Materials Science-Poland, Vol. 22, No. 3, 2004

Effect of double substituted *m*-barium hexaferrites on microwave absorption properties

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The complex permeability (μ_r^*) and permittivity (ε_r^*) of radar absorbing materials (RAMs) play a key role in determining the reflection and attenuation properties of incident microwaves. Their real (μ' and ε') and imaginary (μ'' and ε'') components and relationship with microwave absorbing properties have been investigated in the frequency range 8–16 GHz for doped M-type barium hexaferrites in polychloroprene (CR) matrices. Individual and simultaneous substitutions of Fe^{3+} ions by Co^{2+}, Ti^{4+}, and Mn^{3+}, and of Ba^{2+} ions by La^{3+} and Na^+ make possible the use of these materials as RAMs, due to frequency dependence of μ_r^* of hexaferrite, responsible for the location of its natural resonance. A double substitution of Ba^{2+} and Fe^{3+} (LaNaCoTiMn-BaHF) resulted in the best microwave absorption (99.9%) at the frequency of 15 GHz.

Key words: *microwave absorbing materials; doped ferrites; composites; waveguide*

1. Introduction

The reduction of military platform radar cross-sections has been a major challenge since the second world war. Possible solutions for reducing the radar signatures of targets include the design of objects with small cross sections or the use of radar absorbing materials (RAMs) for covering the metallic surface. In this way, microwave absorbers have been widely used to prevent or minimize electromagnetic reflections from large structures such as aircraft, ships and tanks, and also to cover walls of anechoic chambers [1–4].

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The main problem in designing a magnetic absorber is related to the choice of the material, preferentially with control over some magnetic and dielectric properties, such as permeability (μ), permittivity (ε) and the dissipation factor (tanδ) [5]. The use of hexaferrites as RAMs has been widely cited in literature during the last two decades. The choice of polychloroprene (CR) as the material for the elastomeric matrix was due to its favourable properties, including excellent resistance to ageing, sea water and flame retardant behaviour, which allows using it for naval applications [6–8].

A basic formula of hexagonal ferrites is $MeFe_{12}O_{19}$, where Me is a divalent metal such as Ba or Sr. The substitution of Fe^{3+} ions by Co^{2+}, Ti^{4+}, and Mn^{3+} makes possible the use of these materials as RAMs in the frequency range from 8 to 16 GHz. In the same way, individual or simultaneous substitution of Ba^{2+} ions by La^{3+} and Na^{+} can also change the magnetic behaviour of these materials, allowing their application as RAMs at various frequencies [3, 4].

2. Experimental

Synthesis and characterization of ferrimagnetic materials. In this work, M-type barium hexaferrites of the basic composition $BaFe_{12}O_{19}$ (BaHF) were synthesized by the mixing oxide route. In order to obtain the composition $BaFe_{10.2}Co_{0.85}Ti_{0.85}Mn_{0.1}O_{19}$, referred to as CoTiMn-BaHF, Fe^{3+} ions were partially replaced by Co^{2+}, Ti^{4+} and Mn^{3+} ions. In the same way, Ba^{2+} was substituted by La^{3+} and Na^{+}, resulting in the composition $Ba_{0.8}La_{0.10}Na_{0.10}Fe_{12.0}O_{19}$ (LaNa-BaHF). The composition $Ba_{0.8}La_{0.10}Na_{0.10}Co_{0.85}Ti_{0.85}Mn_{0.1}Fe_{10.2}O_{19}$ (LaNa CoTiMn-BaHF), resulting from the simultaneous substitution of Fe^{3+} and Ba^{2+}, was also prepared. Raw materials used for obtaining the stoichiometric mixtures, with 99.9% purity, were cobalt oxide (CoO), barium carbonate ($BaCO_3$), iron oxide (Fe_2O_3), sodium carbonate (Na_2CO_3), lanthanum hydroxide ($La(OH)_3$), manganese oxide (Mn_2O_3), and titanium oxide (TiO_2) [6, 8–10].

A small amount of $La(OH)_3$ present in barium hexaferrite is known to form an anisotropic magnetoplumbite structure with optimum ferromagnetic properties [10].

Mixing was carried out in a ball mill for 24 h, using Y-TZP as the milling media. After mixing, the slurry was dried at 100 °C. All samples were calcined in air at 1200 °C for 2 h, except LaNaCoTiMn-BaHF, which was calcined for 2½ h.

The powders obtained were characterized by X-ray Diffraction (XRD, Brucker-AXS D5005), Scanning Electron Microscopy (SEM, Leica S440), and Vibration Sample Magnetometry (VSM 4500, EG & G Princeton Applied Research) [8].

Preparation of composites with polychloroprene by bulk process. The composite specimens for measuring microwave absorber properties were prepared by mixing, molding and curing mixtures of barium hexaferrite powders with polychloroprene (CR, neoprene W of Du Pont, density 1.21 g/cm^3) and the additives of vulcanization. This resulted in a barium hexaferrite:polychloroprene concentration of 80:20 by weight. The processing was carried out in a Berstorff mill at room temperature, with velocities of 22 and 25 rpm (back and forward). Vulcanized samples 4.00×4.00×0.15 cm^3 in size were obtained by compression molding in a hydraulic press at 150 °C and 6.7 MPa. The curing times were determined from the data obtained with a Monsanto Rheometer TM100 [8].

*Measurement system for transmission/reflection. P*roperties of the microwave absorber were evaluated in the frequency range of 8–16 Ghz using the Transmission/Reflection method (T/R) [11], after tightly inserting the vulcanized samples into a rectangular waveguide. Using the data obtained from each of the measured samples (ε', ε'', μ' and μ''), expected values of the microwave reflectivity level were determined by measuring variations of the reflection loss (dB) versus frequency (GHz) using an HP 8510 network analyzer system [8, 12].

In microwave absorption measurements a rectangular waveguide was used as the transmission/reflection medium. The waveguide sample holder (22.86×10.16 mm^2) was fabricated by cutting the flange from an X-band standard waveguide 8 mm in length. The measurement calibration procedure adopted typical waveguide standards: a $\lambda_{gm}/4$ off-set ("line"), a short circuit ("reflect"), and a "thru" measurement (where λ_{gm} is the guided wavelength at the geometric mean frequency for the X-band). In order to avoid undesirable resonances during the measurements, the thickness of the samples was limited to 1.0–2.0 mm.

3. Results

Figure 1 shows the hysteresis curves for doped (LaNa-BaHF, CoTiMn-BaHF, LaNaCoTiMn-BaHF) and undoped (BaHF) barium hexaferrites.

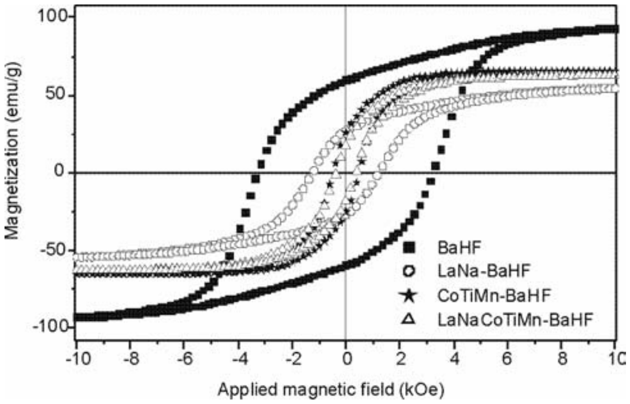


Fig. 1. Hysteresis curves for doped and undoped barium hexaferrites

As can be seen, the doped hexaferrites in comparison to the undoped ones show a reduction in the coercive field (H_c). A high value of H_c for undoped hexaferrite (3.26 kOe), in addition to its high anisotropy (1350×10^3 A·m^{-1}), places this material among magnetically hard ones. On the other hand, small values of H_c for CoTiMn-BaHF (0.50

kOe), LaNa-BaHF (1.18 kOe), and LaNaCoTiMn-BaHF (0.40 kOe), in addition to smaller values of their anisotropy, classify these materials as magnetically soft. Consequently, the addition of dopants is responsible for the reduction of the magnetic hardness and magnetization of barium hexaferrites. Among the doped barium hexaferrites, La-NaBaHF shows the highest magnetic hardness.

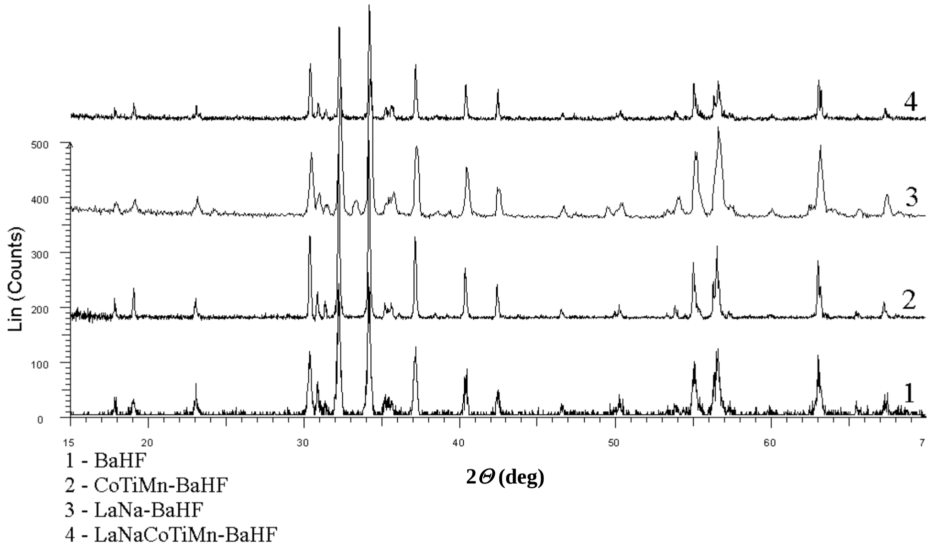
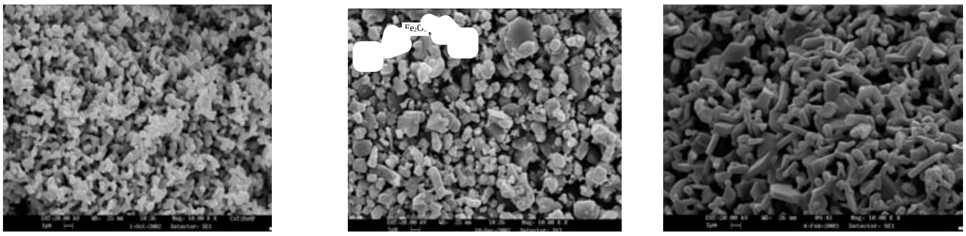


Fig. 2. X-Ray diffraction curves for doped and undoped barium hexaferrites

Figure 2 shows X-ray diffraction curves for the doped and undoped hexaferrites, in agreement with those given in JCPDS Card No. 43-0002, confirming the magnetoplumbite structure for these materials. The peaks for the doped barium hexaferrites appear at the same positions as the ones for the undoped hexaferrite, but with different intensities. According to JCPDS Card No. 33-0664, hematite (Fe_2O_3) is shown to be present besides the hexaferrite phase for the LaNa-BaHF composition, although lanthanium orthoferrite is reported in literature to be the second phase [13]. The presence of this second phase can be attributed to differences in the sizes of Ba^{2+}, Na^{+}, and La^{3+} ions. In LaNa-BaHF, two cations of Ba^{2+} (1.34 Å) are substituted by one La^{3+} (1.05 Å) and one Na^{+} (0.97 Å). In this way, the introduction of La^{3+} and Na^{+} changes the interatomic distances and super-exchange interactions, which results in precipitation of hematite or lanthanium orthoferrite as the second phase.

The presence of hematite as the second phase in the formation of LaNaBaHF can be responsible for the largest reduction in magnetization.

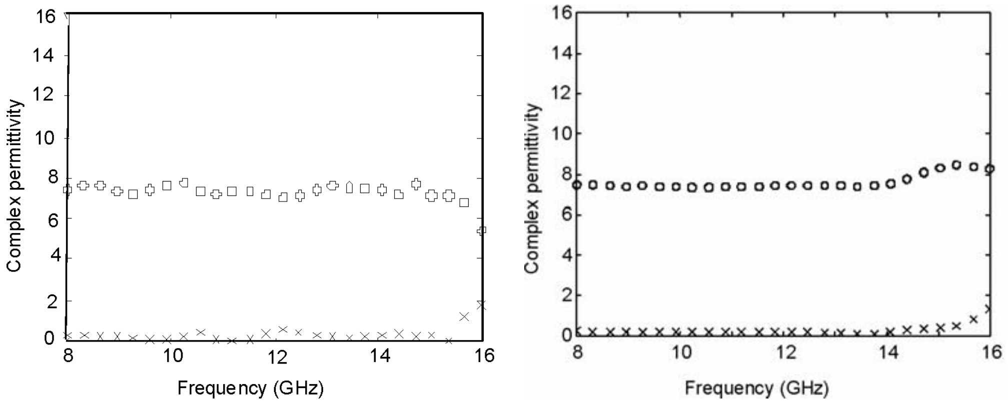
SEM micrographs of the doped ferrites are shown in Figure 3. The presence of the second phase (hematite) in the form of small particles is observed only in Figure 3b, for the LaNa-BaHF composition, which is in accordance with X-Ray results. The presence of larger hexagonal particles, visible in Figure 3c, can result from longer calcination times.



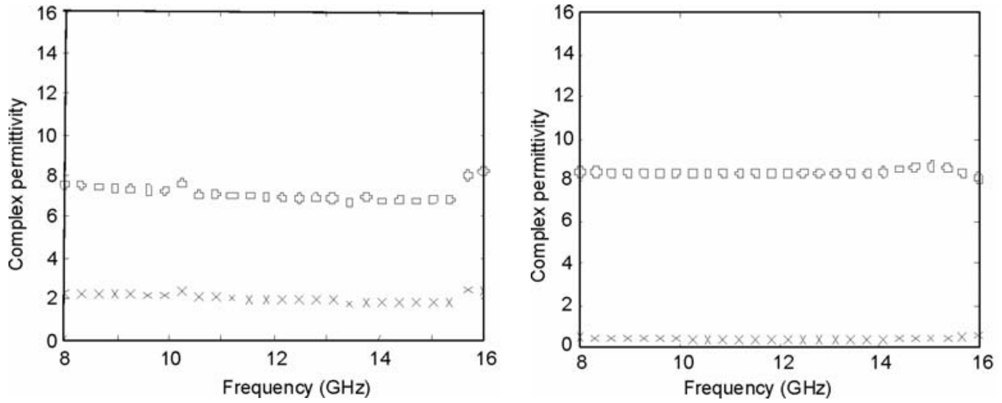
a) CoTiMn–BaHF b) LaNa–BaHF c) LaNaCoTiMn–BaHF

Fig. 3. SEM images of doped barium hexaferrites

The frequency dependencies of real and imaginary parts of the complex permittivity (ε' and ε'') and complex permeability (μ' and μ'') for barium hexaferrite:polychloroprene composites are shown in Figures 4 and 5.



a) BaHF:CR b) CoTiMn-BaHF:CR

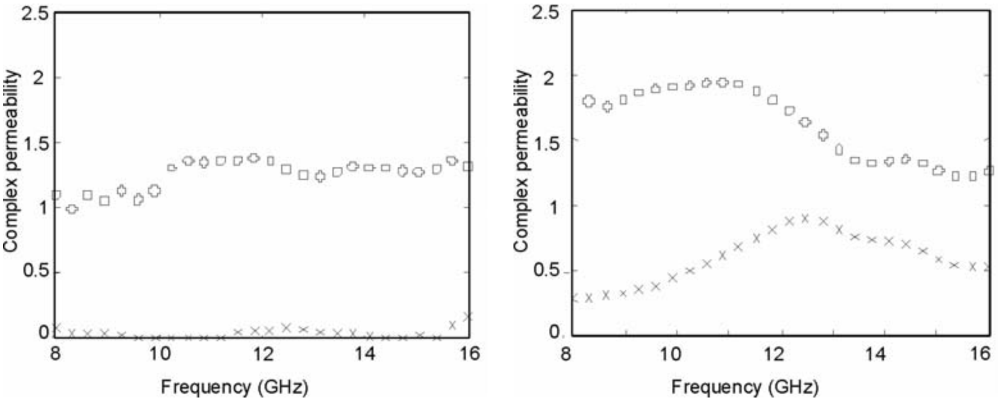


c) LaNa-BaHF:CR d) LaNaCoTiMn-BaHF:CR

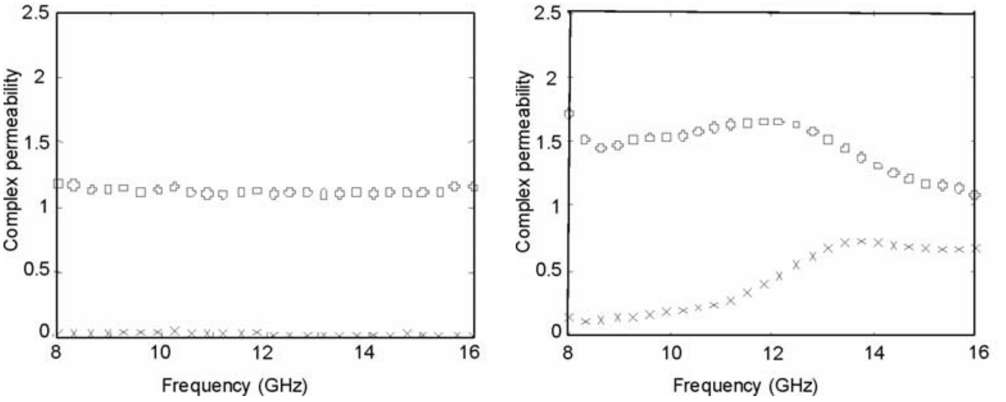
Fig. 4. Dispersion of the real (ε', 0) and imaginary parts (ε'', X) of the complex permittivity of barium hexaferrite:polychloroprene composites

The permeability of hexaferrite:polymer composites depends on the composition of the hexaferrite, the nature of the polymer, and the operation frequency [14].

Dielectric properties of polycrystaline hexaferrite:polychloroprene composites result from the heterogeneous structure of hexaferrites, which may contain low-conductivity grains separated by higher-resistivity grain boundaries as proposed by Koops [15].



a) BaHF:CR b) CoTiMn-BaHF

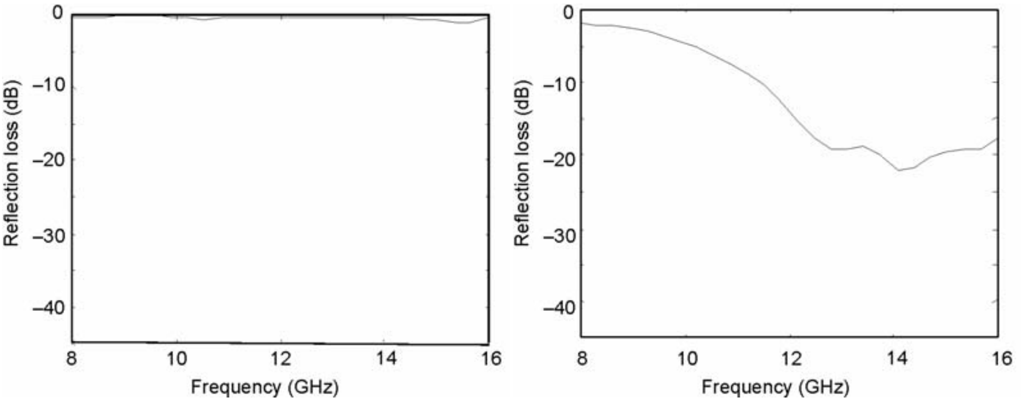


c) LaNa-BaHF d) LaNaCoTiMn-BaHF

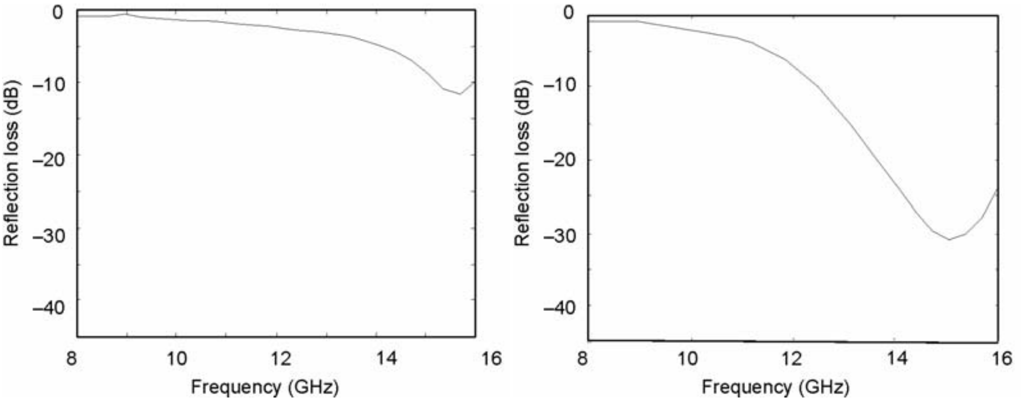
Fig. 5. Dispersion of real (μ', 0) and imaginary parts (μ'', X) of the complex permeability of doped barium hexaferrite:polychloroprene composites

As seen in Figure 5, addition of dopants results in changes in magnetic resonance as compared to the composite BaHF:CR (Fig. 5a), which is illustrated by variations in the values of μ' and μ''.

Reflection losses of doped and undoped hexaferrites are shown in Figure 6. Ferrites absorb microwaves at different frequencies due to various interactive loss mechanisms, mainly related to magnetization. The greatest microwave absorption for doped barium hexaferrite:polychloroprene composites can be attributed to the reduction of H_c and increase in permeability values as compared to BaHF:CR which does not absorb in the analyzed frequency range (it absorbs at 45 GHz). The composite LaNa-BaHF:CR shows the poorest microwave absorption, which can be attributed to the presence of hematite. The presence of this second phase may be responsible for the disappearance of magnetic resonance and for the increase in the values of ε'' (Fig. 4c). The CoTiMn-BaHF:CR composite (80:20) exhibits a reflection loss smaller than –10 dB in the frequency range of 12–16 GHz, whereas the LaNaCoTiMn BaHF:CR composite exhibits the highest microwave absorption (99.9 %) at 15 GHz.



a) BaHF:CR b) CoTiMn-BaHF:CR



c) LaNa-BaHF:CR d) LaNaCoTiMn-BaHF:CR

Fig. 6. Reflection loss (dB) of doped barium hexaferrite:polychloroprene composites, thickness 1.5 mm

4. Conclusions

Addition of dopants resulted in a reduction in the coercive field and magnetization of barium hexaferrites. Different composites of doped barium hexaferrites:polychloroprene obtained from the substitution of Fe^{3+} and Ba^{2+} can be prepared to be used as microwave absorbers in the frequency range of 8–16 GHz, according to the natural ferrimagnetic resonance illustrated by variations in μ' and μ''.

Dual substitution of Ba^{2+} and Fe^{3+}, which occurs in the composite 80:20 of LaNaCo-TiMnBaHF:CR, produces a better RAM at 15 GHz, as compared to individual substitutions, with the reflection loss of –30 dB (microwave absorption of about 99.9 %).

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Received 16 June 2004
Revised 30 July 2004