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Millimeter wave transmittance/absorption measurements on micro and nano hexaferrites

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Millimeter wave transmittance measurements have been successfully performed on commercial samples of micro- and nano-sized particles of $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ hexaferrite powders and nano-sized particles of $BaFeO_2$ and $SrFeO_2$ powders. Broadband millimeter wave transmittance measurements have been performed using free space quasi-optical spectrometer, equipped with a set of high power backward wave oscillators covering the frequency range of 30 – 120 GHz. Real and imaginary parts of dielectric permittivity for both types of micro- and nanoferrites have been calculated using analysis of recorded high precision transmittance spectra. Frequency dependences of magnetic permeability of ferrite powders, as well as saturation magnetization and anisotropy field have been determined based on Schlöemann's theory for partially magnetized ferrites. Micro- and nano-sized ferrite powders have been further investigated by DC magnetization to assess magnetic behavior and compare with millimeter wave data. Consistency of saturation magnetization determined independently by both millimeter wave absorption and DC magnetization have been found for all ferrite powders. These materials seem to be quite promising as tunable millimeter wave absorbers and filters, based on their size-dependent absorption. [http://dx.doi.org/10.1063/1.4973597]

I. INTRODUCTION

Ferrites and garnets are mostly ferromagnetic oxides with dielectric and magnetic properties that are useful and important for microwave and millimeter wave (MMW) applications.[1] M-type hexagonal barium ferrite with stoichiometric chemical formula $BaFe_{12}O_{19}$ has been well established as a low cost permanent magnets[2] and high density magnetic recording media.[3] A free space magneto-optical approach has been successfully employed to study ferrites at millimeter wave frequencies.[4] This technique enables the acquisition of precise transmission spectra for determining the dielectric and magnetic properties of both isotropic and anisotropic ferrites from a single set of direct measurements. This paper examines the complex permittivity and permeability of micro- and nano-sized powdered barium and strontium hexaferrites and nano-sized particles of $BaFeO_2$ and $SrFeO_2$ powders in a broadband MMW frequency range from 30 to 120 GHz, encompassing the ferromagnetic resonance

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frequency of these materials. Micro- and nano-sized ferrite powders have been also investigated by DC magnetization at room temperature to assess magnetic behavior and compared with millimeter wave absorption, based on magneto-optical approach.

A. Samples preparation

Ninety-nine percent pure barium ($BaFe_{12}O_{19}$) and strontium ($SrFe_{12}O_{19}$) microferrite powders have been developed by Advanced Ferrite Technology GmbH with the average fine particle size of 3 μm. Barium (99.5% pure) and strontium (99.8% pure) ferrite nanopowders with the same stoichiometric chemical formulas as for microferrites have been developed by Sigma-Aldrich, Inc. The average fine particle sizes of both barium and strontium nanoferrites are reported by the manufacturer to be less than 50 nm. Ninety-nine percent pure barium ($BaFeO_2$) and strontium ($SrFeO_2$) iron oxide nanopowders have were developed by American Elements with the average fine particle size of 60 nm. The samples of different effective specific gravities (densities) have been prepared by uniformly packing ferrite powders in specially fabricated transparent plane parallel Mylar walls containers with the thickness of 12 mm to ensure the accuracy of millimeter wave measurements.

B. Measurements technique

Free space MMW quasi-optical spectroscopy techniques, including technical details and measurement uncertainties analysis, have been successfully employed and presented by several scientific groups.[4–7] Present study presents the characterization of the frequency dependent electromagnetic material properties studied by a free space transmittance millimeter wave spectrometer. High vacuum, high power backward wave oscillators (BWO's) were used as the sources of coherent radiation, continuously tunable from 30 to 120 GHz. A pair of pyramidal horn antennas and a set of polyethylene lenses along the propagation path from the source antenna to the receiver antenna form a Gaussian beam focused onto the sample. A simplified schematic diagram of the MMW spectroscopic system is shown in Fig. 1.

The mathematical relationships between transmittance and reflectance spectra, and refractive and absorption indexes are presented below (see, also Refs. 5 and 6),

$$\begin{aligned}
&T = E\frac{(1-R)^2 + 4R\sin^2\psi}{(1-RE)^2 + 4RE\sin^2(\alpha+\psi)} && R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}\\
&\varphi = \alpha + \arctan\frac{ER\sin^2(\alpha+\psi)}{1 - ER\cos^2(\alpha+\psi)} && + \arctan\frac{k}{n^2 + k^2 + n} - \arctan\frac{k}{n+1}\\
&E = \exp\left(-\frac{4\pi kdf}{c}\right) && \alpha = \frac{2\pi ndf}{c}\\
&n + ik = \sqrt{\varepsilon^*\mu^*} && \psi = \arctan\frac{2k}{n^2 + k^2 - 1}
\end{aligned} \tag{1}$$

where c is the speed of light, n is the refractive index of the sample material, k is the absorption index, μ is the complex permeability of the sample material, ε is the complex dielectric permittivity, T is the transmittance, R is the reflectance, φ is the phase of the transmitted wave, and ψ is the phase of reflected wave. The millimeter wave measurements have been performed in a frequency sweep mode. After obtaining the transmittance spectra of the ferrite materials, optimization procedures were applied to extract the best-fit dielectric and magnetic parameters of the measured samples (see

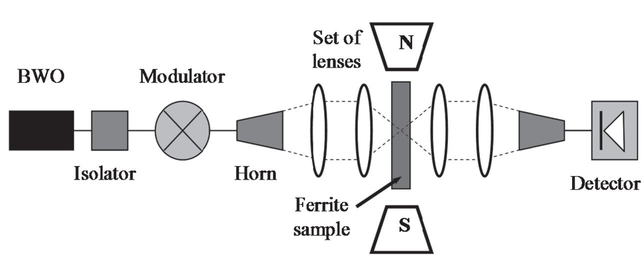

FIG. 1. Schematic diagram of the free-space quasi-optical millimeter-wave spectrometer operated in transmittance mode.

Refs. 4, 7, 8 for more details). Note, that in order to get better transmittance interferogram spectra, the errors can be significantly reduced by imposing the following restrictions on the sample dimensions $D^{1/2} \geq 8\lambda$ and $d \leq 3\lambda$.[4–8] Here, λ is the wavelength, D and d are the cross section and thickness of a plane-parallel specimen, respectively.

II. RESULTS AND DISCUSSION

Transmittance spectra of all barium and strontium ferrite micro- and nano-powdered materials have been recorded in millimeter waves and are shown in Fig. 2. Values of the effective specific gravities are shown in the inset of the graph.

Quite deep (down to opaque) and relatively wide absorption zone in transmittance spectra has been observed for both barium and strontium microferrites. This deep absorption is the natural ferromagnetic resonance that shifts to millimeter wave range due to the strong magnetic anisotropy of barium and strontium ferrites. Experimentally observed width of the absorption line does not reflect the actual width of ferromagnetic resonance line.[4,8] Experimental width is supposed to be broadened because of saturation of the absorption line, the phenomenon, which is well known in optics. For the nano-sized barium and strontium hexaferrite materials as well as barium and strontium iron oxide nanopowders, absorption in MMW due to ferromagnetic resonance is also observed. Periodic structure observed in all transmittance spectra at the frequencies above the zone of deep absorption allows calculation of the dielectric constants of all materials (see, Table I, below).

For the calculation of complex magnetic permeability, Schlömann's equation[9] for partially magnetized ferrites has been used:

$$\mu_{\text{eff}} = 2/3 \left\{ \left[(\omega/\gamma)^2 - (H_{\text{a}} + 4\pi M_s)^2 \right] \Big/ \left[(\omega/\gamma)^2 - H_{\text{a}}{}^2 \right] \right\}^{1/2} + 1/3 \quad (2)$$

where ω is the frequency, H_A is anisotropy field, $4\pi M_S$ is saturation magnetization, γ is the gyromagnetic ratio. Demagnetizing factors are determined by the theory of Schlömann's model for nonellipsoidal bodies.

Best matching has been done by varying three parameters: saturation magnetization, anisotropy and gyromagnetic ratio. Anisotropy can be easy determined by the frequency of the deep absorption zone f_{Res} in the transmittance spectra. Saturation of magnetization strongly depends on absorption level at ferromagnetic resonance. The millimeter wave transmittance data is used to compute the μ_{eff} as above. From this μ_{eff} we have modeled the values of anisotropy field and saturation magnetization. Frequency dependences of complex magnetic permeability for barium and strontium micro- and nano-sized powdered samples are shown in Figs. 3 a, b and Figs. 4 a, b.

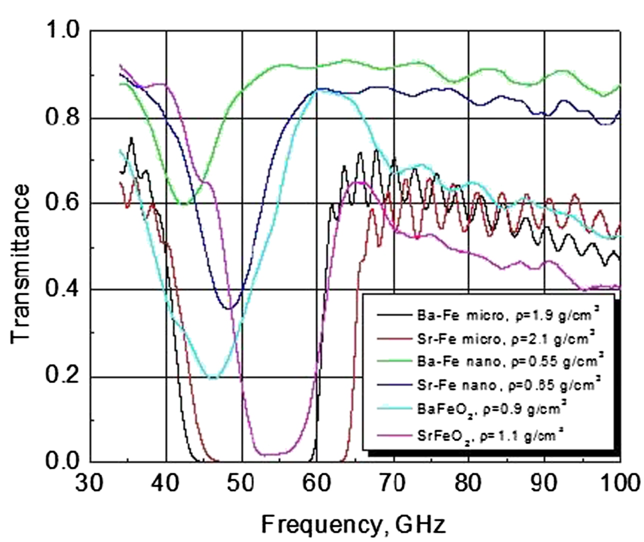

FIG. 2. Millimeter wave transmittance spectra of all barium and strontium ferrite micro- and nano-powdered materials under study.

TABLE I. Dielectric constant and magnetic parameters of micro- and nanoferrite powders.

Sample	ε'	ε"	f_{Res} (GHz)	H_A (kOe)	$4\pi M_S$ (kG) (Magneto-optics)	$4\pi M_S$ (kG) (Magnetic moment)
$BaFe_{12}O_{19}$ micro $\rho = 1.9$ g/cm^3	4.4	0.04	49.2	17.6	1.4	1.56
$SrFe_{12}O_{19}$ micro $\rho = 2.1$ g/cm^3	5.7	0.055	53.1	19.2	1.55	1.69
$BaFe_{12}O_{19}$ nano $\rho = 0.55$ g/cm^3	1.9	0.01	42.5	15.3	0.55	0.65
$SrFe_{12}O_{19}$ nano $\rho = 0.6$ g/cm^3	2.15	0.012	48.2	17.1	0.85	1.02
$BaFeO_2$ nano $\rho = 0.9$ g/cm^3	2.2	0.04	46.1	16.5	0.46	0.58
$SrFeO_2$ nano $\rho = 1.1$ g/cm^3	2.5	0.05	54.5	19.5	0.63	0.84

Both barium and strontium microferrite materials show quite strong anisotropy field of H_A = 17.6 kOe and H_A = 19.2 kOe, respectively. These values are similar to previously reported and known from the literature solid barium and strontium hexaferrite materials.[4,8,10–13] Saturation magnetization of $4\pi M_S$ = 1.4 kG for barium microferrite and of $4\pi M_S$ = 1.55 kG for strontium microferrite are found to be rather low in comparison with previously studied solid barium and strontium hexaferrite materials.[4,8,10–13] Similar behavior has been observed for nanoferrrite powders: relatively strong anisotropy field of H_A = 15.3 kOe and H_A = 17.1 kOe and very weak saturation magnetization of $4\pi M_S$ = 0.55 kG and $4\pi M_S$ = 0.85 kG for barium and strontium nanoferrites, respectively. For of barium and strontium iron oxide nanopowders, relatively strong anisotropy field of H_A = 16.5 kOe and H_A = 19.5 kOe and very weak saturation magnetization of $4\pi M_S$ = 0.46 kG and $4\pi M_S$ = 0.63 kG have also been observed for barium and strontium powders, respectively. Magnetic properties of all powdered materials are shown below in Table I.

Low values of saturation magnetization observed in diluted ferrite materials compared with pure ferrite ceramics can be explained by the presence of a considerable amount of dilution component.[8] Specific gravities (densities) of commercially available pressure-formed (sintered) solid ferrite ceramics and magnets are around 4.7-5.2 g/cm^3 for both barium and strontium ferrites. In the case of pure powdered materials, the presence of the air between micro- and nanoferrite particles can be considered as a dilution component. The values of specific gravities of microferrite powders are found to be about 2.5 times lower in comparison with solid materials. For nanoferrites that difference is even bigger: 5 to 10 times. That dramatic difference in densities of pure solid and powdered

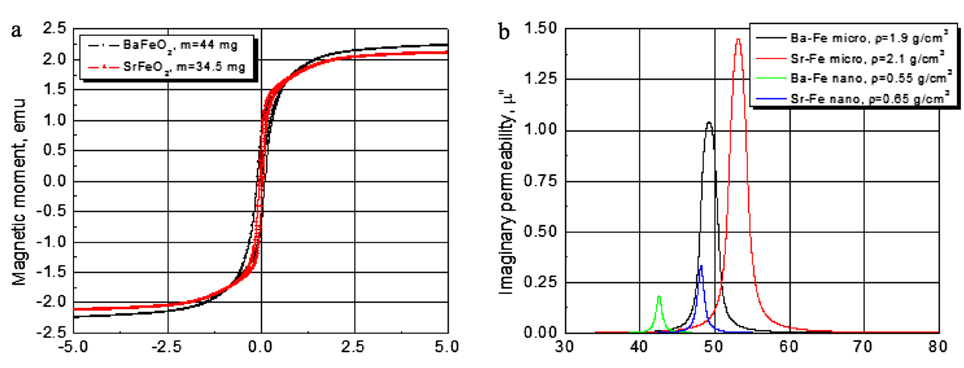

FIG. 3. a. Frequency dependences of real part of magnetic permeability of micro- and nano-sized barium and strontium hexaferrite powders, b. Frequency dependences imaginary part of magnetic permeability of micro- and nano-sized barium and strontium hexaferrite powders.

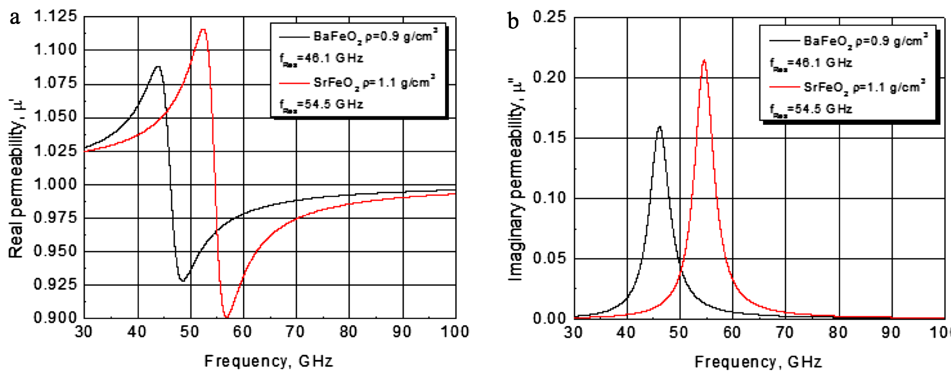

FIG. 4. a. Frequency dependences of real part of magnetic permeability of barium and strontium iron oxide nanopowders, b. Frequency dependences imaginary part of magnetic permeability of barium and strontium iron oxide nanopowders.

ferrite materials explains relatively low MMW absorption at ferromagnetic resonance for nanoferrites (see, Fig. 2.). It has also been shown for nanoparticles that surface spin disorder can result in lower saturation magnetization than is expected for bulk materials.[14,15]

The resonance frequency of nanoferrites is found to be slightly shifted to the lower frequency compare with micro-sized barium and strontium ferrite materials. The resonance phenomena of the ferrites can be described by domain wall motion and spin resonance.[16–18] Domain wall motion resonance is sensitive to both the microstructure of the polycrystalline ferrite (ferrite grain size) and the volume loading of the ferrite (the post-sintering density). The spin rotational relaxation, becoming pronounced in the high frequency range depends only on the volume loading of the ferrite and the dispersion parameters. Commercial milling techniques in magnetic materials technology usually reduce the particle sizes from multi-domain to single domain; however, the particle size of milled powder has a broad distribution of 2 to 5 μm for microferrites. For barium and strontium ferrites, the critical domain diameter is about 1 μm and strong resonances exhibited in the obtained spectra can be accounted for by domain wall motion, as the particle size under study is not sufficiently small to approach single domain characteristics. For nanoferrite powdered materials, the grain size is found to be around 50 nm, i.e. more than ten times less than the domains dimensions (sub-domain size).

Manipulating of the grain sizes and specific gravities of ferrite powders change the ferromagnetic resonance frequency and the level of millimeter wave absorption. Both factors: shift of resonance absorption and level (power) of absorption seem to be very helpful in millimeter wave applications.

Micro- and nano-sized ferrite powders have been further investigated by DC magnetization to assess magnetic behavior and compare with millimeter wave data. Shown in Figs. 5 a, b are hysteresis curves of barium and strontium micro- and nano-sized powdered samples.

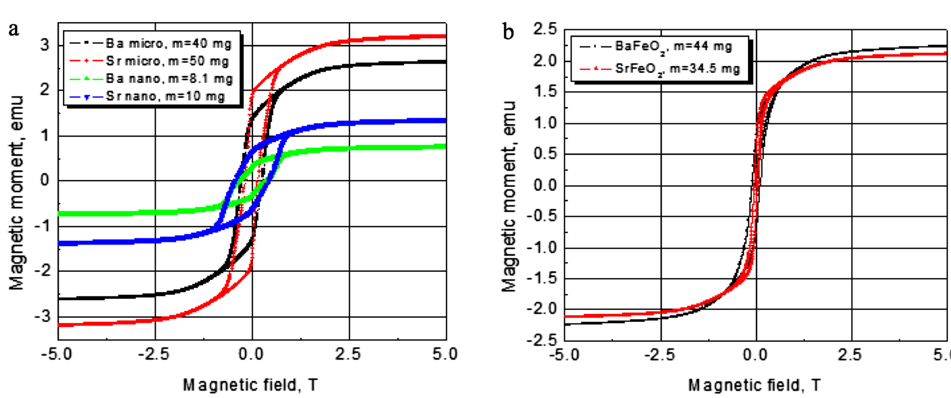

FIG. 5. a. Hysteresis curves of barium and strontium micro- and nano-sized hexaferrite powders, b. Hysteresis curves of barium and strontium iron oxide nanopowders.

Saturation magnetization values, determined from DC magnetization results are found to be slightly higher compare with MMW measurements (~10-15%). It can be attributed to that Vibrating Sample Magnetometer system operates to slightly higher values of densities of powdered samples (~10-15%) due to vibration of the powders. Dielectric constants, resonance frequency anisotropy field, saturation magnetization for all micro- and nano-sized barium and strontium ferrite powders are systemized and presented in Table I.

III. SUMMARY AND CONCLUSION

Micro- and nano-powdered barium ($BaFe_{12}O_{19}$) and strontium ($BaFe_{12}O_{19}$) hexaferrite materials as well as nano-sized barium ($BaFeO_3$) and strontium ($SrFeO_3$) iron oxide powders have been investigated in the millimeter wave range. Broadband transmittance spectra measurements have been performed using a free space, quasi-optical spectrometer. Complex dielectric permittivity and magnetic permeability of micro- and nanoferrites have been calculated from the transmittance spectra.

Absorption zones centered around 49 and 53 GHz have been observed in transmittance spectra of barium and strontium powdered microferrites, respectively, due to natural (spin) ferromagnetic resonance. Pronounced absorption peaks have also been observed at 42.5 and 48.2 GHz for powdered barium and strontium nanoferrites, respectively. Significant absorption peaks have also been observed for barium (46.1 GHz) and strontium (54.5 GHz) iron oxide powders. Magnetic properties, including saturation magnetization and anisotropy field have been determined based on Schlömann's theory for partially magnetized ferrites. Consistency of saturation magnetization determined independently by both millimeter wave absorption and DC magnetization have been found for all ferrite powders.

The presence of air in both micro- and nanoferrite powdered materials has been considered as a dilution component for the pure ferrite. The influence of particle size of ferrites on the ferromagnetic resonance frequency and level of MMW absorption has been found. Tunable millimeter wave absorbers and filters, based on manipulation of the physical properties of micro- and nano-sized powdered ferrite materials, are suggested.

ACKNOWLEDGMENTS

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