SC71129.FR

Chemical and Ceramic Methods Toward Safe Storage of Actinides

Final Technical Report
Contract No. DE-FG07-96ER45617

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BACKGROUND AND SIGNIFICANCE

A very important, extremely-long-term, use for monazite as a radwaste encapsulant has been proposed. The use of ceramic La-monazite for sequestering actinides (isolating them from the environment), especially plutonium and some other radioactive elements (e.g., fission-product rare earths), had been especially championed by Lynn Boatner of ORNL. Monazite may be used alone or, copying its compatibility with many other minerals in nature, may be used in diverse composite combinations.

Overview

The long-term, safe storage of the actinides/transuranic-elements presents a particular problem in that they have extremely long half lives. Encapsulation is necessary for far more than 100,000 years, a period over which the security of caskets etc. cannot be guaranteed, therefore, a geologically long-term-proven rock-like encapsulant is desirable; for this the monazite structure - a mixed rare earth phosphate, more particularly lanthanum phosphate - is a very good prospect. Particular political problems attach to plutonium decommissioning and so this work has specifically addressed a storage medium for that particular actinide.

Before using a particular material as a radwaste encapsulant, it is essential that there exist a basic background of knowledge on the ceramic synthesis and properties of that material. Very few ceramic materials (notably alumina, zirconia, silicon nitride etc.) have, in fact, been studied in sufficient detail to have any security as to what mechanisms are involved in their synthesis/fabrication and material properties.

Geological Occurrence and Stability of Monazite

Monazite is a natural orthophosphate mineral containing light rare earth elements, especially cerium, lanthanum and neodymium, and generally also containing some thorium and uranium appropriately valence balanced by calcium or silicon.

Natural monazite, $(Ln,Ca,Th,U\ldots)(P,Si)O_4$, is often found in the form of relatively large single crystals in granites, gneisses, as an accessory mineral in pegmatites, felsic volcanic ash (Parrish, 1990). and so forth and is one of the most water resistant minerals known - examples exist where it has been washed out of rocks (on to the beach sands of India, Australia, Brazil etc.), then reincorporated into a new generation of rocks with new crystal overgrowths, washed out a second time, then being 2.5-3 billion years old. During this aggressive water treatment it has retained Thorium and Uranium. Where very low levels of water attack have been seen (in more aggressive siliceous waters), the Thorium forms new thorite/huttonite, $ThSiO_4$, or allanite, $(Ca,Ce)(Al,Fe_2)Si_3O_{12}(OH)$, which, in their turn, remain immobile.

Only one other mineral, zircon, has been found to have similar properties. However, unlike zircon and many other natural rad-element hosts, monazite is never metamict in nature. At low temperatures the damage done by the radiation from uranium and thorium is progressively annealed out and this has recently been an intensive study on the part of the Boatner/Ewing groups. The monoclinic crystal structure of monazite (Mullica, 1984, Ni, 1995) is shared by several other compounds, notably huttonite, thorium silicate (Taylor, 1978), which also have the properties of not being found metamict, and are also known to be very stable in the presence of water. The most detailed report ever written on monazite (Boatner, 1988), contains all the details up to that time – recent work: (Meldrum, 1998, Meldrum, 1999, Salje, 1999, Zhang 2000, Zhang 2000, Zhang, 2000, Zhang, 2002). Monazite with nature's billion year geological experiments already carried out, was one of very few ceramic like materials that is seriously considered for the encapsulation of radioactive waste and, in particular, actinides.

Many of the actinide phosphates, and especially plutonium phosphate, have the monazite crystal structure and will form solid solutions with the mineral-type version. Several ceramic waste forms have been demonstrated to have far superior water leach resistant properties for high-level radioactive waste than do glass forms, which have hitherto been considered in the USA for low level wastes. A book (Lutze, 1988) is probably the best single resource for details to the radioactive waste encapsulation work that went on from about 1978 until 1988 – including the particular work done at Rockwell Scientific (formerly Rockwell science center but hereinafter RSC) over several years on several tailored ceramic waste forms. Details of other considered waste forms are enumerated therein. This book would surely be one of the first places consulted by anyone in the future, newly entering this field of study.

In addition to their geological persistence, proven natural ability to incorporate both thorium and uranium, and their resistance to permanent radiation damage, monazites also exhibit the relatively unusual characteristic of a negative temperature coefficient of solubility. Accordingly, unlike most materials that have been considered as nuclear-waste-disposal materials, monazites become less soluble as the temperature of an aqueous ambient increases rather than becoming more soluble. Monazites are also highly refractory substances with melting points which exceed that of alumina in some cases (Hikichi, 1987), and they are thermally stable from the compositional point of view until they reach their melting points.

Resistance to Radiation Damage

In addition to its established extreme stability in the geological environment, monazite, because it frequently incorporates significant concentrations of radioactive thorium and uranium, has been subjected to displacive radiation damage extending over long geological time periods. In spite of this exposure to long-term radiation damage, monazites are always found in a crystalline state rather than as an amorphous or metamict mineral. Relatively recent research using synthetic monazite crystals has shown that this occurrence is due to the ability of monazite to recover readily from displacive damage events at near-ambient temperatures. Even when the near-surface region of synthetic monazite crystals is deliberately rendered amorphous by high-dose, heavy-ion bombardment in an accelerator, the leach rate of the ion-damaged, amorphous phase of the material in aqueous media remains extremely low.

Natural monazite samples, even those with high thorium (Ueda, 1957) or uranium (Gramaccioli, 1978) contents, always give well defined characteristic X-ray diffraction patterns. This led to the general perception that monazite does not go metamict. The physics of alpha decay implies that on the order of 1000 atomic displacements occur per event (Malow, 1979). Thus, for a crystal not to appear metamict, this damage must anneal out by some combination of radiation enhanced diffusion and low temperature thermal diffusion on a time scale short compared to the irradiation rate.

Natural (Karioris, 1981) and synthetic (Ehlert, 1983) monazite samples have been metamictized by Ar ion bombardment. Synthetic monazite samples have also been made metamict by U fission (Vance, 1982). Karioris (1981) found that gentle annealing at 200°C for 20 hours restored their samples to a fully crystalline condition. Vance (1982) stated that 8 days at 200°C produced partial recrystallization, but was not more quantitative. Ehlert and others (1983) used differential scanning calorimetry to quantify the stored energy and recovery rate versus temperature. Indeed the stored energy in monazite is modest and the recovery rates at low temperatures are high. This provides a satisfying explanation of the high degree of crystallinity observed in ancient monazites with high Th or U contents. Recent work (Begg, 2000, Meldrum, 1998, 1999, Salje, 1999, Zhang, 2000, 2002, Weber, 1997) has continued to illuminate these details.

However, there are data in the literature which, taken at face value, raise concerns about this satisfying picture. (Ueda, 1957) found that the x-ray patterns of his monazites shifted and somewhat sharpened on annealing at 400°C and 800°C, and in one specimen further changes were observed on annealing at 1800°C. (Ghouse, 1968) reported that the x-ray pattern of a monazite from India sharpened on annealing at 1130°C. Finally, (Vance, 1982) reported density changes and x-ray line sharpening on annealing 11 natural monazite samples from various localities at 950°C and 1100°C.

The above results suggest that some radiation damage may persist to high temperatures in natural monazites. There is a simple way to rationalize such a hypothesis. Now that many electron microprobe analyses are available (Forster, 1995) we know that natural monazites are highly variable in composition and exhibit complete, or near complete solid solubility with huttonite, $ThSiO_4$, and brabantite, $CaTh(PO_4)_2$. They are also frequently compositionally zoned in various ways and on a variety of scales (Parrish, 1990; Wark, 1993). On the basis of very limited transmission electron microscopy Kucha (1980) even suggested very fine scale segregation. The monazites used in the above radiation damage and annealing studies were not always analyzed or examined for homogeneity.

Cartz (1981) have shown that ion irradiated huttonite is much harder to anneal than monazite. No comparable data exists for brabantite. Natural monazites may plausibly contain regions that are easy to anneal and regions that are hard to anneal.

However, it seems equally plausible that the above high temperature annealing effects have nothing to do with radiation damage. They may simply result from reductions in internal strain that was caused by growth inhomogeneities or low temperature segregations.

To the extent that one might want to incorporate four-valent actinide cations in monazite using huttonite or brabantite type substitutions, it is important to understand how such substitutions might affect radiation damage resistance. More generally it is important to establish whether self annealing completely removes radiation damage in monazite or whether, for example, some crystallite misorientation develops with time.

Use for Storage of Actinides

For the specific case of the disposal of actinide elements, other than thorium and uranium, monazites are particularly attractive (Boatner, 1988, Ewing, 1996), since plutonium, americium, and curium all form orthophosphate compounds having the monoclinic monazite crystal structure. Accordingly, monazites are compatible with the non-naturally-occurring actinides from the crystal-chemistry point of view. In the monoclinic monazite structure (space group $P2_1/n$, No. 14, Z = 4), the lanthanide (or actinide) ions are nine-fold coordinated with the surrounding oxygens, phosphorous is four-fold coordinated to oxygens and the oxygens are one-fold coordinated to phosphorus and two- or three-fold coordinated to lanthanum (see the picture of the crystal structure below) and it has been suggested that this irregular coordination may be associated with the ability of the structure easily to incorporate

chemically diverse cations, including thorium and uranium. (Having nine-fold weak bonds around La may also account for the ready annealing detailed earlier - rare earth orthophosphates in the second half of the transition series have the tetragonal zircon structure in high-temperature form and in this case each lanthanide cation is eightfold coordinated with oxygen). Natural samples demonstrate near complete solid solubility of $CaTh(PO_4)_2$, brabantite, in monazite (Forster, 1995), while laboratory studies demonstrate complete solid solubility of $CaU(PO_4)_2$ at elevated temperatures (Podor, 1995).

For application to the storage of fissile actinides, such as plutonium resulting from the dismantling of nuclear weapons, monazites are also attractive from the standpoint of criticality issues since isotopes of Gd and other lanthanide isotopes with extremely large neutron-cross-sections may be incorporated in a tailored $LnPO_4$ host-crystal system.

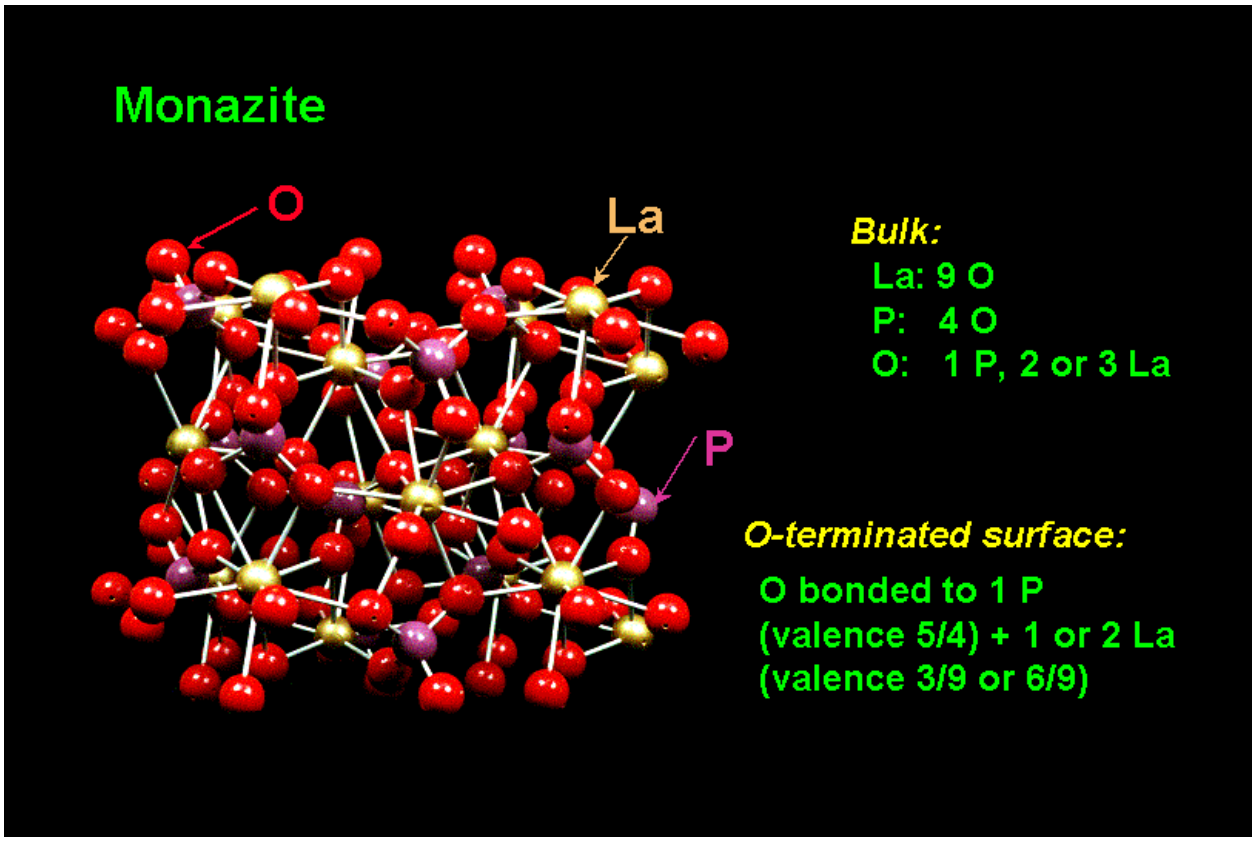
As a result of the cumulative favorable chemical and physical characteristics noted above, monazites were proposed a number of years ago as a high-level nuclear waste form, and much of the work associated with their development for this purpose has been summarized (Boatner, 1988). Following the deliberations of the appointed panel and the decision to proceed with borosilicate glass for the low level wastes from the Defense Waste Processing Facilities, organized research on monazites, and on most other so-called "alternative" waste forms came quickly to an end (Hench Panel, Final Report: Alternate Waste Form Peer Review Panel, Report No. 3, USDOE/TIC-11472. 1984). These developments are one of the subjects considered in a report of a National Academy of Sciences panel entitled "Barriers to Science: Technical Management of the Department of Energy Environmental Remediation Program," 1996. This report points out that, as a result of decisions made during and following the Hench Panel report, approximately fifteen years of potential progress in the development of "alternative" nuclear waste forms were lost.

When sustainable research on most nuclear waste forms came to an end, it had advanced to the point where methods for the controlled formation of some precursor powders had been developed and used to produce ceramics containing chemical simulants of certain types of U.S. defense wastes as well as commercial light water reactor wastes. Ceramics of this type were formed by both cold pressing and sintering methods and by hot pressing. The chemical durability of these ceramics was compared to that of borosilicate glass waste forms based on various frit compositions, (Harker in Lutze, 1988).

At the juncture represented by the publication of the "Monazite" chapter in "Radioactive Waste Forms for the Future" (Lutze, 1988), the primary monazite waste form issues concerned the development of a fundamental understanding of: the sintering mechanisms involved in the formation of high-density monazite ceramics, of the physical and chemical properties of grain boundaries in these ceramics, of the identification of sintering aids that could be used to lower the ceramic processing temperatures, and of understanding the interactions associated with additives used to promote densification of these materials. An additional significant research area concerned the development and understanding of precipitating monazite phases in an efficient and economic manner. These

remain the outstanding fundamental research issues that are still germane to the practical formation of high-density monazite ceramics whose properties can be optimized for a given type of radioactive waste - including plutonium originating from dismantled nuclear weapons.

Crystal structure of monazite



The Fig. shows the monoclinic crystal structure of monazite. Red balls are oxygen, all connected to tetrahedral purple phosphorus. Gold, lanthanum, is in an irregular 9-fold coordination.

Competing/Alternative Systems (Zircon)

It would seem that monazite should be one of the very best candidate radwaste hosts for a thorough ceramic study as detailed herein; however we should further compare it with zircon, $ZrSiO_4$, the other natural host phase for actinide elements, which is comparably stable with monazite in a variety of geological environments (Silver, 1982, Ewing, 1995). Zircon does not self anneal at low temperatures, but the higher temperature annealing of natural radiation damage has been extensively studied by optical, X-ray and TEM techniques. For low degrees of damage it seems to anneal back to the single crystal state; at intermediate levels of damage, new zircon crystallites nucleate in the

amorphous regions and the crystals anneal to a mosaic state; while with high levels of damage, the samples anneal to ZrO_2 and SiO_2, which persist as separate phases to at least 1200°C (McLaren, 1994; Murakami, 1991, Woodhead, 1991). Since high levels of damage do not accumulate in monazite, we expect it to maintain a well ordered state.

Another seemingly big advantage of monazite over the otherwise attractive zircon is the precipitation and preparation of monazite with the very necessary 1:1 La:P ratio from, for example, aqueous solutions. Which is to say that monazite can be prepared stoichiometric and crystalline at low temperatures. Recent work here: (Oelkers, 2002), Kijkowska, 2003, Wang, 2003).

Deviations from stoichiometry lead to unwanted secondary phases and/or grain boundary impurities/phases/glasses. Zircon on the other hand does not easily form crystalline and stoichiometric under mild conditions. Monazite resists taking part in reactions that produce glassy phases preferring to remain usually as a distinct crystalline phase. In ceramic processing zircon frequently produces glassy phases containing silica, for example in the reaction of zircon and alumina (Moya, 1991), under conditions where monazite and alumina do not react at all. This exemplifies, by the way, the superior ability for a lanthanide to hold on to phosphate over and above the ability for zirconium to hold on to silicate. Zircon is also a well known constituent of ceramic glazes (e.g., Grum-Grzhimajlo, 1992), whereas monazite is not.

Gaps in Knowledge

Hitherto, before our group at RSC became interested in monazite for composites etc., there had been few detailed ceramic consolidation studies on materials such as lanthanum monazite (Abraham, 1980, Floran, 1981), which has a stability in oxygen up to its high melting point of 2074°C (higher than alumina), and is eminently an important refractory material. Alumina is one of a handful of materials where extensive sintering studies have been carried out and the study of this still benefits as recent work continues to contrive a careful break down of the many mechanisms simultaneously occurring, using slowly evolving (and mutating) critical testing that cannot always appear quickly as on demand (e.g. the recent issue of J. Am. Ceram. Soc. April 2003).

Thorough sintering and related studies have been carried out on only very few other ceramic materials notably silicon nitride, mullite and, somewhat piecemeal, on magnesia, zinc oxide and a few ferroelectrics. As befitting their different chemistries, bonding and crystal types, etc., all of these turn out to be very different, one from another and from alumina. It would be impossible to generalize much about sintering phenomena from a study of only a few of these. Moreover, the actual details of the understanding of sintering phenomena in a well-studied case, for example, alumina, have had to be modified over the years, as better model experiments (not mathematical model fitting!) have elucidated particular tricky aspects of the underlying many-fold, interacting mechanisms (e.g., Harmer 1991 and 1996). For example, the dependence of diffusion on density and grain size, the dependence of grain size on porosity, the dependence of pore size and mobility on surface or grain boundary diffusion, which in turn depends on location, whether on the grain boundary or within a crystal and so forth. And, with all the extra complexity that

small amounts of liquid or glass and second phases will introduce, any real appreciation of this complexity demands individual studies of any new ceramic in great detail.

Little is understood about microstructure evolution in low symmetry crystalline materials such as monazite. Mechanisms of grain growth and therefore kinetics of such processes can be strongly dependent on details of crystal symmetry and grain boundary structure. In high symmetry crystal systems, such as cubic metals, (Exner, 1979) and to a lesser extent, hexagonal (or rhombohedral) materials, such as alumina (Harmer, 1992, 1993) and silicon nitride (Clarke, 1978), grain boundary structure and morphology can strongly determine microstructure. Grain boundaries in such materials can often be aligned with a specific crystal plane in one of the pair of grains that the boundary joins (e.g., many boundaries in alumina can be parallel with a basal plane in one of the grains (Porter, 1986)). In higher symmetry systems, e.g., cubic systems, so called special boundaries such as coincident site lattice boundaries can develop with a concomitant low grain boundary energy due to improved fit between the two crystal lattices. (Ballufi, 1981).

Many experiments must be done so that intelligent breakdowns enabling separation of the various mechanisms can be achieved. Whereas in alumina, mostly solid state phenomena can be studied (although we don't by any means underrate the possibility that much work in the past actually concerned low levels of liquid being present (Ho, 1987)) in, for example, silicon nitride, liquid phase mechanisms are the most important.

This work is particularly timely because renewed and widespread interest in the properties of monazites has been stimulated by the recent activities of the RSC group in the course of the research on the identification of phases which could provide weak interfaces for ceramic matrix composites. For 20 years an oxidatively stable weak interface for ceramic matrix composites had eluded discovery but monazite has been found to fit the bill (Morgan, 1993, 1995, Marshall, 1994). Work in this area has established that, in fact, the stable monazite phase does not interact significantly with a surrounding alumina matrix thereby providing the desired weak interfaces which result in improved mechanical characteristics in ceramic composites. This work has had a major impact in the ceramic-composites field, and at the present time, about thirty research groups have investigated lanthanum monazite additives for applications in ceramic composites, to the degree that a whole session at an American Ceramic Society annual meeting was devoted to it. In the course of this recent research, new routes for the precipitation of monazites have been discovered which, with additional development, can have a direct bearing on the practical formation of monazite nuclear-waste ceramics.

Finally, it is important to note that, completely independent of their obvious application to the storage of plutonium and other actinides, or to other forms of radioactive waste, monazites are potentially important high-temperature ceramics in their own right. Owing to their essentially unique combination of physical and chemical characteristics (as outlined above), when fully developed, monazite ceramics could find applications in: the disposal of non-radioactive hazardous (e.g., heavy-metal) wastes; as high-temperature structural ceramics for use in corrosive and

demanding environments such as those associated with fossil-fuel processing technologies; in petroleum-exploration systems; in nuclear-power systems, or in transportation technologies. Monazite is of known importance also for luminescent materials, scintillators (Wojtowicz, 1994), catalysts (Pemba, 1990), catalyst substrates and for electrochemical electrodes (e.g., Fournier, 1995 and refs. therein).

Basic studies to understand the nature and to become familiar with monazite as a ceramic material were, of course, a major motivation in this work, but, during this activity, as the history of science well illustrates, that major moves are anticipated to be made by the hands-on-learning-by-doing and quite unexpected serendipitous engineering tricks that will inevitably be discovered. Good evidence exists that the scientific process is a social activity (Kingery, 1991), which benefits from the excitement of scientific interactions and intellectual exchanges. This is a slow development process and good networking takes time to establish the communication required for particular technological advances and it cannot certainly be produced on short term demand (notwithstanding that the traditional budgeting and proposal routes seem to demand it). We would hope therefore for long term, stable, studies to commence in this arena.

Aside

Lest it be thought that rare-earths are "rare" (and, therefore, expensive), this is definitely not the case. Nowadays, many of 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 by-products. The large-scale use of Nd in the recently developed Nd-B-Fe magnets (e.g., in automobiles) 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 preferred source mineral, bastnaesite, are present in the U.S.A. and the P.R.C.; mineral monazite itself is not endorsed as a source of cheap lanthanides because of the expense of safely discarding the high thorium content; in Australia this route has recently been abandoned.
Another possible cost saving approach would be to use "mixed-rare–earth" phosphate; this consists of a mixed $(La,Ce,Pr\ldots)PO_4$ with the rare earths left over after the "goodies" have been removed. As far as we can guess, this ,material would suffice as well as pure $LaPO_4$. Materials analogous to this are already used in the metallurgical industry.

It is always beneficial to have an industrial base related to developments such as the prospective ceramic radwaste forms. In the last 5 years or so, it has become increasingly apparent that monazites and xenotimes (specifically here La-monazite) are previously-unrecognized/ becoming-interesting ceramic materials with unusual (actually somewhat peculiar!) properties. Monazite melts without decomposition (in a closed system) at 2074ºC and, being compatible with most other common ceramic oxides such as alumina, mullite, zirconia and YAG, it is useful as an enabling weak interface in oxidatively stable, oxide/oxide fiber ceramic composites for engine use, possibly as machinable ceramics, as a "high temperature starch" on space shuttle blankets, and for other uses – see RSC references for much more detail of other ceramic uses for monazite.

Research Objective

The routine "ceramic" behavior/performance (viz.sintering/densification/grain-growth/strength/ hardness etc.) of pure and doped La-monazite has not hitherto been studied in any great detail. Therefore, the intent here was 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. The sine-qua-non of ceramic studies and reliable manufacture is the synthesis and availability of consistent starting powders and precursor chemicals that always reproduce the desired ceramic outcome. This has generally been a more neglected (i.e., underfunded!) side of ceramic studies (many years passed before pure reproducible powders of alumina or silicon nitride became available, long after it was appreciated that these were extremely useful ceramics, whereupon how quickly research results consistently improved!).

We have attempted to demonstrate that monazite is a practical, reasonable and economic solution for this problem.

Why Mother Nature "likes" monazite:

Natural, monoclinic monazite, ([La^{3+},Ce^{3+},Nd^{3+}, Th^{4+},U^{4+}, Ca^{2+}, etc.][P^{5+},Si^{4+}, etc.]O_4), occurs:

- with a very wide range of solid solutions
- and can be billions of years old
- and is very resistant to water attack
- therefore, it is present as placer deposits (washed out by rivers) on the beach sands of India, Brazil, Australia
- sometimes washed out, reconsolidated,
  overgrown with new monazite, and washed out a second time
- yet still containing Th^{4+} and U^{4+}
- which are coupled substituted by Ca^{2+} or Si^{4+} (even the end member brabantite, $CaTh(PO_4)_2$, has the monazite structure)
- quite resistant to radiation damage and metamictization (monazite is normally not metamict in nature)
- the mineral can host neutron poisons, such as Gd, in solid solution

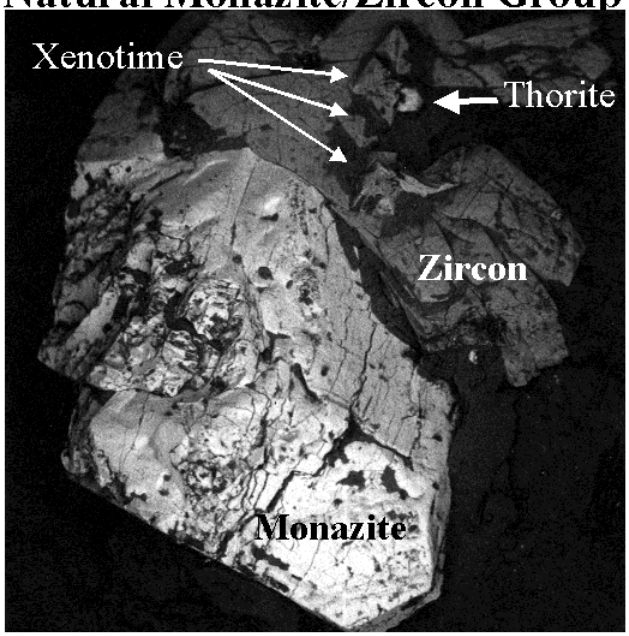
Moreover:

- pure synthetic $PuPO_4$ also has the monazite structure
- in which Pu^{3+} is strongly stabilized over Pu^{4+}
- e.g., on heating $Pu^{4+}{}_2P_2O_7$*, in air,* it converts to normal $2Pu^{3+}PO_4$, monazite
- but anyway, some Pu^{4+} could be stabilized by coupled-substitution with Ca^{2+} or Si^{4+}

Why *we "like"* the "ceramics" of monazite for long-term disposal/storage is because monazite is known to resist metamictization and deleterious volume expansion more than other mineral forms considered for radwaste disposal and readily self-anneals/crystallises above ~400°C. $PuPO_4$ itself has the monazite structure; the PO_4^{3-} unit strongly stabilizes actinides and rare earths in their trivalent states, e.g., as Pu^{3+}, which as phosphates are very insoluble. For example, when $Pu^{4+}{}_2P_2O_7$ is heated in air $2Pu^{3+}PO_4$ is formed. But, Pu^{4+} can also be coupled-substituted with Ca^{2}+ (as $La_{1-2x}Pu_xCa_{2x}PO_4$) as for the natural Th^{4+} case.

Previous "work by Mother Nature":

Natural Monazite/Zircon Group



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

Experimental and Results

We have

1) Concentrated on the reproducible and semi-automatic production of large quantities of La-monazite (up to ~3kg/week) using methods adaptable to the large scale. Several techniques have been tried to produce a heavy, agglomerated, aqueous precipitated powder of both monoclinic monazite, $LaPO_4$, and its hexagonal hydrated precursor rhabdophane, $LaPO_4.{}^1/_2H_2O$. The precipitations are carried out very slowly over several days in large plastic bins (such as are used in commercial kitchens) using hospital type peristaltic intravenous drip systems; very slow precipitations allow us obtain heavy (i.e. agglomerated), well crystalline precipitates. The process is designed to allow a simple automatic washing procedure. *Fines* are beneficially recycled to serve as *seeds* in the ensuing precipitation step. Mainly two precipitation methods, where either lanthanum or phosphorus are maintained in excess, have been tried. Either way, it has been found that it is quite hard to remove <~1% excess phosphorus, which always occurs in the precipitates; we have now found methods to adjust the stoichiometry exactly to La:P, 1:1.

Our X-ray diffraction pattern of pure rhabdophane was accepted by the joint committee on powder diffraction standards and appears as PDF 46-1439

2) Studied the preparation of $LaPO_4$ from various stable aqueous solution precursors such as:
from La nitrate and phosphorous (sic) acid
from La nitrate and methyl phosphonic acid
from La nitrate and phytic acid (aka inositol hexaphosphate)

Of these, phytic acid, is likely to be the most important when dealing with plutonium, actinides or other nuclear waste due to its well-known complexing ability.

Phytic acid is a hexa-dibasic acid, $[H\text{-}C\text{-}O\text{-}P(\text{-}OH)_2(=O)]_6$, that forms acid soluble complexes with many cations which can be precipitated by raising the pH. It is readily available from seeds soybeans, rapeseed, etc. (up to 100,000 tons a year could be produced as a by-product according to the U.S. Department of Agriculture!) where it stores Mg, Ca and phosphate prior to germination. It is a by-product of the food industry e.g., rapeseed oil – phytic acid = canola oil. Mixed with radioactive elements and La, it sequesters them; on heating, doped monazite is produced as a reactive powder for ceramic processing.

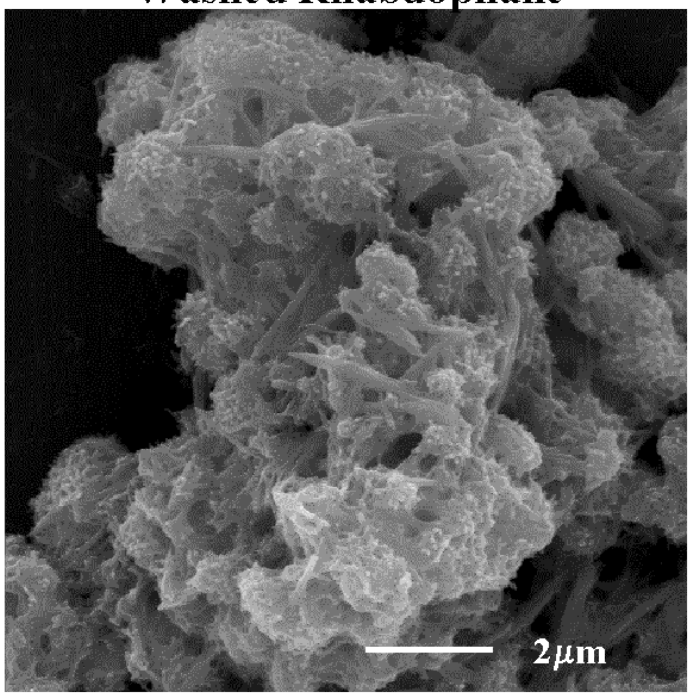
Some tests with other non aqueous complexing agents (e.g. tributyl phosphate – well known in the actinide separation business) were deemed unattractive at this stage of research.

Powders and Sintering/Grain-Growth

After considerable, concentrated work, taking about two years in all, we were able to produce fairly uniform, nanophase, stoichiometric rhabdophane starting powders. As was the case for the classic silicon nitride, this has not been a particularly simple matter. Recent powders now perform much better in most of our usages than the earlier preliminarily produced powders.

This is the SEM appearance of our standard rhabdophane ($LaPO_4.{}^1/_2H_2O$) which is now made in multi-kg amounts by slowly precipitating La nitrate solution (in excess) with phosphoric acid. Notice that the material is desirably highly agglomerated so that extensive washing to remove excess phosphate is facilitated.

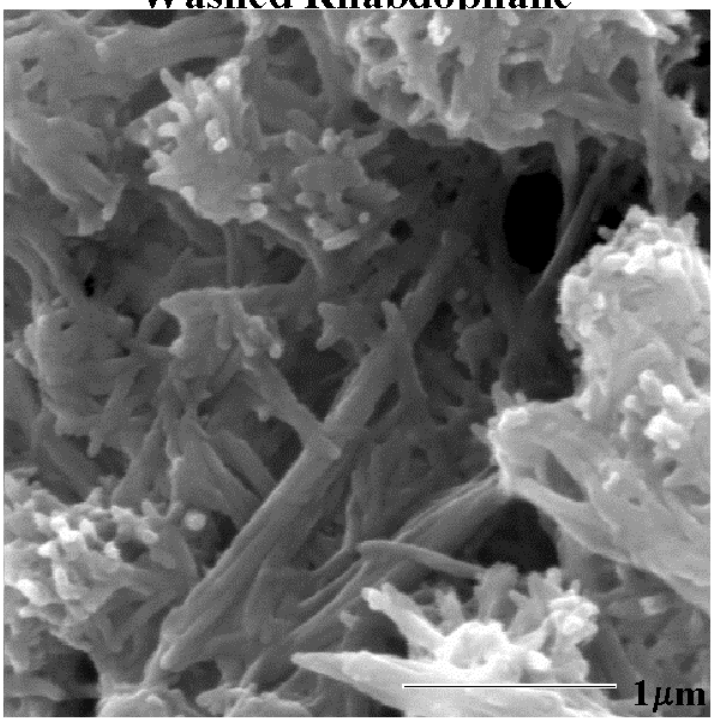
Washed Rhabdophane



Typical aggregate of needles and modified needles

This depicts the same material at larger magnification:

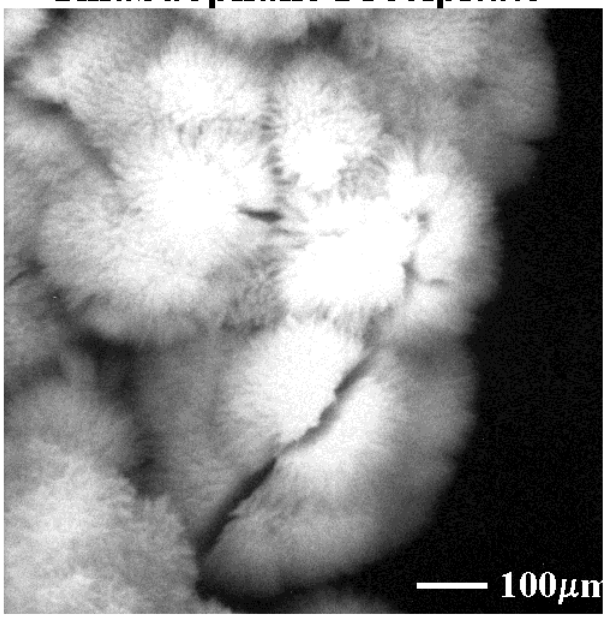
Washed Rhabdophane



Note clumping and modification of initially precipitated long needles.

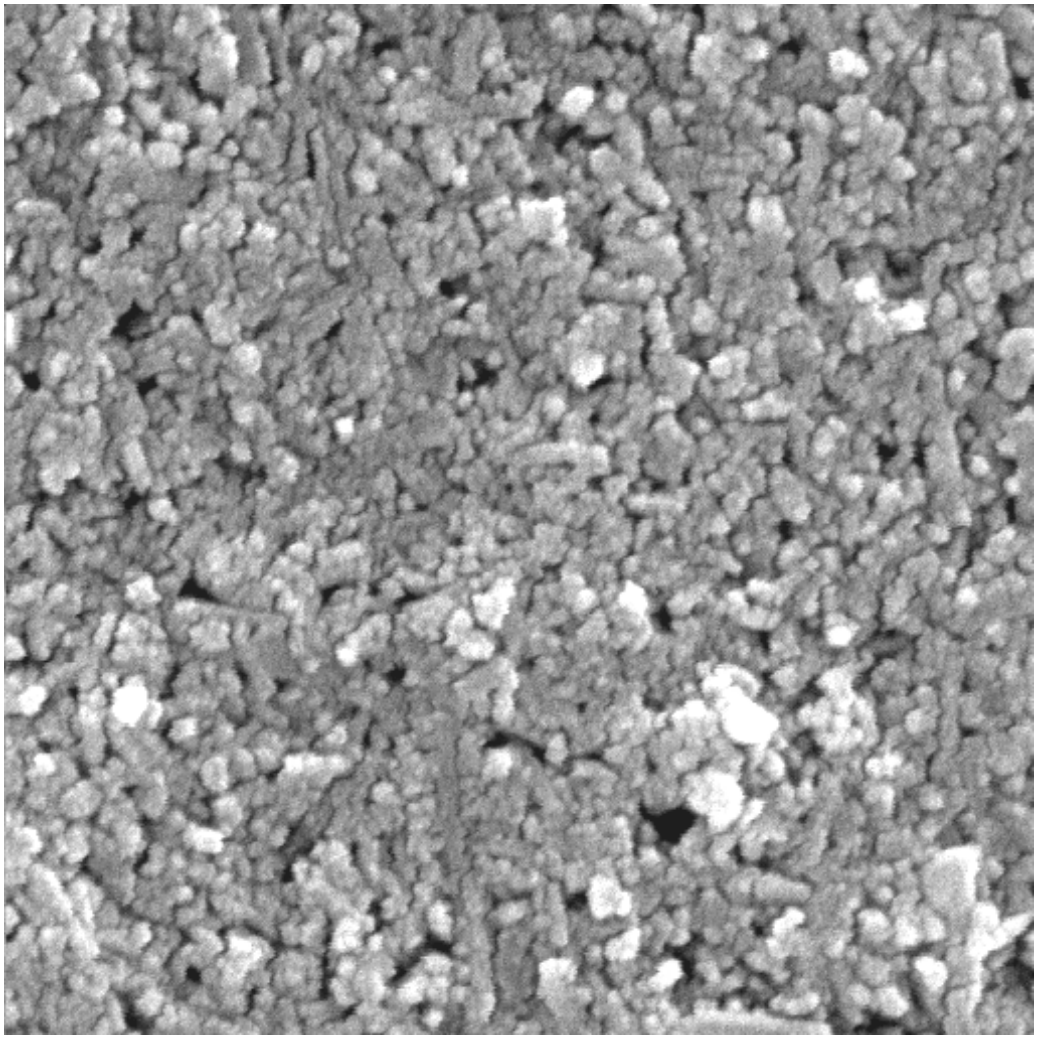
Earlier precipitates were done with phosphoric acid in excess and have a different appearance:

Rhabdophane Precipitate



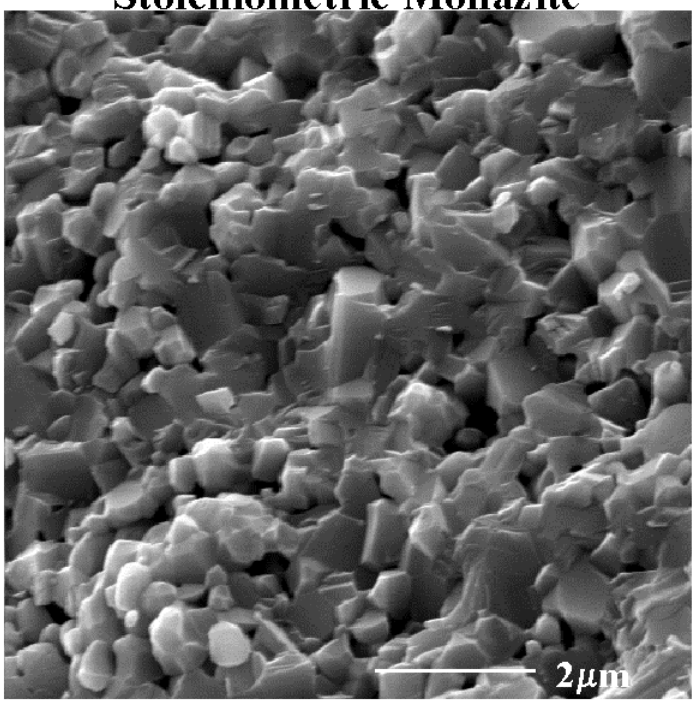
Spereulitic precipitate made up of fine rhabdophane needles.

The 1:1 La:P rhabdophane powder is prefired to 900°C and wet milled before colloidal-consolidation/pressure-filtration (typically) to a dense green body as depicted below:



10μm

Stoichiometric Monazite



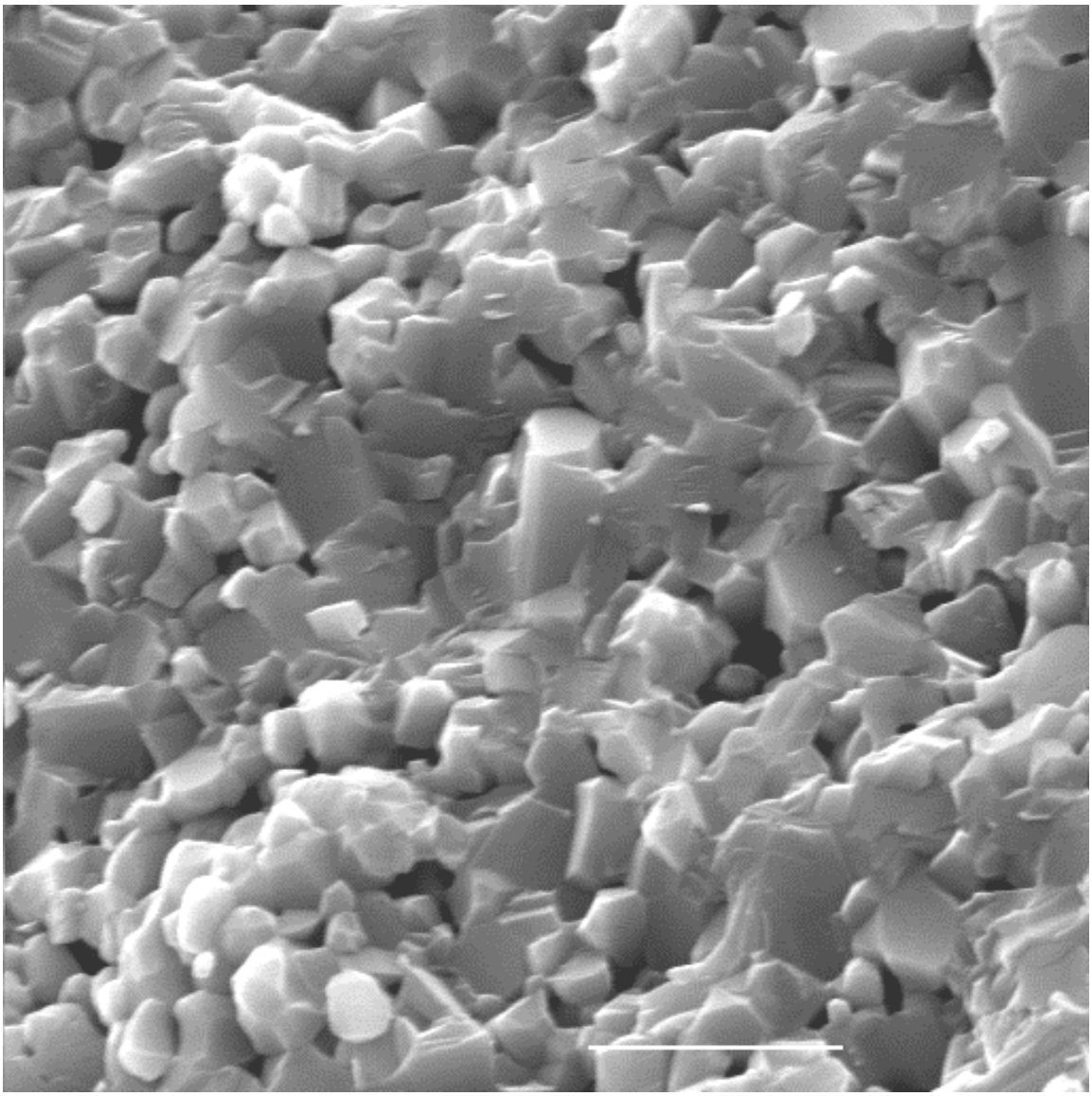
Uniaxially cold pressed and fired at 1200 C.
Fracture surface.

Over many years the ceramic community has concluded that, to achieve a high final density after firing, the single ineluctable requirement is to start with a dense, uniformly packed, fine particle, unagglomerated, green body; this

we have achieved. Monazite pellets are always embedded in powders (viz. in a “powder bed”) of their same composition to protect from the furnace atmosphere contamination as discussed elsewhere.

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

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

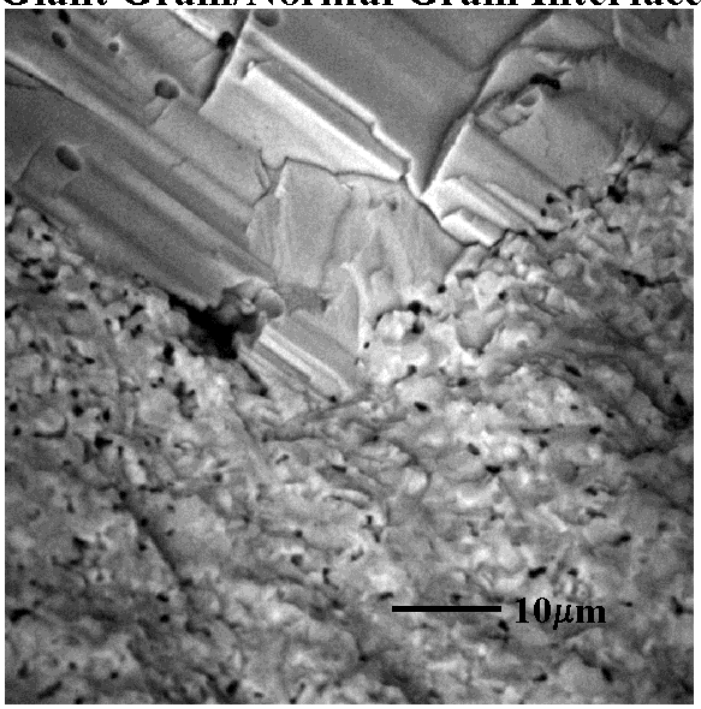


2μm

At this temperature, even with a small excess of phosphate, discontinous grain-growth is not usually apparent.

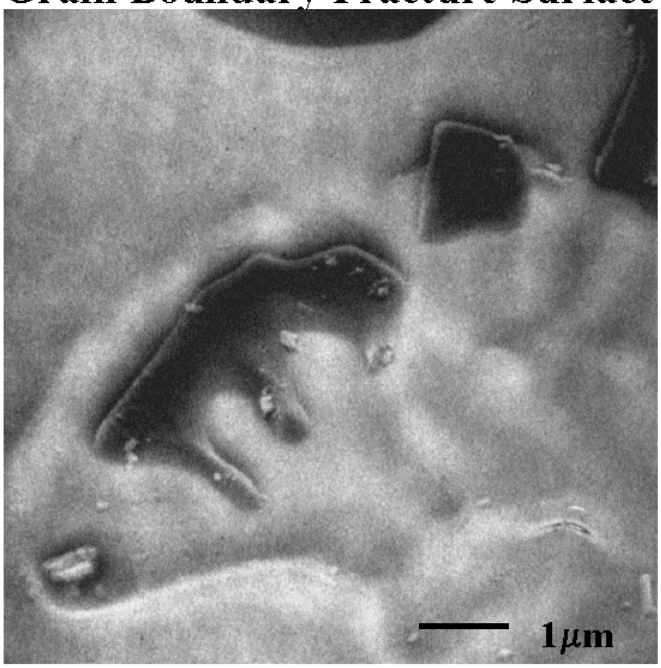
But, at higher temperature, by 1400°C, discontinuous grain growth readily occurs:

Giant Grain/Normal Grain Interface



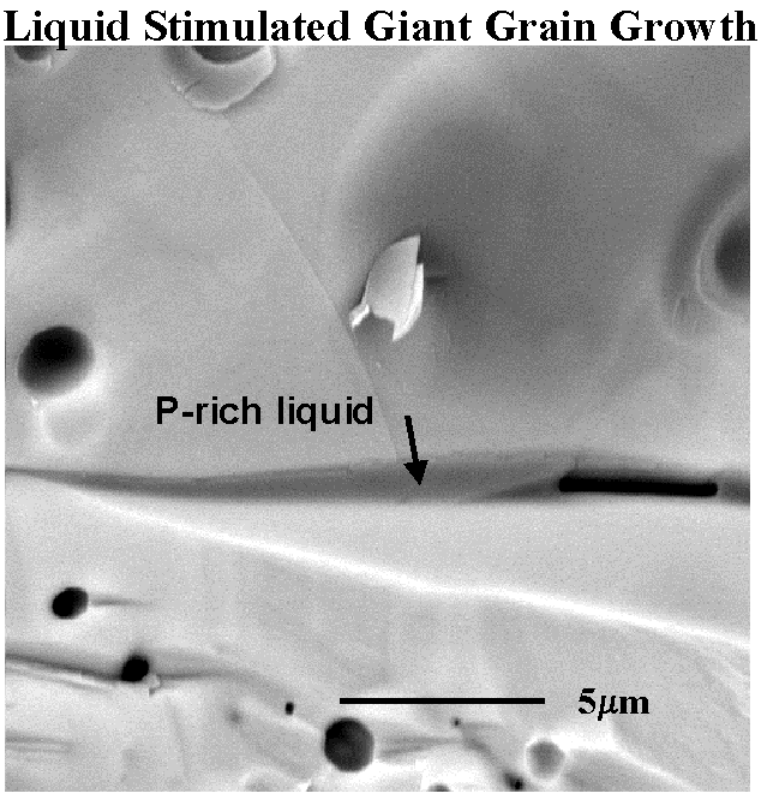
-- caused by very low levels of eutectic liquid phase above 1050°C (see phase diagram later) on the grain-boundaries as seen below:

Grain Boundary Fracture Surface

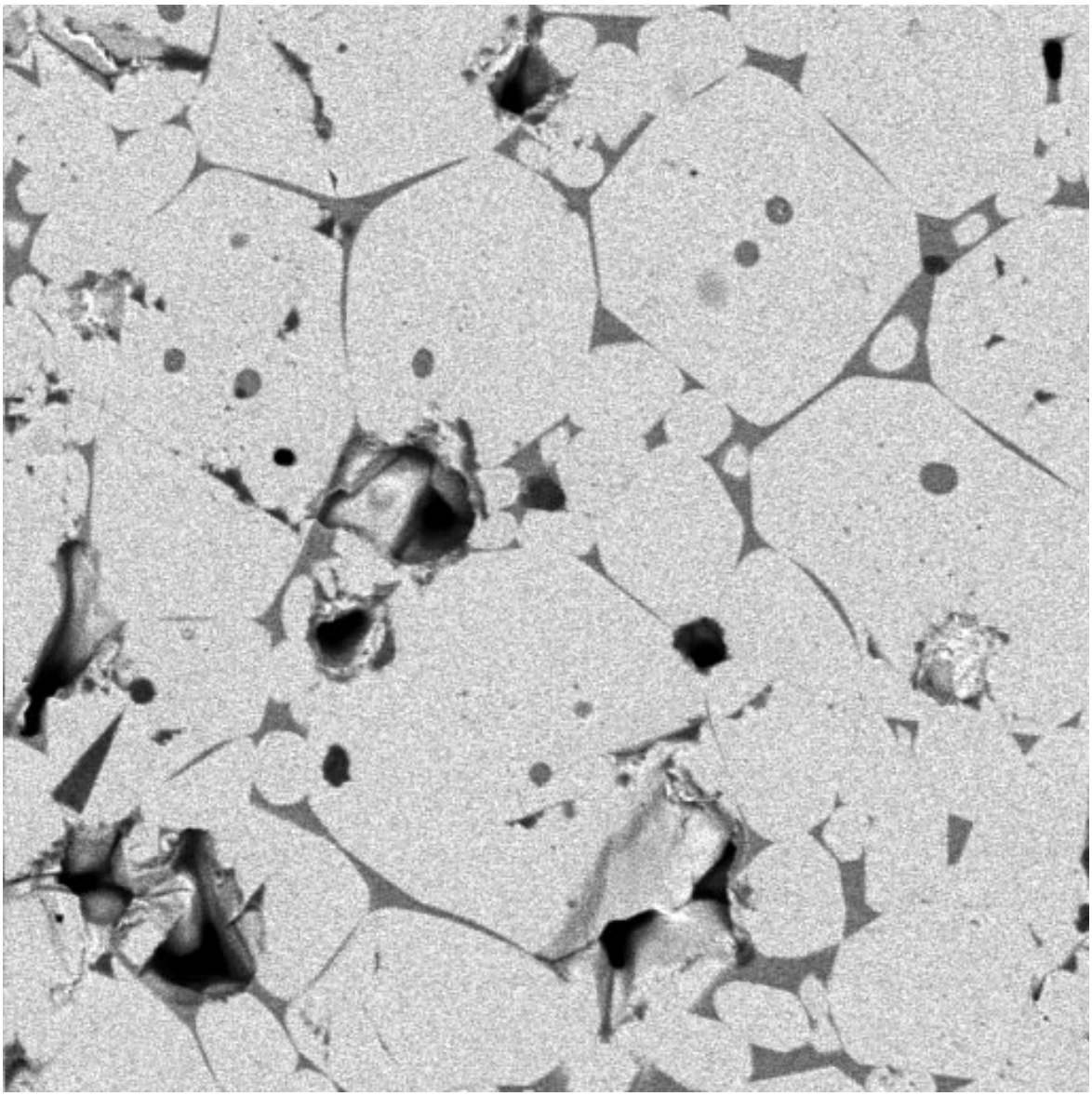


P-rich liquid only partially wets monazite resulting in grain boundary porosity.

and in an orthogonal view here:



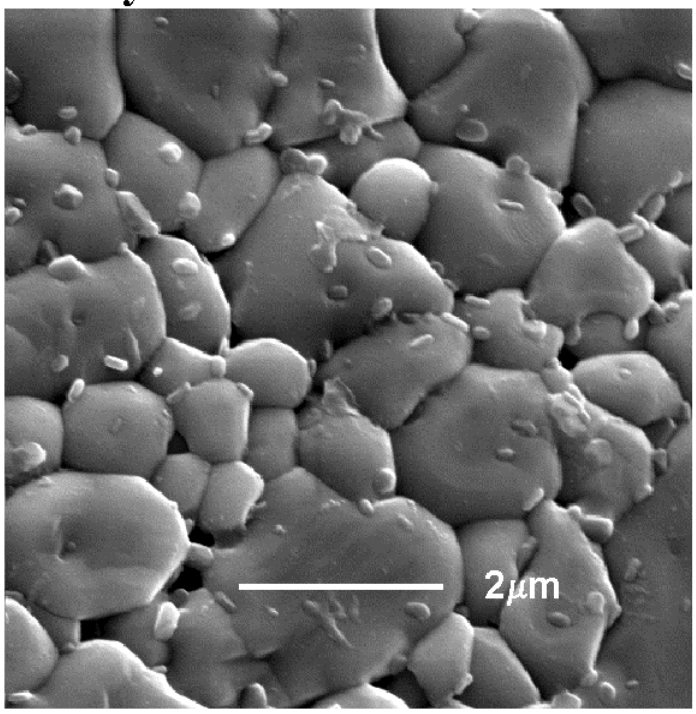
Polished Section in P-rich Monazite



50μm

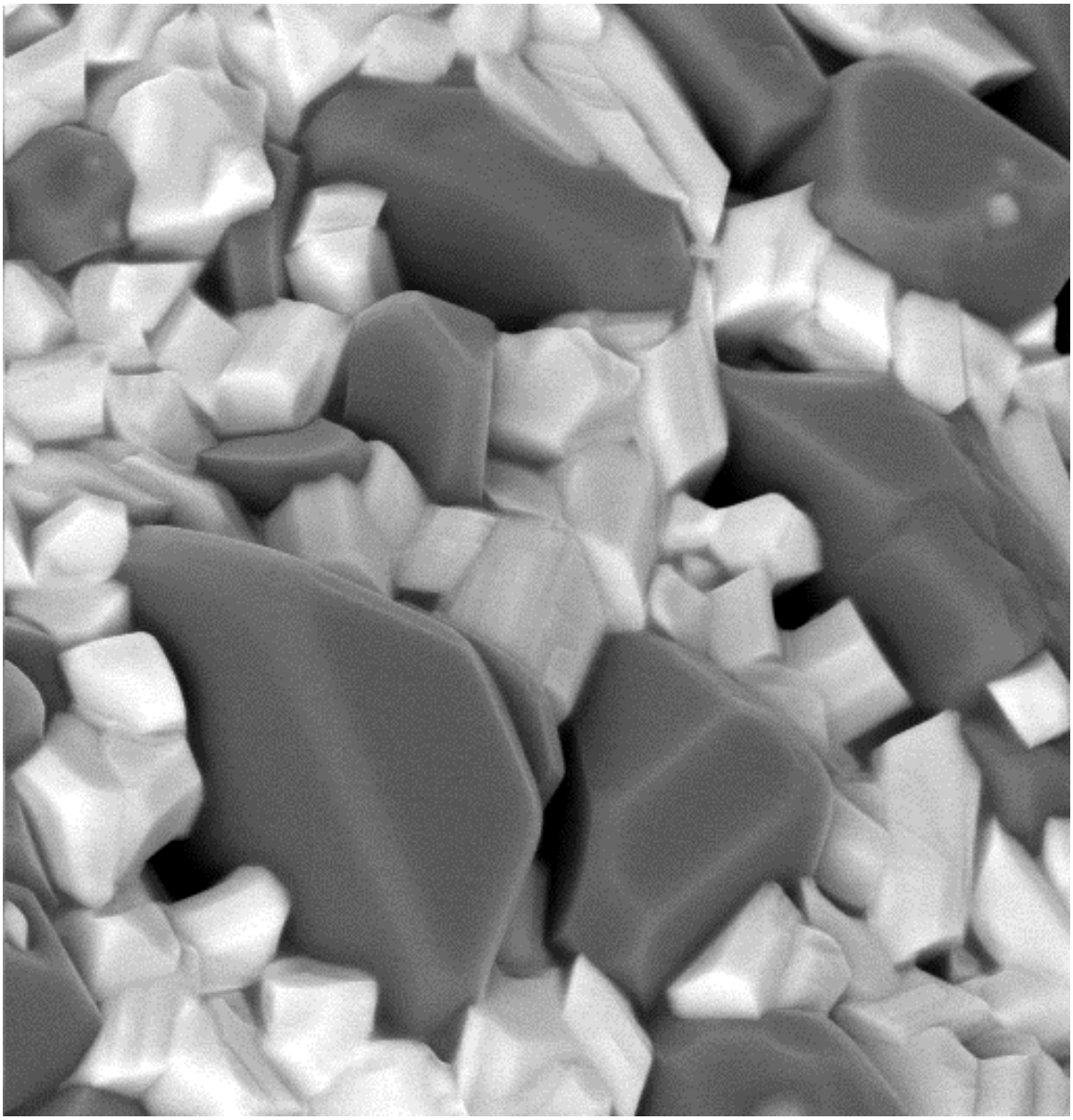
However, small additions of ~<4% Al^{3+} (typically as aqueous aluminum nitrate) remediates this (normally) unwanted feature:

Thermally Etched Monazite/4% Alumina

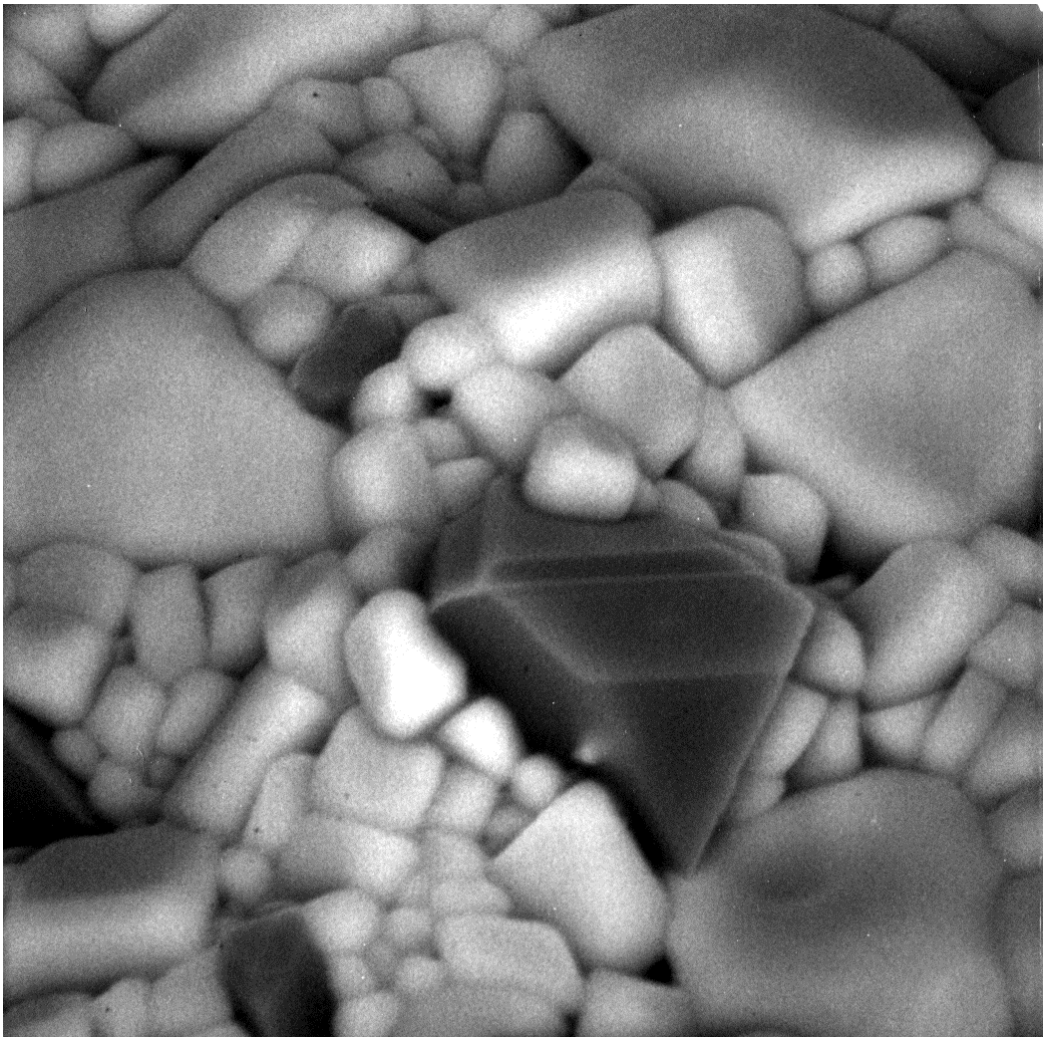


Monazite is phase compatible with hundreds of other minerals(excepting only other very basic minerals such as those with high alkali content). Here are some synthetic cases where monazite is compatible with minerals that are also important ceramics.

Monazite/Alumina at 1600° C

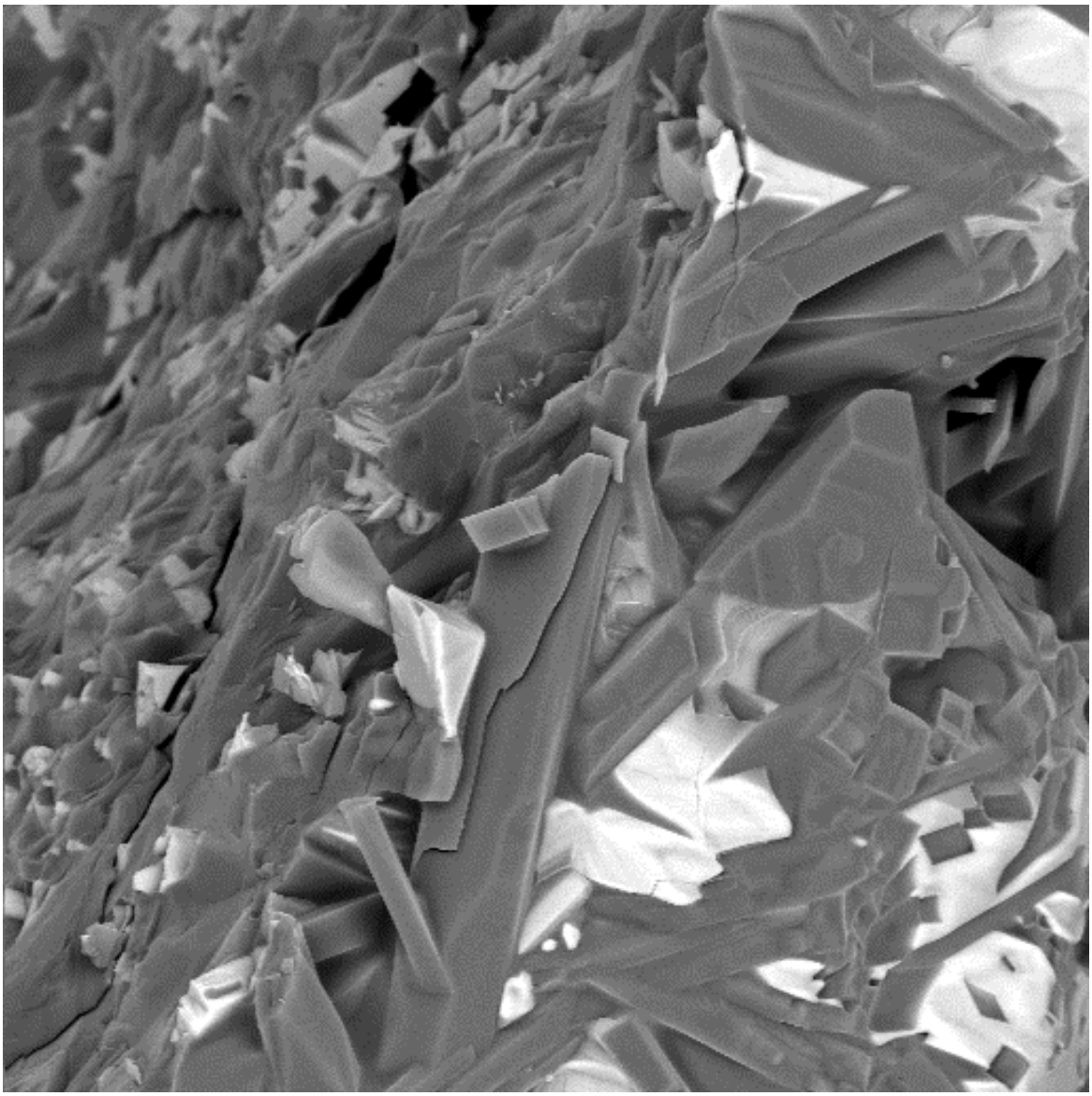


Spinel and Monazite



Compatibility with spinel at 1400ºC

Monazite/Mullite 1600ºC

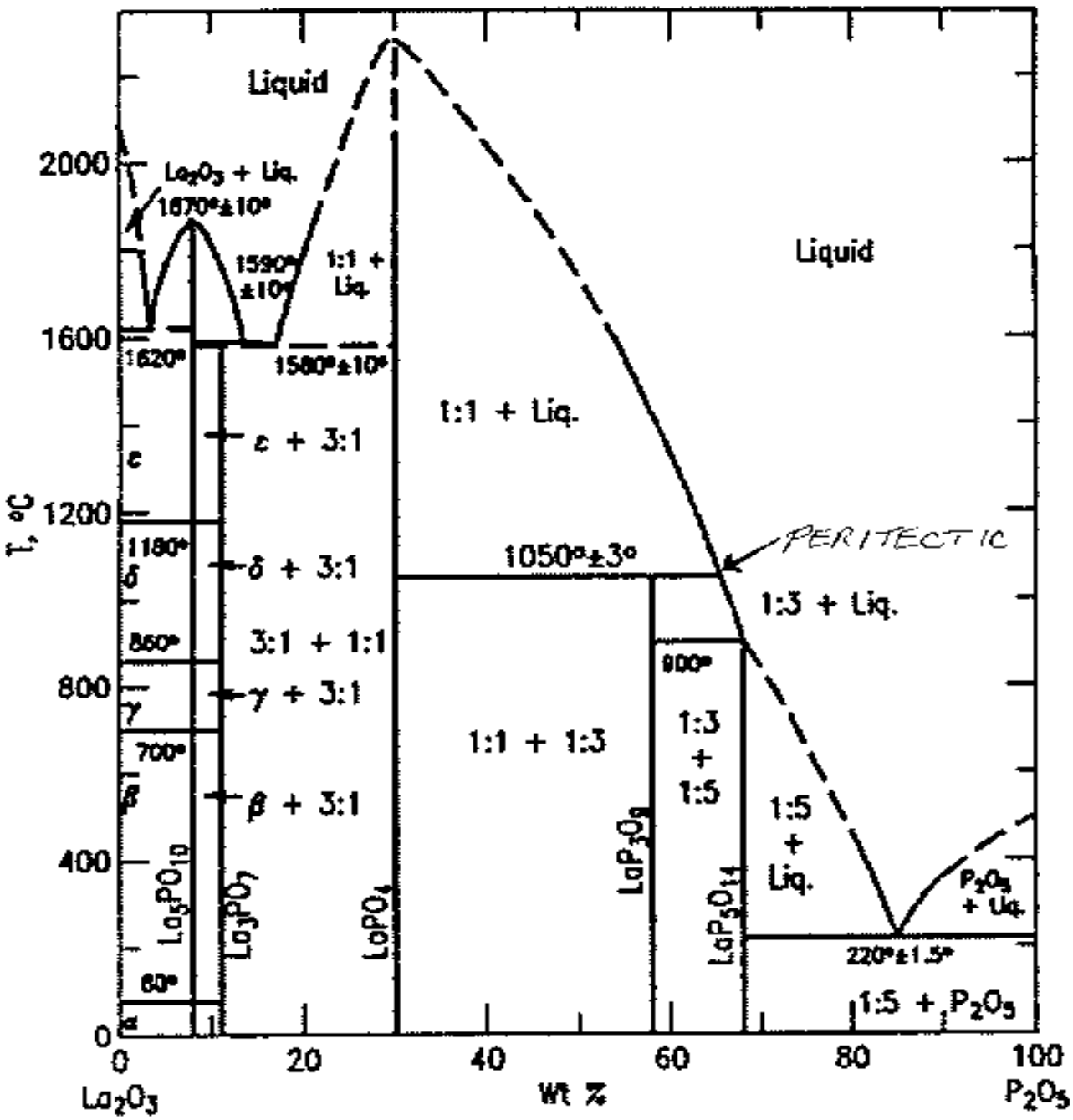


20μm

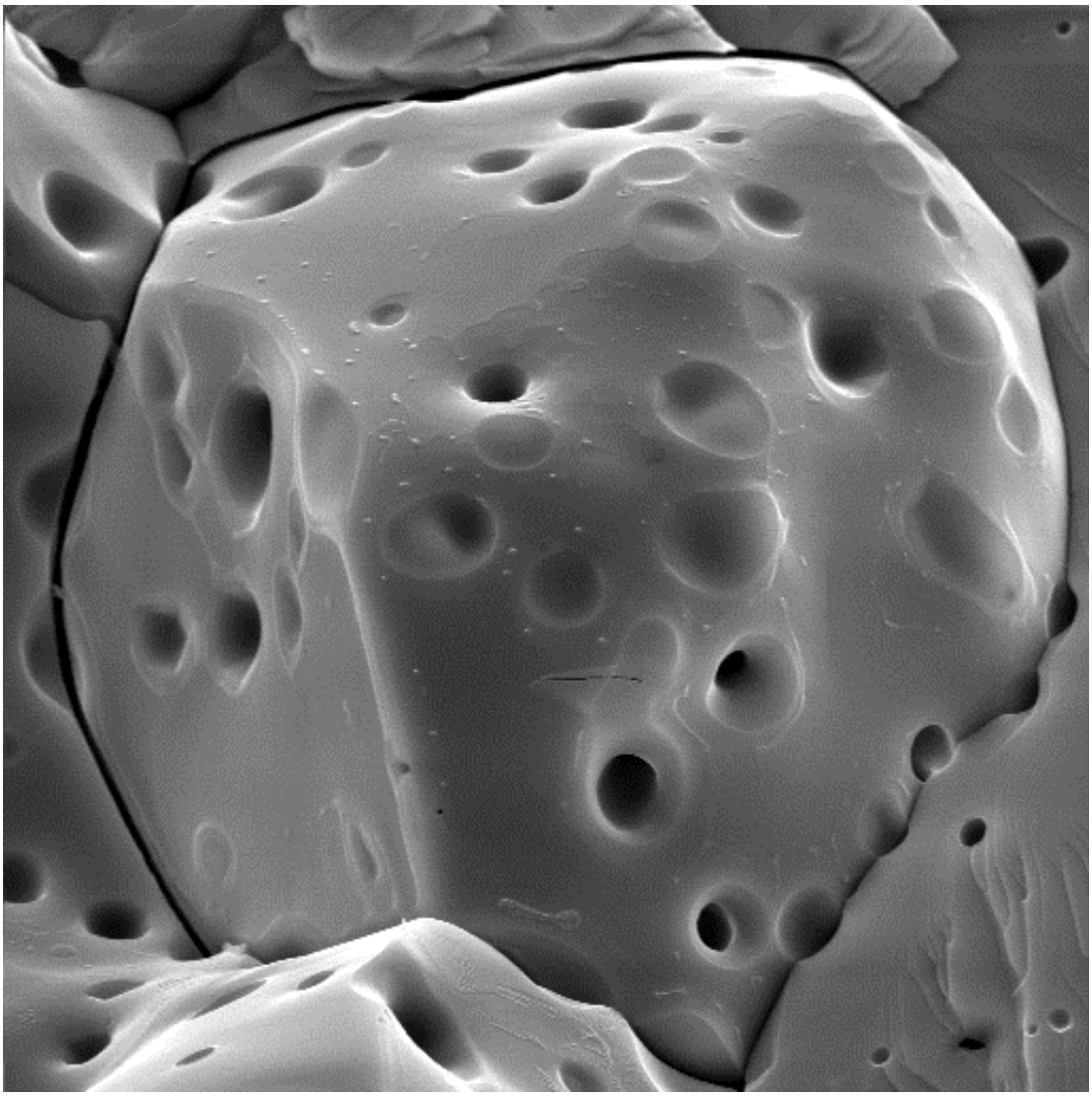
Not shown are compatibilities we have seen with zirconia, YAG, "$LaAl_{11}O_{18}$", $AlPO_4$ and many others.

As mentioned, when powders contain small amounts of excess P, a peritectic liquid will form above 1050ºC, as indicated in the phase diagram:

La_2O_3-P_2O_5


Liquid
Liquid
La_2O_3 + Liq.
1870°±10°
1590° ±10°
1:1 + Liq.
1620°
1580°±10°
1:1 + Liq.
ε + 3:1
ε
1180°
δ + 3:1
δ
1050°±3°
PERITECTIC
1:3 + Liq.
860°
3:1 + 1:1
900°
γ + 3:1
γ
1:1 + 1:3
1:3 + 1:5
700°
β + 3:1
β
1:5 + Liq.
P_2O_5 + Liq.
La_5PO_{10}
La_3PO_7
$LaPO_4$
LaP_3O_9
LaP_3O_{14}
220°±1.5°
60°
α
1:5 + P_2O_5
t, °C
0
400
800
1200
1600
2000
0
20
40
60
80
100
La_2O_3
Wt %
P_2O_5

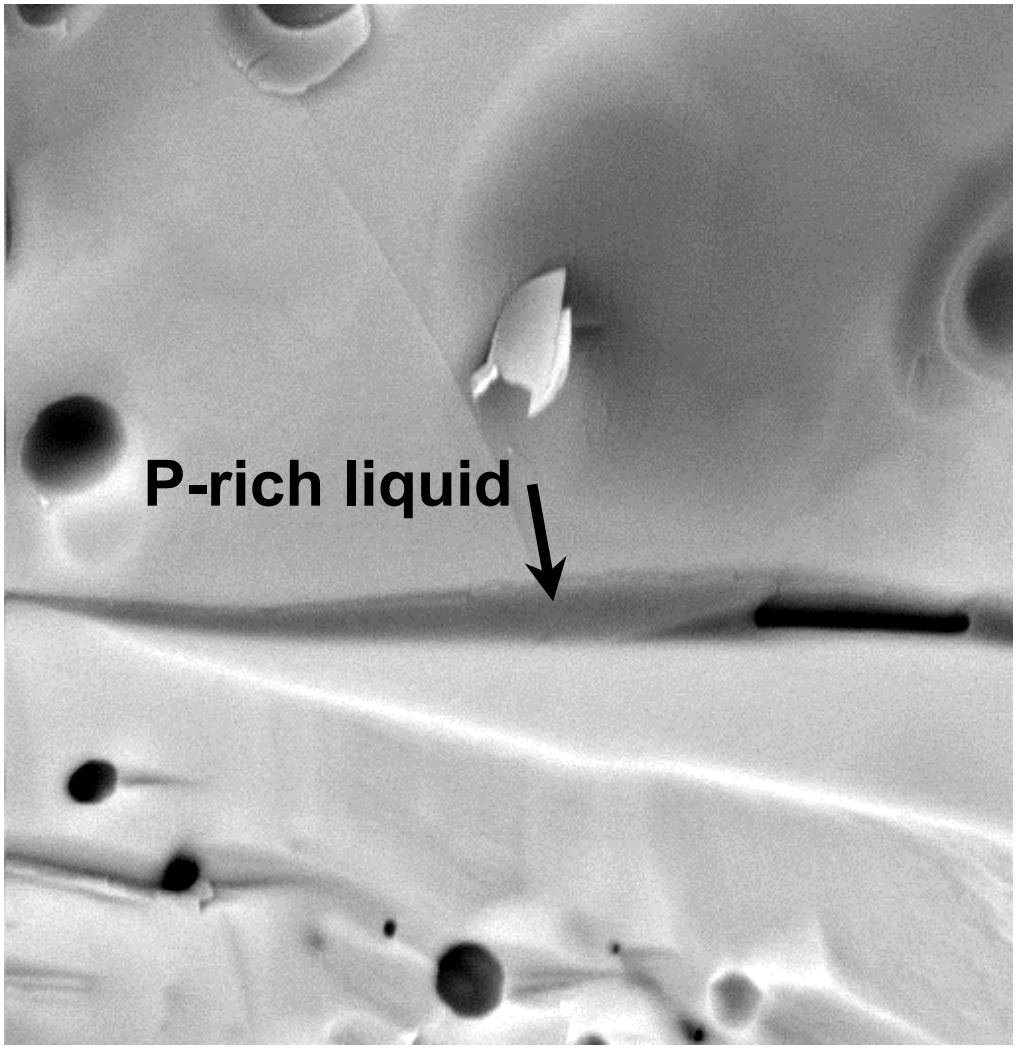
Separated $LaPO_4$ Grain



5μm

The partially wetting liquid, with a thickness of ~1000Å, is easily seen along the separated boundaries as well as the imprint of liquid, that has detached to the adjacent neighboring grain; this represents <0.5% by volume of the sample.

Liquid Stimulated Abnormal Grain Growth



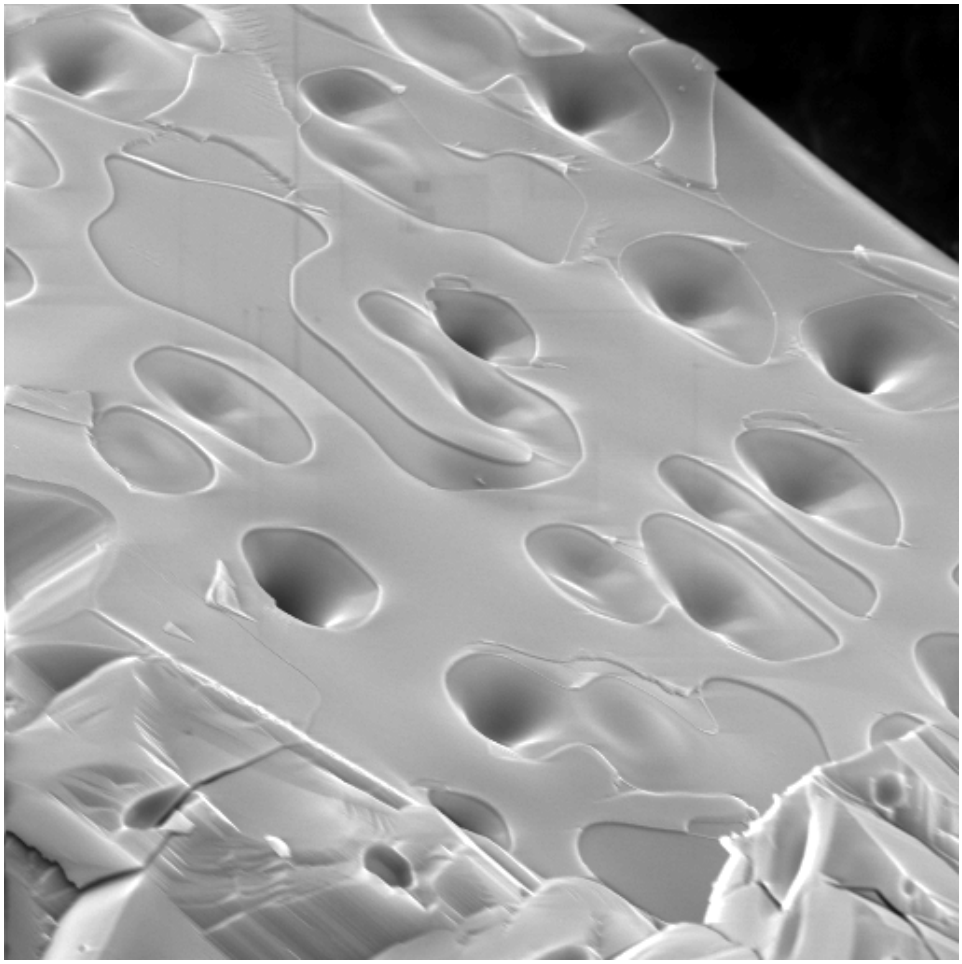
5μm

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

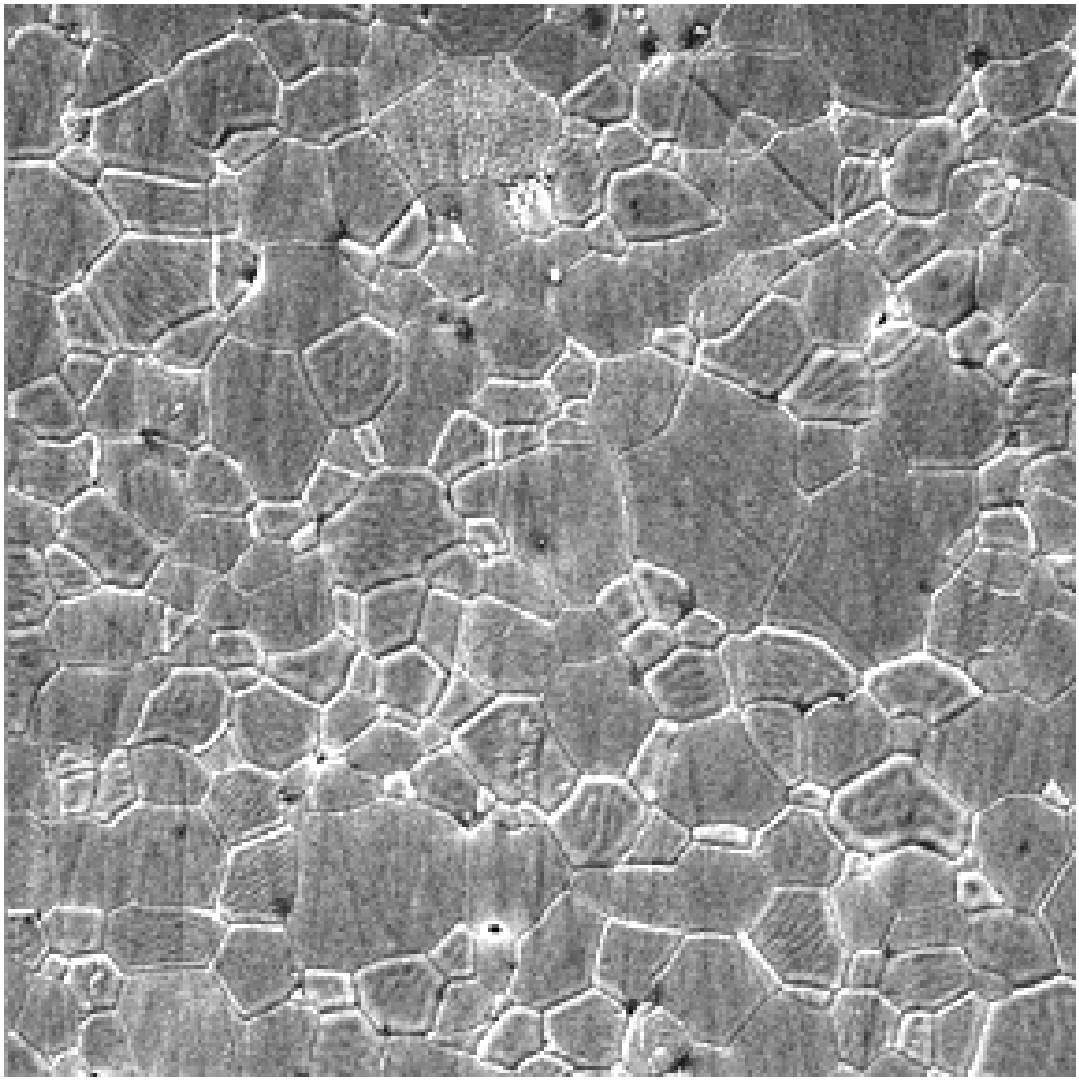
1μ

This liquid remnant has scavenged impurities within it to levels that can be seen by EDS, in a carbon coated specimen, we find low levels of Fe, Na, Al, Si, in that order, adding up to <10% in the liquid and so only <0.05% in the ceramic. This liquid does not occur on all boundaries. Curiously, although many ceramics have contained low levels of liquids (the high temperature superconductors are notorious examples), few observers seem to track it down and extract the

information it contains. Cleavage of the giant grains, which can be >>100μm, reveals internal trapped porosity characteristic of "breakaway" discontinuous grain-growth.

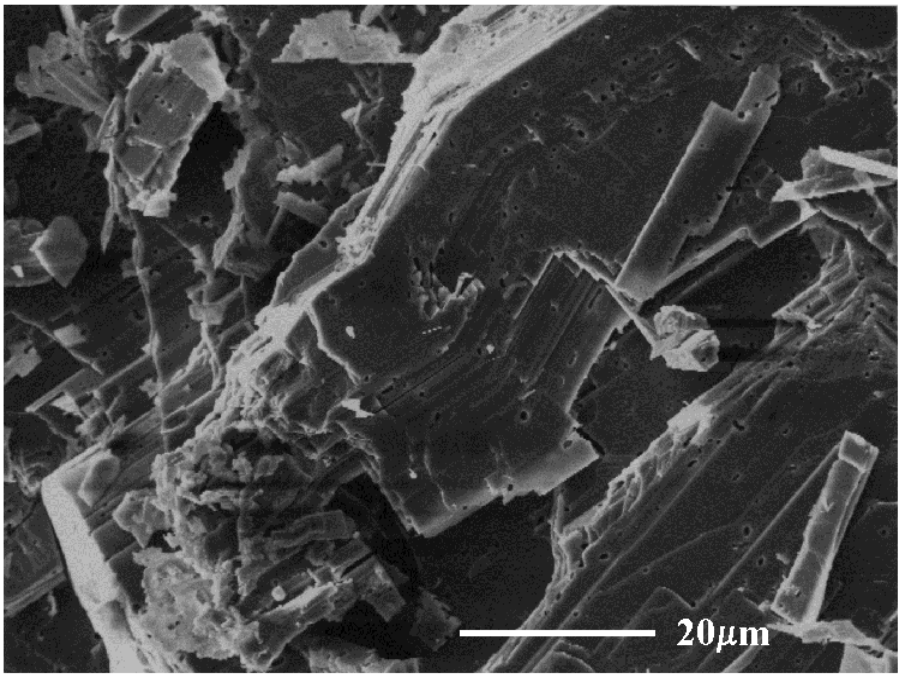


When powders are stoichiometric, so that no peritectic liquid sintering occurs, then fine grained dense ceramic is produced by sintering to 1200ºC. Further heating to 1400ºC then causes little extra grain growth.



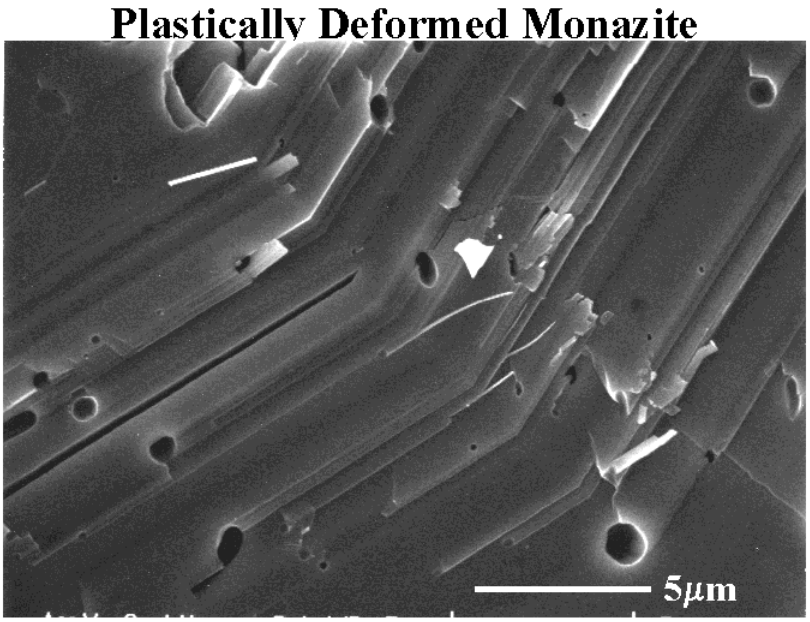
Monazite shows considerable plasticity including upon fracture:

Monazite Fracture Surface



Room temperature fracture shows both plastic and brittle regions.

Region at larger magnification with deformation twins:



Kink bands produced by room temperature deformation

Subsequent to this work, in our related composites, a recent publication has appeared detailing more plastic phenomena in monazite, (Davis, 2003).

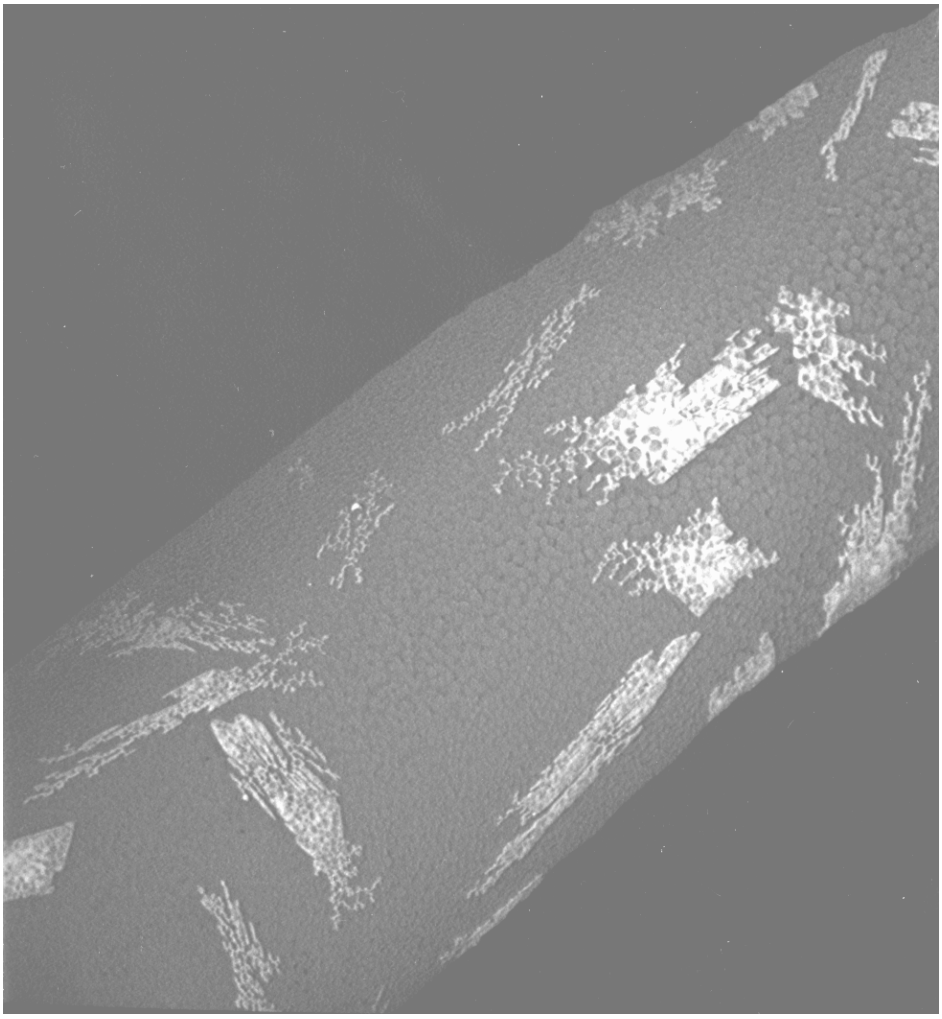
New type of ceramic test for stoichiometry

We have developed a very simple and sensitive test for analyzing whether a particular monazite powder has any excess P above the usually-desired 1:1 La:P ratio. An Al_2O_3 Saphikon® fiber is embedded in a pellet of the starting powder and heated overnight to 1200ºC or 1400ºC. When there is excess P (as in this case where an industrially available powder had been separately analyzed as 1:1.004), a deposit of $AlPO_4$ with included monazite is readily observable upon the fiber, – this sometimes degrades the strength of the fiber and other fibers, e.g., the Nextel types, and so is undesirable in our associated oxide/oxide composites work. This technique is assisted by the fact that pure monazite cleanly separates from the fiber leaving any areas where the peritectic liquid has slightly reacted with the fiber and left some bonded $AlPO_4$ and attached monazite.

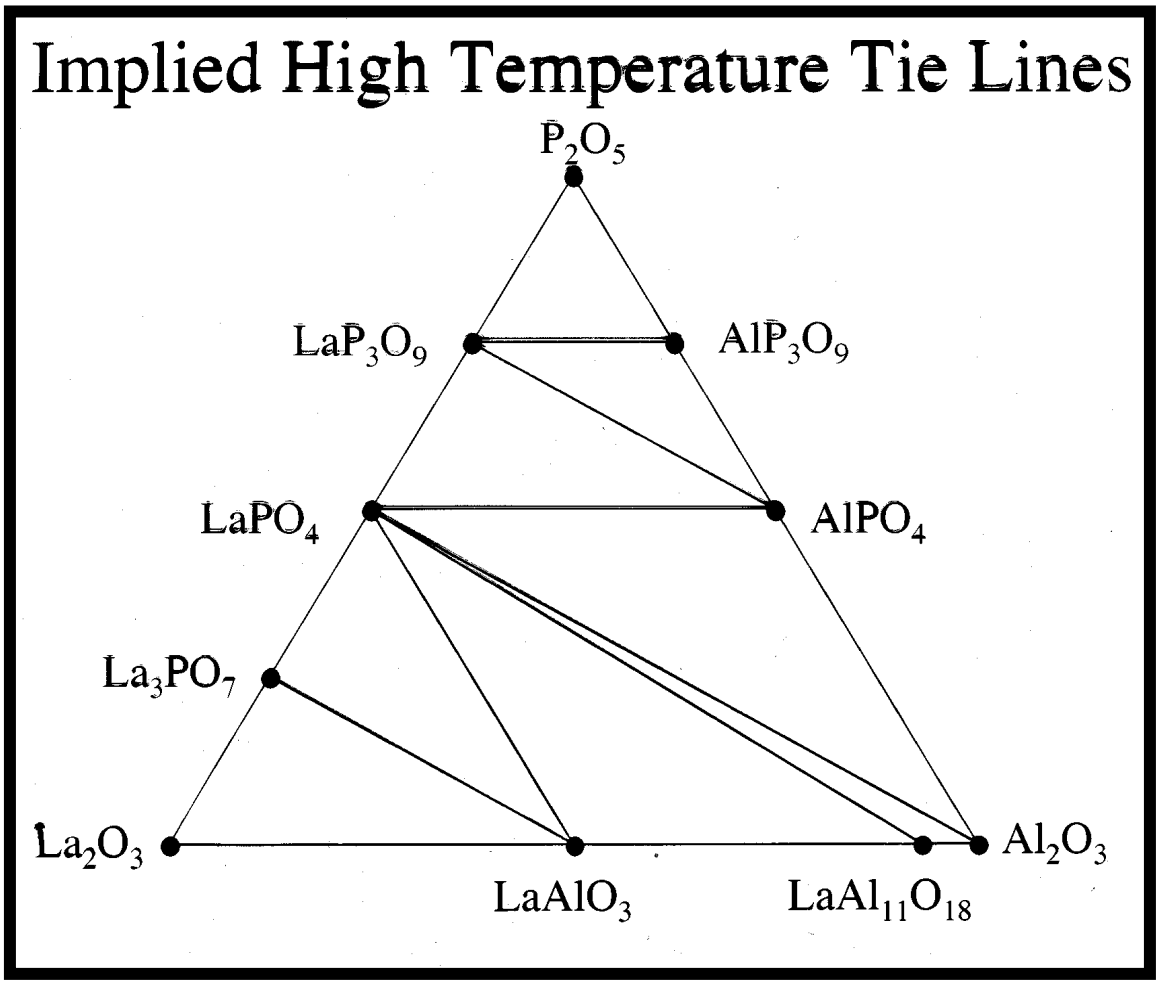
Similarly, when solutions are used to deposit monazite as fiber coatings, should these have excess La, then obvious $LaAlO_3$ or "$LaAl_{11}O_{18}$" is formed on the Saphikon fiber. Excess lanthanum above stoichiometry more regularly weakens fibers.

This type of test could find wide utility for detecting very low levels of impurities in ceramic powders when the compatible detector fiber (or platelet, particle etc.) is judiciously chosen to have the right chemistry to surface react, assuming that the impurity is sufficiently diffusively mobile at high temperatures. Alternatively very low levels of a reactive "scavenger" could sequester and neutralise the bad effects of particular impurities, or excess P, as small additions of Al (as nitrate, hydroxide, oxide etc.) are seen to do. Although this research has had a very applied goal in mind, several generally useful new basic ceramic techniques have been discovered.

This SEM micrograph shows traces of $AlPO_4$ deposited upon a sapphire fiber embedded in monazite, fired to 1200°C, and then the weakly bonded monazite removed. Back scatter electon image shows the light monazite remaining on the $AlPO_4$ regions.



As a result of these and other tests, we have been able to assemble a tentative ternary phase diagram of the La_2O_3-Al_2O_3-P_2O_5 system:



Other uses – helpful for economy of scale in powder production

It has been shown in other work (see refs.) that the interfaces between monazites (more specifically $LaPO_4$) and xenotimes and conventional ceramic materials: alumina, mullite, zirconias and others, are weak/"quasi plastic" and easily debond under stress. This counterintuitive discovery (as many phosphates are used as strong binders in ceramics) has pointed the way to several interesting and practical results. It engenders sliding/pull-out when alumina or mullite type fibers are coated with monazite in a ceramic matrix composite (CMC) making them notch insensitive with much distributed damage and with "plastic-like" stress-strain curves. Very "woody"/brushlike failure has been observed. High temperature testing and long-term stability tests in air look extremely promising.

Monazite, xenotime and these other ceramics are phase compatible to very high temperatures, e.g., monazite/alumina up to at least 1750ºC in air. Morphological and debonding characteristics have been examined up to 1600ºC.

Weak interfaces also lead to "machinable" diphasic ceramics containing monazite by a mechanism, which was originally anticipated to be similar to that known in Macor® by distributed micro-fracture of weak-planes/interfaces. Moreover, monazite itself appears to be machinable; perhaps related also to the "quasi?" plasticity. This has led to several group investigations [Davis, (1998), Begg, (2000), Hikichi, (2002), Min, (2002), Wang, (2003), Wang, (2003)].

. Conjectures as to the reason why these interfaces are weak have been tentatively advanced based upon classical bonding ideas, but the details remain to be studied. Monazite is also being tested as a "high-temperature-starch" on space-shuttle blankets (replacing ceramic tiles) where the weak interfaces allow stiffening without embrittlement and better atmospheric re-entry performance.

Contamination from $MoSi_2$ Heating Elements in Furnace

Because we are working with very pure $LaPO_4$, whose sintering/densification/grain-growth etc. is very sensitive to stoichiometry and to impurities (that effect low melting peritectics), we soon noticed a puzzling irreproducibility in results. Because of previous experiences, this soon became conjectured to be due to the common furnace element, $MoSi_2$, contamination.

To check this out, trays of La_2O_3, which can absorb both of the suspected Mo and Si, were inserted into the furnace, sitting atop the monazite containing crucibles. After 10 overnight runs at 1200ºC, the La_2O_3 powder was discolored. An X-ray diffraction pattern of the surface powder readily showed the presence of La_4MoO_9 (PDF 23-1144), with traces of La_6MoO_{12}. The grains of La_4MoO_9 could be recognized in the SEM of the powder by their "wormy" morphology, and their composition confirmed by EDS. In wide area scans of gold-coated, dilute, bulk powder, the Mo could easily be missed due to the overlap of its strongest line X-ray fluorescent line with Au.

THERE IS A SIGNIFICANT PICK-UP OF MOLYBDENUM THAT CERTAINLY AFFECTS RESULTS.

At the research level the problem is overcome by having scavenger powders in the furnace and by surrounding samples with "powder-beds"1 of the same powder*. We seriously wonder how many reported, curious ceramic results have been influenced by this, often undetected, and/or ignored, effect! Again this is a contribution to general ceramic phenomenology.

An alternative monazite waste form (a grain) to that of a dense ceramic.

We have found that the liquid remains between the large grains can be leached out with aqueous bases. Figures below show a "before and after" leaching; afterwards no sign of liquid remains nor is any excess of phosphorus found. This means we can make a grain (analogous to the natural beach sands) that is preleached; the leachant, containing any plutonium, would be cycled back to the precipitation step. Such a grain form may perhaps have an even lower subsequent leachability in a repository than a bulk ceramic; it has essentially already been "proof-tested".

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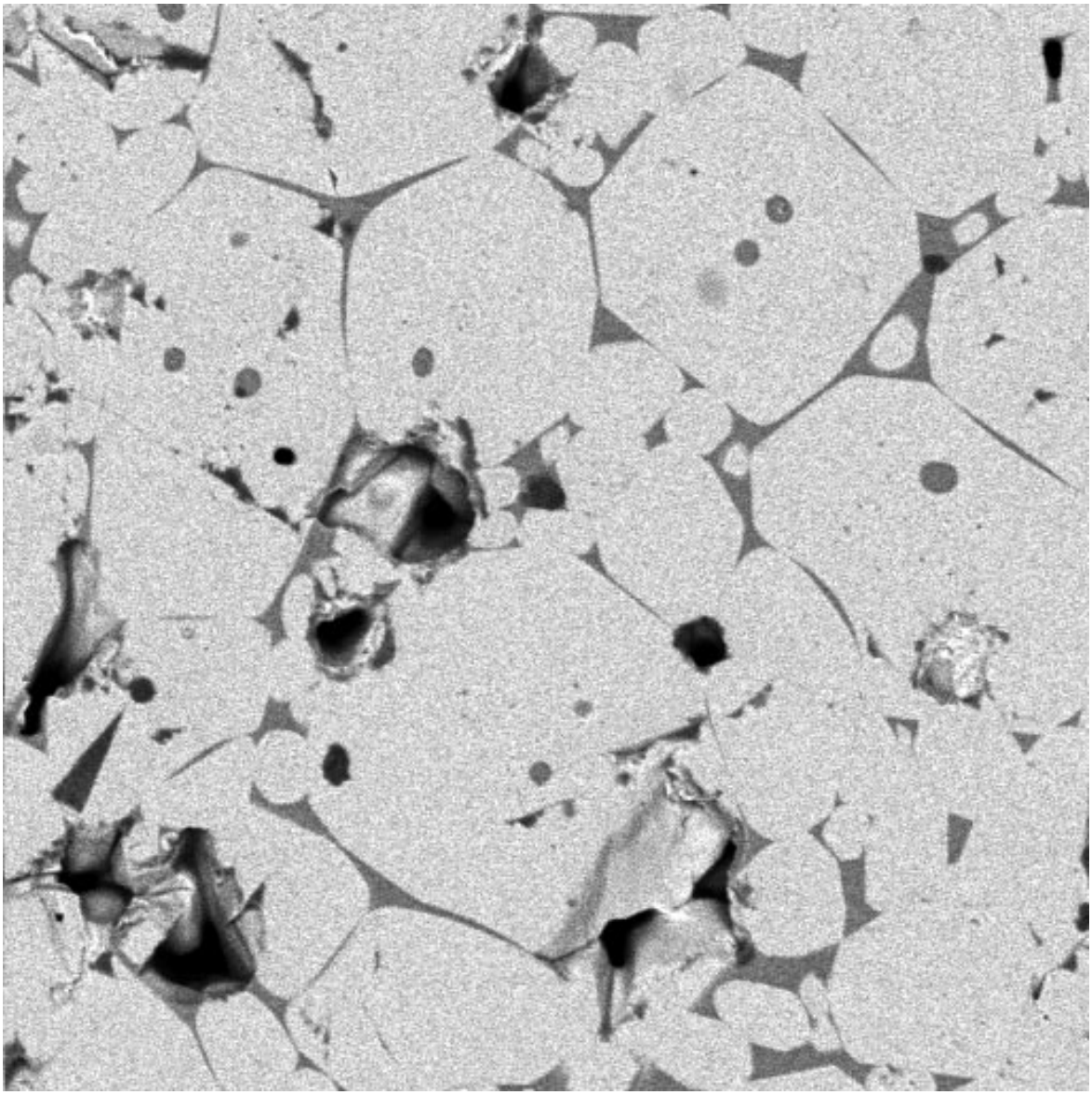
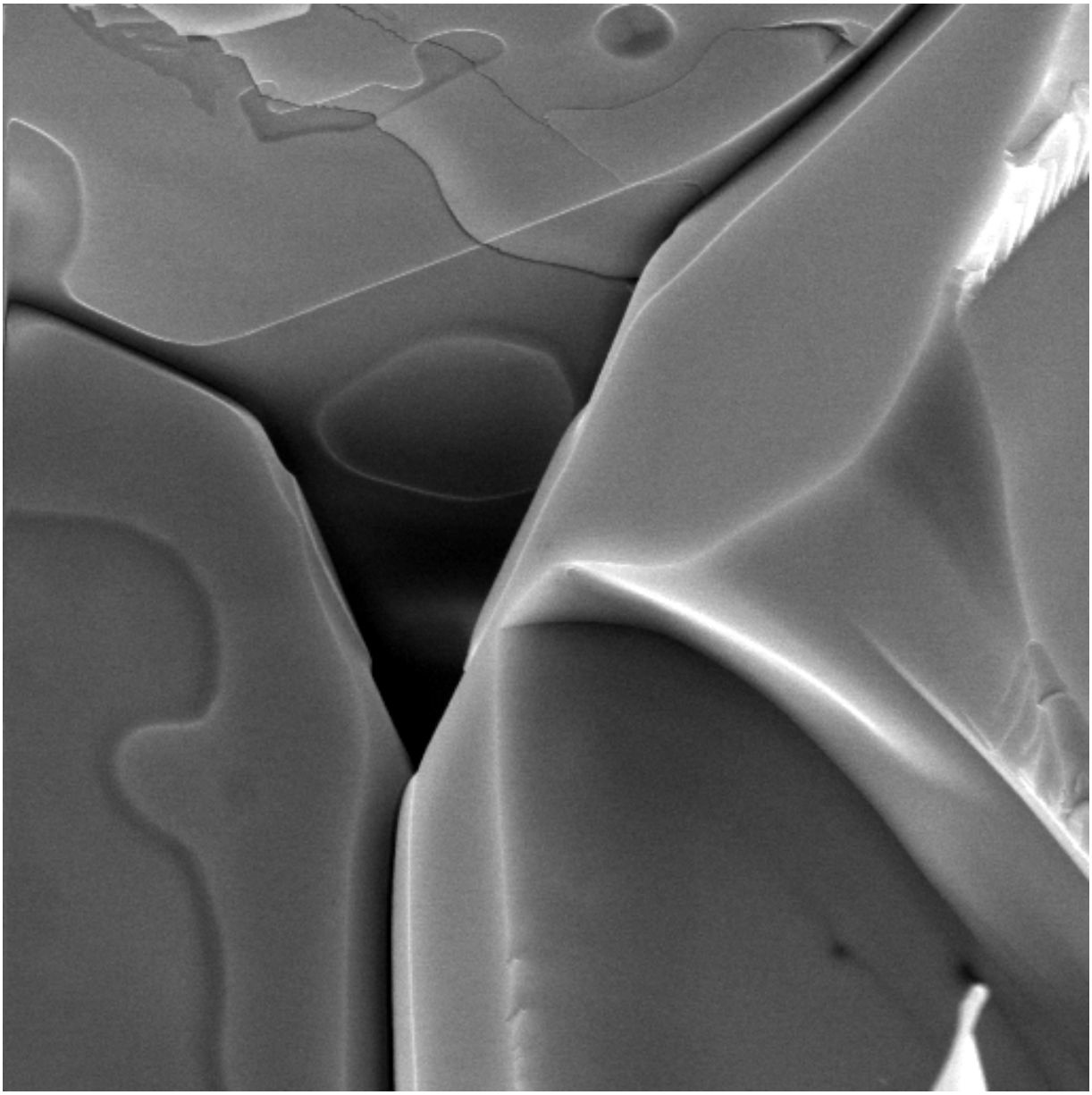
* PEDM was one of the first to realize the importance of this and has been using buffer-beds (powder-beds) since: P. E. D. Morgan, *"The Sintering of Zinc and Cadmium Sulfides",* Sintering and Related Phenomena, Intl. Conf., Notre Dame, Ind., June (1965), Gordon and Breach, 861-894, 1967, Ed., C. G. Kuczynski

Polished Section in P-rich Monazite



50μm

Fracture Surface after TMAH Wash



5μm

Conclusions

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). Much of the unusual behavior relates to the presence of a phosphorus-rich peritectic liquid above 1050°C (somewhat similar to the action of the glass in silicon nitride) which occurs with the easy incorporation of excess P in the precipitated $LaPO_4 \cdot {}^{1}/_{2}H_2O$ precursor powder; methods have been discovered to avoid this as desired.

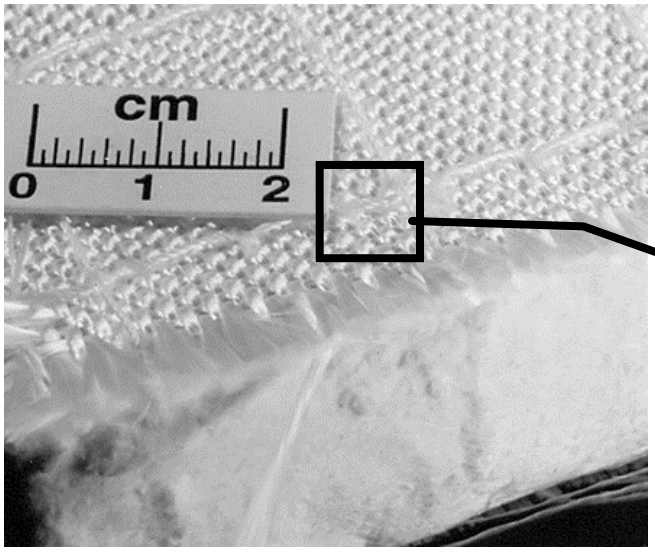
It appears that monazite can be easily made in a dense, fine-grained ceramic form, or as a large-grained (sugary) form (mimicking the natural beach sands), and suitable for possible long-term, >100,000 years, disposal of Pu, other actinides, and some fission products.

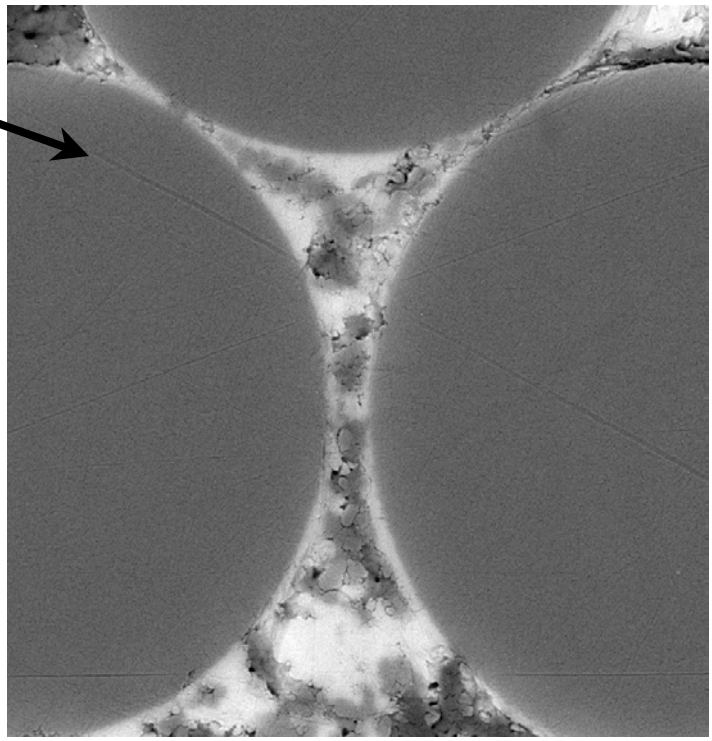
As we mentioned, monazite seems to have some unexpected and quite peculiar properties, cf. it's plasticity, (compared to traditional ceramics) in that regard this work may be compared with the early days of silicon nitride research - that material took 30 years from concept to their use as roller bearings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

The necessarily fundamental nature of this ceramic work has contributed also significantly to knowledge that may be (partly) serendipitously applicable to energy conservation material problems, such as for oxide/oxide composites (for combustor liners or candle filters etc.), which have been under investigation in other DoE programs (e.g. the CFCC program).

Monazite in these other applications has had an impact in other important areas, such as machinable ceramics and for space orbiter blankets; we include below two pictures (without comment) that are from one of our related presentations – see Davis (1999):

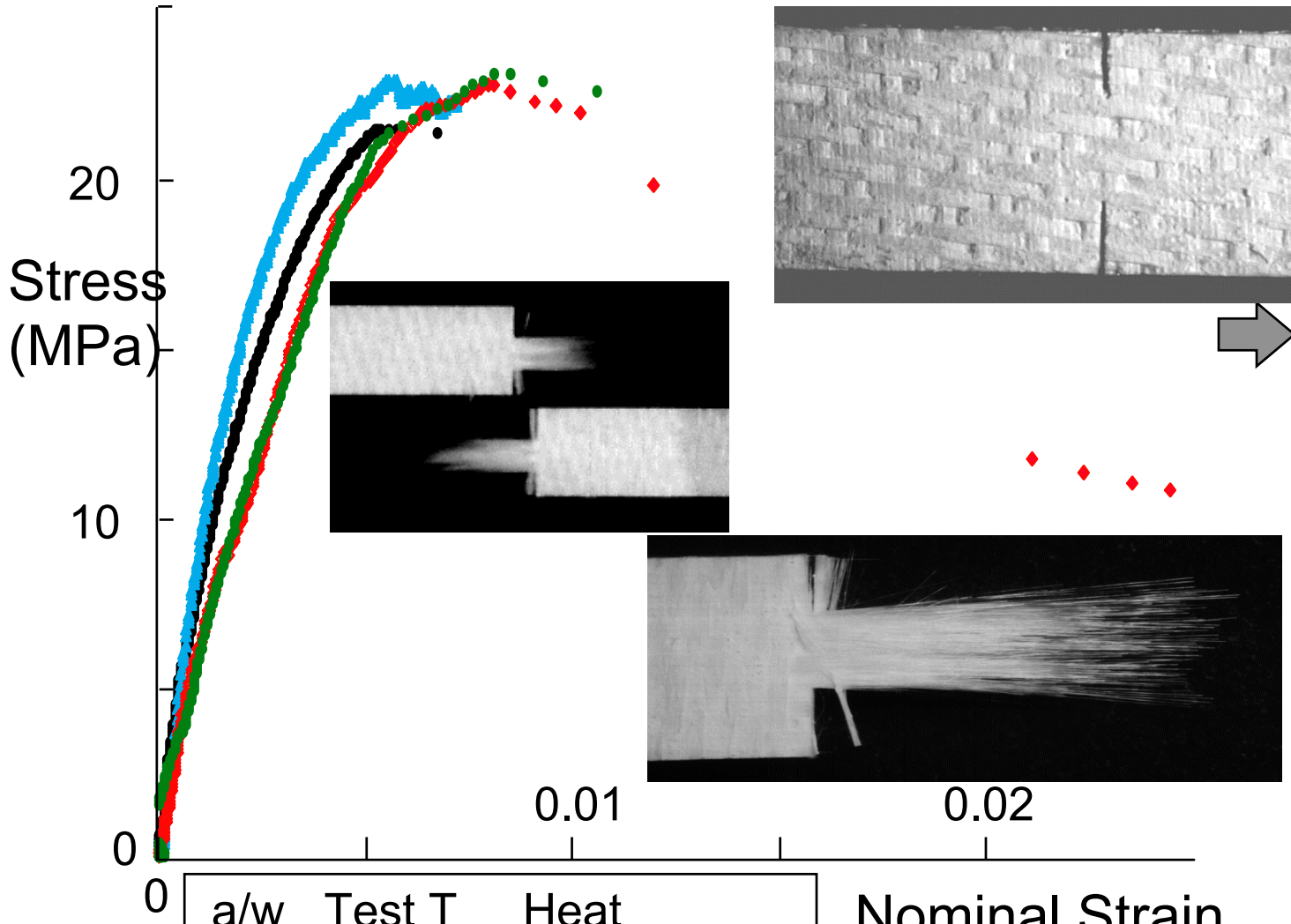
Oxide CMCs:
Thermal protection





Al_2O_3 fiber / Al_2O_3-$LaPO_4$

Edge notch tension



a/w	Test T	Heat
.35	RT	1100*C/1h
.32	1025*C	1100*C/1h
.52	RT	1100*C/1h
.54	RT	1100*C/24h

RSC Publications Concerning Monazite

P. E. D. Morgan and D. B. Marshall, *"Ceramic Composites of Monazite and Alumina",* J. Am. Ceram. Soc. **78** 1553-63 (1995). [over 100 known citations – a "citation classic"]

D. B. Marshall and P. E. D. Morgan, *"Ceramic Composites Having a Weak Bond Interphase Material Selected from Monazites and Xenotimes"*, US Patent 5,514,474, 1996.

A. Cazzato, M. Dolby, D. Daws, J. Davis, P. Morgan, J. Porter, S. Butner and B. Jurf, *"Monazite Interface Coatings in Polymer and Sol-Gel Derived Ceramic Matrix Composites",* Cer. Eng. & Sci. Proc. **18** [3] 269-78 (1997).

S. M. Johnson, Y. Blum, C. Kanazawa, H.-J. Wu, J. R. Porter, P. E. D. Morgan, D. B. Marshall and D. Wilson, *"Processing and Properties of an Oxide/Oxide Composite",* Key Eng. Mat. 127-131 231-238 (1997).

D. B. Marshall and P. E. D. Morgan*, "Fibrous Composites Including Monazites and Xenotimes",* US Patent No. 5,665,463, 1997.

D. B. Marshall, P. E. D. Morgan and R. M. Housley, *"Debonding in Multilayered Composites of Zirconia and $LaPO_4$",* J. Am. Ceram. Soc. **80** 1677-83 (1997).

P. E. D. Morgan, D. B. Marshall, J. B. Davis and R. M. Housley*, "The Monazite Enabling Interface for Oxidatively Stable Ceramic Matrix Composites",* 6th Int. Symp. Ceram. Matl. and Components for Engines, 679-682 (1997).

J. B. Davis, D. B. Marshall, R. M. Housley and P. E. D. Morgan*, "Machinable Ceramics Based on $LaPO_4$ and $CePO_4$",* J. Am. Ceram. Soc. **81** 2169-75 (1998).

Y. Konishi, T. Kusunose, P. E. D. Morgan, T. Sekino and K. Niihara*, "Fabrication and Mechanical Properties of Al_2O_3/ $LaPO_4$ Composite",* The Science of Engineering Ceramics II, Proc. 2nd Int. Symp. Sci. Eng. Ceram. 161-3 341-4 (1998).

D. B. Marshall, P. E. D. Morgan, R. M. Housley and J. T. Cheung, *"High Temperature Stability of the Al_2O_3 and $LaPO_4$ System",* J. Am. Ceram. Soc**. 81** 951-6 (1998).

D. B. Marshall and P. E. D. Morgan, *"Interface Control for Oxide Composites",* Ceramic Microstructure: Control at the Atomic Level*,* Eds. A. P. Tomsia and A. Glaeser, Plenum Press NY 1998, p 83-91.

J. B. Davis, D. B. Marshall, K. S. Oka, R. M. Housley and P. E. D. Morgan, *"Ceramic Composites for Thermal Protection Systems",* Composites A – Appl. Sci. and Manufacturing, **30** 483-88 (1999).

J. B. Davis, D. B. Marshall and P. E. D. Morgan, *"Oxide Composites of Al_2O_3 and $LaPO_4$",* J. Eur. Ceram. Soc. **19** 2421-2426 (1999).

J. B. Davis, D. B. Marshall, K. S. Oka, R. M. Housley and P. E. D. Morgan, *"Ceramic Composites for Thermal Protection Systems",* Composites A – Appl. Sci and Manufacturing, **30** 483-88 (1999).

D. B. Marshall, J. B. Davis, P. E. D. Morgan, J. R. Waldrop and J. R. Porter , *"Properties of La-Monazite as an Interphase in Oxide Composites",* Z. Metall. **90** 1048-52 (1999).

J. B. Davis, D. B. Marshall and P. E. D. Morgan, *"Monazite Containing Oxide/Oxide Composites",* J. Eur. Ceram. Soc. **20** 583-7 (2000).

D. B. Marshall, J. R. Waldrop and P. E. D. Morgan, *"Thermal Grooving at the Interface Between Alumina and Monazite",* Acta Mater. **48** 4471-4 (2000)

D. B. Marshall, J. B. Davis, "Ceramics for future power generation technology: fiber reinforced oxide composites," Curr. Opin. Solid State Mat. Sci., **5** 283-289 (2001)

J. B. Davis, R. S. Hay, D. B. Marshall, P. E. D. Morgan, A. Sayir, *"Influence of interfacial roughness on fiber sliding in oxide composites with La-Monazite Interphases",* J. Am. Ceram. Soc. **86** 305-316 (2003)

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Powder Diffraction Pattern of $LaPO_4$, (La)-Monazite

2θ(°)	d (Å)	I/I_0	h k l
17.030	5.202	41	$1\ 0\ \bar{1}$
18.375	4.825	78	1 1 0
18.870	4.699	77	0 1 1
21.190	4.190	162	$1\ 1\ \bar{1}$
21.525	4.125	69	1 0 1
24.990	3.560	89	1 1 1
25.245	3.525	174	0 2 0
26.860	3.317	725	2 0 0***
28.200	3.164	w	1 2 0***
28.640	3.114	1000	0 0 2
28.900	3.089	w	0 2 1
29.720	3.004	212	2 1 0
30.110	2.9656	36	$2\ 1\ \bar{1}$
30.970	2.8852	326	0 1 2***
33.33	2.688	w	1 2 1
34.360	2.6079	80	$2\ 0\ \bar{2}$ ***
35.570	2.5219	4	2 1 1
36.405	2.4659	38	1 1 2
36.685	2.4478	68	$2\ 1\ \bar{2}$
37.120	2.4201	70	2 2 0
37.475	2.3979	10	$2\ 2\ \bar{1}$
38.225	2.3526	19	$1\ 2\ \bar{2}$
39.880	2.2587	23	$3\ 0\ \bar{1}$
40.850	2.2073	172	0 3 1***
41.810	2.1588	137	$1\ 0\ \bar{3}$ ***
42.110	2.1441	147	2 2 1***
42.730	2.1144	27	3 1 0
43.055	2.0992	6	$2\ 2\ \bar{2}$
44.215	2.0468	11	1 3 1

44.795	2.0216	4	0 1 3
45.690	1.9841	183	2 1 2***
46.020	1.9721	w	3 1 -2
46.380	1.9562	62	3 0 1***
47.530	1.9115	122	$2\ 3\ \overline{1}$ ***
48.170	1.8876	161	$1\ 3\ \overline{2}$ ***+ 3 1 1
48.435	1.8779	173	3 2 0***
49.420	1.8427	9	$1\ 2\ \overline{3}$
49.875	1.8270	6	1 1 3
50.325	1.8117	43	0 2 3
51.455	1.7745	119	$3\ 2\ \overline{2}$ ***+ 2 3 1
52.030	1.7562	124	1 3 2***
52.120	1.7533	w	2 3 -2
52.500	1.7416	43	$2\ 2\ \overline{3}$ + $3\ 0\ \overline{3}$ ***
53.610	1.7082	119	1 4 0***
54.770	1.6747	7	$1\ 4\ \overline{1}$
55.175	1.6633	50	4 0 0
56.210	1.6351	46	$4\ 0\ \overline{2}$ ***
56.530	1.6266	13	1 4 1
56.815	1.6192	81	4 1 0
56.900	1.6169	w	3 3 0
57.385	1.6044	24	3 1 2
57.835	1.5930	6	$1\ 3\ \overline{3}$ + $4\ 1\ \overline{2}$
58.250	1.5826	14	0 0 4
59.135	1.5611	26	2 4 0
59.685	1.5480	30	$3\ 3\ \overline{2}$
60.070	1.5390	21	$2\ 1\ \overline{4}$
62.110	1.4932	5	3 2 2
62.515	1.4845	11	$4\ 2\ \overline{2}$
62.760	1.4793	29	2 4 1
63.025	1.4737	13	2 2 3
63.470	1.4645	12	$2\ 4\ \overline{2}$

64.420	1.4452	4	0 2 4
65.375	1.4263	8	$3\ 1\ \overline{4}$
66.730	1.4006	28	$4\ 2\ 1 + 3\ 3\ \overline{3}$
67.685	1.3832	66	$4\ 3\ \overline{1}$ ***+ 3 4 0 + 1 5 0
68.640	1.3662	22	$1\ 4\ \overline{3} + 4\ 2\ \overline{3} + 1\ 5\ \overline{1}$
69.295	1.3549	36	1 2 4 ***
69.535	1.3508	60	4 0 2 + 3 3 2***
70.020	1.3426	31	$5\ 1\ \overline{1}$
70.220	1.3393	50	$1\ 3\ \overline{4}$ ***+ 2 3 3
70.995	1.3266	24	$4\ 1\ 2 + 2\ 4\ \overline{3}$
71.550	1.3176	17	2 0 4 ***
72.140	1.3083	28	5 1 0
72.525	1.3023	18	2 5 0
73.190	1.2921	37	$1\ 5\ \overline{2} + 1\ 4\ 3 + 0\ 5\ 2$ ***
73.660	1.2850	22	$4\ 1\ \overline{4}$ ***
74.040	1.2794	8	$1\ 1\ \overline{5}$
74.990	1.2655	7	$2\ 1\ \overline{5}$
75.730	1.2550	28	$5\ 2\ \overline{2} + 4\ 3\ \overline{3}$
76.330	1.2466	46	5 2 0 + 5 0 1*** + 1 5 2 + 0 1 5
76.840	1.2396	22	$3\ 3\ \overline{4}$ ***
77.215	1.2345	7	2 2 4
77.685	1.2282	5	$3\ 0\ \overline{5}$
78.915	1.2121	9	4 4 0
79.875	1.1999	22	$3\ 5\ \overline{1}$
81.555	1.1794	34	0 6 0*** + 0 4 4
82.495	1.1683	30	2 5 2 ***
83.245	1.1597	44	5 3 0***
83.595	1.1557	15	$2\ 5\ \overline{3} + 4\ 4\ 1$
84.065	1.1505	6	$1\ 6\ \overline{1}$
84.360	1.1472	5	3 5 1

84.680	1.1437	5	$4\,3\,\overline{4} + 5\,1\,\overline{4}$
85.290	1.1371	6	$4\,4\,\overline{3}$
85.815	1.1314	20	$6\,0\,\overline{2}$ ***
86.005	1.1294	16	$2\,3\,\overline{5} + 1\,4\,4$
86.550	1.1237	7	$5\,1\,2 + 6\,1\,\overline{1}$
86.825	1.1209	4	4 2 3
87.290	1.1161	6	0 3 5
87.700	1.1119	34	2 6 0***
88.340	1.1055	5	0 6 2
89.270	1.0964	29	6 1 0***
90.215	1.0873	3	$4\,2\,\overline{5}$
90.635	1.0834	12	5 2 2
91.175	1.0784	23	$6\,2\,\overline{2} + 6\,1\,\overline{3} + 4\,5\,0$
91.545	1.0750	12	$2\,6\,\overline{2}$
92.120	1.0698	17	$5\,4\,\overline{2}$ *** $+ 1\,1\,\overline{6}$
92.785	1.0638	3	5 4 0
93.575	1.0569	15	2 4 4 + 4 3 3
93.935	1.0538	8	2 5 4
94.925	1.0454	4	$5\,0\,\overline{5}$
95.540	1.0403	12	$2\,4\,\overline{5}$
96.185	1.0350	19	$1\,2\,\overline{6} + 4\,0\,4$***
96.960	1.0288	5	$5\,4\,\overline{3}$
97.410	1.0253	21	$6\,3\,\overline{1} + 2\,6\,2 + 5\,3\,2 + 5\,0\,3$
98.165	1.0194	5	5 4 1
98.725	1.0151	11	$3\,5\,\overline{4} + 6\,1\,\overline{4}$
99.535	1.0090	16	$3\,4\,\overline{5} + 6\,2\,1$
100.590	1.0012	8	$1\,6\,3 + 4\,0\,\overline{6}$ **
100.850	0.9994	8	2 3 5
101.705	0.9933	6	$1\,7\,\overline{1} + 4\,2\,4$
102.410	0.9883	4	3 5 3

103.090	0.9837	11	5 5 $\overline{1}$ + 1 3 $\overline{6}$
103.675	0.9797	7	6 0 2
104.000	0.9775	16	4 5 2
104.340	0.9753	8	3 4 4
105.115	0.9702	5	5 5 0 + 6 1 2 (392) + (337)
106.220	0.9631	18	1 7 $\overline{2}$ (733)
106.620	0.9606	10	4 5 $\overline{4}$ *** (1042)
107.205	0.9570	16	4 6 $\overline{2}$ (992)
107.875	0.9529	5	7 0 $\overline{3}$ (503)
108.970	0.9464	8	0 6 4 + 2 0 6 (878) + 378)
109.340	0.9442	15	7 1 $\overline{3}$ + 0 5 5 + 1 7 2 + 6 2 2 (565)+(293) + (706) + (490)
109.550	0.9430	12	2 7 $\overline{2}$ + 7 1 0 (524) + (584)
110.095	0.9398	13	7 2 $\overline{2}$ (943)
112.385	0.9271	5	1 3 6 (797)
113.080	0.9233	8	4 6 $\overline{3}$ + 3 7 $\overline{1}$ + 1 4 $\overline{6}$ (210) + (492) + (749)
113.645	0.9203	5	3 7 0 (532)
114.135	0.9178	3	1 1 $\overline{7}$ (326)
114.990	0.9134	5	1 5 5 (711)
115.545	0.9106	8	7 0 1 (853)
115.940	0.9086	11	2 7 2 (814)
116.130	0.9077	11	4 5 3 + 5 2 $\overline{6}$ (270) + (860)
116.780	0.9045	8	6 3 2 (?) (110)
117.550	0.9008	3	7 3 $\overline{2}$ (255)
118.425	0.8967	4	5 5 $\overline{4}$ + 3 6 3 (273) + (558)
119.095	0.8936	5	4 4 4 (592)
119.640	0.8911	6	5 2 4 (753)

CuK_α radiation: α_2 stripped, fixed slit. Diffractometer.

Monoclinic: S.G.: $P2_1/n$ (14); h 0 l: h + l = 2n; 0 k 0: k = 2n.

a = 6.8375 ± 0.0007Å, b = 7.0763 ± 0.0007Å, c = 6.5063 ± 0.0006Å,
β = 103.24°
(Compare with a = 6.8313 ± 0.0007Å, b = 7.0705 ± 0.0007Å, c = 6.5034 ± 0.0006Å,
β = 103.27° as for Y. Ni, J. M. Hughes and A. N. Mariano, "Crystal chemistry of the monazite and xenotime structures", Am. Min. 80 (1995) 21-6 and a = 6.8366 ± 0.0007Å, b = 7.0769 ± 0.0007Å, c = 6.5095 ± 0.0006Å,
β = 103.23° for PDF 32-493)

Common structure type, isotypic with phosphates of the larger rare earths (La-Tb), bismuth and plutonium, and with (La-Nd,Bi,Pu)AsO_4, $LaVO_4$, $SrCrO_4$, $PbCrO_4$, $SrSeO_4$, $PbSeO_4$, and others.

Synthesized from rhabdophane $LaPO_4$.~$0.5H_2O$, precipitated with excess concentrated phosphoric acid from strong lanthanum nitrate solution, filtered,washed and fired to 1200°C in air for 17hours.

Pattern and cell parameters refined to maximum agreement of (h k l) assignments with higher intensity (h k l)'s in calculated pattern from data in: D. F. Mullica, W. O. Milligan, D. A. Grossie, G. W. Beall and L. A. Boatner, *"Ninefold Coordination in $LaPO_4$: Pentagonal Interpenetrating Tetrahedral Polyhedron"*, Inorg. Chim. Acta. **95** (1984) 231-236.

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