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Sandia National Laboratories

Chemical Precipitation of Nb-doped $Pb(Zr_{0.95}Ti_{0.05})O_3$ powder

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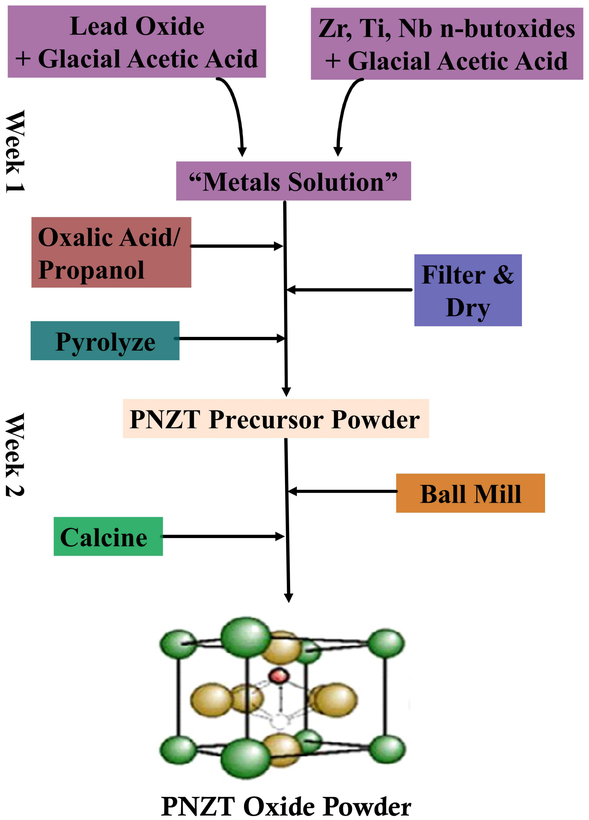
Advantages of chemical precipitation (chem-prep) process to produce PNZT powder:

- Chem-prep process requires mixing molecular precursor solutions together.
  - Cations mixed intimately, leading to a homogenous product.
  - Requires additional thermal processing steps to remove organic species prior to calcine.
  - Chem-prep can establish proper stoichiometry without subsequent adjustment.
- Alternate method requires mixing individual metal oxides together prior to solid state reaction.
  - Product powders are less homogenous.
  - Inhomogeneity is not completely addressed.
  - Inhomogeneous regions cause yield problems due to performance requirements.
  - Stoichiometry adjustments required after testing final powder. Iterative approach.

Process Flow
10kg batch size

PZT 95/5 Target Stoichiometry



1. Metals Solution Preparation

$PbO + 2\ CH_3COOH \rightarrow Pb(CH_3COO)_2 + H_2O$

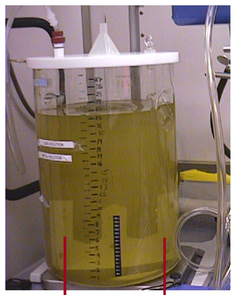
- Metals solution (29kg) is prepared by mixing together separate solutions – one solution for each cation (Pb^{2+},Nb^{5+},Zr^{4+},Ti^{4+})
- Each solution is provided through a vendor except for the Pb acetate which is prepared manually by reacting Lead oxide with glacial acetic acid (very exothermic).

Reagents

Creation of Metals Solution

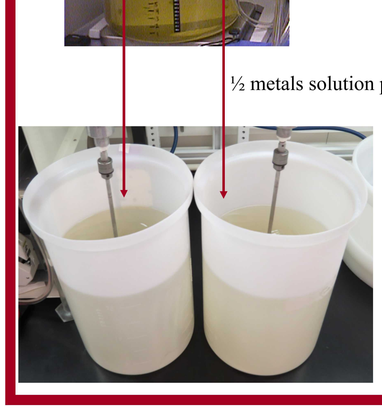
2. Chemical precipitation reaction

Metals solution + Oxalic acid solution → Metal oxalate precipitate (slurry in n-propanol)



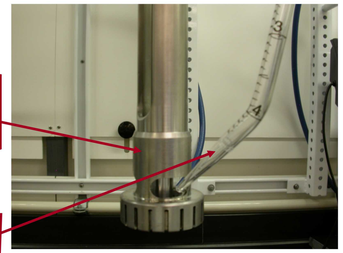
½ metals solution per oxalic acid solution

- Metals solution reacted in two aliquots (serial reactions), one aliquot per oxalic acid solution.
- Two reactions necessary due to limited volume in reaction station.



- Oxalic acid solution is prepared in two sub-lots by dissolving oxalic acid in two tanks each filled with 26L n-propanol.

- Shear mixer incorporated at reaction station provides energy and mixing to help reaction kinetics.
- Shear mixer head immersed in oxalic acid solution
- Pipette injects metals solution into shear head.



- Reaction station
- Metals solution
- Oxalic acid solution
- Oxalate precipitate (slurry)

3. Oxalate Dry

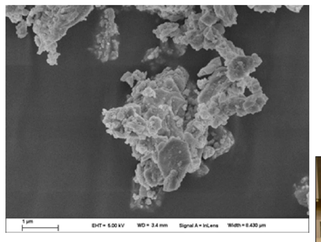
- n-propanol separated from the precursor oxalate
- The separation occurs in two steps:
  1. Slurry sits in Buchner funnels overnight under vacuum.
  2. Slurry paste loaded into glass trays and dried at 88˚C|48h.

4. Pyrolysis

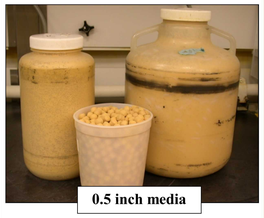
- Oxalate is decomposed in an atmosphere supplied furnace at 400˚C for 16h
- Organics are driven off as CO_2

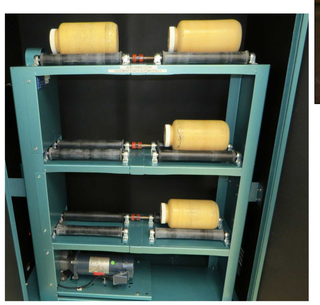
- Mixture of metals oxides remain (precursor powder to PNZT).

5. Ball mill



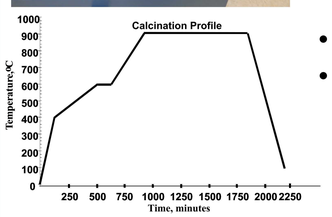
- Agglomerates form in pyrolysis furnace run.
- These agglomerates implement them selves as defects in the final ceramic body.





- Agglomerates reduced by milling 15 hours in jars loaded with ZrO_2 milling media.

6. Calcine



- The milled powder fired in alumina crucibles 600˚C|2h, 900˚C|16h.
- Oxides undergo solid state reaction to form PNZT perovskite crystal structure.
- Grain size ~5um.
- Powder yield 96%

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