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Chemical and Ceramic Methods Towards the Safe Storage of Actinides

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Background and Significance

A very important use for monazite, aristotypically $LaPO_4$, as an extremely-long-term radwaste encapsulant has been earlier proposed. The use of ceramic La-monazite for sequestering actinides (isolating them from the environment), especially plutonium, and also some other radioactive elements (e.g., fission-product rare earths), had been especially championed by Dr. Lynn Boatner of ORNL. Monazite could be used alone, or, mimiking/utilizing its compatibility with many other minerals in nature, could be used in diverse composite ceramic combinations.

In order to attain this goal, the ceramic science of how reproducibly to prepare monazite powder, or its precursors, how to incorporate the radwaste component, how to consolidate or otherwise prepare the ceramic form and all other stages of the process, must be studied and understood. Bearing in mind that a safe waste form must be remotely processed, simplicity of the minimized steps is very desirable. Such simplicity, while not necessarily readily attainable at the bench, would be engendered by generated basic understanding so promoting its practical accomplishment at the operating stage.

Overview

The long half-lives of the actinide/transuranic-elements presents a particular problem for their long-term, safe-storage. Encapsulation is necessary for far more than 100,000 years, a period over which the security of containment (or nations!) etc. cannot be guaranteed, therefore, a geologically-long-term-proven rock-like encapsulant is desirable; for this the mineral monazite - a mixed rare earth phosphate, more particularly lanthanum and/or cerium phosphate (and likely containing some balanced divalent and quadrivalent elements), is an excellent prospect. Particular political problems attach to plutonium decommissioning and so this study has specifically borne in mind that particular actinide.

Before using a particular rock-like mimicking ceramic as a radwaste encapsulant, it is essential that there exist a basic background of knowledge on such material's ceramic synthesis and properties. Very few ceramic materials (notably alumina, zirconia, silicon nitride etc.) have been studied in sufficient detail to have much confidence as to what mechanisms are involved in their synthesis/fabrication and material properties. However, because of its developing interest for phosphors, oxide composites, machinable ceramics and others, monazite is being now quite aggressively studied in these several contexts.

It is always beneficial to have an allied industrial base related to material 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 usefully peculiar!) properties. Monazite, MP 2074ºC, being compatible with most other common ceramic oxides such as alumina, mullite, spinel, zirconia and YAG, is useful as an enabling weak interface in oxidatively stable, oxide/oxide fiber ceramic composites for engine use, in machinable ceramics, as a "high temperature starch" e.g. on space shuttle blankets, and for other uses – see RSC references near end of document for much more detail of these new ceramic uses for monazite. The necessary major force making for ready availability and cheapness of materials is the economy-of-scale brought about by many varied uses.

Geological Occurrence and Stability of Monazite

Monazite is a natural orthophosphate mineral containing rare earth elements, especially cerium, lanthanum, neodymium and minor other light rare earth elements, and generally also containing some thorium and uranium appropriately valence balanced by calcium (more usually) and/or silicon (less usually).

Natural monazite, $(Ln,Ca,Th,U\ldots)(P,Si)O_4$, is widely found, often in the form of relatively large crystals, in granites, gneisses, as an accessory mineral in pegmatites, basalts, carbonatites, felsic volcanic ash (Parrish, 1990) and so forth; the frequency of its occurrence in many rock types attests to its compatibility with very many other mineral species. It ranks as one of the most water resistant minerals known - examples exist where it has been washed out of rocks (e.g. becoming the beach sands of India, Australia and Brazil), 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 – retained daughter products are used to date the crystals. Where low levels of aggressive (hot) siliceous water attack have been noted, the thorium and rare earths form new thorite/huttonite,

$ThSiO_4$, or enter allanite, $(Ce,La,Y,Ca)Al_2Fe(SiO_4)(Si_2O_7)O(OH)$ which, in their turn, also remain immobile.

One other mineral, zircon, has been found to have competitive properties but is found, like several other U and Th mineral hosts, to be metamict (partly or completely amorphous). Monazite is never found 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 under 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 isotypic minerals, notably huttonite, thorium silicate (Taylor, 1978), which is also known to be very stable in the presence of water. A most detailed report on monazite (Boatner, 1988), contains much detail up to that time – more 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, is one of very few ceramic-like materials ***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 heretofore been considered in the USA only to be suitable for low level wastes. In France, where glass forms for high level waste have (mistakenly we think) been manufactured, a growing interest in monazite is now apparent. 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 (hereinafter RSC*) over several years on several ceramic waste forms specifically tailored for particular waste streams[#].

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* now a division of Teledyne Corporation (TDY)

being actually the first ones to find pyrochlore and murataite, both still under study, and others in these tailored forms.

Several other considered waste forms are enumerated therein. This book would surely be one of the first records 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 decreasingly soluble as the temperature increases in an aqueous ambient.

Monazites are highly refractory substances with surprisingly high melting points (exceeding e.g. alumina) (Hikichi, 1987); they are thermally stable from the compositional/structural point of view, with no phase transformations until they reach their melting points, $ThSiO_4$ excepted.

Resistance to Radiation Damage

Favorable, in addition to its unexcelled 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 the longest geological time periods. In spite of this exposure, natural monazites, even those with high thorium (Ueda, 1957) or uranium contents (Gramaccioli, 1978), are always found to be crystalline rather than amorphous/metamict, manifesting always reasonably well defined characteristic X-ray diffraction patterns. Recent research, using synthetic monazite crystals, has shown that this characteristic is due to the ability of monazite to recover readily from displacive damage events at near-ambient temperatures and may relate also to its recently discovered surprising plastic nature (for a ceramic-type material).

Natural (Karioris, 1981) and synthetic (Ehlert, 1983) monazite samples have been metamictized by Ar ion bombardment. Yet gentle annealing at only 200°C for 20 hours restored these samples to a fully crystalline condition. Moreover, even when the near-surface region of synthetic monazite crystals is thusly rendered amorphous by high-dose, heavy-ion bombardment in an accelerator, the leach rate of the ion-damaged phase in aqueous media remains extremely low. The physics of alpha decay implies that on the order of 1000 atomic displacements occur per decay event (Malow, 1979). Thus, for a crystal not to appear metamict, this damage must anneal out by some combination of radiation-damage-enhanced-diffusion and low temperature thermal diffusion on a time scale short compared to the irradiation rate.

Synthetic monazite samples have also been rendered metamict by U fission (Vance, 1982). Vance stated that 8 days at 200°C produced partial recrystallization, but was not more quantitative. Ehlert and others (1983) employed 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; so, ancient monazites with high Th or U contents are crystalline. Works (Begg, 2000, Meldrum, 1998, 1999, Salje, 1999, Zhang, 2000, 2002, Weber, 1997) have continued to illuminate these details.

However, there are data in the literature which, taken at face-value, raise concerns about this otherwise satisfying picture. (Ueda, 1957) found that the X-ray patterns of his natural 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.

Although the above results might suggest that some radiation damage may persist to high temperatures in natural monazites there may be alternative explanations; from electron microprobe analyses (Forster, 1995), we know that natural monazites are highly variable in local composition and exhibit complete, or near complete, solid solubility with huttonite, $ThSiO_4$, and brabantite, $CaTh(PO_4)_2$. They are 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 such deviations from homogeneity. The fact that the X-ray changes were observed at very high temps perhaps indicates that diffusive homogenization was happening. Cartz (1981) has shown that ion irradiated huttonite is harder to anneal than monazite. No comparable data exists for brabantite. Natural monazites could plausibly contain regions that are easy to anneal and regions that are harder to anneal.

It does seem plausible that the above high temperature annealing effects have little to do with radiation damage. They may simply result from annealing away internal strain that was caused by growth inhomogeneities or low temperature segregations or, as we lately learn (Hay, 2003), by the ready plasticity of monazite.

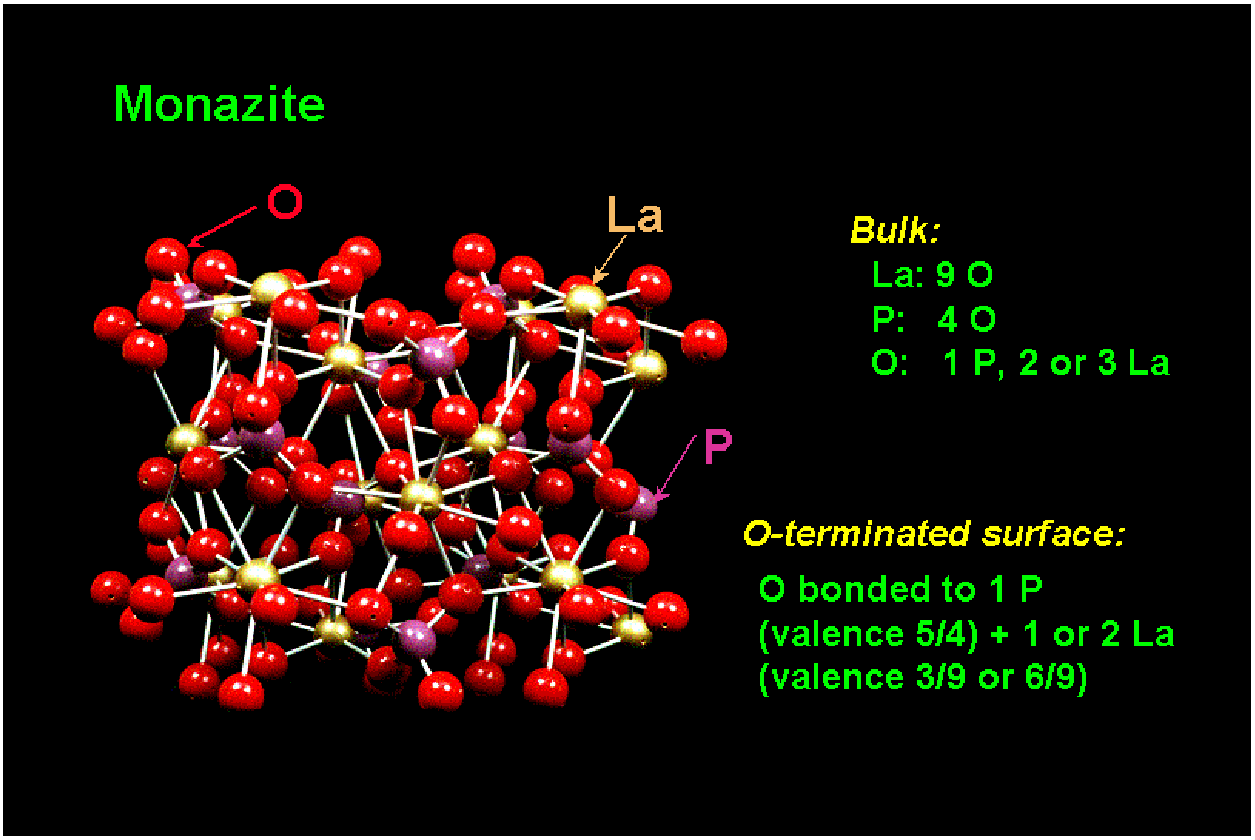
To the extent that one does want to incorporate four-valent actinide cations in monazite using huttonite or brabantite type substitutions, it is important to understand how such substitutions might affect radiation damage resistance. More generally it is important to establish whether self-annealing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

Use for Storage of Actinides

For the specific case of the disposal of actinide elements, aside from thorium and uranium, monazites are particularly attractive (Boatner, 1988, Ewing, 1996) since plutonium and curium themselves readily form monoclinic monazite crystal structured orthophosphates. Other actinides e.g. americium, like U preferring a four-valent state, are incorporated with divalents for charge balance. Accordingly, the non-naturally-occurring actinide monazites are friendly from the crystal-chemistry point of view, and should facilitate high waste loadings. Natural samples demonstrate near complete solid solubility with $CaTh(PO_4)_2$, brabantite (Forster, 1995), while laboratory studies demonstrate complete solid solubility with characteristically green $CaU(PO_4)_2$ at elevated temperatures (Podor, 1995).

In the monoclinic monazite structure (space group $P2_{1/n}$, No. 14, Z = 4), the lanthanide (or actinide) ions are very irregularly nine-fold coordinated with the surrounding oxygen, phosphorus is tetrahedrally four-fold coordinated to oxygen, and oxygens are one-fold coordinated to phosphorus and irregularly two-or-three-fold coordinated to lanthanum (see the model of the crystal structure below); 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 (every La-O bond is structurally distinct!), may possibly account for the ready annealing and plasticity detailed earlier; heavier rare earth orthophosphates have the more symmetrical tetragonal zircon structure with each lanthanide cation in more regular eight-fold coordinated sites.

Crystal structure model of monazite



Red balls are oxygen, all connected to tetrahedral **purple-colored phosphorus.** **Gold-colored lanthanum,** is in a maximally irregular 9-fold coordination to oxygen (all 9 bonds are inequivalent).

For application to the storage of fissile actinides, such as plutonium resulting from the dismantling of nuclear weapons, monazites are attractive from the standpoint of criticality issues since isotopes of Gd and other lanthanides with extremely large neutron-cross-sections may naturally 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 an appointed panel (Hench Panel, Final Report: Alternate Waste Form Peer Review Panel, Report No. 3, USDOE/TIC-11472. 1984) 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 other so-called "alternative" waste forms came quickly to an end. 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 some processed commercial light water reactor wastes. Ceramics of this type were formed by both cold pressing and sintering methods and by hot-pressing or hot-isopressing. The chemical durability of these ceramics was compared to that of borosilicate glass waste forms based on various frit compositions, (e.g. Harker in Lutze, 1988). Some concerns of volatile and anionic contaminants were not laid to rest before the demise of the programs, nor were minor glass forming problems sufficiently tackled.

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.

Competing/Alternative Systems (e.g. Zircon)

Although it would seem that monazite should be one of the very best candidate radwaste hosts for a thorough ceramic study as detailed herein, 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 so is often found in nature to be metamict; 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). In fact, there is now some doubt as to whether zircon is a truly stable ambient pressure phase. This raises flags of concern regarding other hosts where a solid solution, formed under the conditions of ceramic firing, may not be a truly stable phase at lower temperatures, and could undergo deleterious exsolutions. A chilling (to that heavily invested research community) example of this phenomenon is the recent doubt cast that any Y-doped cubic zirconia is truly stable at lower temps.

Zircon does not easily form crystalline and stoichiometric under mild conditions. Deviations from stoichiometry and other causes lead to undesirable second-phases and/or grain-boundary impurities/phases/glasses. 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. Zircon is also a well known constituent of ceramic glazes (e.g., Grum-Grzhimajlo, 1992), whereas monazite is not. This exemplifies, by the way, the superior ability for lanthanides/actinides to hold on to phosphate over and above the ability for zirconium to hold on to silicate. Glassy grain-boundary phases, which usually leach more readily than the crystalline host, compromise the waste-form.

Gaps in Knowledge

Hitherto, before our group at RSC invented the ways that monazite could be used for oxide composites etc. (Marshall, patents 1996, 1997), there had been few significant 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 should thus eminently be an important refractory material, very unreactive in some corrosive environments (notably acidic ones). Alumina is one of a handful of materials where extensive beneficial ceramic studies have been carried out and its prototypical study continues; recent work contrives to a careful breakdown of the many mechanisms simultaneously occurring using slowly evolving (and mutating), occasionally critical, inventive testing that rarely appears quickly on funding demand (e.g. the issue of J. Am. Ceram. Soc. April 2003).

Extensive sintering and related (often not very good, as time is revealing) studies have been carried out on only a very few other ceramic materials notably silicon nitride, mullite, zirconia and, somewhat piecemeal, on magnesia, zinc oxide and a few ferroelectrics. As befits 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 e.g. 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/critical (decision-making) experiments (not mathematical model fitting!) have elucidated particularly 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 negotiation of this quicksands demands individual studies of any new ceramic material in considerable detail. Luckily, the growing diversity in monazite research in several other ceramic areas, encouraged somewhat by work at RSC, is helping here.

Little is understood about microstructure evolution in low symmetry crystalline materials such as monazite. Mechanisms of grain-growth and 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/rhombohedral/trigonal materials, such as alumina (Harmer, 1992, 1993) and silicon nitride (Clarke, 1978), grain boundary structure and morphology are known strongly to determine microstructure. Grain-boundaries in such materials can often be aligned with a specific crystal plane on one side of the boundaries (e.g., many boundaries in alumina are parallel with a basal plane on one side 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 capable between the two crystal lattices. (Ballufi, 1981).

Many experiments need to 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 was concerned with low levels of liquid being present (Ho, 1987)) in, for example, silicon nitride, liquid phase mechanisms are ineluctably 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. Although for 20 years an oxidatively stable weak interface for ceramic matrix composites had eluded discovery, now 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 can result in improved mechanical characteristics in ceramic composites.

Our work here has impacted the ceramic-composites field where, at the present time, about thirty research groups have investigated lanthanum monazite additives for applications in ceramic composites; a dedicated session at an American Ceramic Society annual meeting was devoted to it. Large-scale work is proceeding (mostly in the PRC) on monazite containing machinable ceramics. 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.

The work, alluded to above, has elicited the seemingly big advantage of monazite over the e.g. otherwise attractive zircon, the simplifying ability to directly precipitate monazite from, for example, aqueous solutions, which is to say that monazite can be prepared stoichiometric and crystalline at low temperatures (a significant endeavor of our work here discussed later); recent other work here: (Oelkers, 2002, Kijkowska, 2003, Wang, 2003). Practically all other proposed hosts cannot be precipitated conveniently at low temps but must be synthesized at high temps by firing with the consequent possibility that they are not truly stable at low temps and may have various ceramic defects so entailed.

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). Work associated with these other interests cannot but usefully augment the monazite-as-radwaste host research endeavors. It must be better to utilize a familiar, generic material rather than a niche one in terms of understanding and economy-of-scale considerations (history thus confirms!).

Basic studies to understand and 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, major moves were anticipated to be made by the hands-on-learning-by-doing whereby quite unexpected serendipitous engineering tricks would inevitably be discovered. Good evidence exists that the scientific process is a social activity (Kingery, 1991), which benefits from the excitement of scientific, competitive 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 traditional budgeting and proposal routes seem to demand it). We would hope therefore for long term, stable studies to commence and persist in this growing arena.

Aside

Lest it be thought that rare-earths be "rare" (and, therefore, expensive), this is definitely not the case. Nowadays, many of the less common lanthanides are removed from mixed rare earth; 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 need for Nd nowadays for Nd_2BFe_{14} magnets (used e.g., in automobiles, computers, audio equipment, toys, on refrigerator doors, ha!) has further exaggerated this. Finding a profitable outlet for the La and Ce (from the world's famous largest RE mine in Baotou, Inner Mongolia) undoubtedly explains the quite intense interest in the state-initiative research in machinable monazite ceramics in the PRC, in several of their "Key State Labs."

Large deposits of the preferred source mineral, bastnaesite with only low-levels of Th, are present in the U.S.A. and the PRC; mineral monazite itself is not itself endorsed as a source of cheap lanthanides because of the expense of safely discarding the high thorium content; in Australia this route has, indeed, recently been abandoned. Another possible cost saving approach would be to use "mixed-rare–earth" phosphate; this consists of a mixed $(La,Ce,Pr\ldots)PO_4$ whatever rare earths are left over after all the otherwise useful "goodies" have been removed. As far as we can intuit, this material would suffice equally as well as pure $LaPO_4$. Materials analogous to this are already used in the metallurgical industry.

The increasingly diverse wide-spread use of the rare earths/lanthanides will also ensure cheapness and ready availability via economy-of-scale.

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, zirconia or silicon nitride became available from industry, long after it was appreciated that these were extremely useful ceramics, whereupon how quickly reproducible research results consistently improved!).

We have attempted to demonstrate that nothing in the synthesis or fabrication of monazite is a bar to the practical, reasonable and economic solution for this problem. Indeed, monazite will appear to be a simpler, thus more economic, solution, than using some other hosts.

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:

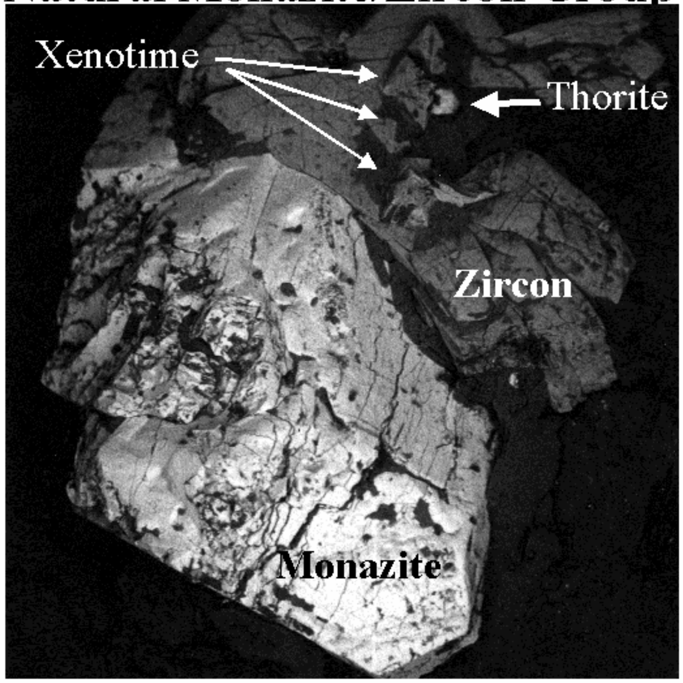
- with a very wide range of solid solutions
- and can be billions of years old
- and is very resistant to water attack
- therefore, it is present in placer deposits (gravels/sands/muds washed out by rivers) on the beach sands of India, Brazil, Australia
- sometimes washed out, reconsolidated by heat/pressure and 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+} (the end member brabantite, $CaTh(PO_4)_2$, also has the monazite structure)
- quite resistant to radiation damage and metamictization (monazite is never metamict in nature)
- the mineral can naturally host neutron poisons, such as some Gd, in solid solution

Moreover:

- pure synthetic $PuPO_4$ also has the monazite structure and is very insoluble
- in which Pu^{3+} is strongly stabilized over Pu^{4+}, the trivalent state is strongly preferred for most of the actinides, U^{4+} somewhat excepted.
- e. g., on heating $Pu^{4+}{}_2P_2O_7$ *in air*, it converts to normal $2Pu^{3+}PO_4$, monazite
- but, in any event, some Pu^{4+} could be stabilized by coupled-substitution with Ca^{2+} or Si^{4+}
- monazite is known to resist metamictization and deleterious volume expansion more than other mineral forms considered for radwaste disposal and readily self-anneals/crystallizes above ~400ºC.
- as most actinides and radioactive rare earths can be integral to the structure (not just entropically encouraged solid solutions), loadings can be high.

“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:

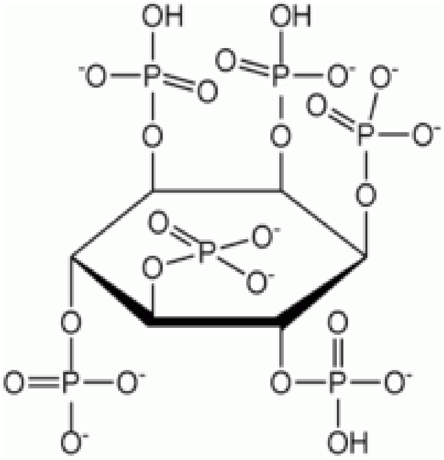
1) Concentrated on the reproducible and semi-automatic production of large quantities of La-monazite (up to ~3kg/week) using methods adaptable to the large scale. Several techniques have been tried to produce a heavy, agglomerated, aqueous precipitated powder of either monoclinic monazite, $LaPO_4$, and its hexagonal hydrated precursor rhabdophane, $LaPO_4.{}^{1}/_{2}H_2O$; we have been unable to directly precipitate the former at 100 °C or less (hydrothermal methods are known for this but are not preferred.). Precipitations of $LaPO_4.{}^{1}/_{2}H_2O$ are carried out very slowly over several days in large plastic bins (such as are used in restaurant 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 for a facile automatic washing procedure. *Fines* (light and less agglomerated) are beneficially recycled to serve as *seeds* in the next batch precipitation. 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 $LaPO_4.^1/_2H_2O$ precipitates; to remove the excess P is quite difficult (excess P may be in the tunnels of the structure) but, we have found analytical and synthetic methods to adjust the stoichiometry exactly to La:P, 1:1.

The X-ray diffraction pattern of our pure rhabdophane was accepted by the Joint Committee on Powder Diffraction Standards (JCPDS) and appears in that file as PDF 46-1439.

2) Studied the preparation of the hydrated $LaPO_4$ from various stable aqueous solution precursors such as:
from La nitrate and phosphorous (sic) acid - recently, preferably, called phosphonic acid
from La nitrate and methyl phosphonic acid
from La nitrate and phytic acid (aka myo-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 phosphate ester acid that forms acid-soluble complexes with many cations which can be precipitated by raising the pH.



It has an advantage over most other complexing agents in having a high P/C ratio (1:1). It is readily available from various 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.

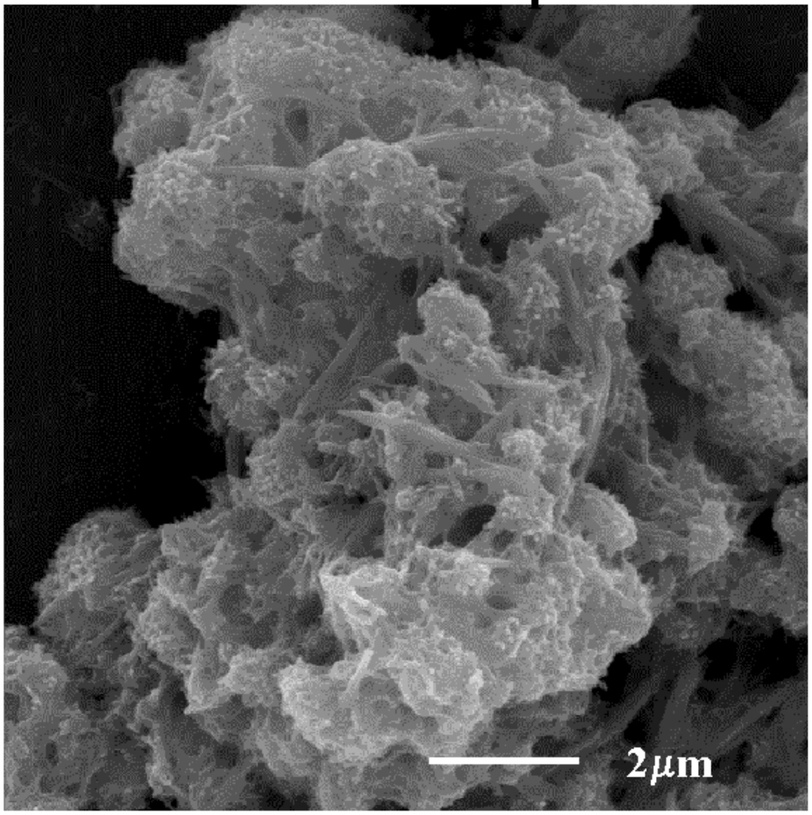
Some tests with other non aqueous complexing agents (e.g. tributyl phosphate – well known in the actinide separation business) were deemed unattractive at this early stage of research.

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 a necessary and worthwhile activity as ceramics can never be more reliable and reproducible than the powders used to make them.

There follows a series of pictures of microstructures illustrating the need for (normally) powders of exactly 1:1 La:P stoichiometry and the consequences of when P is in excess and liquid phase is present above a peritectic.

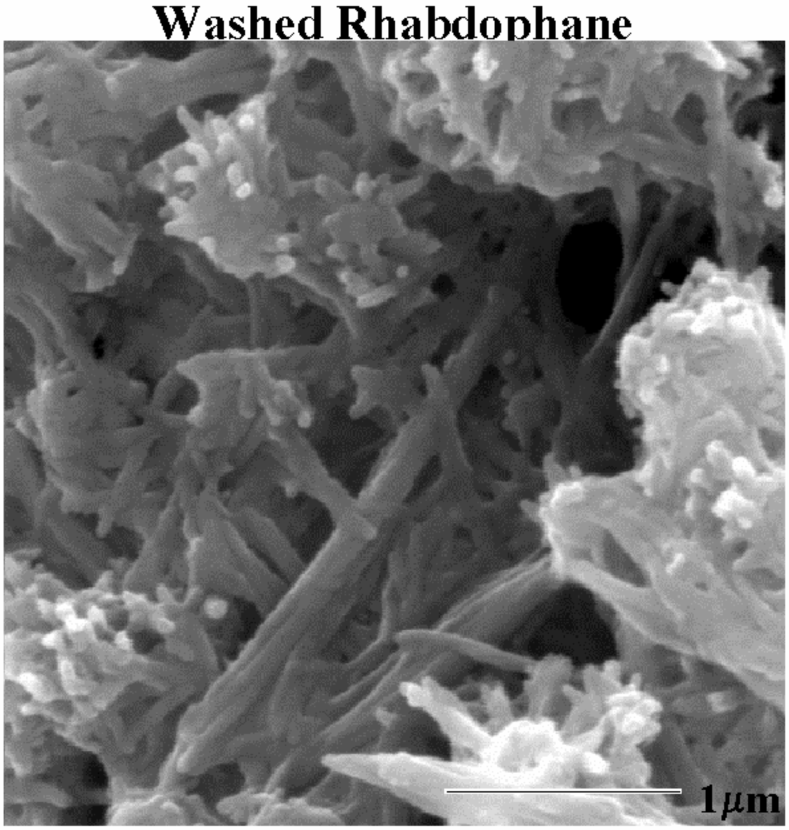
Washed Rhabdophane



Typical aggregate of needles and modified needles

This is the SEM appearance of RSC standard rhabdophane ($LaPO_4.\frac{1}{2}H_2O$) which is now made in multi-kg amounts by slowly precipitating La nitrate solution (usually in excess) with phosphoric acid. Notice that the material is, in this case, desirably highly agglomerated so that extensive sedimentation/washing to aid in removal of excess phosphorus is facilitated (see later comments).

This depicts the same material at higher magnification

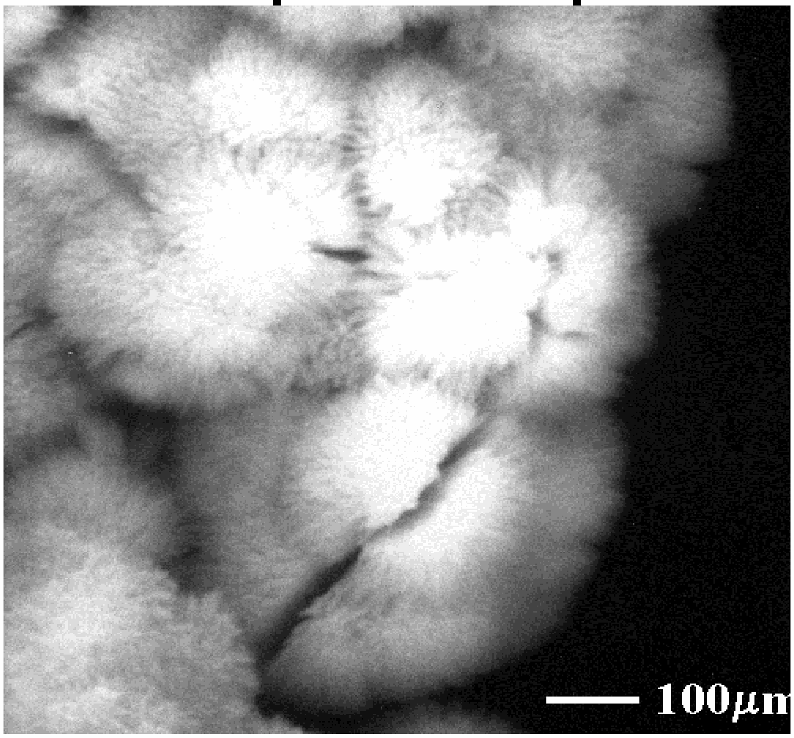

Washed Rhabdophane

Note clumping and modification of initially precipitated long needles.

This material is very easily attrited by standard wet-milling techniques**.** Sedimentation may remove remaining aggregates**.**

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

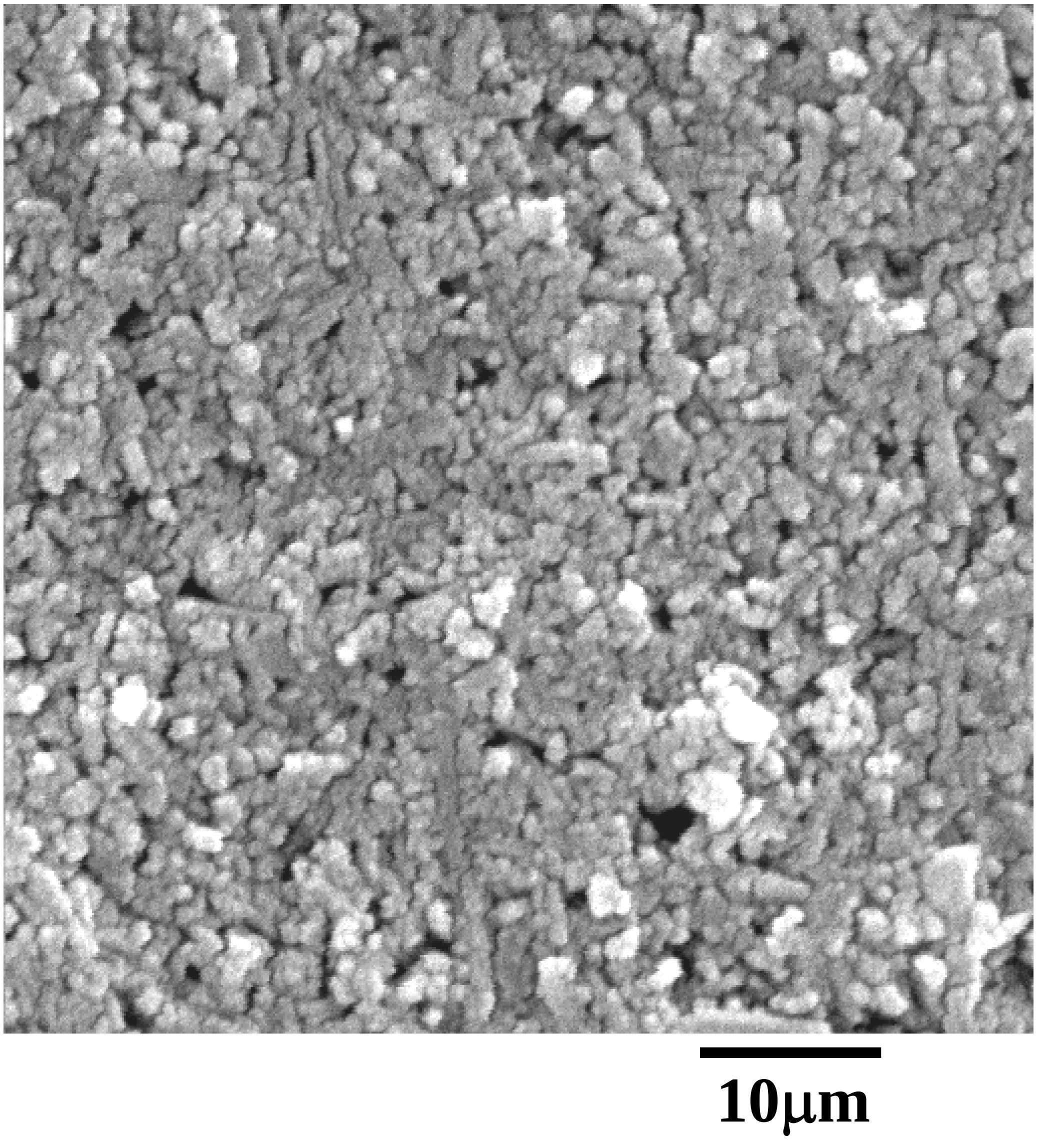
Rhabdophane Precipitate



Spereulitic precipitate made up of fine rhabdophane needles.

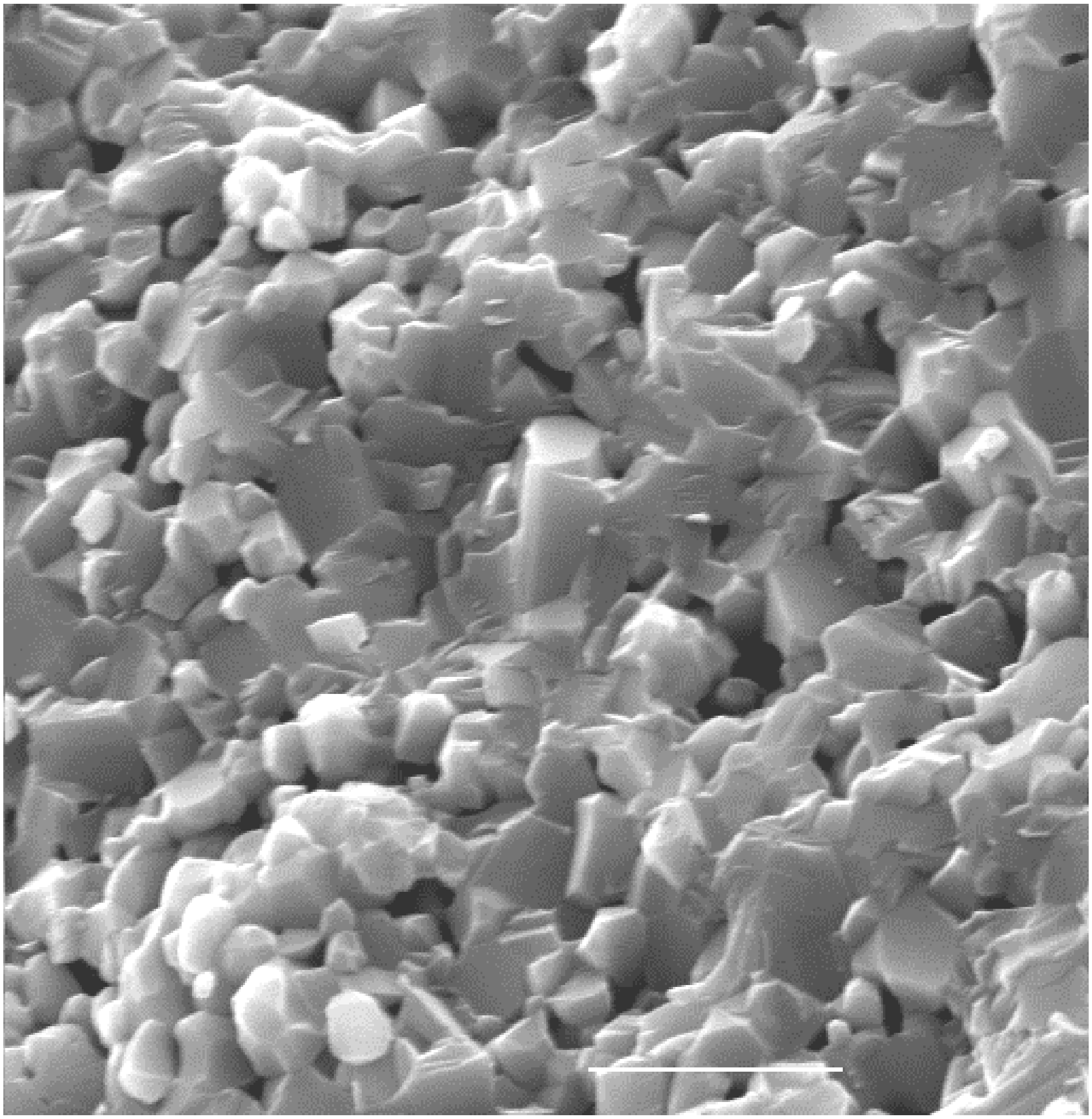
Needles grow out from a nucleus – it follows that “seeding” could be another variable here for control of the morphology.

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



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 them from the furnace atmosphere contamination as discussed elsewhere.

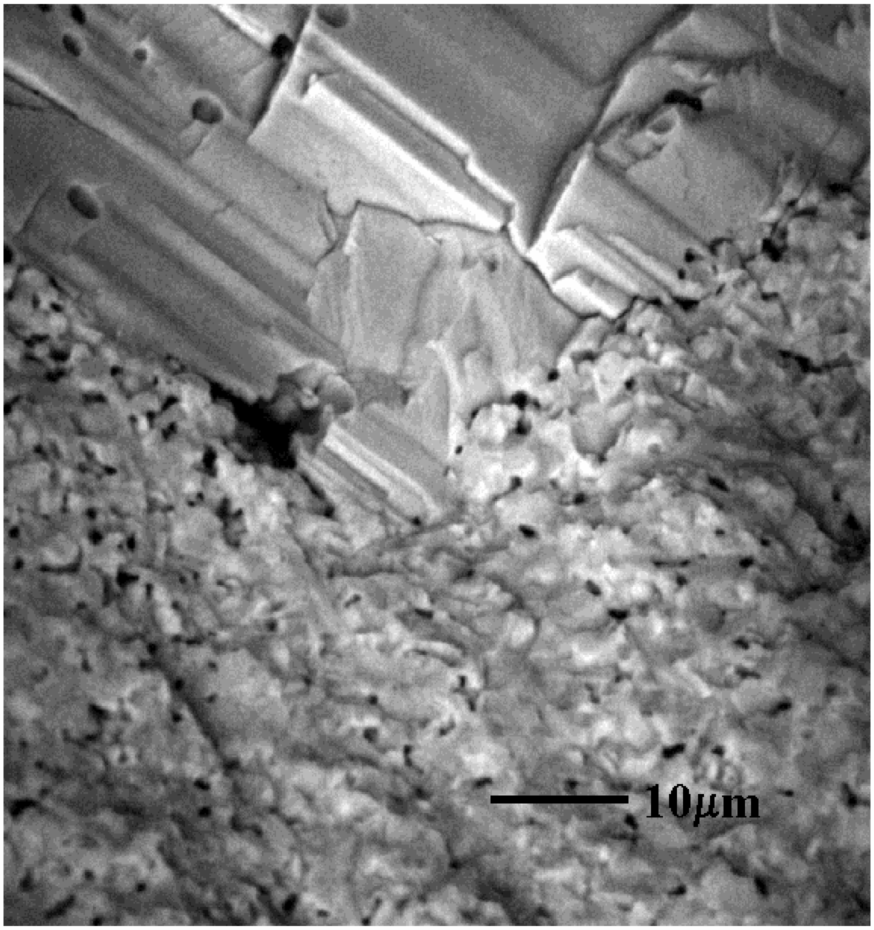
Uniaxially cold pressed and fired at 1200^o C. Fracture surface.



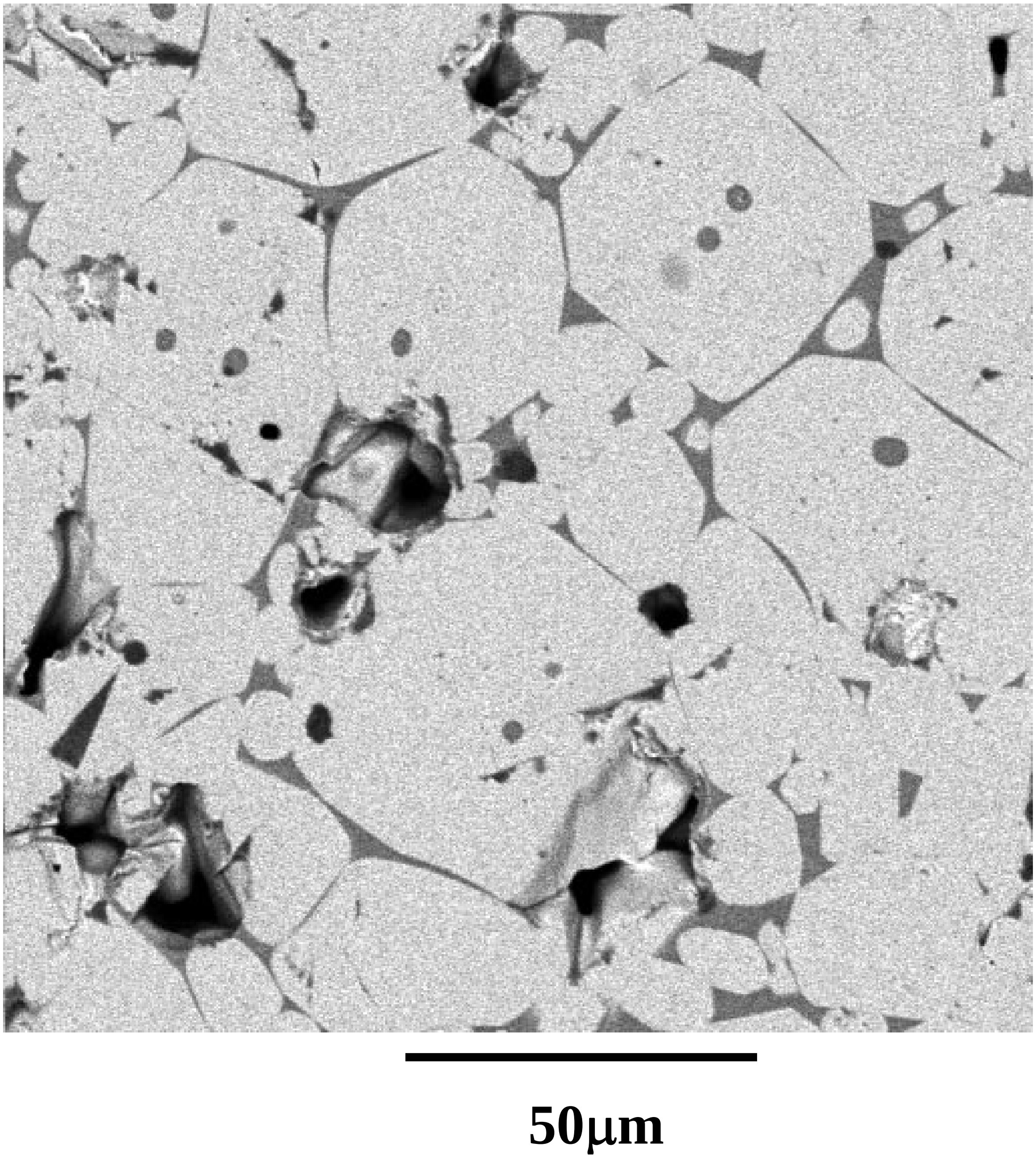
2μm

At this temperature, even with a small excess of phosphorus, discontinuous grain-growth is not apparent.

But, at higher temperature, by 1400^{o}C, discontinuous grain-growth readily occurs, but only when excess P is present:

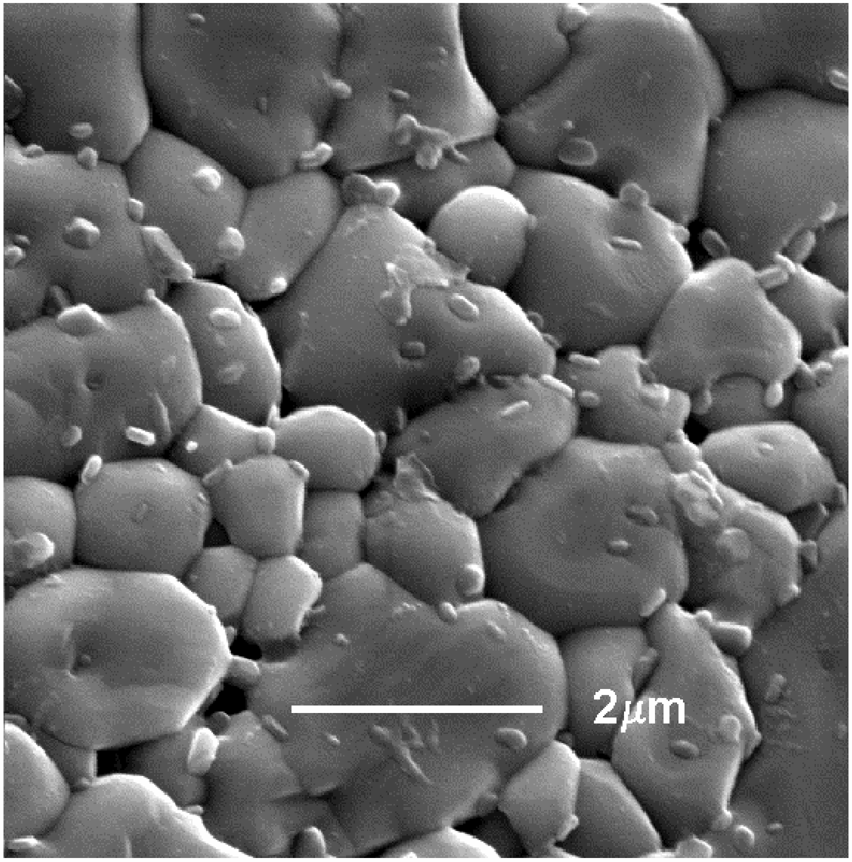

Giant Grain/Normal Grain Interface

Polished Section of P-rich Monazite



Frozen peritectic/eutectic liquid (gray) is clearly visible at the grain boundaries**.**

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

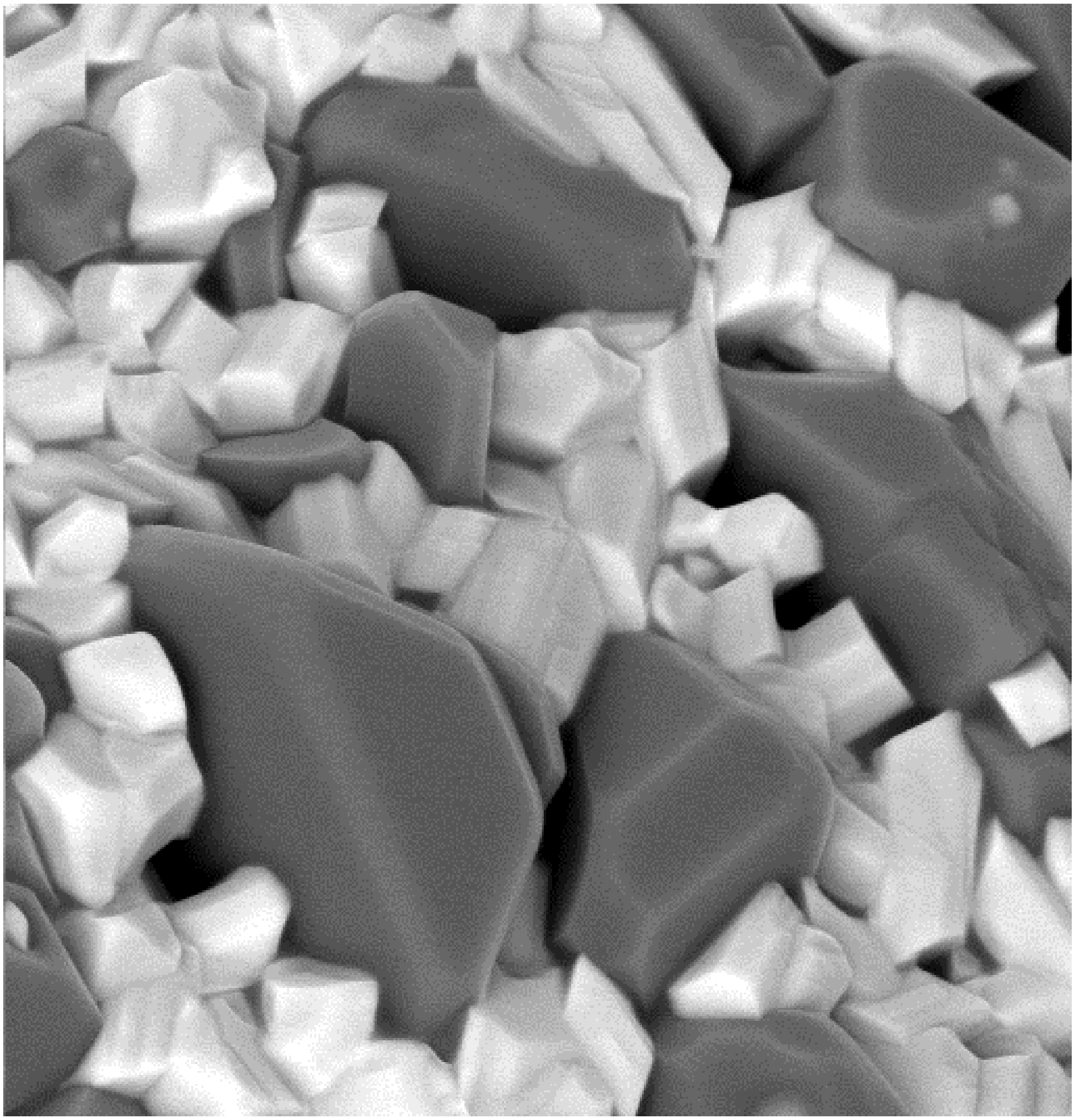


Thermally Etched Monazite/4% Alumina

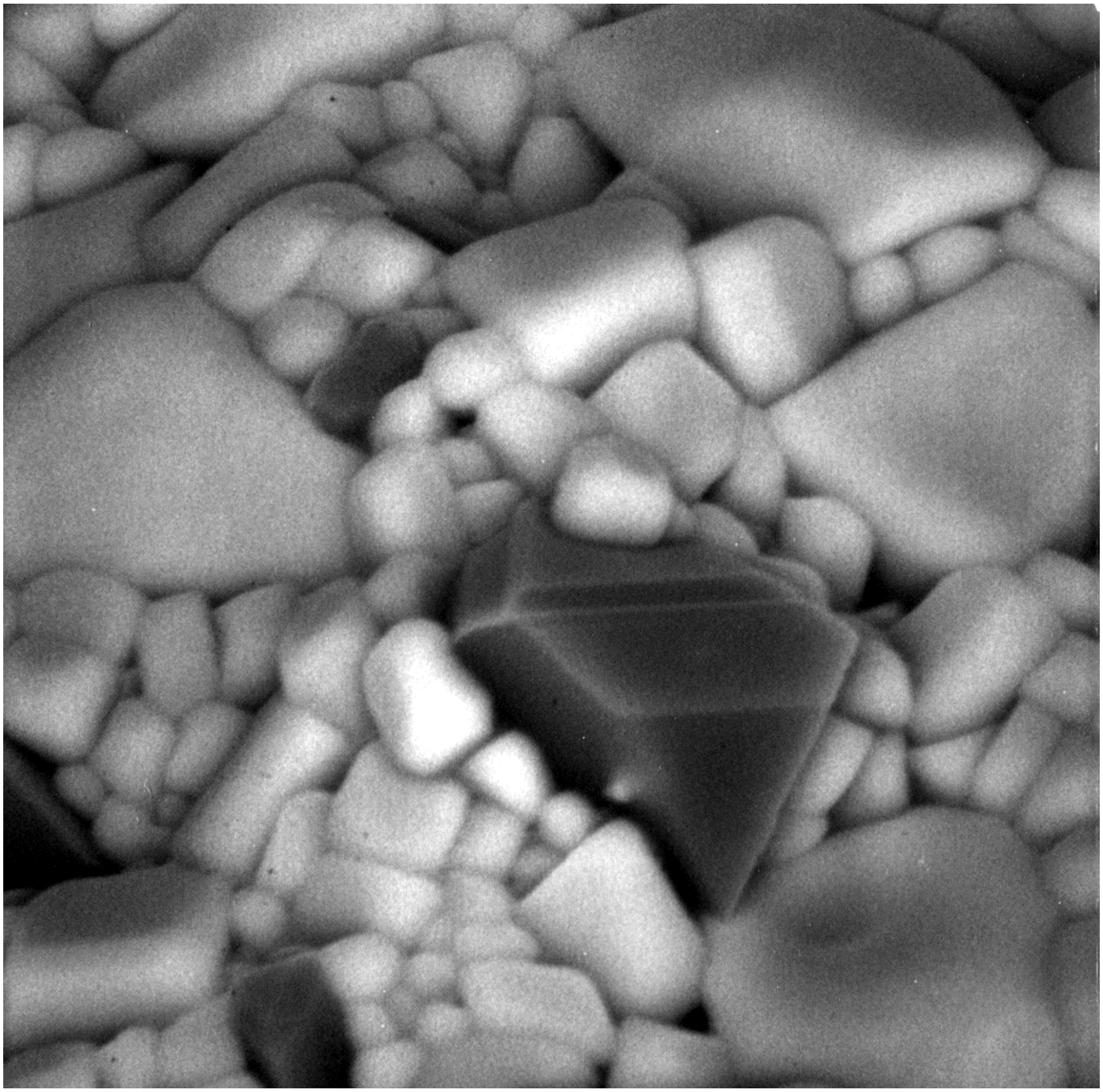
Here the excess P has been sequestered as second-phase, unfaceted $AlPO_4$ with some excess faceted Al_2O_3 remaining; the excess P cannot now form a liquid – see ternary phase diagram later.

Monazite is phase compatible with literally hundreds of minerals (excepting only very basic minerals such as those with high alkali content). Here are some synthetic cases where monazite is compatible with mineral types that are also important ceramics (back-scatter-electron mode so monazite is always the lighter one).

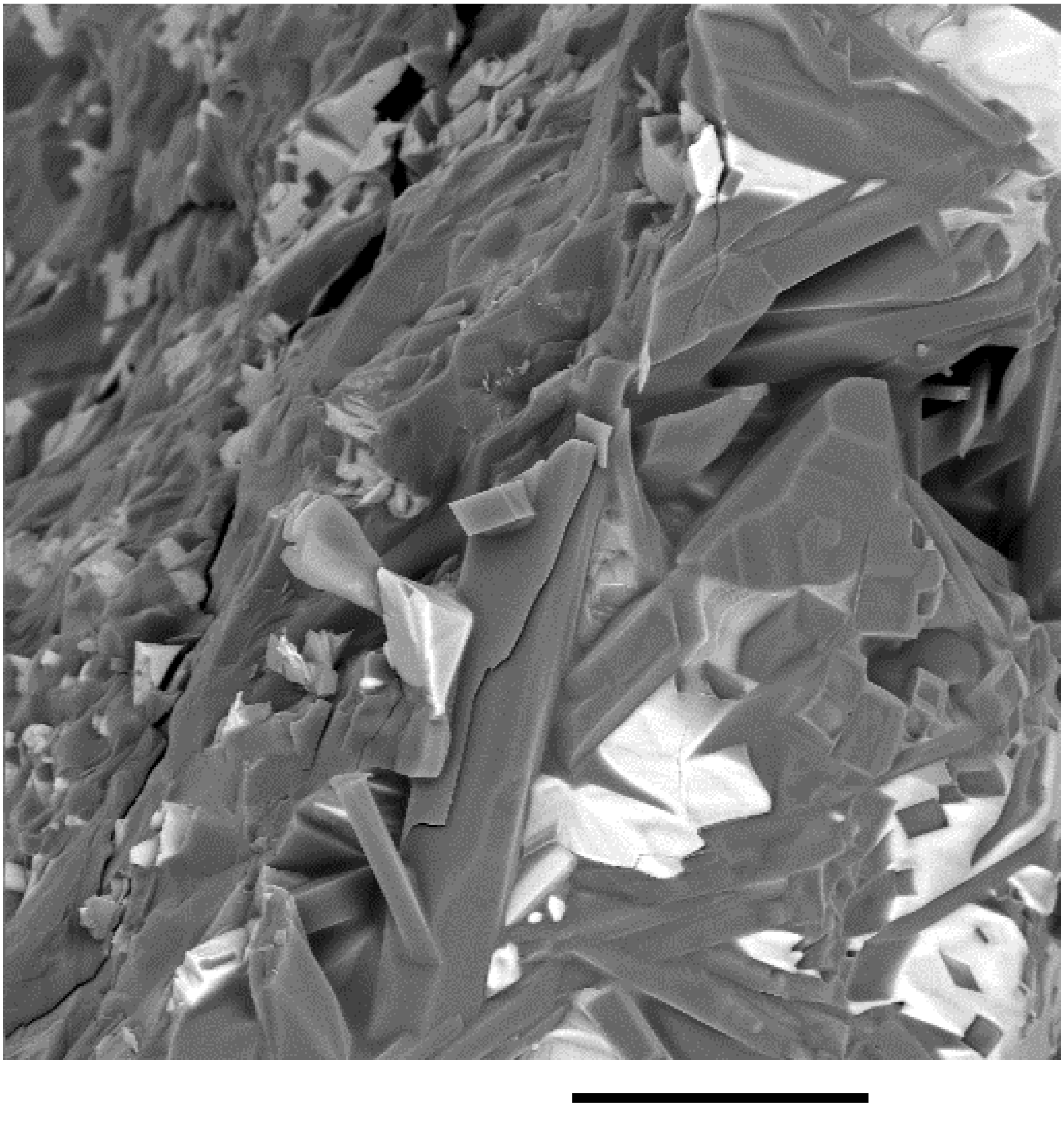
Monazite/Alumina at 1600^{o}C.



Monazite/Spinel at 1400^{o}C.



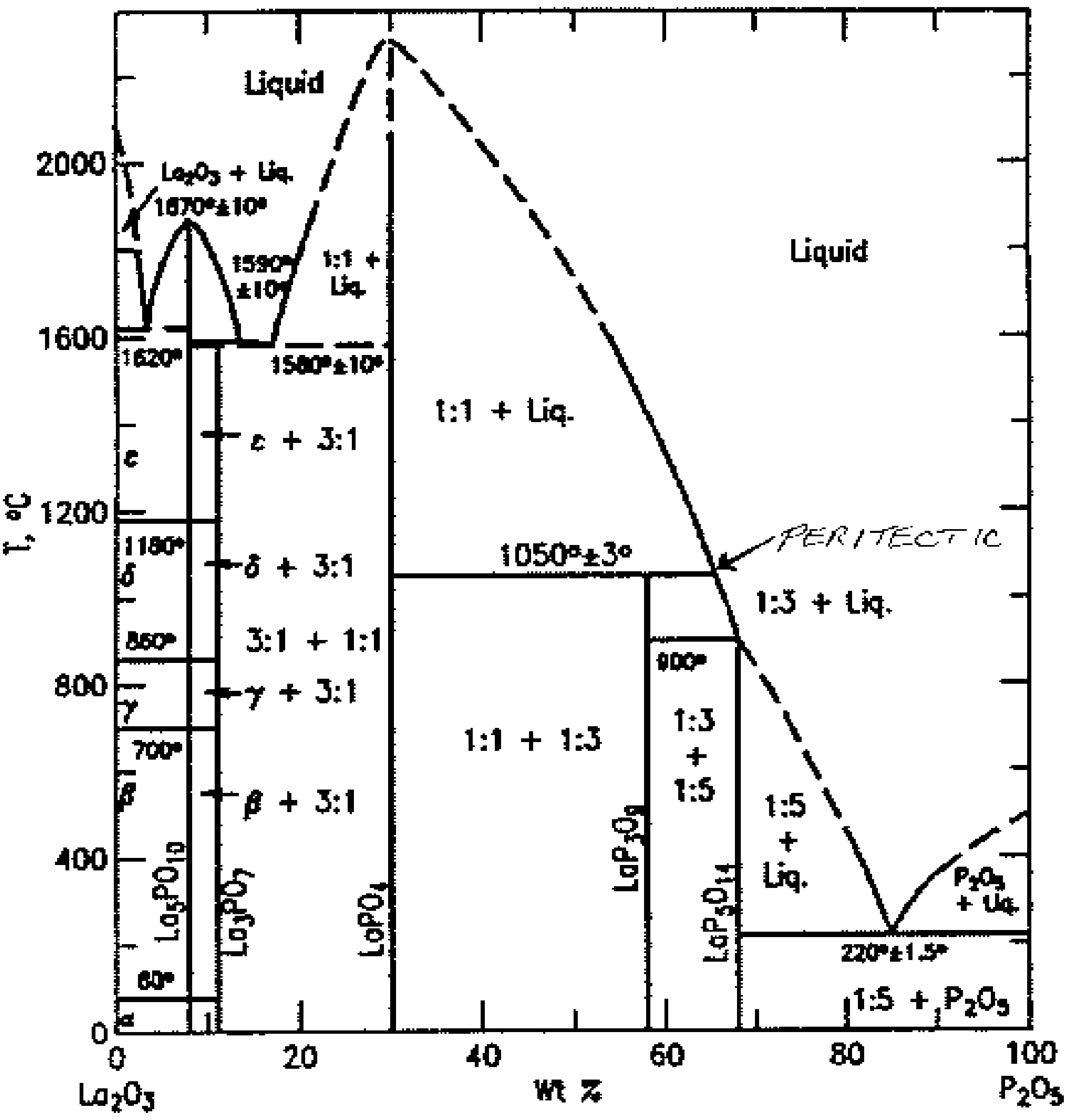
Monazite/Mullite at 1600°C.



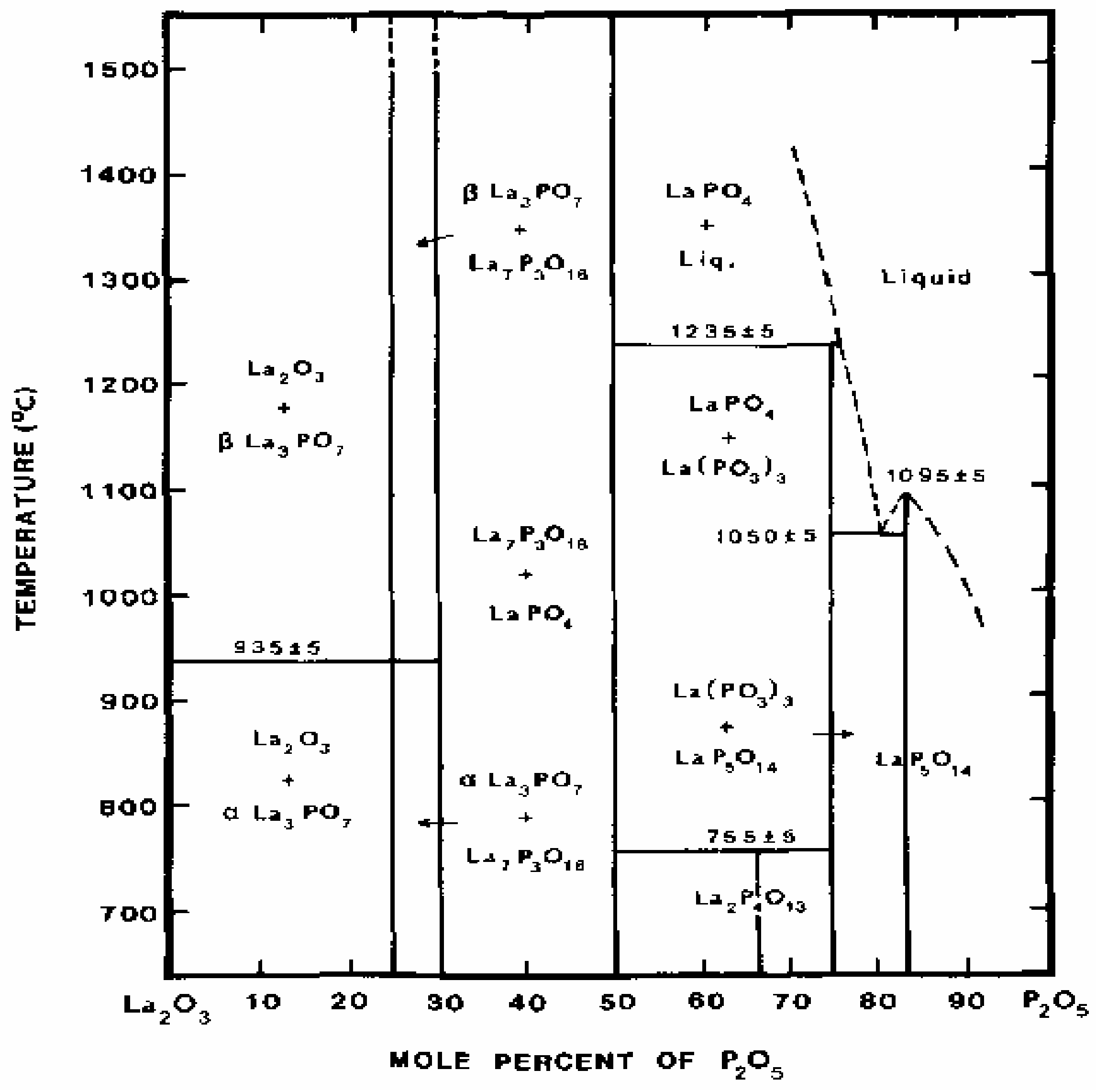
Not shown are compatibilities we have seen with zirconia, YAG, "$LaAl_{11}O_{18}$", $AlPO_4$ and many others.

As mentioned, when powders contain small amounts of excess P, a peritectic liquid is claimed to form above 1050°C, as indicated in this phase diagram (Kropiwnicka, 1988):

La_2O_3-P_2O_5



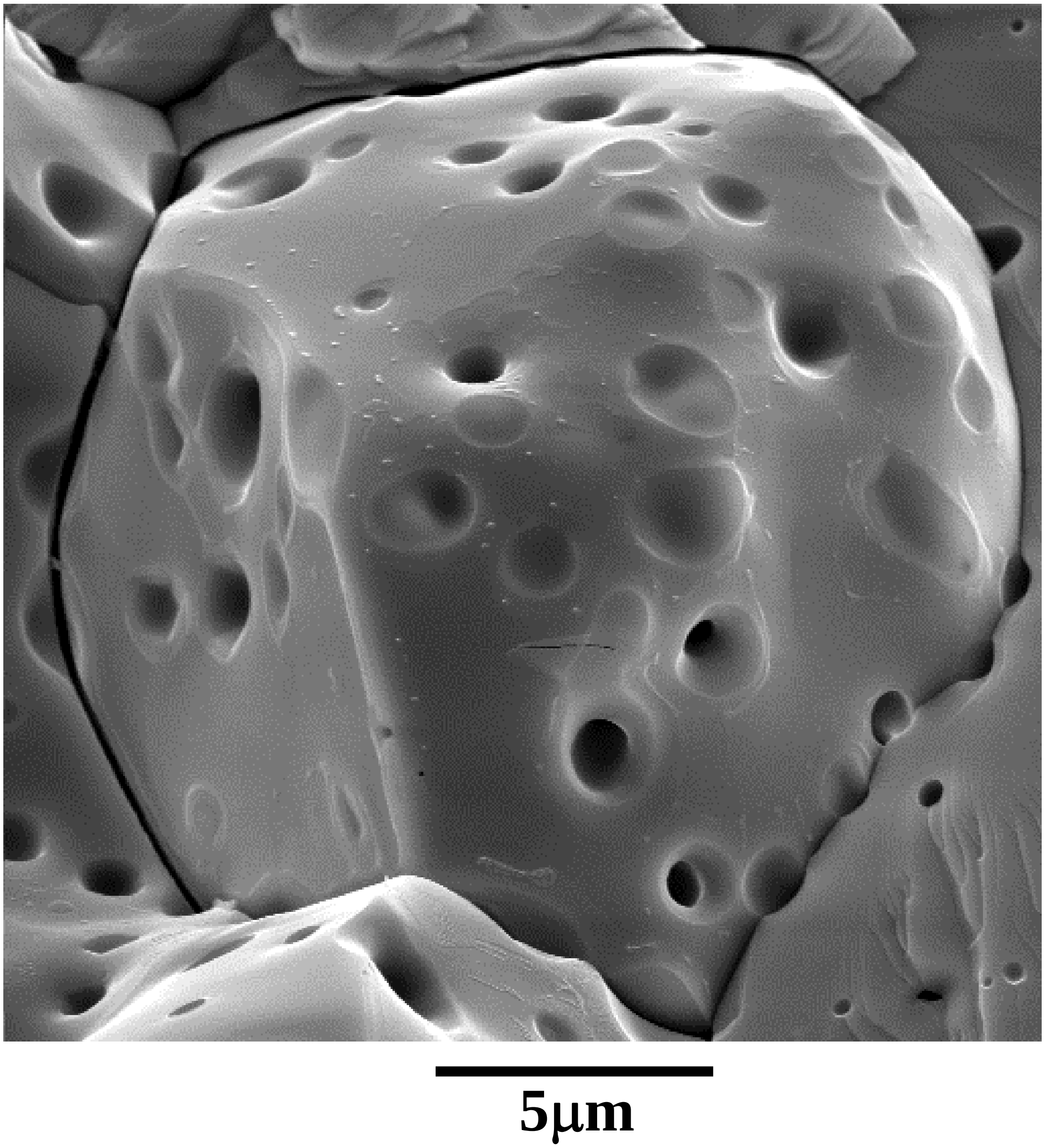
However, since this was originally written we have found an earlier phase diagram (Park, 1984); here the liquid will appear at a higher peritectic at 1235°C although there is a lower eutectic, nearly corresponding to the peritectic in the previous case:



We do generally find the giant grain-growth only occurs above ~1235°C agreeing more with the temperature shown here, above which liquid forms near to $LaPO_4$.

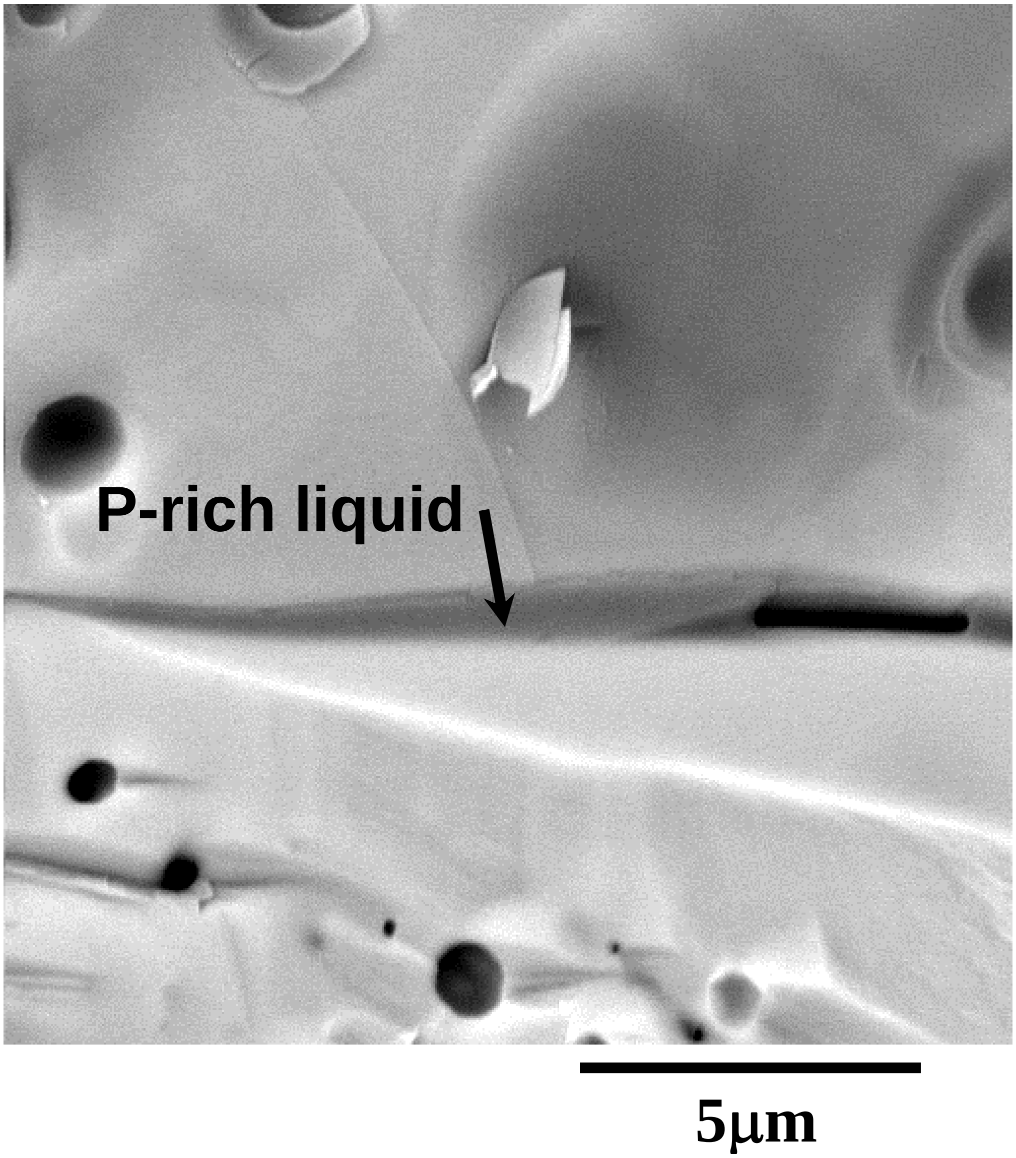
When the giant grains are surrounded by liquid, presumably because of the anisotropic crystal structure, differential shrinkage on cooling leads to separation of the boundaries to produce isolated grains.

Separated $LaPO_4$ grains

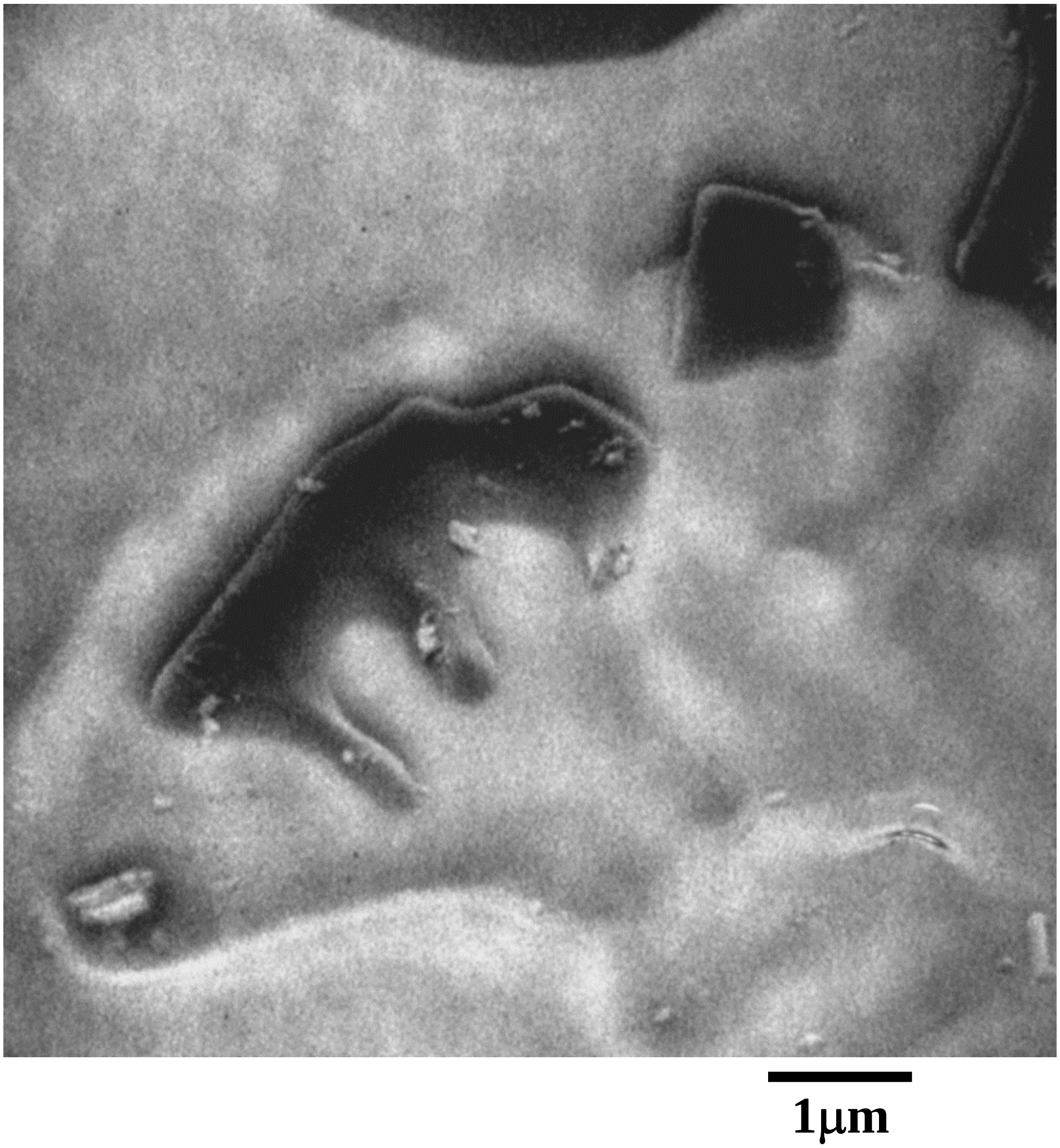


The partially wetting liquid, with a thickness of ~1000Å, is easily seen along the separated boundaries as well as the imprint of liquid, that has detached to the adjacent neighboring grain; this represents <0.5% by volume of the sample.

Liquid between Grains after stimulated “abnormal” grain-growth



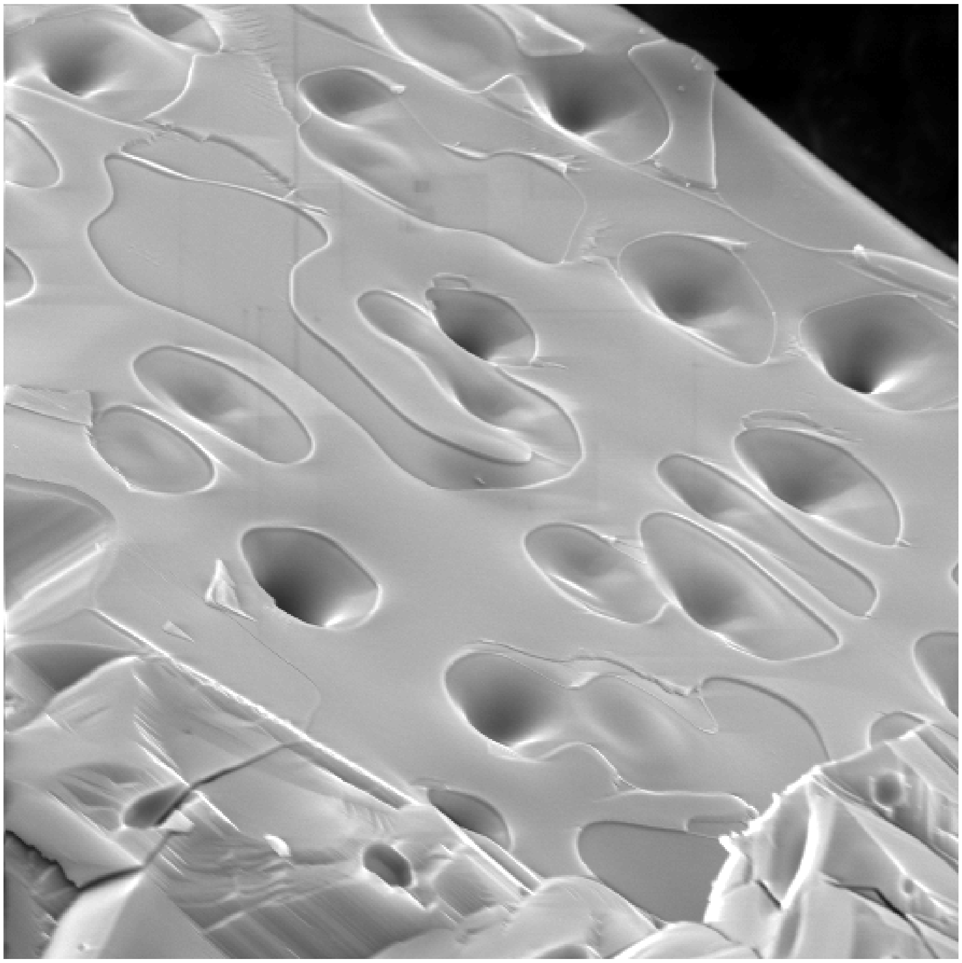
P-rich liquid only partially wets monazite resulting in some grain boundary porosity.



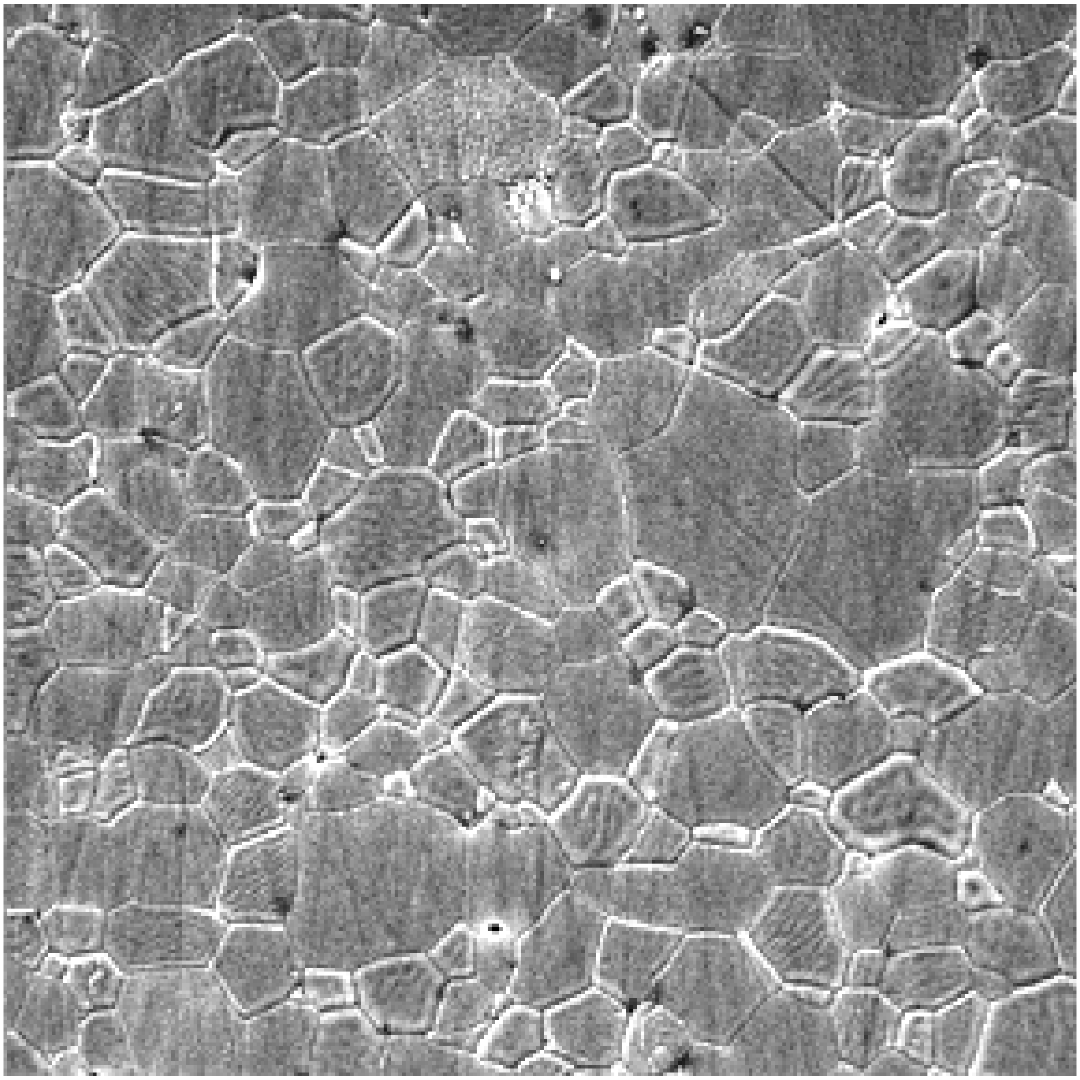
This liquid remnant has scavenged impurities within it to levels that can be readily seen by EDS/EDAX in a carbon coated specimen; we find low levels of Fe, Na, Al, Si, in that order, adding up to <10% in the liquid and so only ~<0.05% in the ceramic; these are elements not expected to much enter the crystal lattice. 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 have tracked this down and extracted the useful information about impurities that the liquid will contain.

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

Another view of the remaining liquid on a separated grain after giant grain-growth.

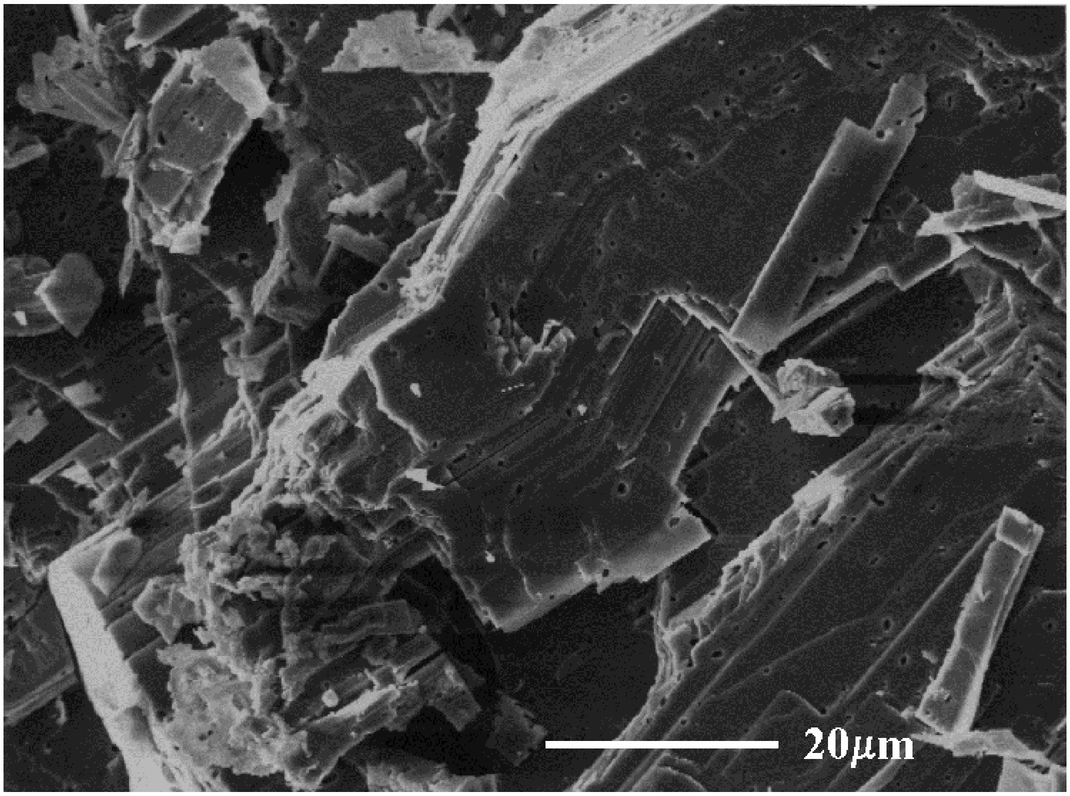


When powders are stoichiometric, so that no peritectic liquid sintering occurs, then fine grained dense ceramic is produced by sintering to 1200°C. Upon further heating to 1400°C, in this case, little extra grain growth occurs.



Monazite, unusually for a ceramic, shows considerable evidence of plasticity upon fracture:

Monazite Fracture Surface

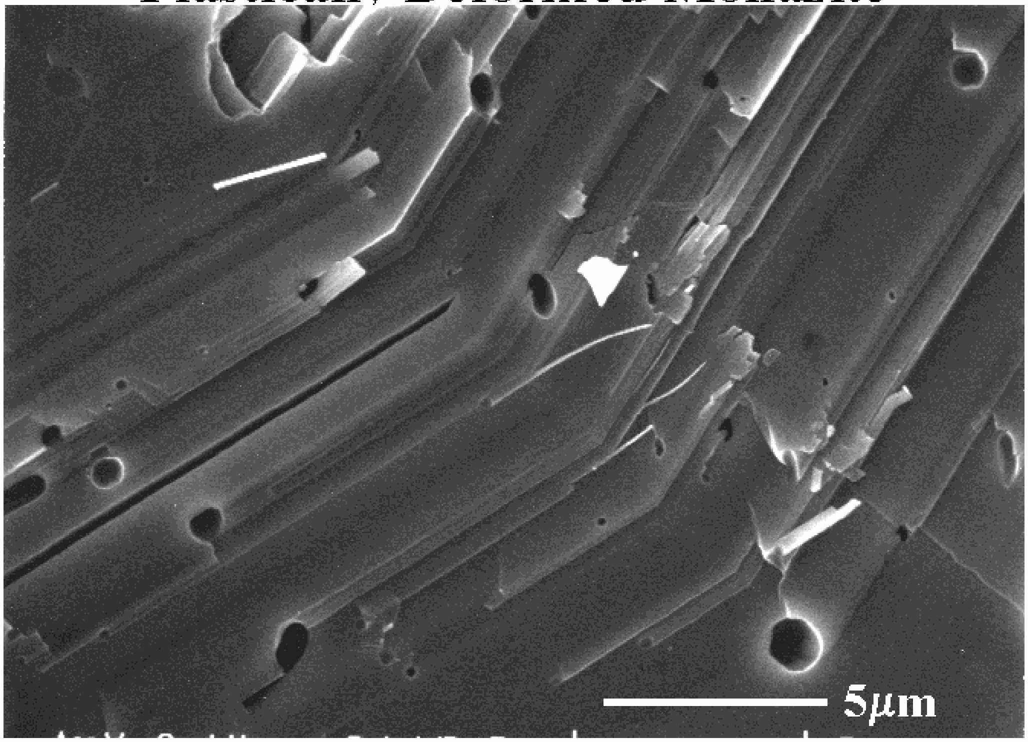


Room temperature fracture shows both plastic and brittle regions.

Most ceramics with high melting points (and, therefore, strong bonding) tend to being brittle.

Region at larger magnification with deformation twins:

Plastically Deformed Monazite



Kink bands produced by room temperature deformation

Subsequent to this work, in our related composites programs, a recent publication has appeared detailing further work on plastic phenomena in monazite, (Davis, 2003) and for creep, (Berbon, 2007).

New 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 compact of the starting powder and heated overnight to 1200ºC or 1400ºC. When there is excess P (as in this case where a purchased 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. Heating to only 1200ºC, produces little effect confirming that it is the liquid that readily reacts.

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

This test (which is basically a ceramic solid/liquid state spot-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. Very low levels only of a reactive "scavenger" can sequester and neutralise the bad effects of particular liquid-forming impurities*; as small additions of Al (as nitrate, hydroxide, oxide etc.) are seen to do wth excess P in this case.

Although this research had a very applied goal in mind, several, generically useful, new basic ceramic techniques have been discovered.

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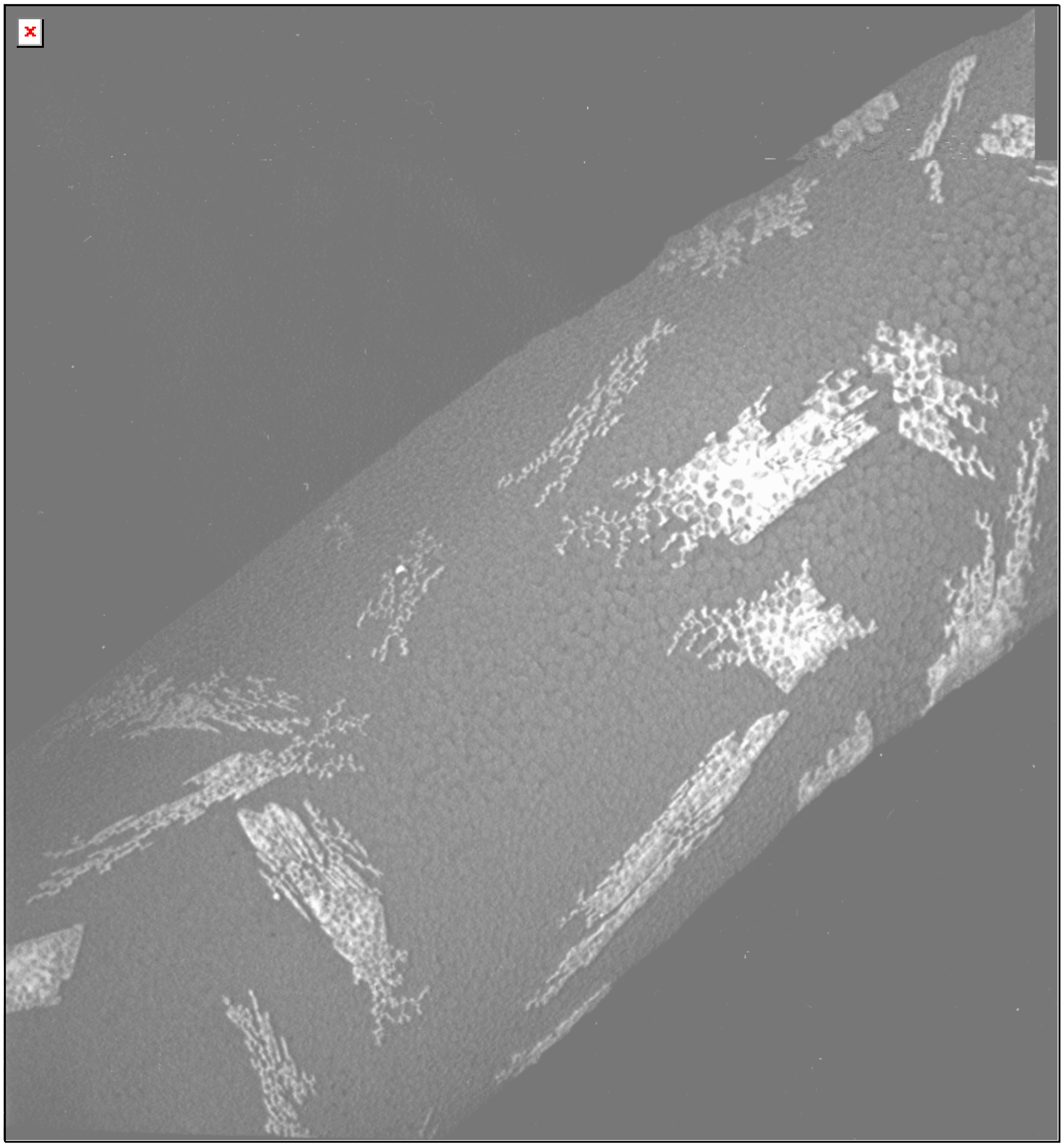
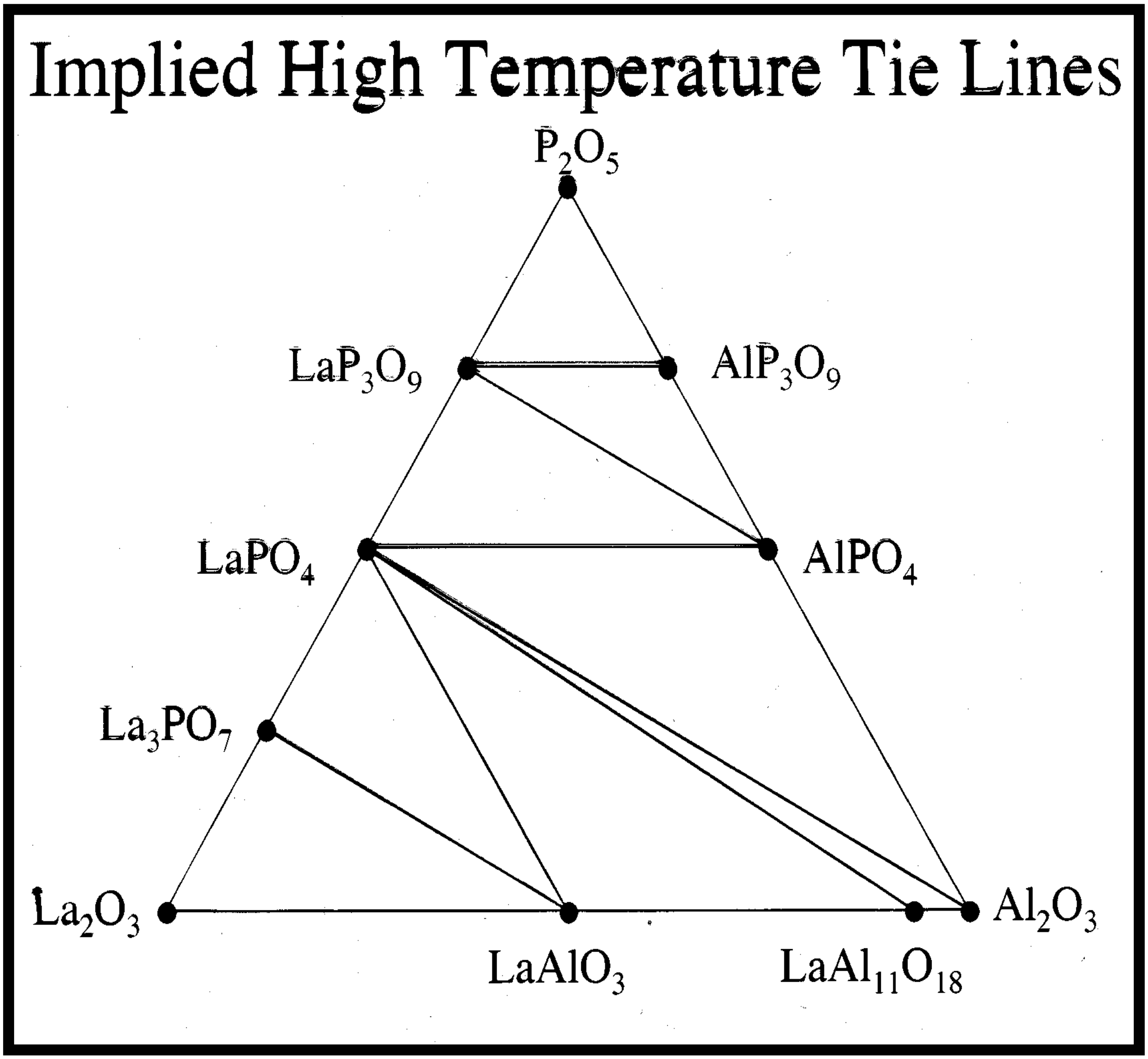
* redolent of arguments about whether Mg additions to alumina control grain-growth by scavenging possible liquid-forming impurities.

This next SEM micrograph shows traces of $AlPO_4$ deposited upon a sapphire fiber embedded in monazite, fired to 1400°C, and then the weakly bonded monazite removed. Back scatter electon image shows the light monazite remaining more strongly bonded to the $AlPO_4$ regions.



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



Notice here that monazite is phase compatible with fully 6 neighbors, even the more distant ones.

Other developing uses – helpful towards economy-of-scale in powder production

It has been shown in other work (see RSC refs.) that the interfaces between monazites (more specifically $LaPO_4$), 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 normally 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, including for engine vortex combustors etc., 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 and now independently confirmed. 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)]. A government initiative at several key-state laboratories in the PRC has evinced the considerable interest there and produced a suite of publications (sometimes only in Chinese so not available through “Web of Science” e.g.).

Monazite is also being tested as a “high-temperature-starch” on space-shuttle blankets (replacing some ceramic tiles) where the weak interfaces allow stiffening without embrittlement and better atmospheric re-entry performance without “flutter”.

Conjectures as to the reason why these interfaces are weak have been tentatively advanced based upon some classical ideas (Morgan 1995), but the details are crying out to be studied.

Contamination from $MoSi_2$ heating elements in furnaces

Because we work 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 puzzling irreproducibilities in results. Because of previous experiences, this soon became conjectured to be due to contamination from the common furnace element, $MoSi_2$.

To check this out, alumina trays containing La_2O_3 powder, which can absorb both of the Mo and Si suspects, were inserted into the furnace, sitting atop the monazite containing crucibles. After 10 overnight runs at 1200ºC, the La_2O_3 powder was yellowed. 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/EDAX. In wide area scans of gold-coated samples, the dilute Mo could easily be missed due to the overlap of its strongest X-ray fluorescent line with Au. The ceramics community has, cavalierly, often ignored contamination from this source.

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 buffer "powder-beds" of the same powder*. We seriously wonder how many reported, curious, ceramic results have been influenced by this, often undetected, and/or ignored, effect (e.g. almost all ceramic creep experiments have been carried out in open furnaces!).

This too serves as another contribution to generic ceramic procedure and phenomenology.

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*PEDM was early to realize the importance of this and has been using scavenger/buffer/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., G. C. Kuczynski

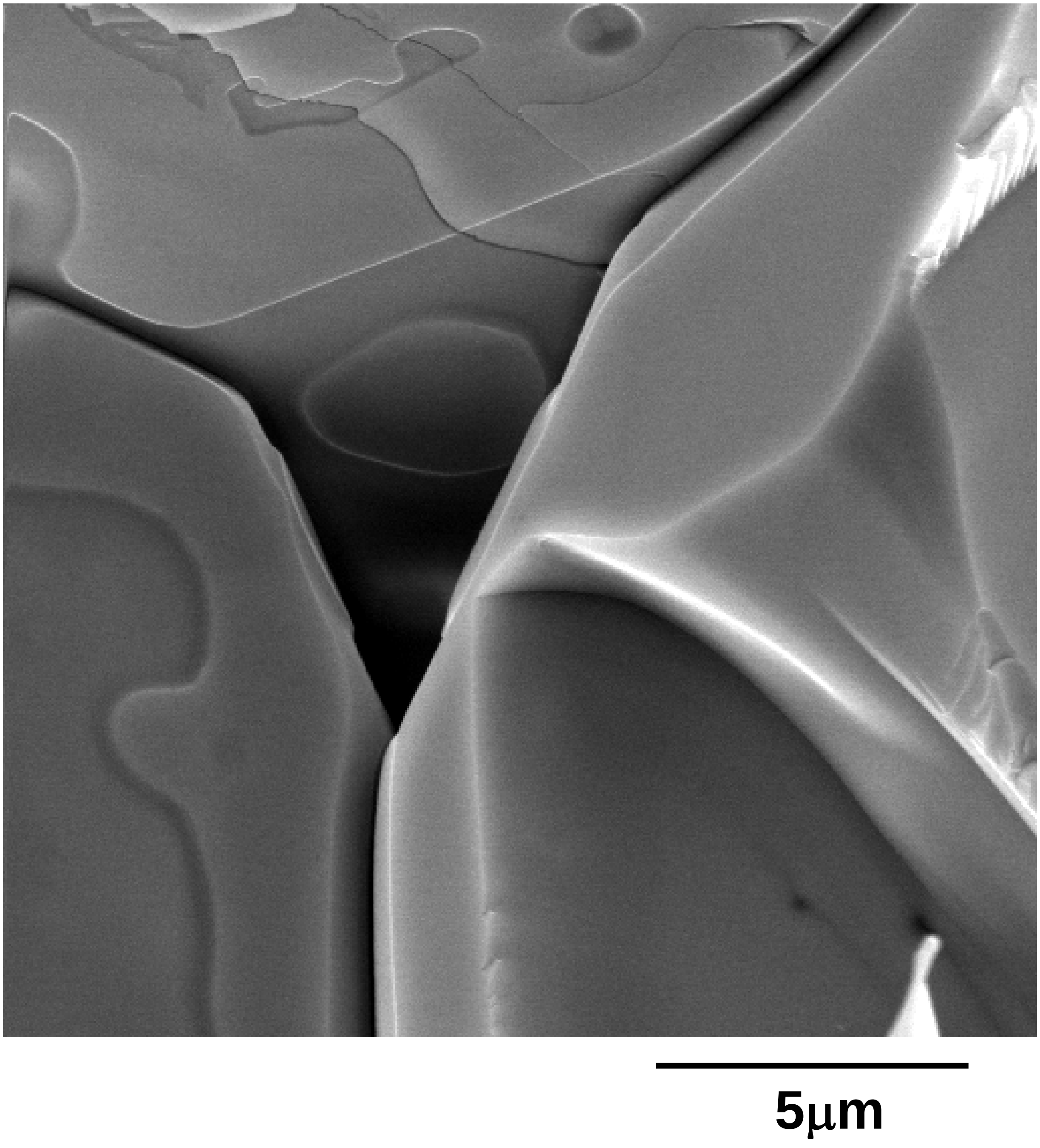
An alternative monazite waste form (a grain/sand) to that of the dense ceramic

We have found that the remains of liquid between the large grains in a monzite ceramic can be leached out with aqueous bases. The next figure shows the result of leaching; afterwards no sign of liquid is left only the voids where it previously was, nor is any excess of phosphorus found. This means we can make a grain (analogous to the natural beach sands) that is pre-leached; the leachant, containing any (say) plutonium, would be recycled back to the precipitation step. Such a grain form may, perhaps, evince an even lower subsequent leachability in a repository than a bulk ceramic would; it has essentially already been "proof-tested" by preleaching. Moreover, it is possible to take such a grain and, using pure La solutions, precipitate an overgrowth of pure $LaPO_4$ upon the grains so that the radiactive components are further isolated from leaching. Overcoating suggestions have been made previously for glass shapes and can partially occur intrinsically as in the case of a recently studied murataite, containing real plutonium, in Russia.

Maybe the beach sands are suggesting to us what to do!

The somewhat poster-like format of this report results from the fact that it was, indeed, abstracted from a series of posters presented at several ceramic oriented meeetings including EMSP ones. This format allows a somewhat, more readable chatty style, and, who knows, actually may be more editorially useful.

Fracture Surface after TMAH Wash



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 ~1235^{o}C (somewhat similar to the action of glasses in silicon nitride) which occurs with the seemingly unavoidable incorporation of ~1% excess, difficult-to-remove, P in precipitated $LaPO_4 \cdot {}^1/_2\ H_2O$ precursor powder; nevertheless, methods have been discovered to remediate this problem; vigilance is required in the processing to assure success.

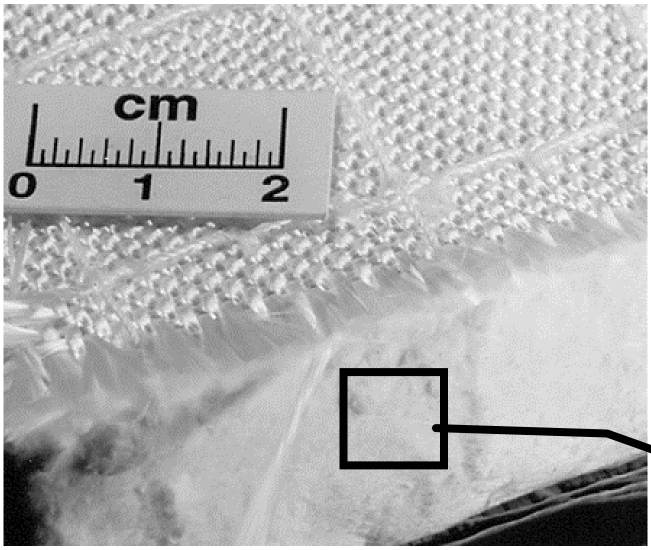
It transpires that 1:1 monazite can be easily processed into a dense, fine-grained ceramic fine-grained form by ~1200^{o}C, or, if containing excess P, into a large-grained (sugary) form by ~1400^{o}C (mimicking natural beach sands). Either of these forms seems eminently suitable for possible long-term, >100,000 years, disposal of Pu, other actinides, and some fission products.

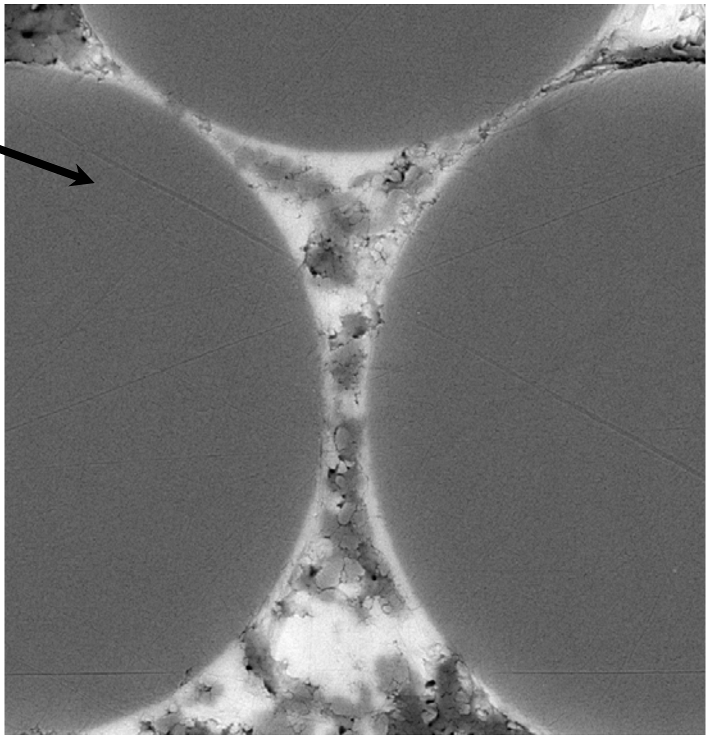
As we mentioned, monazite seems to have some unexpected and quite peculiar properties, e.g. its plasticity, (compared to traditional ceramics); in that regard this work may be compared with the early days of silicon nitride research - that material required 30 years from concept to use, as for roller bearings (in "roller blades" and windmills) and in turbopumps etc. However, hopefully we have learned from the myriad pitfalls that that earlier ceramic community encountered.

The necessarily fundamental nature of this ceramic work (one of the stated missions of EMSP) has contributed significantly also to knowledge that may (at least partly) serendipitously be applicable to other 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) and by other agencies.

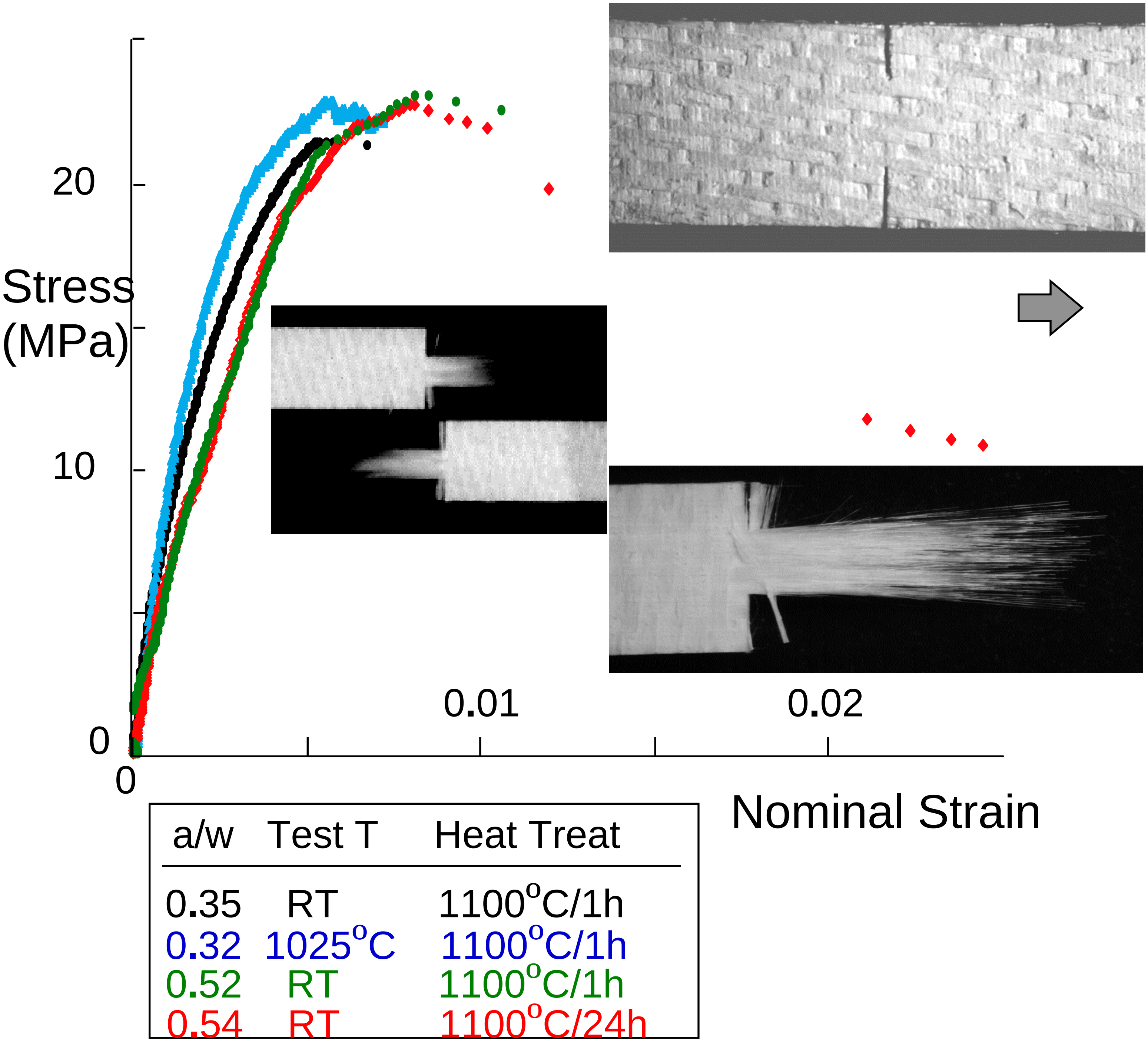
Monazite in this program has had an impact in yet other important areas, such as machinable ceramics and for space orbiter blankets; we include below two pictures (without comment) that are from one of our related efforts – e.g. see Davis (1999) and RSC references:

Oxide CMCs: Thermal protection blankets for the space shuttle





Al_2O_3 fiber/Al_2O_3-$LaPO_4$ matrix



a/w	Test T	Heat Treat
0.35	RT	1100°C/1h
0.32	1025°C	1100°C/1h
0.52	RT	1100°C/1h
0.54	RT	1100°C/24h

a=distance between notches, w-width of specimen

References to monazite for ceramics specifically done at RSC* (inc. patents)

P. E. D. Morgan and D. B. Marshall, *"Ceramic Composites of Monazite and Alumina"*, J. Am. Ceram. Soc., **78** 1553-63 (1995). [>190 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 No., 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). [>70 known citations]

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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 $\bar{1}$ ***
48.170	1.8876	161	1 3 $\bar{2}$ ***+ 3 1 1
48.435	1.8779	173	3 2 0***
49.420	1.8427	9	1 2 $\bar{3}$
49.875	1.8270	6	1 1 3
50.325	1.8117	43	0 2 3
51.455	1.7745	119	3 2 $\bar{2}$ ***+ 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 $\bar{3}$ + 3 0 $\bar{3}$ ***
53.610	1.7082	119	1 4 0***
54.770	1.6747	7	1 4 $\bar{1}$
55.175	1.6633	50	4 0 0
56.210	1.6351	46	4 0 $\bar{2}$ ***
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 $\bar{3}$ + 4 1 $\bar{2}$
58.250	1.5826	14	0 0 4
59.135	1.5611	26	2 4 0
59.685	1.5480	30	3 3 $\bar{2}$
60.070	1.5390	21	2 1 $\bar{4}$
62.110	1.4932	5	3 2 2
62.515	1.4845	11	4 2 $\bar{2}$
62.760	1.4793	29	2 4 1
63.025	1.4737	13	2 2 3
63.470	1.4645	12	2 4 $\bar{2}$
64.420	1.4452	4	0 2 4
65.375	1.4263	8	3 1 $\bar{4}$
66.730	1.4006	28	4 2 1 + 3 3 $\bar{3}$
67.685	1.3832	66	4 3 $\bar{1}$ ***+ 3 4 0 + 1 5 0
68.640	1.3662	22	1 4 $\bar{3}$ + 4 2 $\bar{3}$ + 1 5 $\bar{1}$
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 $\bar{1}$
70.220	1.3393	50	1 3 $\bar{4}$ ***+ 2 3 3
70.995	1.3266	24	4 1 2 + 2 4 $\bar{3}$
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 $\bar{2}$ + 1 4 3 + 0 5 2 ***
73.660	1.2850	22	4 1 $\bar{4}$ ***
74.040	1.2794	8	1 1 $\bar{5}$
74.990	1.2655	7	2 1 $\bar{5}$
75.730	1.2550	28	5 2 $\bar{2}$ + 4 3 $\bar{3}$
76.330	1.2466	46	5 2 0 + 5 0 1*** + 1 5 2 + 0 1 5
76.840	1.2396	22	3 3 $\bar{4}$ ***
77.215	1.2345	7	2 2 4
77.685	1.2282	5	3 0 $\bar{5}$
78.915	1.2121	9	4 4 0
79.875	1.1999	22	3 5 $\bar{1}$
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 $\bar{3}$ + 4 4 1
84.065	1.1505	6	1 6 $\bar{1}$
84.360	1.1472	5	3 5 1
84.680	1.1437	5	4 3 $\bar{4}$ + 5 1 $\bar{4}$
85.290	1.1371	6	4 4 $\bar{3}$
85.815	1.1314	20	6 0 $\bar{2}$ ***
86.005	1.1294	16	2 3 $\bar{5}$ + 1 4 4
86.550	1.1237	7	5 1 2 + 6 1 $\bar{1}$
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 $\bar{5}$
90.635	1.0834	12	5 2 2

91.175	1.0784	23	6 2 $\bar{2}$ + 6 1 $\bar{3}$ + 4 5 0
91.545	1.0750	12	2 6 $\bar{2}$
92.120	1.0698	17	5 4 $\bar{2}$ *** + 1 1 $\bar{6}$
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 $\bar{5}$
95.540	1.0403	12	2 4 $\bar{5}$
96.185	1.0350	19	1 2 $\bar{6}$ + 4 0 4***
96.960	1.0288	5	5 4 $\bar{3}$
97.410	1.0253	21	6 3 $\bar{1}$ + 2 6 2 + 5 3 2 + 5 0 3
98.165	1.0194	5	5 4 1
98.725	1.0151	11	3 5 $\bar{4}$ + 6 1 $\bar{4}$
99.535	1.0090	16	3 4 $\bar{5}$ + 6 2 1
100.590	1.0012	8	1 6 3 + 4 0 $\bar{6}$ **
100.850	0.9994	8	2 3 5
101.705	0.9933	6	1 7 $\bar{1}$ + 4 2 4
102.410	0.9883	4	3 5 3
103.090	0.9837	11	5 5 $\bar{1}$ + 1 3 $\bar{6}$
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 $\bar{2}$ (733)
106.620	0.9606	10	4 5 $\bar{4}$ *** (1042)
107.205	0.9570	16	4 6 $\bar{2}$ (992)
107.875	0.9529	5	7 0 $\bar{3}$ (503)
108.970	0.9464	8	0 6 4 + 2 0 6 (878) + 378)
109.340	0.9442	15	7 1 $\bar{3}$ + 0 5 5 + 1 7 2 + 6 2 2 (565)+(293) + (706) +

			(490)
109.550	0.9430	12	2 7 $\bar{2}$ + 7 1 0 (524) + (584)
110.095	0.9398	13	7 2 $\bar{2}$ (943)
112.385	0.9271	5	1 3 6 (797)
113.080	0.9233	8	4 6 $\bar{3}$ + 3 7 $\bar{1}$ + 1 4 $\bar{6}$ (210) + (492) + (749)
113.645	0.9203	5	3 7 0 (532)
114.135	0.9178	3	1 1 $\bar{7}$ (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 $\bar{6}$ (270) + (860)
116.780	0.9045	8	6 3 2 (?) (110)
117.550	0.9008	3	7 3 $\bar{2}$ (255)
118.425	0.8967	4	5 5 $\bar{4}$ + 3 6 3 (273) + (558)
119.095	0.8936	5	4 4 4 (592)
119.640	0.8911	6	5 2 4 (753)

CuK$_\alpha$ radiation: diffractometer, fixed slit, Li-drifted Si cryogenic detector, α_2 stripped,

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** 21-6 (1995) and a = 6.8366 ± 0.0007Å, b = 7.0769 ± 0.0007Å, c = 6.5095 ± 0.0006Å, β = 103.23° for PDF 32-493

It is a common structure type, isotypic with phosphates of the larger rare earths (La-Tb), bismuth and plutonium, i.e. (La-Tb,Bi,Pu)PO_4, and with (La-Nd,Bi,Pu)AsO_4, $LaPuO_4$, $LaVO_4$, $LaCrO_4$, $SrCrO_4$, $PbCrO_4$, $SrSeO_4$, $PbSeO_4$, $(Ca_{0.5}U_{0.5})PO_4$, $(Sr_{0.5}U_{0.5})PO_4$, $Th(SiO)_4$ and others.

Synthesized from rhabdophane $LaPO_4.{}^1/_2H_2O$, precipitated with excess concentrated phosphoric acid from strong lanthanum nitrate solution, filtered, washed and fired to 1200°C in air for 17 hours.

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** 231-236 (1984).

Also: Y. Ni, J. M. Hughes and A. M. Mariano, *"Crystal Chemistry of the Monazite and Xenotime Structures"*, Am. Min., **80** 21-26 (1995).