Fine particle physics and technology ; some results

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Abstract. The new techniques of fine particle synthesis are shown to lead to better ceramic materials such as yttrium iron garnet (YIG) and ferroelectric lead zirconate titanate (PZT). The densities are greater than 99% of the theoretical density and the grain size can be easily controlled from 2 microns upwards. For YIG this means higher values of the nonlinear spin-wave excitation threshold h_c . For PZT the result is higher values of the tensor component d_{33} and poling voltage. It is also shown that the fine particle systems and the fine-grain microstructure lead to interesting physics results. For PZT the lowering of the peak dielectric constant, the increasing transition temperatures and the decreasing values of d_{33} with decreasing grain size can be understood in terms of the changing low-frequency cut-off of the soft lattice vibration mode. Another interesting result is that for 2000 Å size particles of α -Fe₂O₃ the anisotropy constant is found to be 1.38×10^3 ergs/cm³ from Mössbauer measurements.

Keywords. Fine particle physics ; powder characterisation ; pyrogel process ; spray-dry process ; freeze-dry process ; sol-gel process.

1. Introduction

The large majority of oxides exhibiting ferroelectricity and ferromagnetism find more use as polycrystalline sintered aggregates rather than as single crystals. This has prompted considerable work in the area of ceramic synthesis so as to find ways of reducing the variability aspects, especially, of grain boundaries which are inevitable in ceramics (Palmour *et al* 1978). The single crystal ideal can be partially attained if the sintered ceramics can be made to (1) approach theoretical x-ray density by being pore-free, (2) have uniform and reproducible microstructure, (3) have almost perfect stoichiometry of elemental components, (4) have fairly high lattice and surface diffusion constants for self-diffusion and impurity diffusion.

The most successful way of meeting all the four requirements is to go through one of the "wet" fine particle synthesis routes which have been conceived and developed over the past decade at the Atomic Energy Research Establishment (Harwell), Bell Laboratories (New Jersey) and the Pennsylvania State Materials

Research Laboratory (University Park). In the (i) pyrogel process, (ii) spray dry process, and (iii) freeze dry process one starts with an aqueous solution of the salts in the right proportion. The solution is then sprayed as atomised droplets into an ambient which promotes rapid heat transfer to the droplets (processes 1 and 2) or away from the droplets (process 3). In the first case we obtain dry powder of very finely mixed (at about the atomic scale) of reacted oxides. In the second case we obtain powder at liquid nitrogen temperature wherein each particle aggregate has frozen water which is then removed in a vacuum oven, again yielding finely mixed dry powder.

There is yet a fourth method, sol-gel, wherein the multi-cation oxides are co-precipitated from the soluble salts solution as hydroxides. The finely mixed hydroxides or a single hydroxide complex is then made into a stable sol in water. The sol is then sprayed into an alcohol medium which leads to rapid dehydration and the consequent formation of an "atomically mixed" precursor. The precursor is calcined to give the multi-cation oxide.

We shall show, in what follows, the successful application of three of these processes to two well-known materials; ferrimagnetic yttrium iron garnet (YIG) $\text{Y}_2\text{Fe}_5\text{O}_{12}$ and ferroelectric lead zirconate titanate (PZT) $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$. We shall also show that a fine particle system such as $\alpha\text{-Fe}_2\text{O}_3$ and a fine-grained material such as PZT can lead to interesting physics results.

2. Powder characterisation

It is necessary to characterise the powder obtained by some means so that reproducibility can have meaning. A photo-extinction sedigraph was developed to do this. The basic principle of this instrument is as follows. A homogeneous suspension of the fine particles in a water medium contained in a cell will reduce the transmitted light intensity from I_0 to I_1 given by

$$\log(I_0/I_1) = CS_p l$$

where C is the particulate concentration which is equal to

$$\sum_{d_{\min}}^{d_{\max}} C(d),$$

l is the cell path length, and S_p is the total projected surface area. After a certain time particles larger than diameter d_s will have gone below the horizontal path of the light beam h cm below the top of the suspension. Thus,

$$\log(I_0/I_s) = Cl \sum_{r=0}^{r=s} K_r k_r n_r d_r^2,$$

where k_r is the appropriate shape factor. K_r is the photo-extinction coefficient defined as the ratio of light obscured by the particles in the size range $d_{\min} - d_s$ to the light which would be obscured by particles in the same size range if the laws of geometric optics held. From Stokes' theory we also know that the particles of diameter d_s would have travelled a vertical depth h given by

$$d_s = (18 n/(\rho - \rho_0) g)^{1/2} (h/t)^{1/2}.$$

Thus, by monitoring the intensity of a flat (50 microns width) beam of white light at programmed values of electronically-controlled cell movements for variable h , the per cent undersize distribution of particle sizes can be obtained.

Several other powder characterisation techniques have been used. These are: (1) x-ray sedigraph which is similar, in principle, to the optical sedigraph but which monitors the attenuation of an x-ray beam due to mass absorption, (2) specific surface area due to monolayer surface adsorption by the Braun-Emmet-Teller (BET) technique, (3) x-ray diffraction for phase analysis and particle "size" from the line broadening according to the Warren-Averbach theory, (4) transition electron microscope (TEM) and scanning electron microscope (SEM) photography, (5) thermogravimetric analysis (TGA) and differential thermal analysis (DTA).

3. Sintered material characterisation

The first step was to grind, polish and etch the sintered compacts so that micro-structure could be studied. Also, the density was measured. Then measurements were performed using the following techniques.

3.1. Ferromagnetic resonance

YIG can be represented as

The $3d^5$ electron magnetic moments lead to

$$\vec{\mu} = -\gamma \mathbf{J}$$

where $\gamma = ge/2mc$.

In the magnetic field $\mathbf{H}$, the torque $\mathbf{T}$ is given by

$$\mathbf{T} = \vec{\mu} \times \mathbf{H} = d\mathbf{J}/dt = - (d\vec{\mu}/dt)/\gamma.$$

Thus, the spin or the magnetisation moment M precesses around the field H at a frequency given by

$$\omega = \gamma H.$$

A ferromagnetic resonance spectrometer was developed as shown schematically in figure 1.

3.2. Piezoelectricity

The component of polarisation P_i of a poled PZT ceramic is related to the stress tensor component σ_{jk} by

$$P_i = \sum_j \sum_k d_{ijk} \sigma_{jk}.$$

The tensor component of interest in application is d_{333} . This, in the reduced notation of Mason, is d_{33} and is measured by the technique of Berlincourt *et al* (1960).

Figure 1. X-band ferromagnetic resonance spectrometer.

3.3. Mössbauer spectroscopy

These measurements were made on an ultrastable, precision, spectrometer. The data acquisition system has been developed using an SC/MP microprocessor. It has 1024 channels, each of 24-bit length. The velocity-modulated data is under program control of the microprocessor and minimum hard-wired logic has been used. The input-output functions are performed by an ASR 33 teletype.

4. YIG synthesis and results

Microwave garnet devices require accurate stoichiometry control (Paladino and Maguire 1970) and grain size control (Patton 1970).

4.1. Pyrogel process

A hot spray reactor similar in design to that by Roy *et al* (1977) was set up as schematically in figure 2. The length of the hot zone was 2 meters and the diameter about 85 mm. The aqueous solution of yttrium sulphate and ferrous sulphate in the right proportion for YIG was sprayed from the pneumatic atomiser mounted on the top of the quartz tube. The gas-entrained particles issuing out of the reactor were cooled in a heat exchanger and collected in a bag filter. The hot zone temperatures were controlled by three independent heating modules. The typical temperature of the top zone was 850° C and that of the lower two zones 1150° C.

We report here the studies made on two cases where concentration of the starting solutions were varied. In one case it was 0.1 mol % (the corresponding powder is referred to as HTSS-1) and in the other it was 0.05 mol % (HTSS-2). Other parameters such as liquid flow rate, pneumatic pressure, etc., were varied slightly so as to have a suitable run of the process.

The droplet size distribution on pneumatic spraying is expected to be log-normal with a Sauter diameter given by Nukiyama-Tanasawa expression:

$$d_{\bullet\bullet} = (585/u_r) (\sigma/\rho_L)^{0.5} + 597 (\mu_L/\sqrt{\sigma\rho_L})^{0.45} (1000 Q_L/Q_r)^{0.5}$$

(2)

(3)

Figure 2. Schematic diagram of the hot-spray reactor.

Figure 3. X-ray sedigraphs of the hot-sprayed powders.

where u , is the velocity of gas relative to liquid, Q_L and Q_g are the volumetric flow rates of liquid and gas, σ , ρ_L and μ_L are the surface tension, density and viscosity of the liquid, respectively. The formula gives d_{vs} for HTSS-1 to be 38μ and for HTSS-2 to be 48μ . Figure 3 gives the observed size distribution of the powders obtained from the reactor. It shows that the log-normal distribution is retained. However d_{88} , which corresponds to 80% undersize, is lower for the powder as compared to the estimated droplet size. Figure 3 also includes the size distribution of HTSS-1 after heating at 1050°C for 2 hr. The distribution continued to be log-normal. The aggregate size, however, had grown considerably. Results for HTSS-2 were similar. Figure 4a shows the SEM picture of the powder as obtained from the reactor. The powder appears to be well gelated. Primary particles size as seen from the TEM picture, given in figure 4b, is about $400 \text{ \AA}$. Figures 4c and 4d show the SEM and TEM pictures of the powder after heating at 1050°C for 2 hr. Figure 4c shows that the gelation is still maintained while the primary particle size (figure 4d) went up to approximately 0.4μ .

Thermogravimetric analysis on HTSS-1 and HTSS-2 gave no weight loss up to 1400°C other than the initial moisture loss. This confirmed the complete decomposition of the initial salts. The TGA of powders from the conventional spray dryer showed weight losses corresponding to decomposition of ferrous sulphate and yttrium sulphate at 600°C and 900°C respectively.

X-ray analysis of the powder as obtained from the reactor showed, surprisingly, no detectable YIG phase in HTSS-1 and HTSS-2. Also, no Y_2O_3 phase was seen. The powder contained only YFeO_3 and Fe_2O_3 phases. On heating, the conversion of the powder to YIG phase was observed. The phase composition of the powder, heated at various temperatures, was determined with x-ray diffraction using the method of Klug and Alexander (1954). The results are shown in figures 5a and 5b. There is considerable difference in the rate of formation of YIG in the two cases. In HTSS-1 the formation starts at higher temperature than HTSS-2, but, has more than 90% conversion at lower temperatures. In conventional synthesis of YIG done by Holmquist *et al* (1961) the YFeO_3 phase appears before formation of YIG

Figure 5. Phase compositions at various calcination temperatures.

phase. It, however, does not exceed more than 10% and starts decreasing at 700° C, at which temperature the YIG phase starts appearing. In the synthesis processes employing reactive hot pressing (Blair and Chaklader 1973), pyrolysis of dehydrated amorphous organic precursors (Popma and Diepen 1974), and co-precipitation (Wolf and Rodrique 1958), the data given are not conclusive about the total absence of YFeO₃ as intermediate phase.

Our results indicate that only this method of hot-spraying results in a preponderance of YFeO₃ phase prior to YIG formation. Also, the YFeO₃ phase in this case is stable up to temperature higher than 1150° C.

The powders were calcined at 1125° C for 2 hr before pressing in an isostatic press and sintering. Sintering was done at temperatures between 1300° C and 1400° C in an atmosphere with excess O₂. More than 99% densities were observed above 1350° C. The microstructure after 2 hr of sintering at 1350° C is given in figure 6. The average grain size observed is 2.2 μ .

The saturation magnetisation measurements were performed on a low frequency induction-applied field loop tracer of the type developed by Likhite *et al* (1965). Samples sintered at 1300° C showed magnetisation to be 1650 gauss which increased to 1780 gauss for samples sintered at 1350° C. The latter value corresponds to the standard value reported in literature.

The FMR linewidths were highly dependent on the starting stoichiometry, the best value being 40 Oersted.

The process of hot spraying for several other materials is known to give fine, free-flowing, and highly sinterable powders (Dell 1973; Roy *et al* 1977). These advantages were also realised in this study of YIG. The process, however, when followed for YIG could not give a single-phase material directly, within the limitations of our experimental conditions. Though a separate calcination step was necessary, the powders finally obtained were still fine and more reactive than those

Figure 4. (a) SEM at $3000\times$ and (b) TEM at $44,000\times$ of powder from the reactor, (c) SEM at $3000\times$ and (d) TEM at $9000\times$ of reactor powder heated at 1050°C for 2 hr.

Figure 6. Microstructure at $3200\times$ of thermally etched YIG pellet sintered at 1350°C for two hours. Average grain size is $2.2\ \mu$.

obtained by ball milling. Thus there has been an extensive nucleation of YIG. This particular study also indicates that YFeO_3 phase nucleates before growing and transforming into YIG. From the HTSS runs as well as the conventional spray drying runs at lower temperature the sequential reactions appear to be the following relations :

We think that formation of YIG must be preceded by the formation of YFeO_3 in any other synthesis process also. For instance, in the case of ball milling of oxides (Holmquist *et al* 1961), YFeO_3 phase appears first, increases to 10% and the fall is accompanied by the formation of YIG. The amount of YFeO_3 is less because of less number of nucleation centres. The powders used in that study are not so fine. In the case of reactive hot pressing (Blair and Chaklader 1973) the same fact is borne out for non-stoichiometric compositions. For the stoichiometric composition the data given are insufficient to conclude total absence or presence of YFeO_3 before the formation of YIG. In the process of dehydration of organic precursor followed by pyrolysis (Popma and Diepen 1974), again, the data is not conclusive against this fact. In the method of co-precipitation (Wolf and Rodrique 1958) this fact finds support on the basis of colour change.

To substantiate this point further we spray-dried sulphates at relatively low temperatures (300° C). The SEM of the powder obtained showed gelation. The powder was maintained dry and calcined outside. This gave rise to extensive nucleation. Phase composition curves were similar to that obtained for the hot-sprayed powders. When powders were not maintained dry the gelation was destroyed and the calcination gave rise to Y_2O_3 , YFeO_3 and Fe_2O_3 phases. Thus, the amount of YFeO_3 phase is in direct proportion to the number of nucleation sites.

4.2. Sol-gel process

The method of synthesising YIG by co-precipitation has been mentioned earlier (Wolf and Rodrique 1958). This method of co-precipitating hydroxides of yttrium and iron was not very successful because grain growth during the calcination of the precipitate is not controlled and the first sintering gave a product similar to that by the dry method. For the sol-gel method we follow here, the co-precipitation step found to be more successful is iron hydroxide and yttrium oxalate. This precipitate was then made into a stable sol and then gelled using 2-ethyl hexanol and span-80 surfactant.

Calcination studies of the gelled powder gave results similar to those obtained on pyrogel powders discussed in the previous section. Here also the preponderant intermediate phase was found to be YFeO_3 and was stable to more than 1000° C . This showed that extensive nucleation centres were possible using a sol-gel technique, leading to fine reactive YIG powders. These powders, when sintered at

1350° C, gave more than 99% of the x-ray YIG density with an average grain size of 1.5 microns.

5. PZT synthesis and results

Much work has been done in an effort to obtain a high density, uniform PZT ceramic microstructure using advanced ceramic techniques (Haertling 1964; Schnettler 1973) such as hot pressing and continuous hot pressing. A modified conventional technique by Kim and Hart (1978) has recently been found to be useful.

A sol-gel technique was developed by us for the synthesis of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ materials. Compositions with varying x were made with special attention to $x = 0.52$. To start with, aqueous solutions of "analar" grade $\text{Pb}(\text{NO}_3)_2$, ZrOCl_2 and TiCl_4 were taken in stoichiometric proportions. The presence of ammonium nitrate was found essential to avoid formation of insoluble PbCl_2 . The mixture was then poured into 12N NH_4OH , leading to the co-precipitation of cation hydroxides. The precipitate was then dispersed into water and formed into a stable sol. It was then gelated using 2-ethyl hexanol as a dehydrating agent and span-80 as a surfactant.

From TGA and DTA made on the gel it was seen that only one single decomposition at 300° C exists, indicating the formation of a complex during precipitation. This was consistent with the observation of Biggers and Venkataramani (1978) using co-precipitate from lead acetate, zirconium tetra-*n*-butoxide and titanium tetra-*n*-butoxide. X-ray diffraction pattern of the gel powders calcined at 400° C showed that the material is amorphous. Above 400° C the formation of crystalline PZT starts and is found to be complete after the calcination for 1 hr at 800° C.

In table 1 are given the powder characteristics of one of the gel powders obtained. It shows that the surface area per gram of the powder is reducing, indicating the increase in the particle size with calcination temperature. The specific surface area under the same calcination conditions, however, differs depending upon the concentration of the starting solution. For example, when the concentration was reduced from 94 g/litre to 31.3 g/litre the specific surface area after 1 hr calcination at 800° C changed from 2.20 m²/g to 4.97 m²/g.

Sintering studies of gel powder obtained from various starting concentrations and calcined at 800° C for 1 hr were made. Sintering was done in a platinum cru-

Table 1. Powder characterisation data.

Time/Temp.	Surface area (m ² /g)	Equivalent spherical diameter (Å)	Phase
Gel	35.50	156	Amorphous
400° C/1 hr	14.65	520	Amorphous
600° C/1 hr	7.09	1060	PZT
800° C/1 hr	2.26	2800	PZT

cible sealed by MgO. X-ray diffraction and SEM microstructure showed no detectable second phase in the sintered material. In the region of high densification the particle size of the calcined powder had almost no effect on the sintered characteristics of the material. Typical observations on the effect of sintering time on density is shown in figure 7. Undue rise in sintering temperature results in the reduction of the density as is apparent from the observations given in figure 8. From observations made at various sintering temperatures and soaking times the optimum sintering conditions were found to be 1200° C for 2 hr. Under these conditions the density of 8.1 g/cm³ was obtained and the value of the d_{32} tensor

Figure 7. Sintering at 1200° C for various soaking times.

Figure 8. Sintering for 4 hr for various soaking temperatures.

component as a function of the poling voltage is shown in figure 9. These samples had the remarkably high breakdown voltage of greater than 70 kV/cm at 100° C.

6. Physics

6.1. $Pb(Zr_{0.52}Ti_{0.48})O_3$ fine-grain material

Ever since Anliker *et al* (1954) showed the effect of decreasing particle size on the spontaneous lattice deformation, $(c/a)-1$, of $BaTiO_3$ there have been several attempts to understand particle size effects in ferroelectrics (see Martirena and Burfoot 1974 and references therein). Most of the experimental data were often non-reproducible because of inadequate material characterisation and chemical homogeneity of the fine particles or the sintered polycrystalline materials. Also, a coherent explanation has been lacking due to the intrinsically complex nature of a polycrystalline material.

It is now known, for instance, that the morphotropic phase boundary which separates the rhombohedral and tetrahedral phases at $x \approx 0.52$ in $Pb(Zr_xTi_{1-x})O_3$ does not signify a co-existence region as was supposed by Isupov (1975) and Ari-Gur and Benguigui (1974). This was shown recently by Kakegawa *et al* (1977) by using a "wet-dry" synthesis technique which overcomes compositional fluctuations present in the earlier work. We have improved the synthesis technique by starting with all constituents $Pb(NO_3)_2$, $ZrOCl_2$ and $TiCl_4$ as aqueous solutions. The details will be published elsewhere. The synthesis gave materials of $x = 0.52$ composition as a clean, single-phase tetragonally-distorted PZT of density $> 99\%$ x-ray density with no PbO loss and with a breakdown field in excess of 65 kV/cm. The microstructure could be controlled from 0.5 to 5 μ .

Our measurement on $\epsilon(0)_{\max}$ versus grain size coincide with those of Martirena and Burfoot (1974). Their data are re-plotted in figure 10. The d_{33} measurements were done on the Berlincourt d_{33} meter.

The variation of $\epsilon(0)_{\max}$ with grain size has been attributed by Martirena and Burfoot (1974) to diffuse phase transition. We propose another model.

Figure 9. $Pb(Zr_{0.52}Ti_{0.48})O_3$ sintered at 1200° C for 2 hr.

Figure 10. Variation of the peak dielectric constant and the transition temperature with grain size.

As the grain size decreases the crystalline lattice is not able to sustain low-frequency lattice vibrations. Support for this hypothesis comes from the fact that the zero-phonon fraction, $f = \exp(-\langle x^2 \rangle / \lambda^2)$, in the Mössbauer effect of small gold particles increases with decreasing size (Marshall and Wilenzick 1966). This result was explained by assuming that the density of states $c(\omega)$ is zero below a cut-off value of ω determined by size.

Now, according to Cochran's (1960) theory, $\epsilon(0)_{\max}$, at the phase transition T_c of a ferroelectric is given by the Lyddane-Sachs-Teller relation,

$$\epsilon(0)/\epsilon(\infty) = \omega_{\text{LO}}^2/\omega_{\text{TO}}^2,$$

where the transverse-optic (TO) mode frequency is temperature-dependent or soft and goes to zero as $\omega_{\text{TO}}^2 = c(T - T_c)$ for a second order transition. Since $\epsilon(\infty)$ = square of the refractive index is only weakly temperature-dependent and ω_{LO} is constant, it is expected the low-frequency dielectric constant $\epsilon(0)_{\max}$ should tend to infinity as the particle size tends to infinity. Thus, according to our model the minimum value of ω_{TO} will be a function of particle size, leading to the result shown in figure 10 for changes in T_c and $\epsilon(0)_{\max}$.

The particle-size varying cut-off vibration frequency of the soft mode would lead to varying spontaneous deformation below T_c . These would scale up to values observed by Anliker *et al* (1954) at room temperature.

It has been shown earlier that the axial field gradient V_{zz} at the Ti site in BaTiO_3 is closely proportional to P_z^2 (Bhide and Multani 1965) at various temperatures. Now $P_z = \sum \sum d_{ijk} \sigma_{jk}$. Thus, the piezoelectric modulus d_{333} (or d_{33} in the reduced notation) will be proportional to $\sqrt{V_{zz}}$. Further, V_{zz} is also a function of the spontaneous deformation with V_{zz} decreasing as $(c/a) - 1$ decreases. Similar considerations would apply to isostructural $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ and one must expect d_{33} to be a function of spontaneous deformation and hence with d_{33} increasing with particle size. This is shown in figure 11.

Thus we have seen how a particle-size dependent soft mode can explain the variations in T_c , $\epsilon(0)_{\max}$ and d_{33} .

Figure 11. The variation of d_{33} with grain size.

6.2. Fine particles of $\alpha\text{-Fe}_2\text{O}_3$

The magnetic properties of microcrystals are currently under investigation in many laboratories. Several new phenomena have been found to be associated with fine particles such as speromagnetism (Coe and Readman 1973), surface-sensitive magnetic anisotropy energy barriers (Dumesic *et al* 1975) and pinning of surface spins (Berkowitz *et al* 1975).

We have studied by Mössbauer spectroscopy 300 Å and 2000 Å particles of $\alpha\text{-Fe}_2\text{O}_3$ prepared by spray-drying ferrous sulphate solution followed by calcination. The spectra obtained are shown in figure 12.

$\alpha\text{-Fe}_2\text{O}_3$ has the corundum structure D_{3d}^2 . At room temperature the spins lie in one of the vertical planes of symmetry, making a small angle with the basal plane. At temperatures below 260° K, for bulk $\alpha\text{-Fe}_2\text{O}_3$, the spin is aligned along the [0001] axis. The spin-flip transition temperature has been found to lower with decreasing particle size (Schroeder and Nininger 1967). Also, from the data of Kundig *et al* (1966) it is found that the hyperfine field is lower for 180 Å particles than the bulk value. However, this result has not been taken seriously by the authors nor is the measurement precise.

Our measurements show that the hyperfine field is reduced by 3.75% when the particle size is 2000 Å. This is seen in the middle spectrum of figure 12 which is for an admixture of 300 Å and 2000 Å particles. The first spectrum shows the usual supermagnetic behaviour. For small particles there is a high probability that the magnetisation vector will spontaneously change direction at a rate faster than the Mössbauer nuclear excited state lifetime. This relaxation time has been suggested by Neel (1949) to be given by

$$\tau = \tau_0 \exp (KV/kT),$$

Figure 12. Particle-size dependent Mössbauer spectra of α - Fe_2O_3 .

where K is the anisotropy constant, V is the particle volume and k is the Boltzmann constant. Kundig *et al* (1966) have used this relation to determine K for 180 Å particles to be 4.7×10^4 ergs cm^{-3} .

Recently, Morup and Topsoe (1976) have suggested a theory for the diminished values of the hyperfine field with decreasing size of Fe_2O_3 . They suggest that below the superparamagnetic blocking temperature thermally excited oscillations of the magnetisation around an energy minimum reduce the average magnetisation and, consequently, the magnetic hyperfine field :

$$\begin{aligned} M(T) &= M_0(T) \langle \cos \theta \rangle_T, \\ &= M_0(T) (1 - kT/2KV). \end{aligned}$$

Using this relation we find the anisotropy of the 2000 Å particles of α - Fe_2O_3 to be 1.38×10^3 ergs cm^{-3} . Thus we find the anisotropy constant to be highly size-dependent.

7. Conclusions

It has been shown that the applications parameters can be improved for ferromagnetic YIG and ferroelectric PZT by going through the fine particle route. Also, fine particles and fine-grain microstructure can lead to interesting physics results.

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