IMPROVED POWDERS FOR ADVANCED ELECROCERAMICS

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Introduction: *The need for improved actuator materials*

The case for improvements to ceramic actuator materials (piezoelectric and electrostrictive) is becoming increasingly strong. Mainstream applications are broadening from the traditional sonar and ultrasound markets into almost every technological area. From applications as diverse as micro-positioning, optical switching and acoustic generation to high power transducers for valve switching or adaptive structural control there is a common requirement for improved ceramic microstructures and more predictable performance. The most common material in use today is lead zirconate titanate or PZT ($PbZr_xTi_{1-x}O_3$) and it's doped derivatives. Electrostrictive materials such as the relaxor ferroelectric lead magnesium niobate titanate (PMNT) are also showing increasing practical applicability but are difficult to process in dense single phase form by conventional processes.

A cost effective reduction of defect (porosity) levels and control of composition and grain-size, invariably provide the materials engineering solution whether the key requirement is ultra high reliability, high operating stress levels (electrical and/or mechanical) or ultra small size for micro-fabrication. Whilst many of the finished ceramic properties are dependent on the compaction and sintering procedures used, all rely on the quality and suitability of the milled calcined starting powders. Moreover, we have demonstrated that powders can easily be designed for a particular process route by control of the milling and drying regimes used.

The wide range of electroceramic applications and devices is reflected in the diversity of powders and the routes available with which to process them. By far the most prevalent commercial route, however, is a relatively standard mixed oxide ball milling process. This process, whilst suffering several limitations, is difficult to improve upon within a practical commercial context due to its low cost and simplicity. Highly niche, low volume applications may well justify the use of more exotic processes but increasingly users are demanding *niche-performance* in large volumes at low prices.

Ecertec Ultra-Active powders and defect free ceramics.

The processing of actuator ceramics is often complicated by the fact that the majority are compositions based on lead (Pb). As such, evaporation of Pb leading to compositional alterations is a common problem. Powders with very high surface areas can suffer greatly from Pb loss during calcination and sintering and invariably a compromise must be struck between the competing requirements of press-ability, sintering temperature and finished device density and grain size.

Electroceramic Powder Requirements

Requirements for a good electro-ceramic powder are critically dependent on the application. Usually cost implications overshadow the technical requirements and ultimately the material and the process selected is a compromise. The requirements for an ideal powder are listed below:

- **Commercially viable for volume production processes**
  - The powder must demonstrate appreciable improvements to finished device performance and comparable or reduced costs of production.

- **Fine reactive particles**:
  - Sinter to form almost fully dense ceramic with very low defect levels.
  - Low sintering temperature – reductions in sintering temperature can reduce processing costs generally. In addition, if the sintering temperature can be reduced below approximately 1000 °C then inexpensive base metal electrodes can be used rather than precious metals.

- **Controlled particle size distribution**
  - Highly compactable – to produce high green density parts with minimal binder addition. By carefully controlling the powder particle size distribution and degree of agglomeration, the green compaction characteristics can be optimised.
  - Highly compactable powders require less (porosity forming) organic binders to be added prior to pressing.
  - For tape casting and other wet processing techniques, the particle size distribution affects the flow characteristics, colloidal stability and, as above, the amount of organic binder required.
- **Low contamination**
  - Properties are critically dependent on level of doping (usually a few mol% at most) – Fe, Al, Mg are common milling contaminants that seriously affect dielectric properties and ultimately device performance.

Existing Processes

By far the majority of piezoelectric actuator powders are produced using a standard oxide milling process followed by high temperature solid-state reaction (calcination). There are several available attrition techniques such as jet-milling, vibro-milling and ball milling, the latter being the most common for volume production. The main problems associated with powders produced in this way are the lack of microscopic compositional uniformity and the inability to produce reactive sub-micron powders within reasonable commercial time-scales and costs.

More recently the emergence of practical 'wet chemical methods' have offered the availability of sub-micron ('nano-size') powders. Such materials are however much more expensive and are less suited to large volume production (100's of tonnes) of PZT. Alkoxide hydrolysis (sol-gel) has, however, found practical application in the production of barium titanate ($BaTiO_3$). In this process metal alkoxides $M(OR)_n$ [M:metal, R:alkyl] are mixed in alcohol. Water is added and an hydrolytic reaction produces alcohol and the metal oxide (or hydrate). The powders produced are of exceptionally high purity, stoichiometry and a very fine particle size. In the case of PZT, Pb-alkoxide is difficult to obtain and so a two-stage process is necessary, making it impractical and costly.

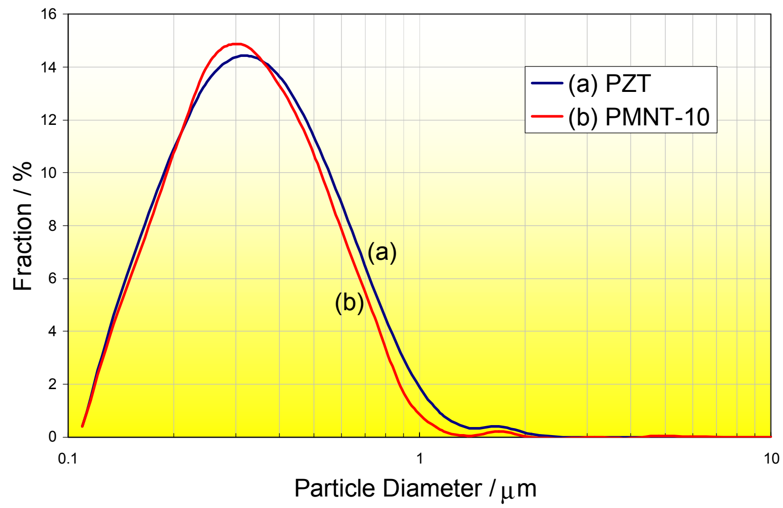

Figure 1. Particle size distributions for Ecertec Ultra-Active HEBM powders: (a) piezoelectric PZT and (b) electrostrictive PMNT (PMN-10mol% Ti)

Co-precipitation is another route used to produce ultra fine electroceramic powders with good chemical homogeneity. A precipitant is added to a solution containing the appropriate metal salts. The resultant precipitate is then usually subjected to thermal dissolution to obtain the required metal oxide powder. Again, the exception to this is barium titanate, which can be produced directly by precipitation. Co-precipitation, like sol-gel synthesis, is expensive, sensitive to processing variables and difficult to scale to large volume production.

There is clearly a requirement for improved piezoelectric (and electrostrictive) powders with production costs comparable to those of large-scale ball milling but with characteristics and physical properties more akin to chemically prepared material. High energy bead milling (HEBM), sometimes known as attritor milling, provides a practical solution to most of these requirements and is indeed starting to feed into commercial processes.

High Energy Bead Milling (HEBM)

High energy bead (or attrition) milling is more efficient than ball milling and is capable of operating in the sub-micron range. A high energy bead mill comprises of a chamber (usually with a volume of a few litres) that is approximately 50%, by volume, full of small (<1 mm) toughened zirconia beads. Powders are suspended in a slurry (either aqueous or solvent based) and are re-circulated through the chamber in which a rotating paddle agitates the media.

The mill may either be run as a single pass continuous process or as a re-circulating batch process. Alternatively, several mills may be arranged in series to provide a multistage single pass continuous process.

The high energy and high efficiency of the milling chamber also means that the process is extremely fast. In our laboratories, we have shown that no further milling takes place after approximately 20 minutes – i.e. this is the maximum time required. For many applications we have demonstrated milling times of less than 10 minutes. These times compare extremely favourably to ball milling which even after 24 hours produces a product with a particle size 10-20 times larger than HEBM.

For ultra–high purity powders the chamber is lined with a toughened zirconia liner, which has

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operated for over 5 years with no chipping and no discernable weight loss. The media are similarly robust and are almost never subject to chipping or disintegration because of their small size and high density. With this arrangement, the purity of the product powder is dictated solely by the purity (usually via cost) of the starting oxides. This offers considerable flexibility to manufacturers on all volume scales. For producers not wishing to make ultra high purity powders other linings may be used that are less expensive such as silicon nitride or sacrificial polymer linings.

To summarise, the principle advantages of HEBM for the production of actuator materials are:

- Cost effective - capital & operational costs are very similar to those for ball milling once volumes are sufficiently large.
- Speed of process – a reduction of 24 hours to 20 minutes offers considerable cost savings and production flexibility improvements.
- Sub-micron particle size and controllable particle size distribution.
- Resultant powders are highly active and will sinter at much reduced temperatures bringing further cost benefits.
- Virtually zero contamination (with toughened ZrO_2 linings)
- Purity is controllable via purity of starting reagents.
- Product purity can be directly dictated by cost targets. (Unlike chemical methods where one obtains ultra pure product regardless of whether it is necessary for the final application).
- Single process and technology that is directly scaleable from prototyping to volume.
- Continuous or batch capable.

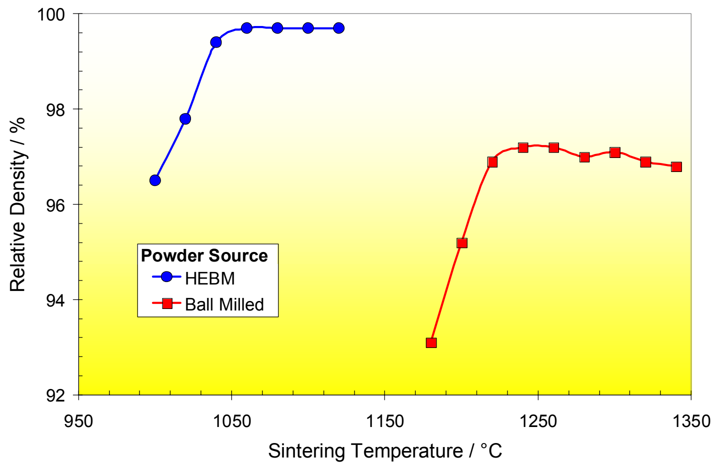

Figure 2. Relative density as a function of sintering temperature for PMNT (10mol% Ti) produced by ball milling (24 hr) and HEBM (20 mins).

HEBM Powder Properties

Ecertec Ltd. and the Electroceramics research group have refined the HEBM process with particular reference to piezoelectric and electrostrictive actuator powders. These ultra active powders themselves are sold commercially for research and prototyping work. Ecertec also produces a range of defect free electroceramics (DFE) that are produced from these powders and demonstrate the performance improvements possible. Ecertec ceramics are specialist products and are used commercially for micro-fabrication, electro-optic modulation and ultra reliable actuators. The HEBM process is, however, more widely applicable and can represent straightforward time and cost savings to many production regimes whilst improving the quality and reproducibility of the finished ceramic product.

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Figures 1 and 2 demonstrate the dramatic improvements possible to both powder and finished ceramic as a result of employing HEBM as part of the process. Figure 1 shows typical particle size distributions from piezoelectric PZT and electrostrictive PMNT-10. Both powders are highly unimodal and are typical of HEBM electroceramics with a d_{50} of 200 – 300 nm. Figure 2 shows the effect of utilising either HEBM (20 minutes) or ball-milled (24 hours) powders on sintered device density and sintering temperature - all other parts of the fabrication process were identical.

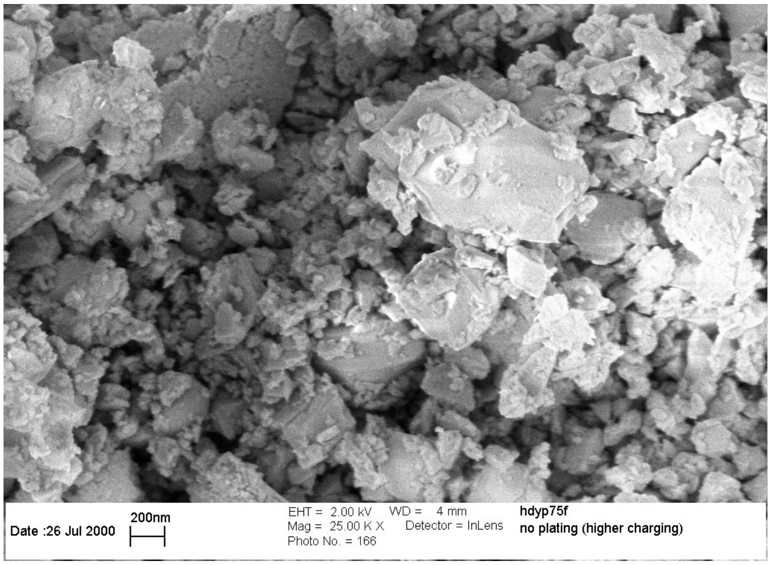

Figure 3. Scanning Electron Micrograph of an Ecertec Ultra-Active PMNT agglomerated powder - produced using the HEBM process.
Photograph courtesy of H. Daniel Young, Naval Research Laboratories, Washington DC, 20375-5345. USA.

Clearly HEBM produces powders that sinter to higher bulk densities at much reduced temperatures when compared to ball milling. Ultra-fine unimodal particles however can pose severe pressing and compaction problems. Ecertec ultra-active powders can be agglomerated to various degrees dependant on the compaction (or casting) requirements. Figure 3 shows a scanning electron micrograph of one such powder, designed with a range of sub-micron particle sizes to aid die flow and compaction.

The dense, defect free ceramics produced from HEBM powders show improvements to the generated strain and force, and also to the reliability and reproducibility. Ceramic actuators usually fail via catastrophic failure emanating from a critical microstructural defect. Failure may either be purely mechanical fracture, electrical breakdown of insulation resistance or more commonly a combination of the two. Removal of such key defects roughly doubles the electric breakdown field (as shown in Figure 4) and reduces the variability, thus allowing the actuator to be safely driven at higher electric fields. This is important for both high reliability power actuators and for multi-layer actuators (either tape cast or cut and bonded) in which the ceramic layer thickness' can be less than 50 µm.

	Sintered Ceramic Properties		
Powder Source	Relative Density / %	Mean Electrical Breakdown Strength, E_b / MV m^{-1}	Standard Deviation
Ball Milled (24hr)	96.8	1.97	0.134
HEBM (20 mins)	99.7	4.01	0.089

Data for 100 PZT discs (25 mm diameter, 1 mm thick), 50 from each powder route. Samples were sintered to maximum attainable density.

Figure 4. Improvement to electrical breakdown field strength for PZT ceramics produced by ball milling and HEBM

Ecertec Ltd. and Powder Science at Leeds

Ecertec Ltd. was formed in 2000 after 7 years of commercial work by the Electroceramics research and consulting group (LUEC) in the Department of Materials, University of Leeds. Ecertec develops materials and devices, processes and technologies for a wide variety of ceramic actuator and electro-optic applications. Our team of consultants and engineers have an unrivalled experience in design and integration of piezoelectric and electrostrictive materials and devices in application areas as diverse as aerospace systems and piezo-audio

Particle science and technology has long been an area of excellence at the University of Leeds. The formation of Ecertec Ltd., the Particle and Colloid Engineering Centre (PACE) and a major new initiative with BNFL (BNFL-University of Leeds Research Alliance in Particle Science and Technology) are leading to a significant enhancement of facilities, research capability, education and academic expertise in particle science and technology.

Further Reading

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K. Uchino, "Piezoelectric Actuators and Ultrasonic Motors", Kluwer Academic Publishers, 1997.

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