NISSHIN SEIFUN

Preparation and property control of fine powder in dry processes

Dr. Satoshi Akiyama
Manager
Nisshin Seifun Group Inc.

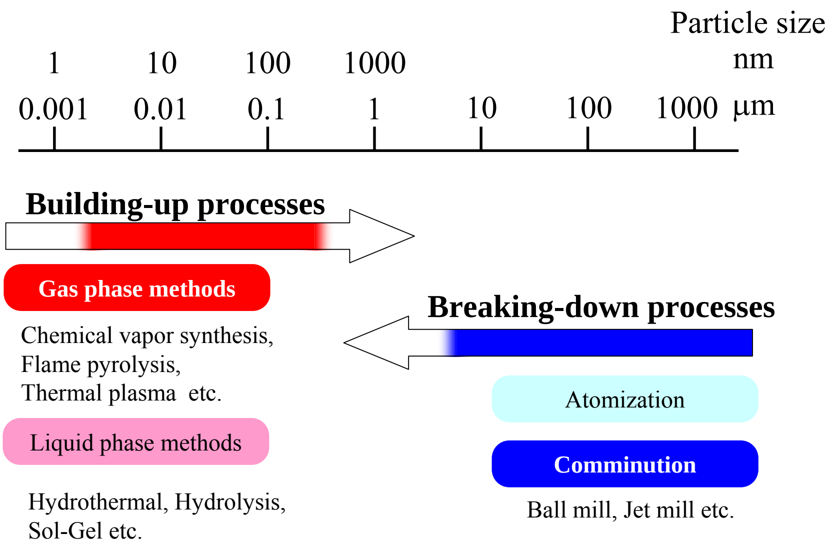
Dr. Carl Ishito
President
AAAmachine, Inc.

Event:	Powder & Bulk Solids (PTXi) 2008
Seminar:	Technical Session 404: Nano powders
Place:	Donald E. Stephens Convention Center, Rosemont IL
Date:	May 8 (Thu), 2008 10:00 AM -11:00 AM

Contents

- **Introduction**
- **Grinding and classification for fine powders**
- **Synthesis of nano powders by RF plasma method**
- **Property control of nano powders**
- **Summary**

Preparation of fine powders



Dry grinding and classification

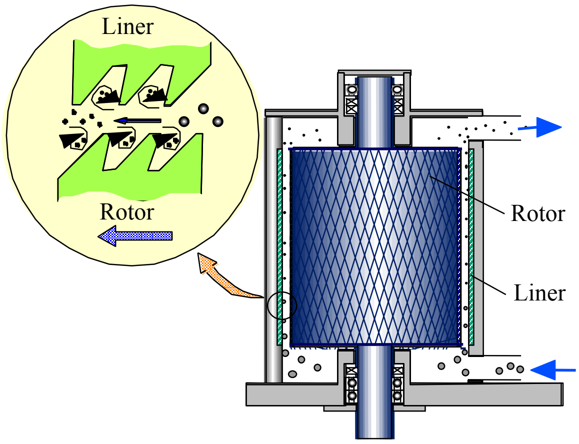
Grinding equipment

- Ball mill
- Mechanical mill (High speed rotor mill)
- Jet mill (Fluid-energy mill)

Classification equipment

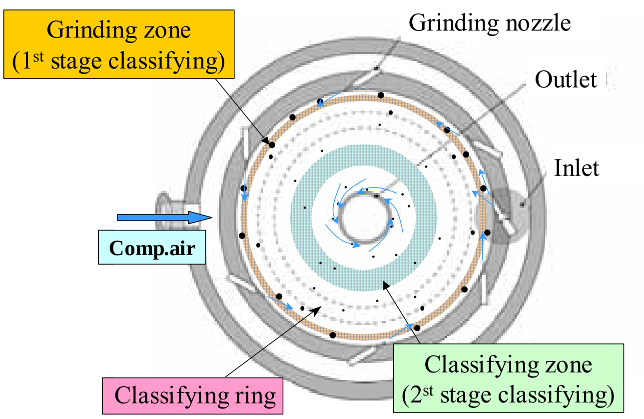
- Inertial classifier
- Free vortex type centrifugal classifier (Centrifugal classifier without a rotor)
- Forced vortex type centrifugal classifier (Centrifugal classifier with a rotor)

Structure of a mechanical mill



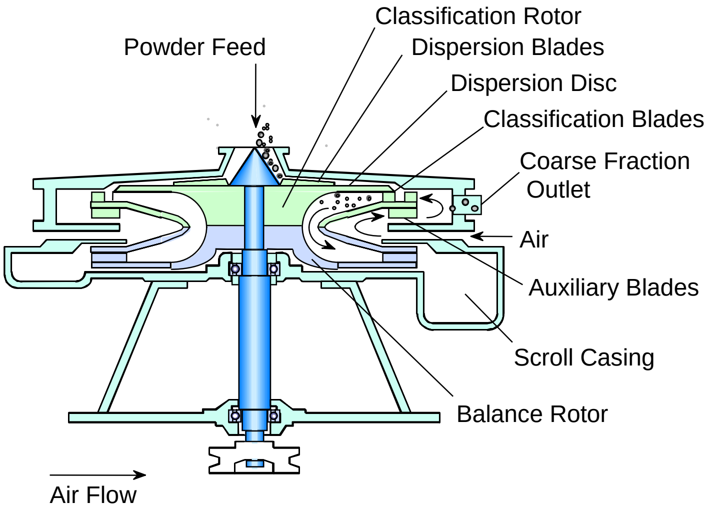
Cross-sectional View (Super Rotor)

Structure of a jet mill



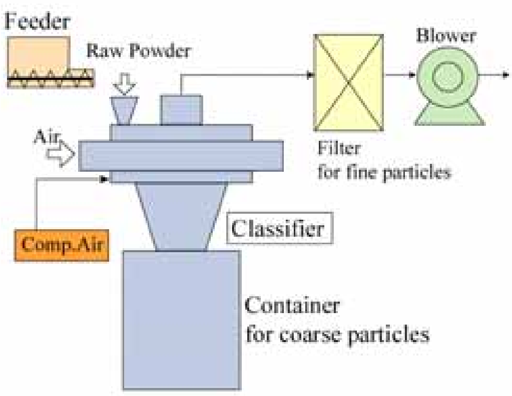
Cross-sectional view (Super Jet Mill)

A forced-vortex-type centrifugal classifier



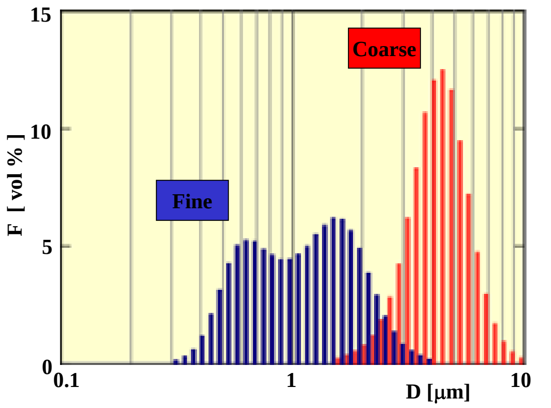
Cross-sectional view (Turbo Classifier)

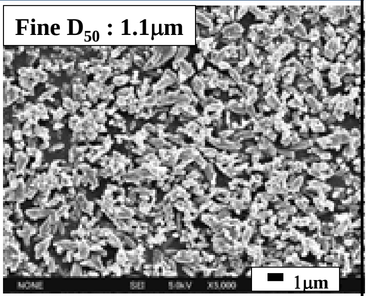
A new free-vortex-type centrifugal classifier

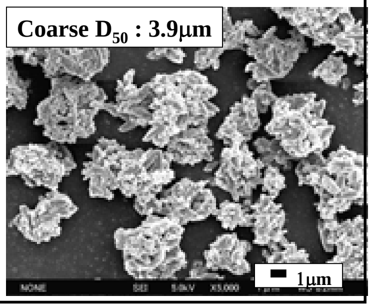


Performance of the free-vortex-type classifier

Calcium carbonate ($CaCO_3$)

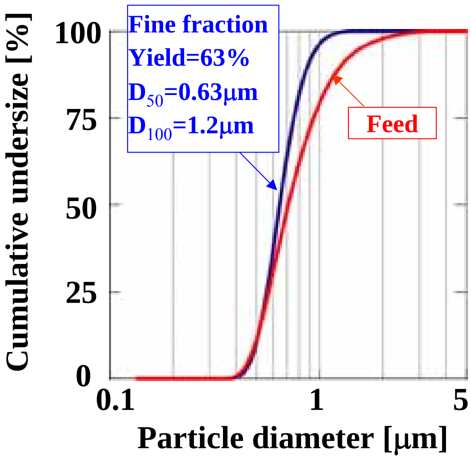


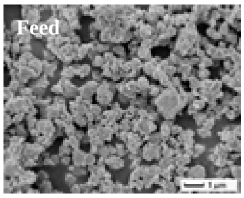


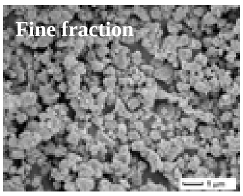


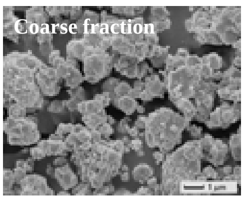
Performance of the free-vortex-type classifier

Barium titanate($BaTiO_3$)

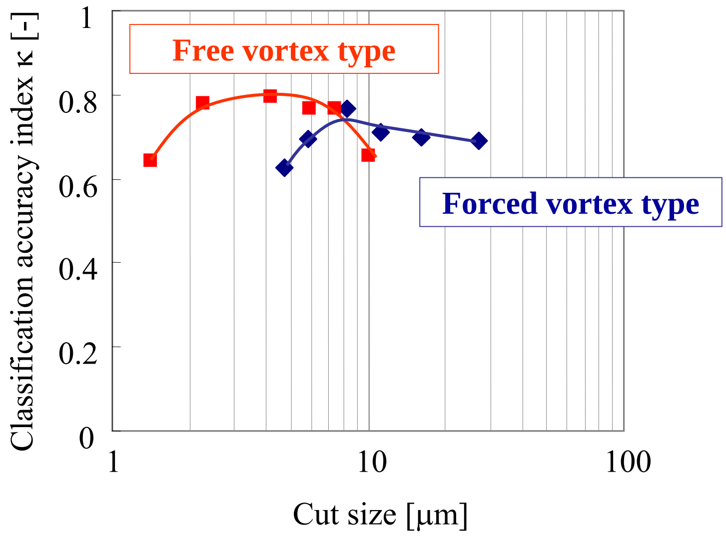




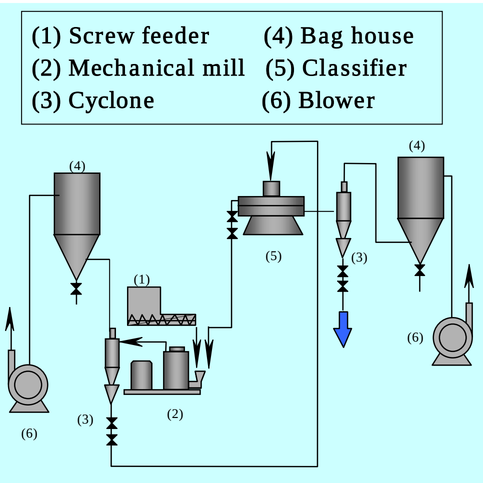




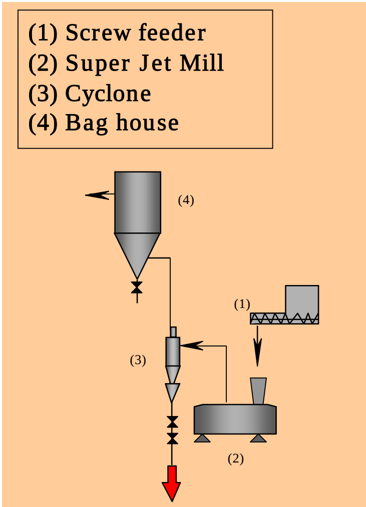
Classification accuracy of the two classifiers



Flowsheets of two grinding systems for toner

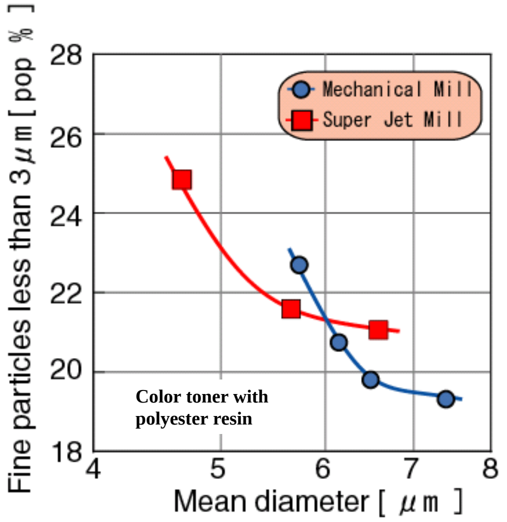


Closed circuit grinding system of mechanical mill and classifier

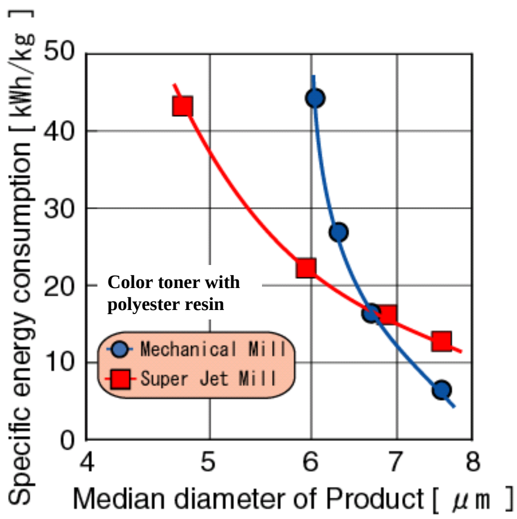


Grinding system of Super Jet Mill

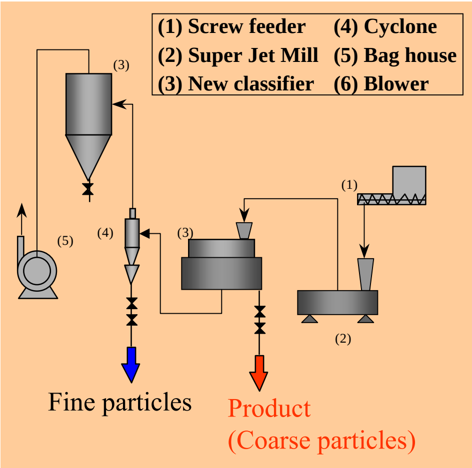
Over-grinding for two grinding systems



Energy efficiency for two grinding systems

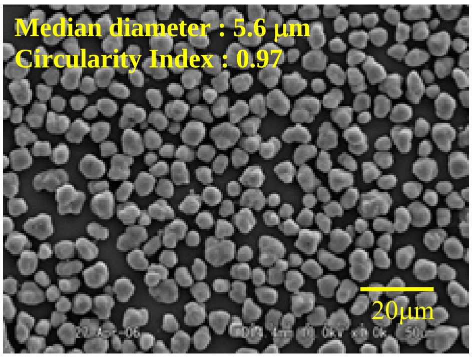


Super Jet Mill system with a new classifier

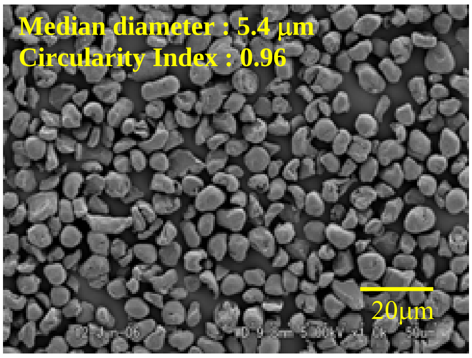


A new classifier for fine classification

Comparison of chemical and pulverized toners

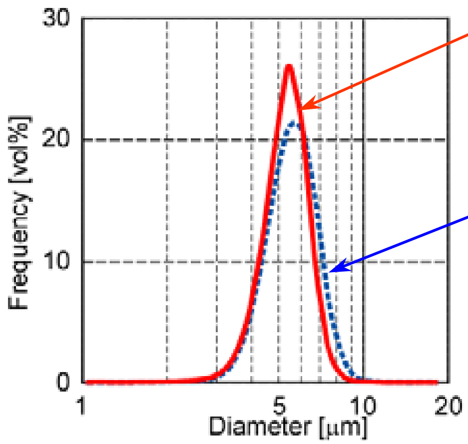


Chemical toner (Building-up process)



Pulverized Toner (Super Jet Mill system)

Comparison of chemical and pulverized toners



Pulverized toner
- Median diameter : 5.4 µm
- Less than 4µm : 26 pop%
- Product yield: 80%

Chemical toner
- Median diameter : 5.6 µm
- Less than 4µm : 24 pop%

Nano powders by a themal plasma method

Apparatus for preparation of nano powders

What's a RF(radio-frequency) thermal plasma?
Experimental setup
Features of nano powders by a RF plasma method

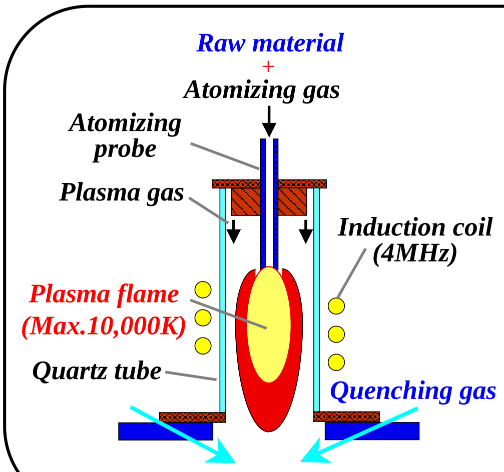
Single component nano powders

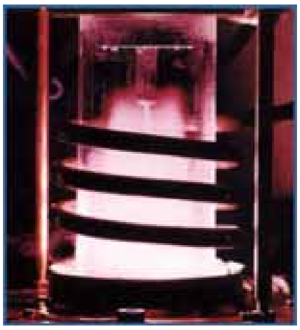
Control of particle size

Composite of nano powders

Synthesis of composite nano powders
Control of the particle size and crystal structure

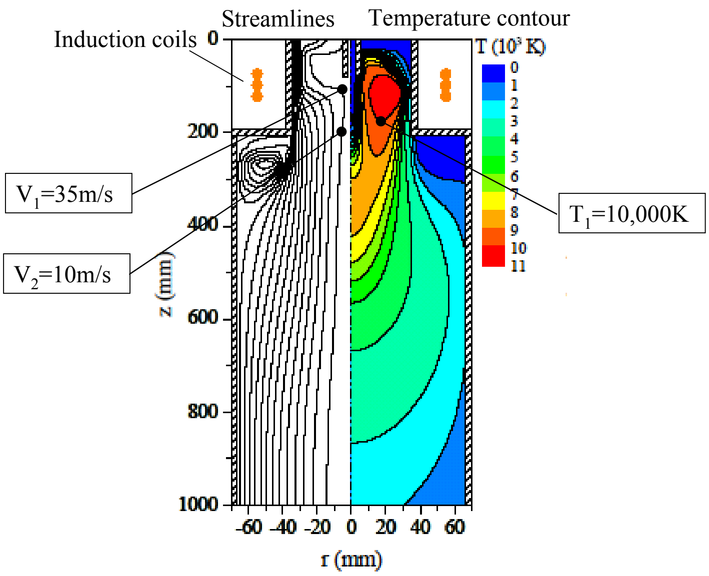
Detailed schematic of RF plasma torch





Plasma in operation

Numerical simulation of a plasma field



R. Ye,J. Li, T. Ishigaki:Thin Solid Films, 4251, 515(2007)

Advantages of RF thermal plasma

Electrodeless

Reduce contamination in nanopowders

Large volume and low velocity of plasma flame

Melt and evaporate raw materials at high throughputs

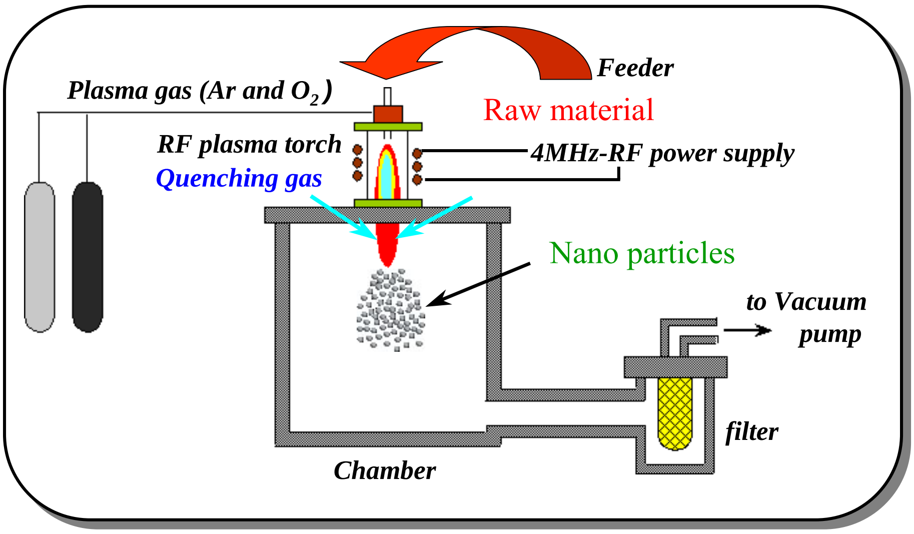
High chemical reaction atmosphere

Oxide, nitride, carbide metal(reduction) etc.

Rapid quenching (quenching rate:10^6K/s)

Preparation of composite materials
Control of particle properties(size and crystal structure)

Manufacturing reactor of nano powders



Control of particle size

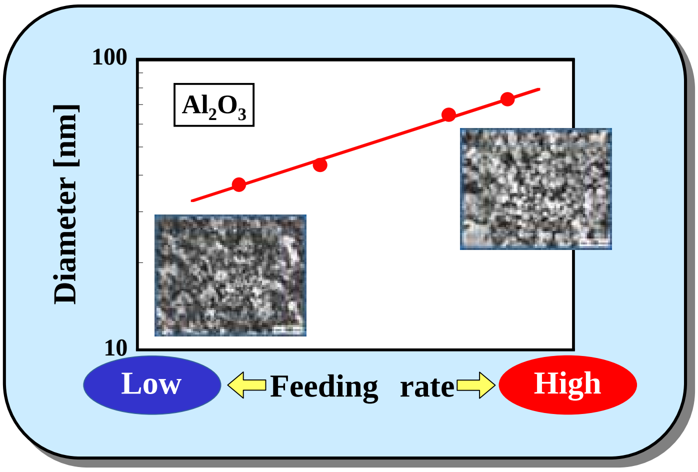
Nucleation and growth of nano powders are influenced by

- **Feed rate of materials**
- **Flow rate of quenching gas**
- **Reactor pressure**
- **Generator power input**
- **Position of probe**

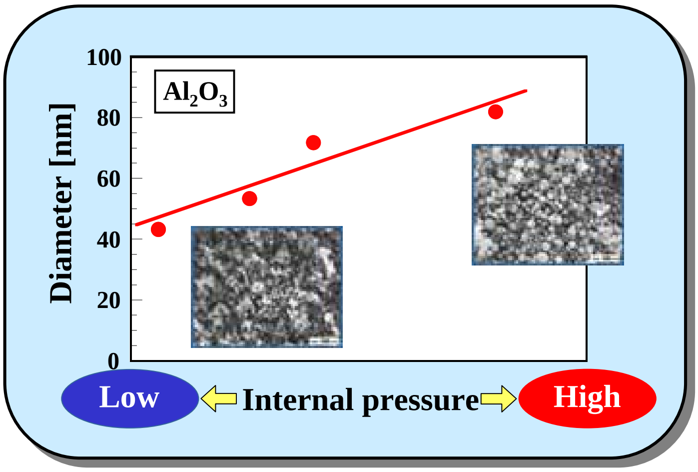
⇩ **adjusting**

Control of particle size

How to control particle size



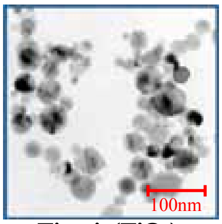
How to control particle size



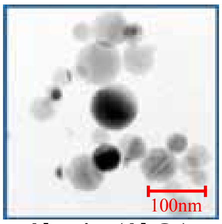
Nano powders prepared by RF plasma

Material	Diameter (BET)	Shape (SEM)	Crystal System (XRD)
SiO_2	10-50nm	Sphere	Amorphous
TiO_2	30-100nm	Sphere	Tetragonal
Y_2O_3	30-80nm	Sphere	Monoclinic
$BaTiO_3$	30-80nm	Sphere	Cubic(Tetragonal)
Ni	50-200nm	Sphere	Cubic
Cu	50-200nm	Sphere	Cubic
TiN	30-60nm	Sphere	Cubic
SiC	30-60nm	anisotropy	Cubic+Hexagonal

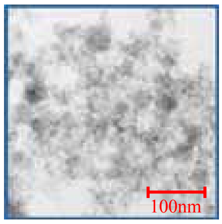
TEM image of nano powders



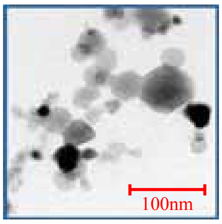
Titania(TiO_2)



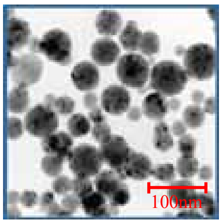
Alumina(Al_2O_3)



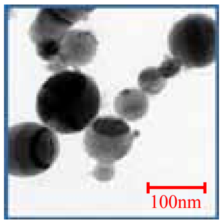
Silica(SiO_2)



Yttria(Y_2O_3)

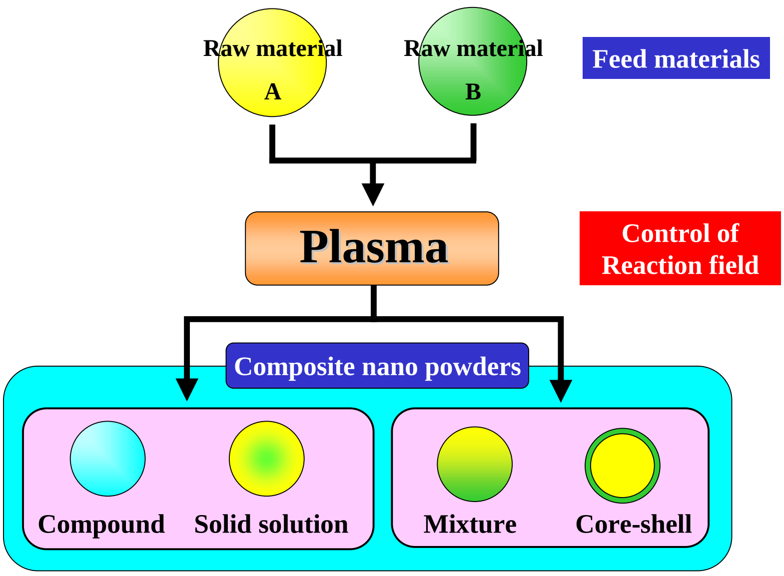


Barium Titanate($BaTiO_3$)

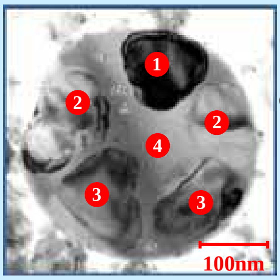


Nickel(Ni)

Preparation of composite nano powders



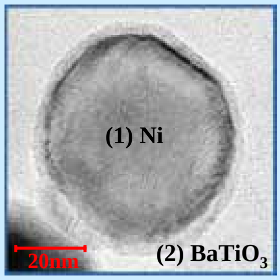
Examples of composite nano powders



Compositions

1. Y_2O_3
2. BaO
3. MgO
4. SiO_2

Mixture



Core-shell structure

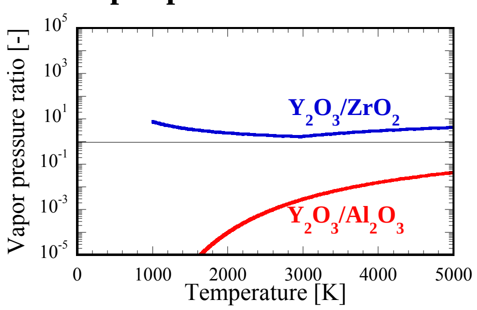
Other examples of composite nano powders

Y_2O_3-Al_2O_3 system

Raw material has a composition of Y:Al= 3:5.
(corresponding to YAG, Yttrium-Aluminum-Garnet)
Large difference of vapar pressure values for each material.

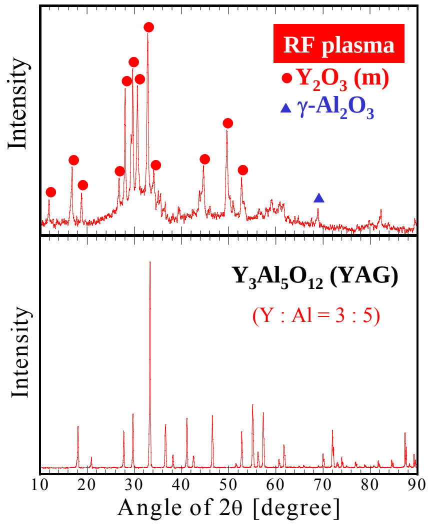
Y_2O_3-ZrO_2 system

Raw materials have compositions of Y : Zr = 0 : 100, 3 : 97, 10 : 90.
Small difference of vapar pressure values for each material.



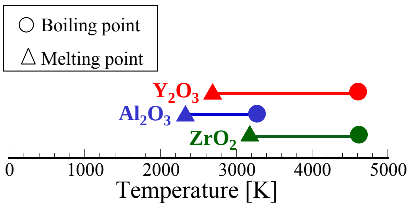
Comparison of the vapor pressure ratio

XRD profiles of Y_2O_3-Al_2O_3 (YAG) system



Two crystallographic phase

High crystallinity of Y_2O_3

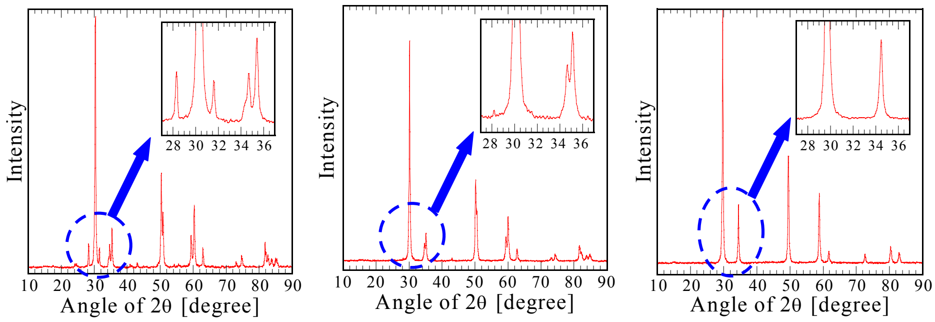


Vapor pressure: Al_2O_3 >>Y_2O_3

→**Mixture of Al_2O_3 &Y_2O_3**

Mixture type is prepared when the materials have a large difference of vapor pressure.

XRD profiles of Y_2O_3-ZrO_2 system



Y_2O_3 : 0 % **mono + tetra**

Y_2O_3 : 3 % **tetragonal**

Y_2O_3 :10 % **cubic**

The solid solution type is prepared when the materials have a small difference of vapor pressure.

The vapor pressure ratio is a key parameter to prepare the composite nano powders

Property control of $BaTiO_3$ nano powders

Barium titanate($BaTiO_3$) ceramics

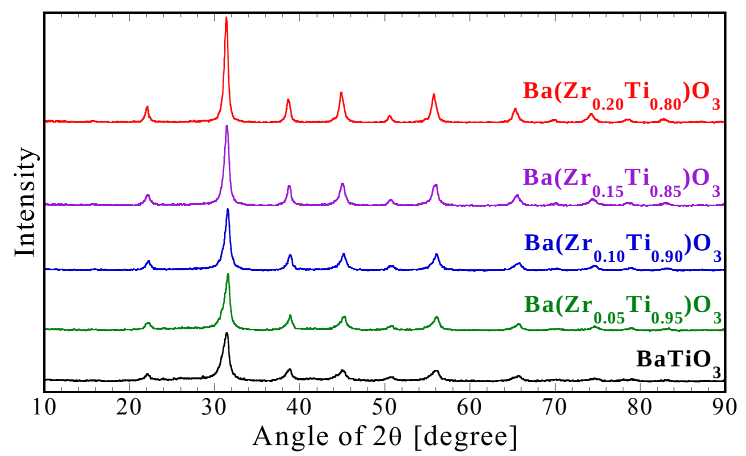
High dielectric constant, Low dielectric loss ・・・

MLCC, Piezoelectric transducers , etc.

Property control of barium titanate(BaTiO3) nano powders by doping Zr

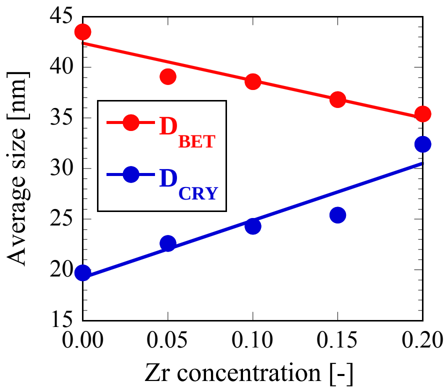
High crystallinity (tetragonal phase)
Narrow size distribution and small size
Weak aggregation

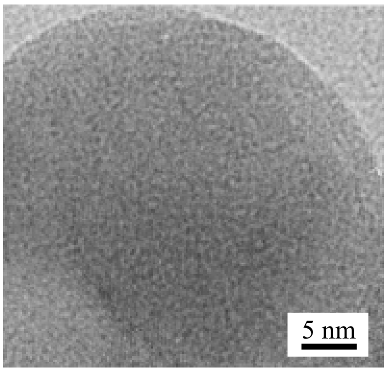
XRD profiles of $Ba(Zr_xTi_{1-x})O_3$ composite



Intensities of Zr doped barium titanate nano powders increase with increasing Zr concentration

Effect of Zr concentration on crystallinity





TEM photo:20% doped BT

The Crystallinity(crystal size) increses and the particle size decreases as Zr concentration increases.

Summary

1) **In order to efficiently prepare fine powders, it is important to use a suitable grinding or classification machine for particle size and characteristics.**
2) **Using grinding and classifying technologies, it is possible to produce toners similar to chemical ones in particle shape and size distribution.**
3) **The RF plasma is a useful method for the synthesis of many kinds of nano powders.**
4) **The vapor pressure ratio is a key parameter to prepare the composite nano powders**
5) **The particle size and crystallinity of barium titanate ($BaTiO_3$) nano powders could be controlled by doping Zr.**

NISSHIN SEIFUN

Thank you very much

for your kind attention.

Experimental conditions (Y_2O_3-Al_2O_3 , -ZrO_2 system)

Plasma gas	100 slpm(Ar), 20 slpm(O_2)
Atomizing gas	10 slpm(Ar)
Plate voltage & current	9 kV, 6A
Power	54 kW
Chamber pressure	50 kPa
Solution	$Y(NO_3)_3$, $Al(NO_3)_3$ (Y : Al = 3 : 5) $Y(NO_3)_3$, $ZrO(C_2H_3O_2)_2$ (Y : Zr = 0 : 100, 3 : 97, 10 : 90)
Solid content of the solution	20 wt%
Solution feeding rate	10 g/min

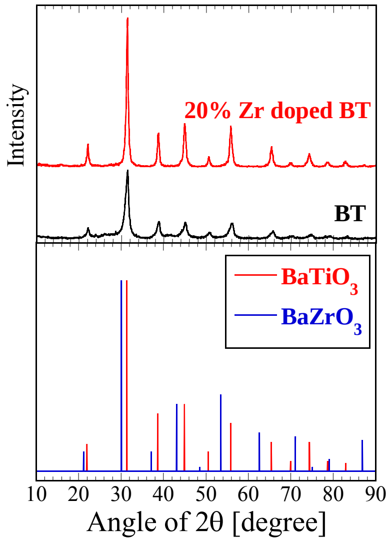
Typical experimental conditions for oxide

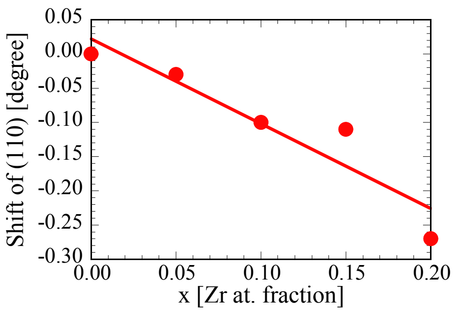
Plasma gas	100 slpm(Ar), 20 slpm(O_2)
Atomizing gas	10 slpm(Ar)
Plate voltage & current	9 kV, 6A
Power	54 kW
Chamber pressure	50 kPa
Feed rate of raw material	500 g/min

Experimental conditions (Ca, Zr doped $BaTiO_3$)

Plasma gas	100 slpm(Ar), 20 slpm(O_2)
Atomizing gas	10 slpm(Ar)
Plate voltage & current	9 kV, 6A
Power	54 kW
Chamber pressure	50 kPa
Suspension	1μm BaO and TiO_2, $ZrO(C_2H_3O_2)_2$ (Ti : Zr = 100 : 0 ~ 80 : 20) 1μm BaO and TiO_2, $Ca(NO_3)_2$ (Ba : Ca = 100 : 0 ~ 90 : 10)
Solid content of the solution	20 wt%
Solution feeding rate	10 g/min

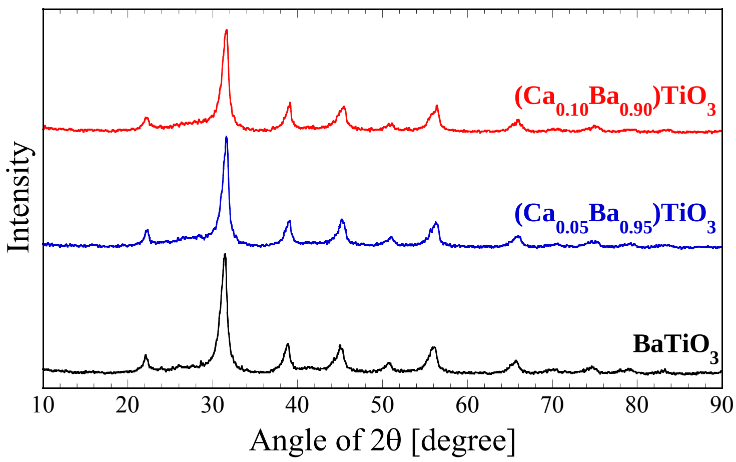
Characteristics of Zr doped $BaTiO_3$





Solid solution nano powders

XRD profiles of $(Ca_yBa_{1-y})TiO_3$ composite



Peak intensities are independent of Ca concentration

Kelvin effect

★ **Pure liquid droplet**

$$\frac{p_1}{p_s} = \exp\left(\frac{4\gamma M}{\rho R T d_p}\right)$$

★ **Containing dissolved materials**

$$\frac{p_2}{p_s} = \left(1 + \frac{6imM}{M_s \rho \pi d_p^3}\right) \exp\left(\frac{4\gamma M}{\rho R T d_p}\right)$$

$$p_1 = p_2 \times \left(1 + \frac{6imM}{M_s \rho \pi d_p^3}\right)$$

$p_1 > p_2$

m : mass of the dissolved materials

The vapor pressure decreases by impurities.

⇩

Acceleration of the physical condensation

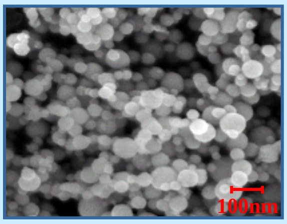
➡ **High crystallinity**

	$BaTiO_3$ <	$CaTiO_3$ <<	$BaZrO_3$
Mp.[K]	**1890**	**2250**	**2770**

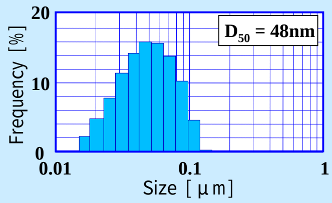
BTO nanoparticles

Analysis of nano-BTO

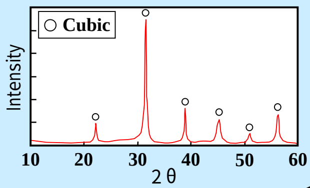
◎ SEM image



◎ Size distribution



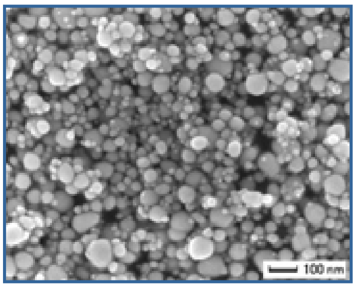
◎ XRD

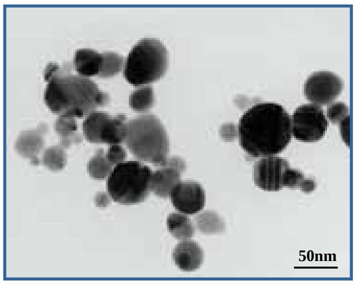


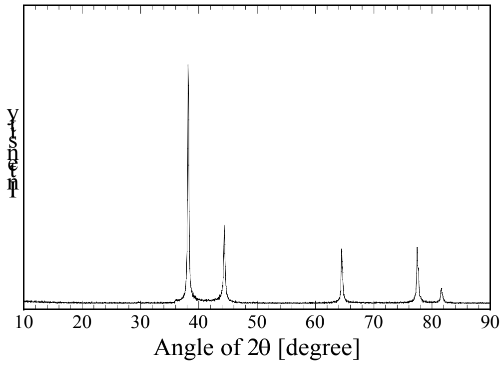
◎ Specific surface area (BET method)

24m²/g (42nm)

Ag nanoparticles







SSA : 14 m^2/g

D_{SSA} : 41 nm

D_{DLS} : 79 nm

Alloy nanoparticles