the solidification behavior of aperiodic solids and crystalline materials. Successful application of these results to growth of single crystals will result in the availability of high quality aperiodic and approximant crystals for structural determination studies and physical property determination in established collaborative efforts both within the Ames Laboratory and internationally.

Significance:

The binary Cd-Yb system is of particular interest because the reported phase diagram (see inset) indicates that the icosahedral phase melts congruently. This phase, $\text{Cd}_{5.7}\text{Yb}$, is the only known aperiodic solid to melt congruently; all other known binary and higher order aperiodic solids melt via a peritectic reaction. The significance of this is that the liquid-solid phase transformation in a congruent-melting system occurs without change in chemistry between the liquid and solid phases. Therefore, there is a direct phase transformation between solid and liquid. Furthermore, two complex crystalline phases exist adjacent to the icosahedral phase in the Cd-Yb phase equilibrium diagram. On the Cd-rich side, a non-congruently melting cubic approximant exists, containing 168-atoms/unit cell with a composition of Cd_6Yb that varies only slightly (3 Cd atoms out of 70) from the $\text{Cd}_{5.7}\text{Yb}$ icosahedral structure. On the Yb-rich side is a congruently melting hexagonal approximant containing 65-atoms/unit cell. These neighboring crystalline approximants of similar chemistry will allow for the investigation of the chemistry/structural stability relationships of aperiodic solids and their crystalline counterparts.



Future Work:

With the basic understanding of the synthesis route that will be acquired in this effort, the physics of solidification for quasicrystalline alloys will be further characterized using high temperature X-ray diffraction at the Advanced Photon Source at Argonne National Laboratory. This work will be in collaboration with M. J. Kramer and D. J. Sordelet and will augment the work on Al-Pd-Mn on local structure and cluster formation. Specifically, the influence of composition variation on the chemical nature and formation of clusters in the liquid will be examined. The use of a binary quasicrystalline system coupled with time-resolved synchrotron X-ray diffraction will allow, quite likely for the first time ever, for the systematic investigation over a range of compositions where the resultant equilibrium solidification product is either crystalline or aperiodic.

Interactions:

Work on synthesis and processing-structure relationships of quasicrystals for surface science investigations continues in collaboration with the Materials Chemistry and Condensed Matter Physics Programs. In addition, numerous international collaborations in the quasicrystal community are on-going focusing on the surface and transport (matter, electronic, thermal) properties of quasicrystals.

Matt Kramer and D. J. Sordelet (M&C) – Structural characterization and Transmission Electron Microscopy

Bruce Cook (M&C) and Clayton Swenson (CMP) – Thermal and electronic transport

E. Belin-Ferre (LCPMR-UMR) – Electronic structure and photoelectron spectroscopy