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Electric and dielectric study of cobalt substituted Mg–Mn nanoferrites synthesized by solution combustion technique

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Abstract

Cobalt substituted Mg–Mn nanoferrites with formulae $Mg_{0.9}Mn_{0.1}Co_xFe_{2-x}O_4$, $x=0.0$, 0.1, 0.2 and 0.3, have been synthesized for the first time by the solution combustion technique. The effects of Co^{2+} ions on the dc resistivity, dielectric constant and dielectric loss tangent of Mg–Mn nanoferrites at room temperature are presented in this paper. X-ray diffraction confirmed the formation of a single phase spinel structure. Particle size was found to increase, 20.9–23.9 nm, with increasing Co^{2+} concentration. The dc resistivity was increased by two order of magnitude with substitution of Co^{2+} ions while the dielectric constant was found to be decreasing with the increasing concentration of cobalt ions. The value of dc resistivity obtained for $Mg_{0.9}Mn_{0.1}Fe_2O_4$ nanoferrite in our work is greater than the value obtained for the same composition prepared by the conventional ceramic technique. Further, the dielectric constant and dielectric loss tangent were observed to be decreasing with the increase in frequency.

Keywords: C. Dielectric properties; C. Electrical properties; Nanoferrites; X-ray diffraction

1. Introduction

Ferrites constitute an important group of materials with a wide range of applications due to their magnetic properties and low dielectric loss [1]. Spinel ferrites play a significant role in microwave control components such as circulators, isolators and phase shifters [2]. The interesting structural, electrical and magnetic properties of spinel ferrites are governed by the choice of cations along with Fe^{3+} ions and their distribution between the tetrahedral (A) and octahedral (B) sites. Substitution of non-magnetic ions at either site alters the A–A or B–B and A–B interactions, which leads to a significant change in their physical properties.

Nanostructured materials are now being studied intensively due to their novel physicochemical properties and in recent years, nanocrystalline ferrites have attracted much interest because of their promising technological applications. The bulk properties of ferrites change as their dimensions are reduced to nanoscale. Mg–Mn ferrites are widely used in the microwave devices due to their high resistivity and low dielectric loss. Microstructure, electric and magnetic properties of Mg–Mn ferrites are highly sensitive to composition, sintering conditions, grain size, amount of additives and the preparation methodology [3–6].

A large number of methods have been developed to prepare substituted Mg–Mn ferrites such as the standard ceramic technique [7], standard solid state reaction technique [8] and citrate precursor technique [9]. Any co-precipitation process is highly pH sensitive. On the other hand, the sol–gel technique is more sophisticated requiring stringent drying conditions and expensive alkoxide precursors. In addition, any wet-chemical synthesis method calcinations require high temperature to obtain the final product of powder with expected crystal structure [10]. Thus, we have chosen the solution combustion method for the preparation of $Mg_{0.9}Mn_{0.1}Co_x$-$Fe_{2-x}O_4$ nanoferrites, because the complex processes, expensive precursors, low production rates are common problems [11] and also there is no report available on the

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study of mixed Mg–Mn nanoferrites by the solution combustion technique.

Amongst the different possible compositions of Mg–Mn nanoferrites, there is minimum spin canting in the $Mg_{0.9}Mn_{0.1}Fe_2O_4$ nanoferrite. In addition, the low content of Mn^{2+} ions present in this nanoferrite minimizes the possibility of the formation of Mn^{3+} ions. However, the presence of Mn^{3+} ions adversely affects the dc resistivity. Therefore, the composition $Mg_{0.9}Mn_{0.1}Fe_2O_4$ has been used as the basic ferrite [12]. The main desirable characteristics of ferrites for use at high frequencies are high dc resistivity and low dielectric loss. The high dc resistivity reduces eddy current losses at high frequencies; thus preventing the attenuation of signals, a highly desirable property particularly for the weak signals.

Although the electric and dielectric properties of mixed Mg–Mn bulk ferrites have been studied extensively [13–17], the available literature on the substituted Mg–Mn nanoferrites is scarce [18,19]. Therefore, in this paper, a maiden attempt has been made to investigate the effects of Co^{2+} ions on the electrical and dielectric properties of Mg–Mn nanoferrites processed by the solution combustion method.

2. Experimental

$Mg_{0.9}Mn_{0.1}Co_xFe_{2-x}O_4$ where $x=0.0$, 0.1, 0.2 and 0.3 were synthesized via the solution combustion technique. The chemical reagents used in this work were ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), manganese nitrate ($Mn(NO_3)_2 \cdot 4H_2O$) and glycine (NH_2CH_2COOH) as a fuel. In a stoichiometric ratio ferric nitrate, cobalt nitrate, magnesium nitrate, manganese nitrate and glycine were mixed in distilled water to obtain precursor solutions. The obtained precursor solution is then heated on a hot plate, at 40 °C with constant stirring, till the solution starts to burn with release of lots of heat. The obtained powder samples were calcined at 500 °C for 4 h. The calcined powders obtained for all the nanoferrites were then pressed into pellets. The prepared samples were sintered at 700 °C for 4 h. The single-phase nature of the prepared samples was checked by X-ray diffraction (XRD) studies, which were made by Cu-K_α radiation of wavelength 1.54 Å using Rigaku-Denki X-ray diffractometer and the microstructures of the fractured surfaces of the samples were studied using QUANTA 250 FFID 9393. The dc resistivity of the samples at room temperature was measured by using a Keithley 2611 system and dielectric studies were made by WAYNER KERR 6500 impedance analyzer.

3. Results and discussions

3.1. Structural analysis

The X-ray patterns of the synthesized $Mg_{0.9}Mn_{0.1}Co_x$-$Fe_{2-x}O_4$, $x=0.0$, 0.1, 0.2 and 0.3, nanoferrites are shown in Fig. 1. The XRD patterns of all the samples reveal a typical cubic spinel structure. The particle size of the nanocrystalline samples was calculated from the broadening of the X-ray diffraction peaks using the

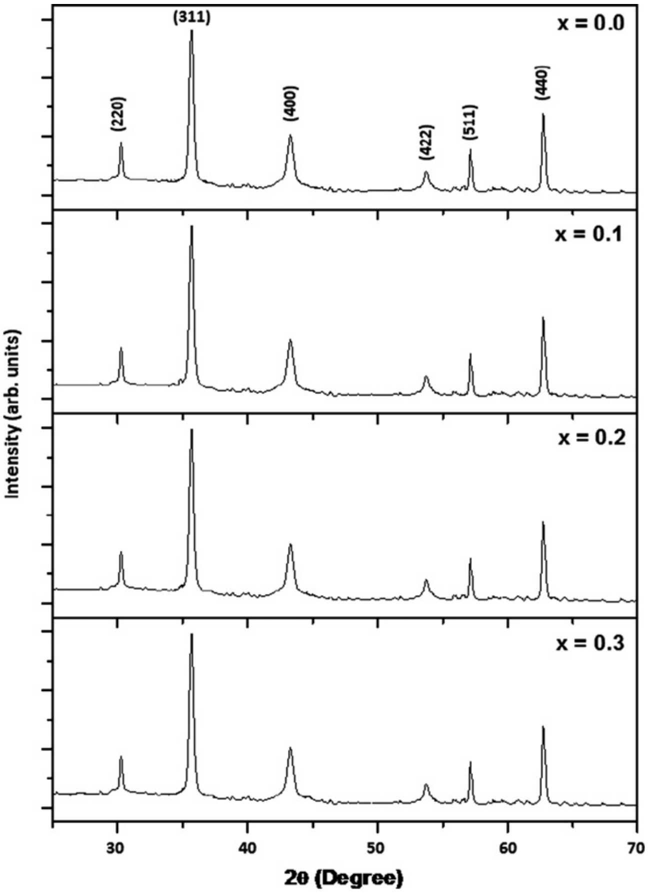

Fig. 1. X-ray diffraction patterns of $Mg_{0.9}Mn_{0.1}Co_xFe_{2-x}O_4$ nanoferrites.

Table 1
Variation of particle size, lattice parameter and X-ray density.

Ferrite composition	Particle size, D (nm)	Lattice parameter, a (Å)	$d_{x\text{-}ray}$ (g/cm^3)
$Mg_{0.9}Mn_{0.1}Fe_2O_4$	20.9	8.35	4.64
$Mg_{0.9}Mn_{0.1}Co_{0.1}Fe_{1.9}O_4$	22.6	8.36	4.63
$Mg_{0.9}Mn_{0.1}Co_{0.2}Fe_{1.8}O_4$	23.8	8.37	4.62
$Mg_{0.9}Mn_{0.1}Co_{0.3}Fe_{1.7}O_4$	23.9	8.39	4.59

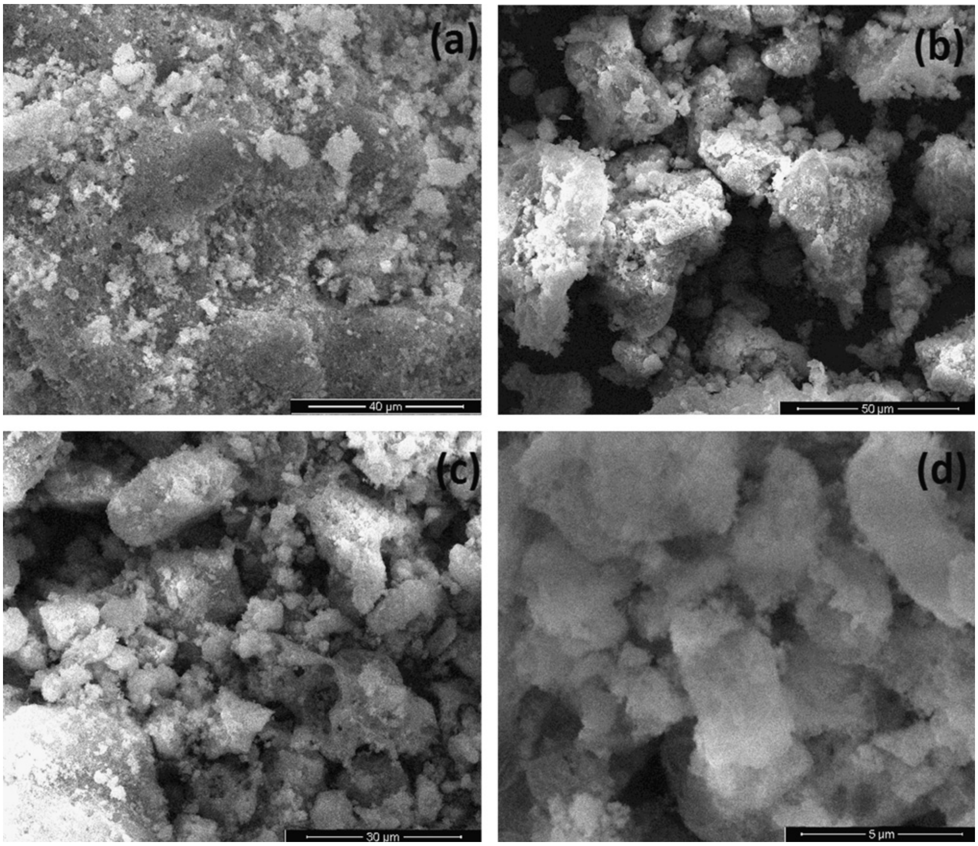

Fig. 2. SEM images of $Mg_{0.9}Mn_{0.1}Co_xFe_{2-x}O_4$ nanoferrites: (a) $x=0.0$, (b) $x=0.1$, (c) $x=0.2$ and (d) $x=0.3$.

Debye–Scherrer equation for the Lorentzian peak [20]

$$D=\frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where D is the particle size, β is the full width at half maximum (FWHM) of the (311) peak, λ is the X-ray wavelength (1.54 Å) and θ is the angle of diffraction. The lattice parameter (a) of the nanoferrites is calculated by using the relation [21]

$$a=\frac{\lambda}{2\sin\theta}\times\sqrt{h^2+k^2+l^2} \tag{2}$$

The X-ray density is determined by using the following relation [21]:

$$\rho_{x\text{-}ray}=\frac{8M}{Na^3} \tag{3}$$

where M is the molecular weight of the sample, N is the Avogadro number and a is the lattice constant.

Table 1 shows the particle size, lattice parameter and X-ray density for all the nanoferrites. It is clear from the table that the particle size and lattice parameter increases with the increase in Co^{2+} ions. It is well acknowledged that the divalent Co^{2+} ions have a strong octahedral site (B-site) preference [2]. The Co^{2+} ions replace an equivalent number of Fe^{3+} ions from the B-site. Further, as the radius of Co^{2+} ions (0.082 nm) is bigger than that of the Fe^{3+} ions (0.067 nm) thus, Co^{2+} ions enter into the B-site which swells the lattice and then enlarges the lattice parameter. In order to confirm the homogeneity of the samples scanning electron micrographs (SEM) were taken. Fig. 2 shows the typical scanning electron micrographs for Co^{2+} substituted Mg–Mn nanoferrites.

3.2. Variation of dc resistivity (ρ) with composition

The variation of dc resistivity (ρ) at room temperature as a function of Co^{2+} concentration in $Mg_{0.9}Mn_{0.1}Co_xFe_{2-x}O_4$ nanoferrites is shown in Fig. 3. The resistivity has been observed to increase with increase in Co^{2+} ions. The observed variations in resistivity can be explained by Verwey's hopping mechanism [22]. According to Verwey, the electronic conduction in ferrites is mainly due to hopping of electrons between ions of the same element present in more than one valence state, distributed randomly over crystallographically equivalent lattice sites [17]. Ferrites structurally form cubic close packed oxygen lattices with the cations at the octahedral (B) and the tetrahedral (A) sites. It is well known that Fe^{3+} ions are moderately reduced to Fe^{2+} ions during sintering of ferrites, which results in the formation of a small amount of Fe^{2+} ions in these samples [23]. Also, a small fraction of Mn^{2+} ions reacts with Fe^{3+} ions to form Mn^{3+} and Fe^{2+} as per the

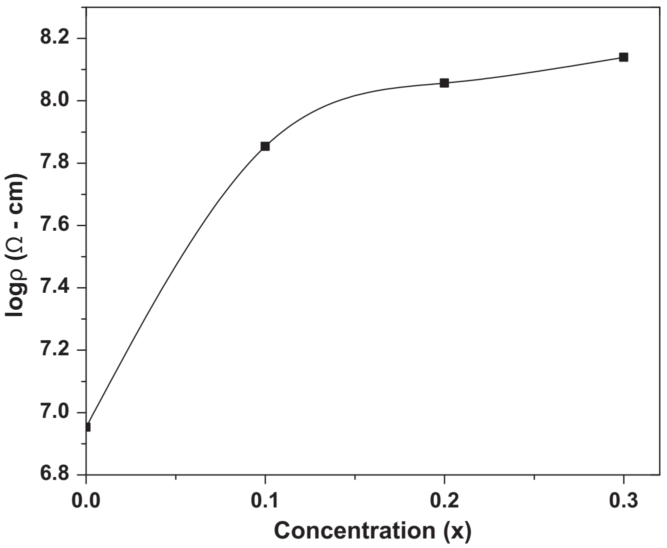

Fig. 3. Variation of dc resistivity with composition for $Mg_{0.9}Mn_{0.1}Co_xFe_{2-x}O_4$ nanoferrites.

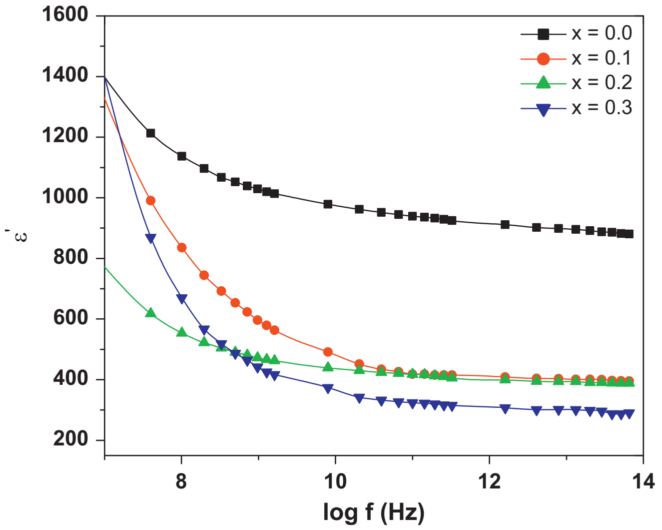

Fig. 4. Variation of dielectric constant with frequency for $Mg_{0.9}Mn_{0.1}Co_xFe_{2-x}O_4$ nanoferrites.

following reaction:

$$Mn^{2+} + Fe^{3+} \rightarrow Mn^{3+} + Fe^{2+} \quad (4)$$

The presence of Fe^{2+}–Fe^{3+} and Mn^{2+}–Mn^{3+} ion pairs of the same element but of different valencies present at the equivalent crystallographic sites results in an increase of conduction due to hopping of electrons in $Mg_{0.9}Mn_{0.1}Fe_2O_4$ ferrites [12]. Since cobalt ions have a tendency to occupy octahedral sites, the addition of Co^{2+} ions in Mg–Mn ferrites directly reduces the number of B-site Fe^{3+} ions thus, limits the degree of conduction by blocking Verwey's hopping mechanism resulting in an increase in resistivity. Further, the value of dc resistivity obtained for $Mg_{0.9}Mn_{0.1}Fe_2O_4$ nanoferrite in this work is greater than the value obtained for the same composition prepared by the conventional ceramic technique [7,17].

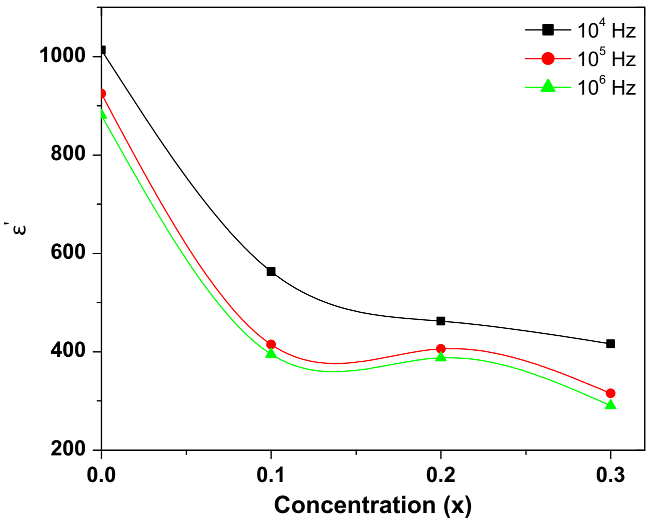

Fig. 5. Variation of dielectric constant with composition at different frequencies for $Mg_{0.9}Mn_{0.1}Co_xFe_{2-x}O_4$ nanoferrites.

3.3. Variation of dielectric constant

Fig. 4 displays the variation of dielectric constant as a function of frequency, 10^3–10^6 Hz, at room temperature for all the nanoferrites. It is seen that the dielectric constant decreases gradually with the increase in frequency and is slightly frequency independent at higher frequencies. This can be explained on the basis of Koop's theory [24], based on the Maxwell–Wagner model for the inhomogeneous double structure [25,26]. According to this model the dielectric structure was supposed to be composed of well conducting grains separated by the poorly conducting grain boundaries [27]. The electrons reach the grain boundary through hopping and if the resistance of grain boundary is high enough, electrons pile up at the grain boundaries and produce polarization. The decrease in dielectric constant with the increasing frequency is because of the fact that the space charge carriers requires a finite time to line up their axes in the direction of an applied alternating field [28]. Thus, if the frequency of the applied field increases, the electrons reverse their direction of motion more often. This decreases the probability of electrons reaching the grain boundary and as a result polarization decreases resulting thereby in the decrease of dielectric constant with an increase in frequency. Fig. 5 shows the variation of dielectric constant with composition. It is evident that the dielectric constant decreases with the increase of Co^{2+} ions concentration. The decrease of dielectric constant with Co^{2+} ions substitution can be explained on the basis of mechanism of polarization process in ferrites, which is similar to that of the conduction process. The whole polarization in ferrites is mainly contributed by the space charge polarization, which is

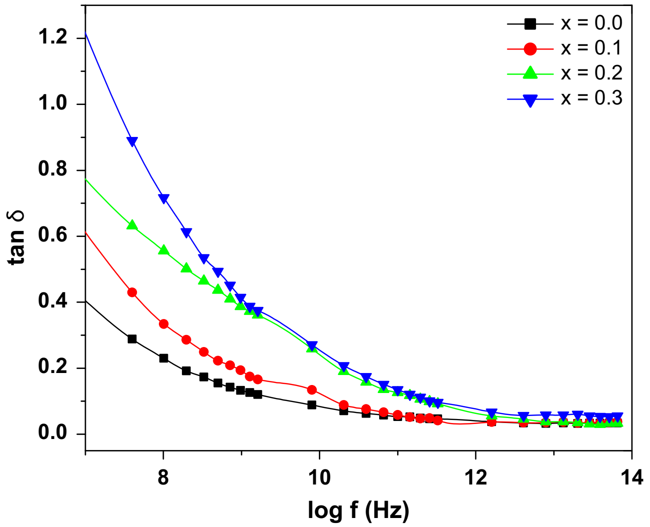

Fig. 6. Variation of dielectric loss tangent with frequency for $Mg_{0.9}Mn_{0.1}Co_xFe_{2-x}O_4$ nanoferrites.

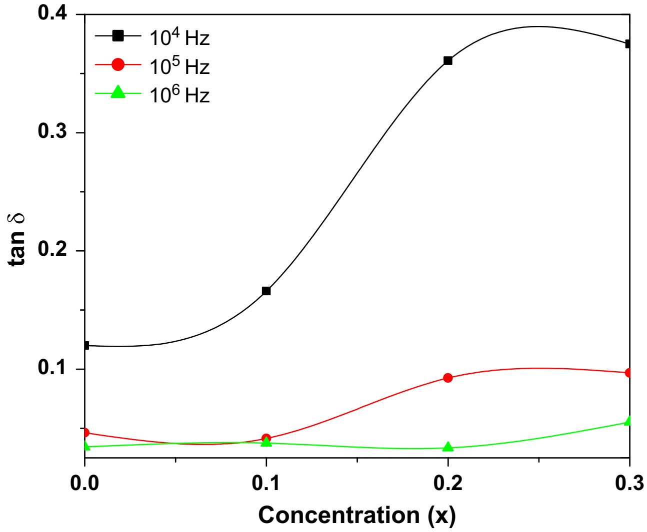

Fig. 7. Variation of dielectric loss tangent with composition at different frequencies for $Mg_{0.9}Mn_{0.1}Co_xFe_{2-x}O_4$ nanoferrites.

governed by the number of space charge carriers, the conductivity in materials [29] and hopping exchange of the charges between two localized states. The addition of Co^{2+} ions reduces the iron ions on B-sites, which is mainly responsible for both space charge polarization and hopping exchange between the localized states. Therefore, increase of Co^{2+} ions content causes a decrease in the polarization, which is accomplished by a decrease of dielectric constant. Further, the value of dielectric constant obtained for $Mg_{0.9}Mn_{0.1}Fe_2O_4$ nanoferrite in this work is comparable to value obtained for the same composition prepared by the conventional ceramic technique [7,17,30].

3.4. Variation of dielectric loss tangent

The variations in dielectric loss tangent versus frequency for $Mg_{0.9}Mn_{0.1}Co_xFe_{2-x}O_4$, $x=0.0$, 0.1, 0.2 and 0.3, nanoferrites are shown in Fig. 6. The decrease in dielectric loss tangent with the increase in frequency is in accordance with Koop's phenomenological model [24]. The dielectric loss tangent arises, if the polarization lags behind the applied altering field and is caused by the presence of impurities and structural inhomogeneities. Fig. 7 shows the variation of dielectric loss tangent with composition. In the present study tan δ studied at room temperature, up to 10^6 Hz, is in the range 10^{-1}–10^{-2}. The low dielectric loss tangent values obtained in the present work is therefore attributed to more structurally perfect and homogeneous ferrites processed by the solution combustion technique.

4. Conclusions

Co^{2+} substituted Mg—Mn nanoferrites were prepared by the solution combustion technique. The particle size, lattice parameter and dc resistivity were increased with the increase in cobalt content. The very low values of the dielectric loss tangent even at high frequency indicate that present nanoferrites have great potential for microwave applications.

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