Electromagnetic properties of $LaCa_3Fe_5Oi_2$ in the microwave range

Electromagnetic properties of $LaCa_3Fe_5O_{12}$ in the microwave range

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Abstract. The X-ray diffraction analysis of the $LaCa_3Fe_5O_{12}$ ferrite (lanthanum ferrite) prepared through high-temperature synthesis via ceramic technology was performed. It was found that ferrites belong to tetragonal system. The electromagnetic response from a flat layer of the composite based on this material under electromagnetic radiation in the frequency range of 0.01–18 GHz was investigated. It is shown that the developed material effectively interacts with electromagnetic radiation. The interaction effectiveness is directly proportional to ferrite concentration. Increased concentration of ferrite leads to growth of the reflection coefficient due to high conductivity of the material and visible decrease in the transmission coefficient in the frequency range of 4–14 GHz.

1. Introduction

A new class of ferrites, lanthanum ferrites, has been intensively studied in the last years. Ferrites of the type $LaM_3Fe_5O_{12}$ (M_3=Mg, Ca, Sr), $TmM_3Fe_5O_{12}$ (M_3=Ca, Sr, Ba), $Tm_2M_3Fe_5O_{12}$ (M_3=Li, Na, K), $ErMFe_2O_{5,5}$ (M–Ca, Sr, Ba) and $YbSrFe_2O_{5.5}$ are distinguished from other ferrites in this class. Their peculiarity lies in the fact that they contain rare earth metals which determine their new unique properties. They are promising for practical application due to a large number of studies of their properties [3–7].

The calorimetric study of the specific heat of the $LaM_3Fe_5O_{12}$ (M_3 = Mg, Ca, Sr) ferrite was carried out in [3]. Synthesis and X-ray analysis of $TmM_3Fe_5O_{12}$ (M_3 = Ca, Sr, Ba) and $Tm_2M_3Fe_5O_{12}$ (M_3 = Li, Na, K) compounds are described in [4,5]. The X-ray study of the double ferrite $ErMFe_2O_{5,5}$ (M–Ca, Sr, Ba) was carried out in [6]. In addition to the X-ray analysis, thermodynamic and electrical properties of $YbSrFe_2O_{5.5}$ and $YbBaFe_2O_{5.5}$ ferrites were studied in [7].

The $LaCa_3Fe_5O_{12}$ ferrite (lanthanum ferrite) is of particular interest. Due to high electrical conductivity and oxygen permeability of the ferrite, solid solutions are promising materials for producing gas electrodes and sensors, and SOFC. They are also used as catalysts for complete oxidation of gas cleaning reactions.

Since the requirements for multifunctionality of the developed materials are growing due to advances in modern science and technology, it is important to assess the result of interaction of the lanthanum ferrite-based composite with electromagnetic radiation (EMR) in a microwave range. The

effectiveness of the interaction between this composite with EMR has not been studied, although it is known that ferrites are widely used as radar absorbing materials for environmental protection of biological objects against harmful effects, for prevention of information leak through radio-frequency channels, noise elimination by means of communication, stealth-technology, etc. [8–12].

The aim of this research is to carry out the X-ray analysis of $LaCa_3Fe_5O_{12}$, to prepare samples and to study the electromagnetic response from a flat layer of the composite based on this material under electromagnetic radiation in the frequency range of 0.01–18 GHz.

2. Experimental procedure

The $LaCa_3Fe_5O_{12}$ ferrite was obtained by high-temperature synthesis via ceramic technology at different temperatures in three stages [13]. The raw material (lanthanum oxide, ferric oxide (III), calcium carbonate) were weighed to the fourth decimal point and stirred. The mixtures were thoroughly grinded and then fired in a furnace, first at 800 ^{0}C for 10 hours, then at 1300 ^{0}C for 10 hours, and finally at 400 ^{0}C for 20 hours. The X-ray analysis of the $LaCa_3Fe_5O_{12}$ ferrite powder was performed using the ARL X'TRA diffractometer (Thermo Fisher Scintific).

Radiophysical measurements of the samples were carried out in the frequency range from 0.01 to 4.00 GHz with the analog meter of the modulus of the transmission transmission coefficient and the voltage standing wave ratio (VSWR) P2M-04 (home made) by "Micran", and the vector network analyzer E8363V (Agilent technologies) was used to perform measurements in the frequency range from 4.00 to 18.00 GHz.

The samples for radiophysical measurements were made of the ferrite powder under study and epoxy resin in the form of disks with an outer diameter of 7 mm and an internal diameter of 3 mm. The thickness of the disk ranged from 0.5 to 2 mm. The disk mold was filled with 3 g of ferrite and 3 g of the binding agent per 30 wt%, 50 wt% and 65 wt% concentration of the substance.

3. Experimental Results

3.1. X-ray diffraction analysis (XRD)

A typical diffraction pattern for the material under study is presented in Figure 1. These diffraction patterns were used for XRD.

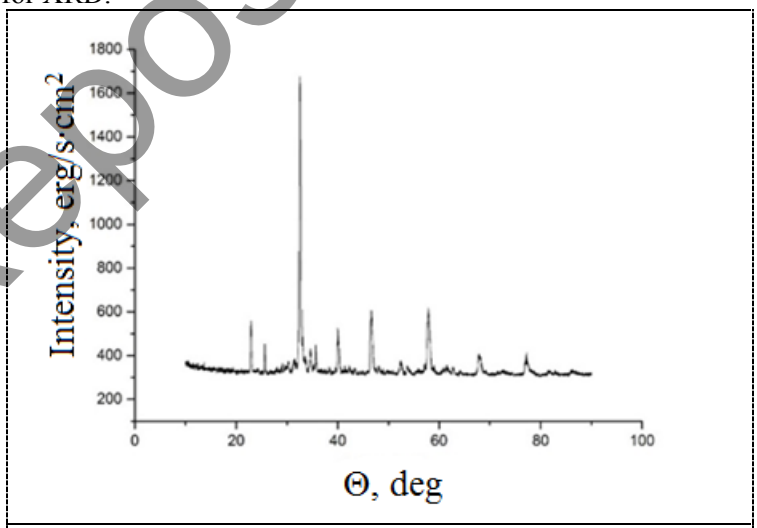

Figure 1. Dependence of the intensity on the scattering angle.

The results of XRD analysis of the $LaCa_3Fe_5O_{12}$ powder are shown in Table 1.

Table 1. Lattice parameters of the $LaCa_3Fe_5O_{12}$ ferrite.

Type of the system	Lattice parameters (Å)		V^o (Å^3)	$V^o_{el.\ cell}$ (Å^3)	Z	Density (g/cm^3)	
	a	c				X-ray	pycnometer
tetra gonal	10.84	16.58	1948.20	243.50	8	5.80	5.82 ± 0.04

where V^o is the volume of the elementary cell;

$V^o_{el.\ cell}$ is the number of formula units per cell;

Z is the number of formula units in a cell.

Homology method [14] was used to carry out indexing of the X-ray patterns (Table 2) of the studied compound powder. A distorted structural type of peroxide was taken as a homologue.

The relationship between the lattice parameters and the interplanar distance in the case of the tetragonal system (a=b) in indexing the X-ray pattern by this method is as follows:

$$\frac{1}{d_{hkl}} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

where a and c are crystal lattice parameters, d is interplanar distance.

In addition to good agreement between the calculated and determined values of $1/d^2$ (maximum deviation of $1/d^2_{calc.}$ from $1/d^2_{exper.}$ should not exceed a probable measurement error), two more criteria can testify to indexing correctness:

a) the ratio of the number of theoretically possible lines in the X-ray pattern to the number of lines found experimentally is to be close to unity, when calculating the number of possible lines, a systematic extinction is considered;

b) good agreement must be observed between the experimental and calculated values of density ($\rho_{calc.}$), i.e. the number of formula units per elementary cell should be close to an integer, which is typically low. The minimal multiplicity of this space group (if it has been determined) can be considered. The number of formula units (Z) is calculated by the equation:

$$Z = \frac{V\rho_{exp.}}{1.66M} \quad (2)$$

where V the cell volume, M is the formula weight.

Otherwise, either $\rho_{exp.}$ or $\rho_{calc.}$ or V are incorrect, i.e. indexing is performed incorrectly. Systematic differences between $\rho_{exp.}$ and $\rho_{calc.}$ can be caused by the presence of a large number of lattice imperfections; however, these cases are extremely rare. In many cases, a simple chemical formula of the compound does not correspond to its stoichiometric formula. The deviation of Z from the integer can be explained by statistical filling of one regular point system with atoms of different types (i.e. random filling of similar positions with different atoms).

The volume of the elementary cells (V^0) for the studied phases was determined by the formula:

$$V^0 = a^2 \cdot c \quad (3)$$

The X-ray (calculated) density ($\rho_{roent/x\text{-}ray}$) of the studied compound was determined by the formula:

$$\rho_{roent} = \frac{1.66 \cdot Mr \cdot Z}{V^0} \quad (4)$$

where Mr is the molecular weight of the compound, Z is the number of formula units in the cell.

The ferrite density was measured by the technique described in [15] in 1 ml glass pycnometer. To measure the sample density, toluene, well wetting the studied substances and chemically inert, was

used as indifferent liquid. It should be noted that the dependence of toluene density on temperature is not significant (ρ^{20}=0.8659 g/cm^3; ρ^{25}=0.8634 g/cm^3).

Table 2. Indexing scheme for the $LaCa_3Fe_5O_{12}$ powder.

I/I_0, %	d, Å	$10^4/d^2_{exp.}$	hkl	$10^4/d^2_{calc.}$
13	3.8739	666.3	220	660.5
8	3.6523	749.6	300	743.0625
4	3.0448	1079	320	1073.313
100	2.7531	1319	400	1321
36	2.6786	1393	410	1403.563
21	2.6500	1424	116	1424.405
7	2.6027	1476	330	1486.125
26	2.5069	1591	206	1589.53
15	2.3928	1747	413	1718.383
15	2.2500	1975	423	1966.07
7	2.2256	2019	306	2002.343
11	2.1947	2076	316	2084.905
5	2.1048	2257	415	2278.063
25	1.9521	2624	434	2623.743
4	1.8780	2835	009	2833.38
18	1.8330	2976	600	2972.25
7	1.7458	3281	603	3287.07
20	1.6909	3498	229	3493.88
4	1.6600	3629	418	3642.283
4	1.6170	3825	2010	3828.25
31	1.5970	3921	615	3929.313
3	1.5392	4221	606	4231.53
13	1.4839	4541	626	4561.78
11	1.4519	4744	617	4768.833
1	1.4448	4791	730	4788.625
13	1.3857	5208	1112	5202.245
5	1.3757	5284	800	5284
7	1.3117	5812	609	5805.63
9	1.2394	6510	664	6504.18

The densities of the compounds were calculated by the formula:

$$\rho = \frac{M_3 - M_0}{\frac{M_1 - M_0}{\rho_1} - \frac{M_4 - M_3}{\rho_2}} \quad (5)$$

where M_0 is the mass of the empty pycnometer, g; M_1 is the mass of the pycnometer filled with water, g; M_2 is the mass of the pycnometer filled with toluene, g; M_3 is the mass of the pycnometer filled with the studied substance, g; M_4 is the mass of the pycnometer filled with toluene and the substance, g; ρ_1 is water density at a specified temperature, g/cm^3 (reference value); ρ_2 is toluene density, g/cm^3.

The densities of the samples were measured 4–5 times, and the results were averaged.

Indices *hkl* were determined analytically (selection, search for sequences of interplanar distances assuming that the inverse square of the distance depends on Miller indices according to formula 1.

3.2. Investigation of the interaction of $LaCa_3Fe_5O_{12}$ with electromagnetic radiation

The dependences in the frequency range of 0.01–4 GHz obtained using different devices (the analog meter of the modulus of the transmission coefficient and VSWR P2M-04 and the vector network analyzer E8363V) coincided. Therefore, we used the data obtained with the vector network analyzer E8363V. The results of radiophysical measurements are shown in Figures 2–4.

Figure 2 shows that the reflection coefficient of $LaCa_3Fe_5O_{12}$ in the studied range depends on the frequency, and it is described by the curve with a maximum which depends on the concentration of ferrite in the composite.

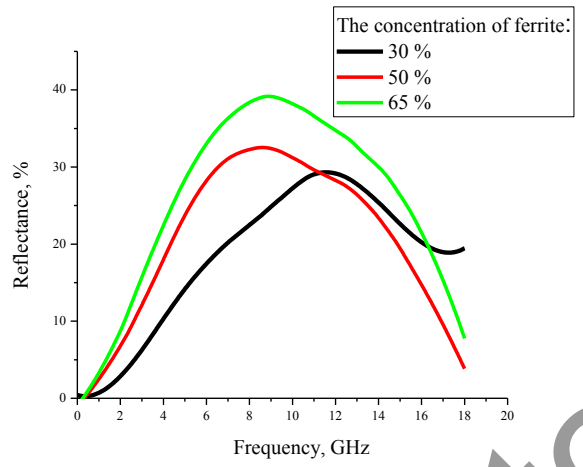

Figure 2. Dependence of the reflection coefficient on the electromagnetic radiation frequency.

The curves of the transmission coefficient relative to frequency are shown in Figure 3, which shows that the transmission coefficient also depends on the concentration of ferrite in the composite, and it is described by the curve with a minimum. The minimum occurs within the frequency range of 6–16 GHz.

The absorption coefficient of the studied material grows continuously as the frequency increases, and as the ferrite concentration in the composite increases, it grows up at a fixed frequency (Figure 4).

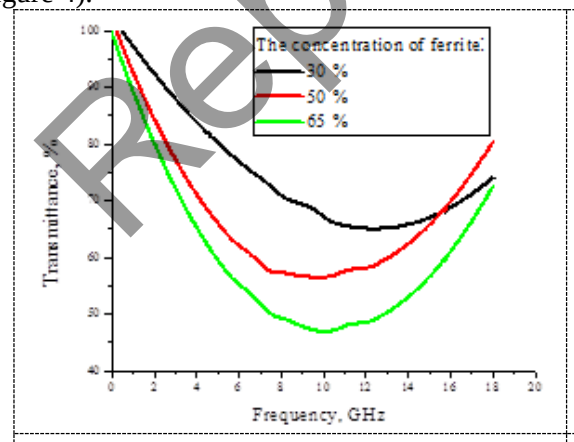

Figure 3. Dependence of the transmission coefficient on the electromagnetic radiation frequency.

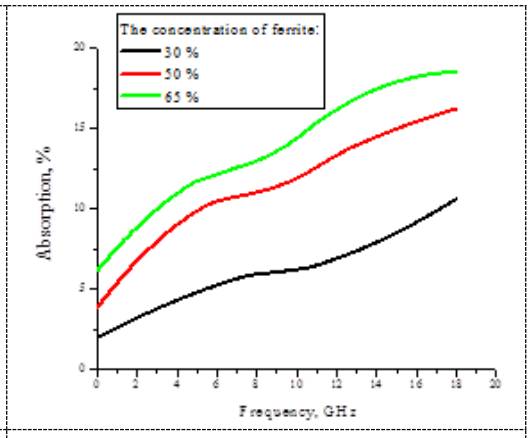

Figure 4. Dependence of the absorption coefficient on the electromagnetic radiation frequency.

4. Conclusions

The obtained results show that LaCa3Fe5O12 ferrites belong to the tetragonal system. The lattice parameters a and c, the elementary cell volume (Vo), the number of formula units per 1 cell (Voel.cell), the number of formula units in the cell (Z) have been determined.

The developed material effectively interacts with electromagnetic radiation. The effectiveness of this interaction is directly proportional to the concentration of ferrite. Increased concentration of ferrite provides growth of the reflection coefficient, which is caused by high conductivity of the material and distinct reduction of the transmission coefficient in the frequency range of 4–14 GHz, which can be used to make screening devices for solving problems of electromagnetic compatibility of modern high-frequency radio equipment. The operating frequency range and effectiveness of interaction with electromagnetic radiation can be changed through selecting the composite thickness.

Acknowledgements

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