Chemical and Ceramic Methods Towards Safe Storage of Actinides Using Monazite

(Preparation of powder/sintering/ densification/grain-growth, etc.)

Peter E.D. Morgan, Robert M. Housley And May-Lin DeHaan

Rockwell Science Center
Thousand Oaks, CA 91360

Research Objective

To study the "ceramics" of monazite (more specifically La-monazite), so as, possibly, to enable its use as a host for sequestering actinides (e.g., plutonium) and other radioactive nuclides.

To demonstrate that monazite is a practical, reasonable and economic solution for this problem.

Introduction

The use of ceramic La-monazite, $LaPO_4$, for sequestering actinides, especially plutonium, and some other radioactive waste elements (e.g., fission-product rare earths), thus isolating them from the environment, has been championed by Lynn Boatner of ORNL. Monazite may be used alone or, as it is compatible with many other minerals in nature, can be used in composite combinations. Natural monazite, (Ce,La,RE,Ca,Th,U…) $(P,Si)O_4$, is often found in granites, gneisses pegmatites and is extremely water resistant - examples are known where the mineral has been washed out of rocks (becoming a placer mineral as on the beach sands of India, Australia, Brazil etc.) then reincorporated into a new generation of rocks with new crystal overgrowths and then washed out yet again - being 2.5-3 billion years old. During this aggressive water treatment it has retained Th and U. Where very low levels of water attack have been seen (in more siliceous waters), the Th forms new thorite/huttonite, $ThSiO_4$, or allanite, e.g., $(Ca,Ce)(Al,Fe_2)Si_3O_{12}(OH)$, and remains immobile. Monazite is known to resist metamictization and deleterious volume expansion more than other mineral forms

considered for radwaste disposal and self-anneals easily above ~400°C (Meldrum et al. 1998).

$PuPO_4$ itself has the monazite structure; the PO_4^{3-} unit strongly stabilizes actinides and rare earths in their trivalent state.

The sine-qua-non of ceramic studies and production is the reliable synthesis of reproducible starting powders and precursor chemicals that consistently reproduce the desired ceramic outcome. This has always been a more neglected (i.e. underfunded!) side of ceramic studies (witness how many years passed before pure reproducible powders of alumina or silicon nitride became available long after it was apparent that these were extremely useful ceramics).

The "ceramic" behavior of pure and doped monazite has not hitherto been studied in any great detail.

Experimental and Results

We have:

1) concentrated on the reproducible and automatic production of large quantities of La-monazite (up to the 10kg/week level) using methods adaptable to the larger scale. Several techniques have been tried to produce a heavy, agglomerated powder by aqueous precipitation of both monoclinic monazite and its hexagonal hydrated precursor rhabdophane, $LaPO_4.^1/_2H_2O$; this is so as to allow a simple automatic washing procedure in a newly designed "conical washer." *Fines* are recycled to serve as *seeds* in the precipitation step. Mainly two precipitation methods, where either lanthanum or phosphorous are maintained in excess, have been tried. Either way, it has been found that it is impossible easily to remove ~2% excess phosphorus, which always occurs in the precipitates; washing with tetramethyl ammonium hydroxide base, however, can remediate this.

2) studied the preparation of $LaPO_4$ from various solution stable aqueous precursors such as:

(i) from La nitrate and phosphorous acid (N.B. *phosphorous* not phosphoric);
(ii) from La nitrate and methyl phosphonic acid
(iii) from La nitrate and phytic acid (aka inositol hexaphosphate).

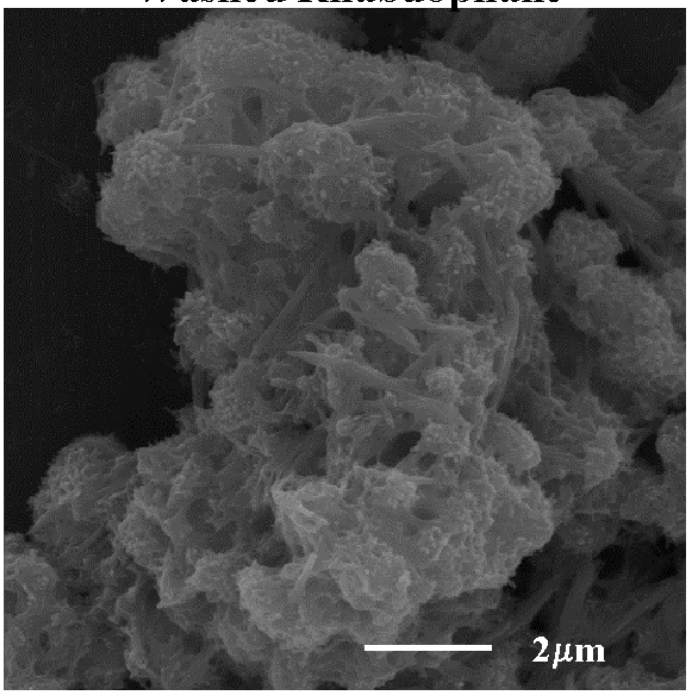
Of these (iii) is likely the most important for plutonium or other nuclear waste due to its complexing ability.

Phytic acid is a poly-dibasic acid that forms acid soluble complexes with many cations which can be precipitated by raising the pH. It is readily available from seeds (soybeans, grapeseed, etc. - up to 100,000 tons a year could be produced as a by-product according to the Department of Agriculture!) where it stores Mg, Ca and phosphate ready for germination. Thus, mixed with radioactive elements and La, it sequesters them; on heating, doped monazite is produced as a reactive powder for ceramic processing.

Studies of sintering/densification so far have shown that with the ~2% excess phosphorus the powders sinter readily via a liquid eutectic above ~1050°C; coincident liquid phase stimulated grain growth is rapid. The stoichiometric powder (i.e. exactly 1:1 La:P) sinters with difficulty and has much less grain-growth at lower temperatures, addition of, e.g., a few percent alumina encourages sintering and inhibits grain growth. In other programs it has been discovered that monazite, surprisingly, shows forms of low temperature plasticity. Not surprising then is that monazite can be fairly easily hot-pressed to high density at approximately 1200°C (but must be protected from reduction by graphite). Studies on hot pressed material are underway.

This is the SEM appearance of our standard rhabdophane ($LaPO_4.^1/_2H_20$) which is now made in multi-Kg amounts by precipitating La nitrate solution (in excess) with phosphoric acid:

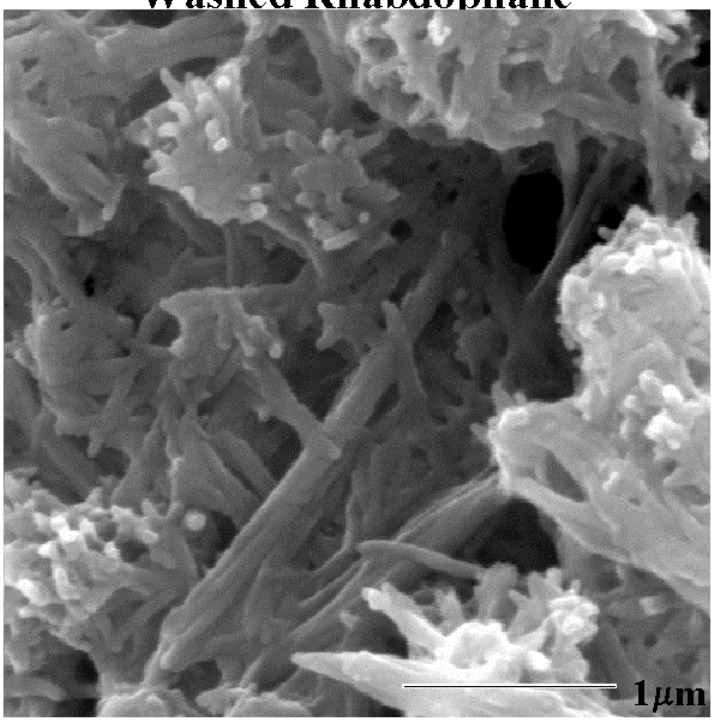
Washed Rhabdophane



Typical aggregate of needles and modified needles

This depicts the material at larger magnification:

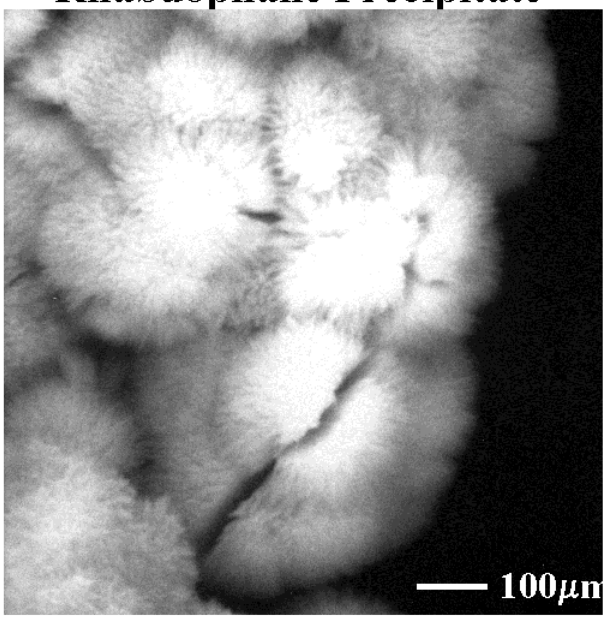
Washed Rhabdophane



Note clumping and modification of initially precipitated long needles.

Earlier precipitates were done with phosphoric acid in excess and have a different appearance:

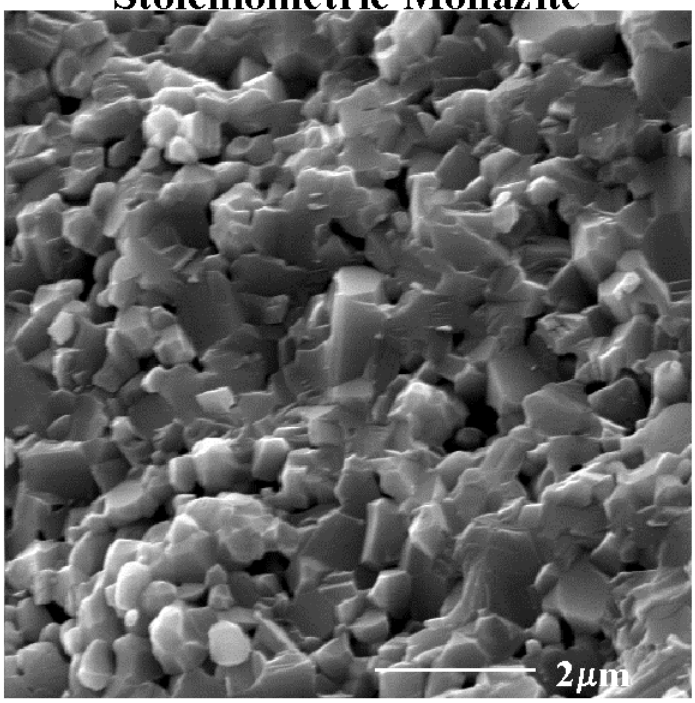
Rhabdophane Precipitate



Spereulitic precipitate made up of fine rhabdophane needles.

This is dense material of almost 1:1 stoichiometry and a fine grain size at 1200°C:

Stoichiometric Monazite



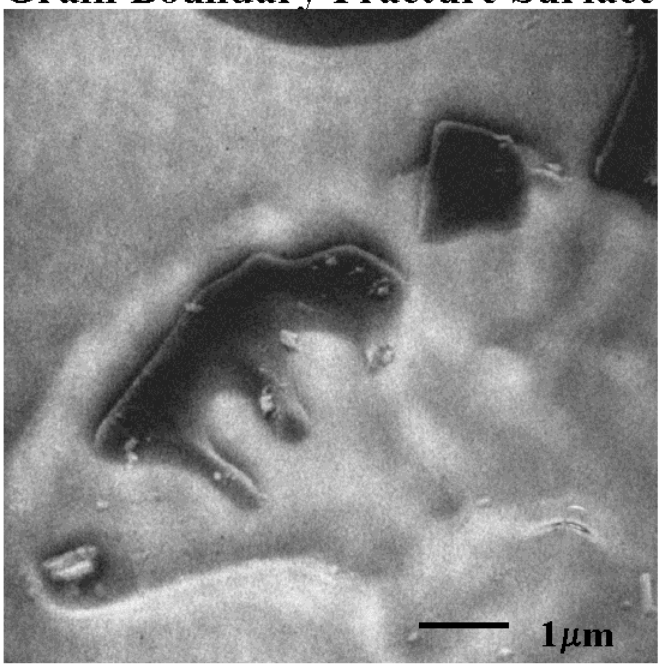
Uniaxially cold pressed and fired at 1200 C.
Fracture surface.

But, at higher temperature, by 1400°C, discontinuous grain growth readily occurs:

Giant Grain/Normal Grain Interface

-caused by very low levels of liquid phase on the grain-boundaries as seen below:

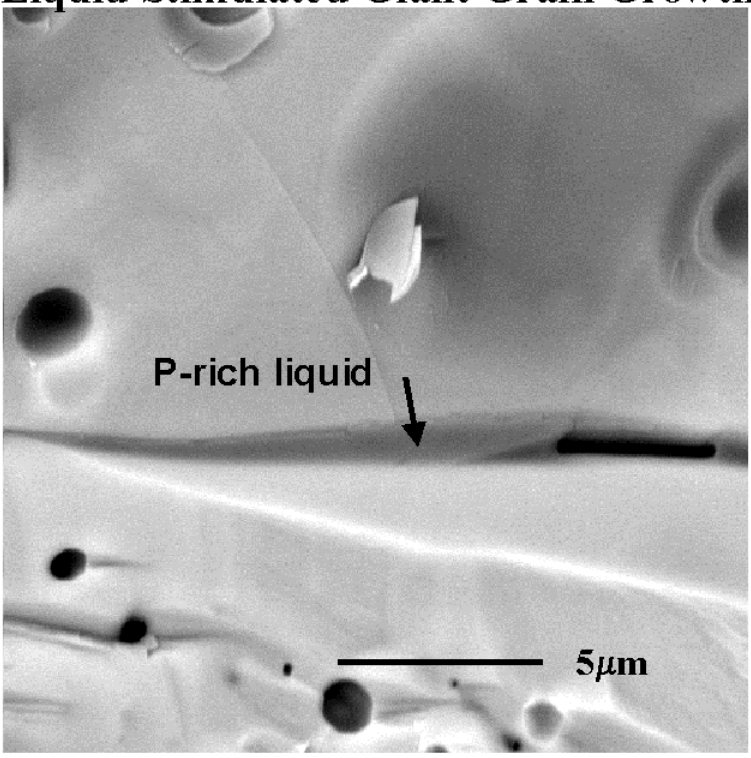
Grain Boundary Fracture Surface



P-rich liquid only partially wets monazite resulting in grain boundary porosity.

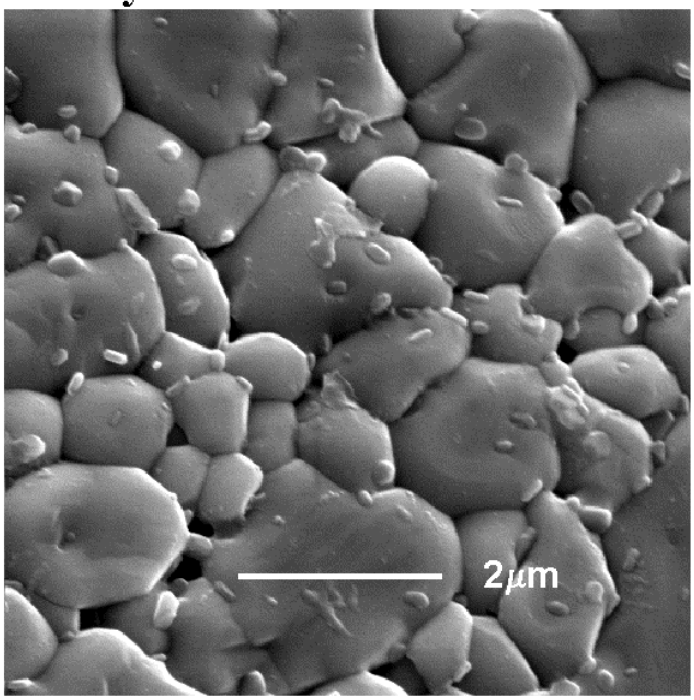
and in an orthogonal view here:

Liquid Stimulated Giant Grain Growth



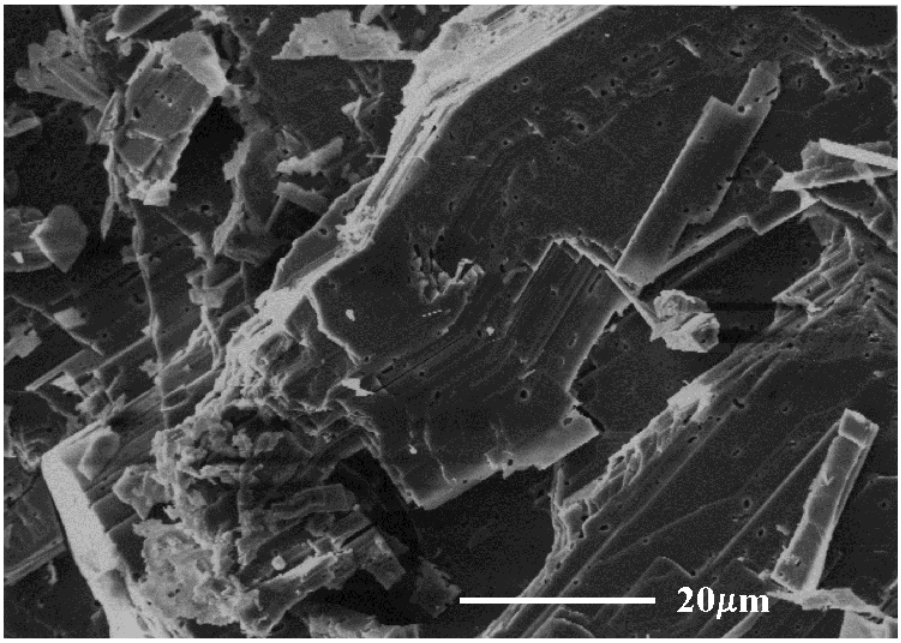
However, small additions of Al^{3+} appear to remediate this (normally) unwanted feature:

Thermally Etched Monazite/4% Alumina



Monazite shows considerable plasticity including upon fracture:

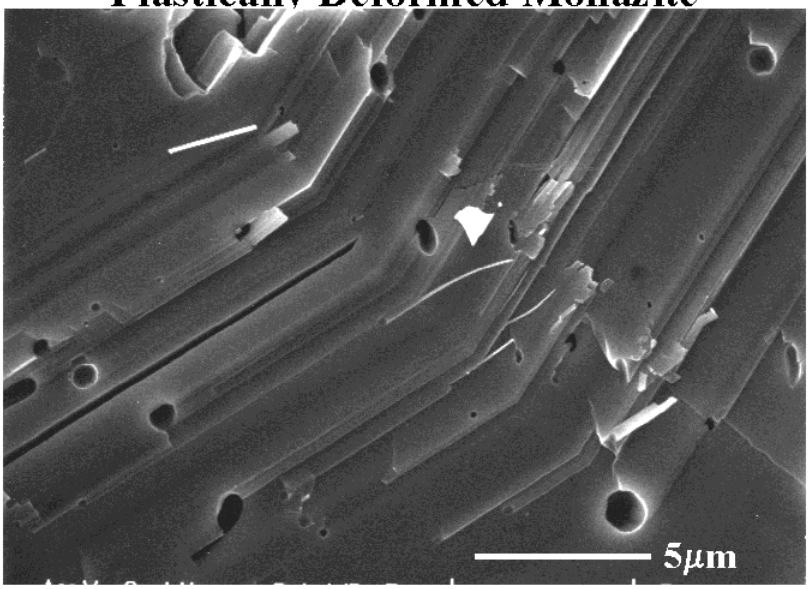
Monazite Fracture Surface



Room temperature fracture shows both plastic and brittle regions.

Region at larger magnification with deformation twins:

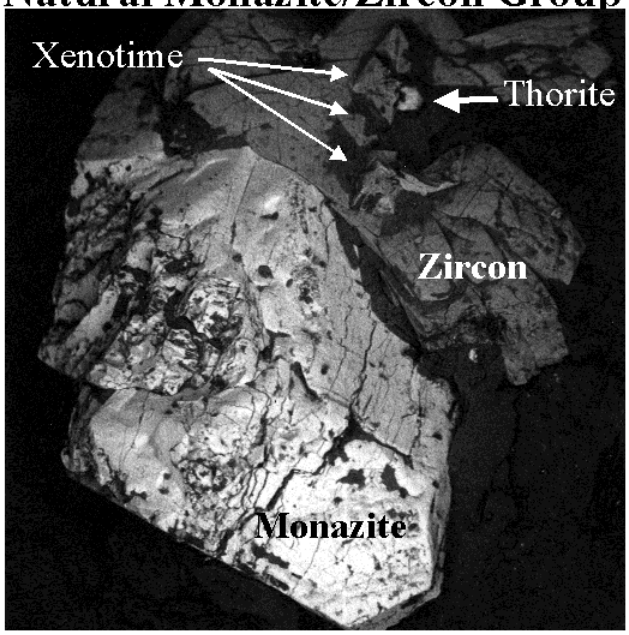
Plastically Deformed Monazite



Kink bands produced by room temperature deformation

Previous work by "Mother Nature":

Natural Monazite/Zircon Group



Natural assemblege of monazite, zircon xenotime, and thorite. Most Th is in monazite.

C o n c l u s i o n s

The "ceramics" of monazite are unusual (more akin to the complexities in, say, silicon nitride than what is found in alumina and other simple ceramic materials). Most of this unusual behavior relates to the easy incorporation of excess P in the precipitated $LaPO_4$ and this is now avoided.

A s i d e

In the last 5 years it has become apparent that monazite (more specifically La-monazite) is an unrecognized/becoming-interesting ceramic material with unusual (actually peculiar!) properties. Monazite melts without decomposition (in a closed system) at 2074°C and, being compatible with other common ceramic oxides such as alumina, mullite, zirconia and YAG, is useful as an enabling weak interface in oxidatively stable, oxide-oxide fiber ceramic composites in engines, possibly as machinable ceramics, as a "high temperature starch" on space shuttle blankets, and others.

Lest it be thought that rare-earths are "rare" or expensive, this is, in fact, not so. Nowadays, the less common lanthanides such as gadolinium, samarium, europium, and terbium, are much used by, e.g., the electronics industry, leaving La and Ce as not-sufficiently-used byproducts. The large scale use of Nd in the recently developed Nd-Fe-B magnets has further exaggerated this. Other uses of the rarer lanthanides, waiting in the wings include the use of Ho in $BaTiO_3$. Large deposits of the source mineral, bastnaesite, are present in the USA and in China; mineral monazite itself is not preferred as a source of lanthanides because of the high thorium content that must be safely disposed of.

This has been part of a two-part program; the other part is at ORNL under Lynn Boatner.

Planned Activities

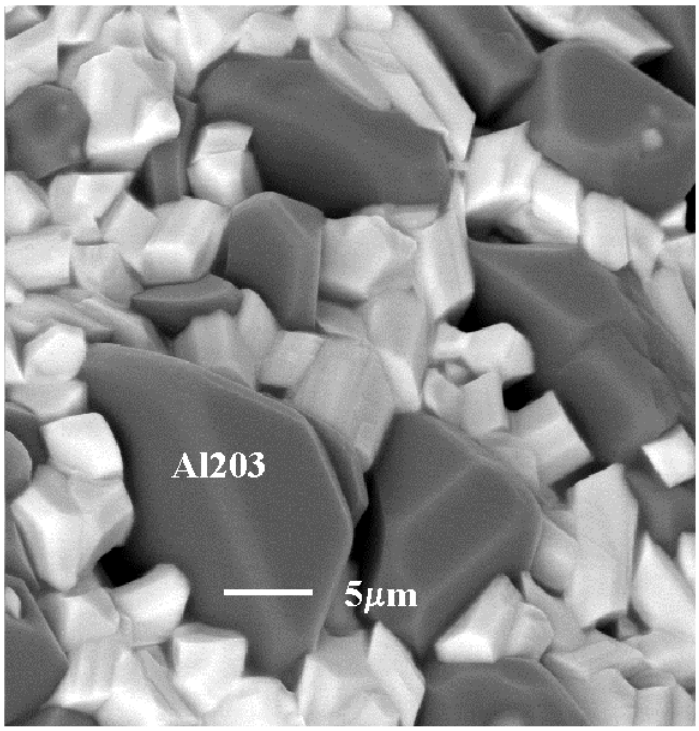
We plan to continue the study of the ceramic behavior (i.e., chemistry of powder, sintering, grain-growth, densification, etc.) of La-monazite, so that the community has ready access to this knowledge via publications.

The aqueous colloidal chemistry of rhabdophane and monazite is presently under study so that good colloidal slips for consolidation by filter pressing to high green density bodies (very necessary for easy densification to high density by pressureless sintering) can be achieved.

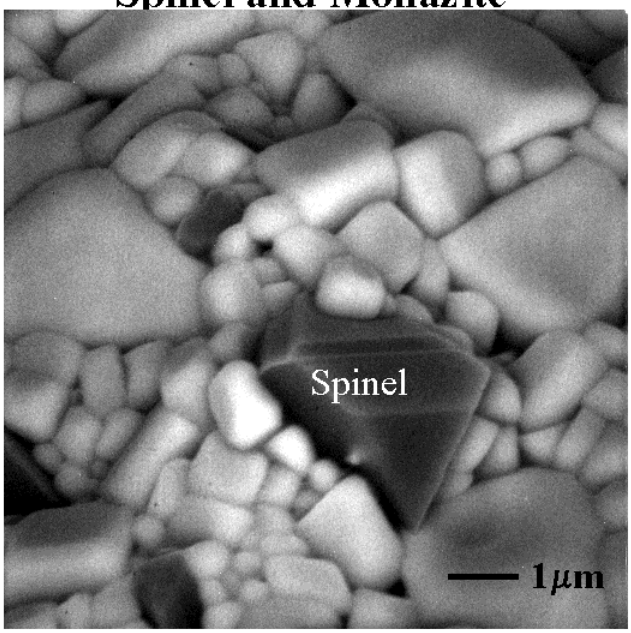
As we mentioned, monazite seems to have some unexpected and quite peculiar properties (compared to traditional ceramics), in that regard this work may be compared with the early days of silicon nitride research - that material took 30 years from concept to their use as roller bearings in turbopumps etc.

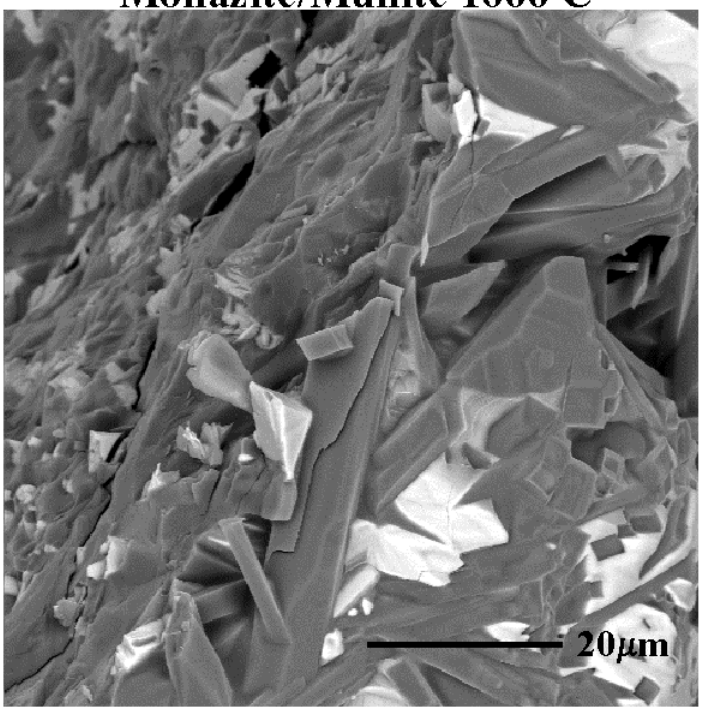
Monazite is phase compatible with most other minerals excepting only other very basic mineral alkalis mostly). Here are some synthetic cases where monazite is compatible with important other ceramics.

Monazite/Alumina at 1600 C



Spinel and Monazite



Compatibility with spinel at 1400 C.

Monazite/Mullite 1600 C