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FURTHER INVESTIGATION ON THE THERMOPHYSICAL PROPERTIES OF SUBSTITUTED LANTHANUM FERRITES

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ABSTRACT

Well-sintered ceramic bodies of different alkaline earth-substituted lanthanum ferrites $L_{1-x}M_xFeO_{3-\epsilon}$ (where $x = 0.1$) have been prepared by the usual ceramic procedure and sintering technique. On these specimens, several measurements were undertaken comprising specific gravity, bulk density, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The results obtained were interpreted and discussed in detail. The thermal stability of the materials investigated was completely evaluated for the first time and correlated with bond strength and the interaction of alkaline earth substituents with the lanthanum ferrite lattice.

INTRODUCTION

The interest of the present investigation is due to the great application of substituted ferrites in storage circuits and in microwave devices such as isolators, circurators and gyrators. The crystal structure of our present substituted lanthanum ferrites ($L_{1-x}M_xFeO_{3-\epsilon}$) can be derived from the cubic perovskite structure ABO_3. The ordering of oxygen vacancies in ABO_3 (1 vacancy per 6 oxygen sites along 101 strings in every other 010 plane as well as a slight shift of the iron atoms in these planes) leads to a structure with alternating sheets of (BO_6) octahedra and (BO_4) tetrahedra [1]. The correlation of both structures predicts a succession of perovskite-like sheets of (MO_6) octahedra [2,3].

Mori [4] studied the phase transformation in $BaFeO_3$ containing Fe^{4+} ions. Correlation with the oxygen content, and the transformations are actually related to oxidation–reduction of iron ions ($Fe^{3+} \rightleftharpoons Fe^{4+}$).

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Yamamura et al. [5] studied the relations between oxygen vacancies and structures in the solid solution of the system $Sr_{1-x}M_xFeO_{3-\epsilon}$ (M = La^{3+}, Y^{3+}, Bi^{3+} and In^{3+}). They found that the presence of oxygen vacancies in the solid solution played an important role for the stabilization of a perovskite-type structure with cubic symmetry.

The electrical and optical properties of some stoichiometric perovskite-structure materials have been studied [6]. Recently, Abou Sekkina and Aiad [7] investigated the semiconducting and spectral properties of lanthanum modified di-lead ferrites.

This paper is aimed at evaluating the effects of various substitutions in ferrite lattices on their thermophysical properties with an attempt to evaluate the optimum preparative conditions for the production of sintered ferrites of good thermal stability for the electronic industry.

EXPERIMENTAL

Material preparation

There are a number of methods for the preparation of ferrites. The calcination of mixed salt particles is the only one being used to a great extent. With this conventional ceramic technique, the starting materials ($MgCO_3$, $SrCO_3$, $BaCO_3$, Fe_2O_3 and La_2O_3 of extra pure grade, purity > 99.80%) are first intimately mixed as well as possible in an agate mortar for 1 h in exact ratios to give the final formula ($L_{1-x}M_xFeO_{3-\epsilon}$), where M = Mg, Sr, Ba and $x = 0.1$. The dry powder mixture was calcined at 900°C for 3 h, quenched to room temperature and finely ground in an agate mortar. Small cylindrical disks of the materials were formed (1.0 cm diameter, 0.2 cm thickness) by pressing under hydraulic pressure (1000 kg cm^{-2}). The formed disks were dried at 120°C for 10 h and then fired at 1150°C for 6 h. These were proved to be the most suitable conditions to avoid partial decomposition of the ferrites formed into α-Fe_2O_3 beside the decomposition products. The correct preparation and the choice of the most suitable conditions were controlled by following each preparation with X-ray diffraction measurements.

X-ray diffraction measurements (XRD)

The Cu-K_α X-ray diffraction patterns of the prepared ferrite samples were carried out using a Shimadzu X-ray diffractometer Model XD-3 (Japan). The ground sample was pressed on the standard sample holder for better briquetting and the holder was fixed in the automatic sample changer. A Geiger Mueller tube was adjusted at a rate of 2° min^{-1}. The amplifier counter output was recorded simultaneously on a chart set at a speed of 10 mm min^{-1}. The diffraction peak was taken to be the average of the position of the positive and negative halves of the Debye–Scherrer ring.

Differential thermal analysis (DTA)

These measurements were undertaken in order to evaluate the calorific change as a function of temperature variations to detect the thermal stabilities of ferrites prepared. A Shimadzu DTA system (Shimadzu 30 series of thermal analysis instruments) was used. Measurements were undertaken at room and elevated temperatures up to 900 °C, using pure alumina as reference material which is thermally stable.

Thermogravimetric analysis (TGA)

In order to detect the thermal stability of the investigated ferrites, they were subjected to thermogravimetric analysis as carried out manually using a Sartorius electric balance, electric muffle furnace and vacuum desiccator. The measurements were undertaken at room and elevated temperatures up to 800 °C, and thermogravimetric curves were drawn, which were found to be straight lines for all samples investigated indicating a high thermal stability for all of them.

Denisty measurements

Pyknometric density measurements

A known weight (W_1) of very finely ground sample was introduced into the pyknometer of W_2. The bottle was completed with distilled water. The pyknometer was subjected to a moderate vacuum pump (10^{-2} mm Hg) to remove the trapped air. After the liquid had completely penetrated through all the sample pores, the pyknometer was then gently thermostated at 30 °C and weighed (W_3). The solid was removed and the pyknometer was filled completely to the mark, at the same thermostating temperature (30 °C), with liquid alone and weighed (W_4). Thus, the density (true) of the test sample (ρ) was $W_1\rho'/(W_4 - W_3 + W_1)$ (g cm^{-3}) at 30 °C where ρ' is the density of distilled water at 30 °C.

Bulk density measurements

The density of the sintered product was measured in the solid state without its destruction, by calculating the sample volume, taking its dimensions and weighing. This method was very similar to that previously used by Atkin and Fulrath [8] as it implies no destruction of the well-sintered ferrite bodies and is directly related to the degree of sintering and thus could be used as the sintering parameter of the present ferrite samples.

RESULTS AND DISCUSSION

The room temperature Cu-K_α X-ray diffraction patterns of the substituted ferrites are graphically collected in Fig. 1 and analysed in Table 1. The interplanar spacing (lattice spacing) calculations were performed using the most intense lines. These peaks were used in preference to the others because of the increased accuracy. It can be easily seen that: (a) substitution of La^{3+} with Mg^{2+} results in decreased interplanar spacings; (b) substitution of Mg^{2+} with other alkaline earth ions (Sr^{2+}, Ba^{2+}) is accompanied by a gradual decrease in $2\theta°$ values, i.e. an increase in the interplanar *d*-spacings in the direction from Mg to Sr to Ba substitution, partially in place of La in the ferrite lattice. This could plausibly be explained on the basis of the increased ionic radii of the alkaline earth elements in the same forementioned direction. That is to say in the direction from Mg^{2+} (0.65 Å), to Sr^{2+} (1.13 Å) to Ba^{2+} (1.35 Å). The noticeable difference in the case of Mg^{2+} substitution is in accordance with its large difference in ionic radius with

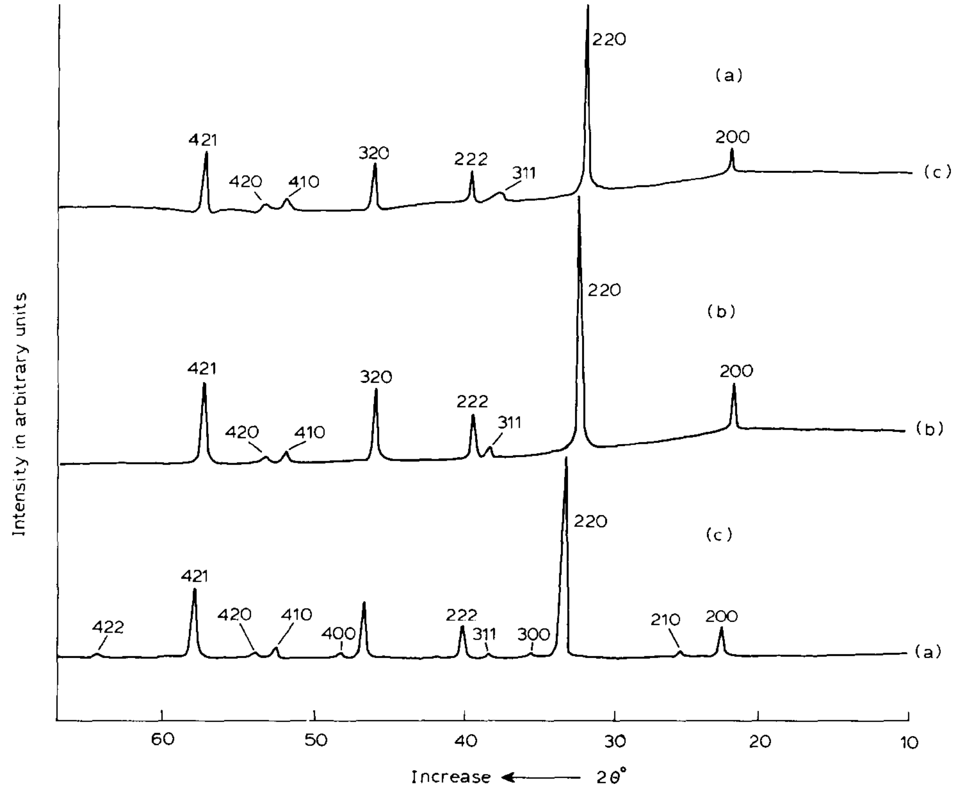

Fig. 1. Room temperature X-ray diffraction patterns of: (a) $Mg_{1-x}La_xFeO_{3-\epsilon}$; (b) $Sr_{1-x}La_xFeO_{3-\epsilon}$; (c) $Ba_{1-x}La_xFeO_{3-\epsilon}$ ($x = 0.9$).

TABLE 1

The obtained room temperature Cu-K_α X-ray diffraction analysis of (1) Mg-; (2) Sr- and (3) Ba-substituted La-ferrites

(1)			(2)			(3)		
I/I_0	d (Å)	hkl	I/I_0	d (Å)	hkl	I/I_0	d (Å)	hkl
16	3.9138	200	20	3.9482	200	17	3.9482	200
100	2.7362	220	100	2.7775	220	100	2.7944	220
18	2.2521	222	18	2.2521	222	22	2.2629	222
30	1.9473	400	–	–	–	–	–	–
3	1.8937	410	6	1.7508	410	8	1.7508	410
6	1.7446	420	3	1.7113	420	3	1.7143	420
3	1.7083	421	30	1.5988	421	34	1.5988	421
36	1.5938	422	–	–	–	–	–	–

respect to Sr^{2+} ion. The effect of smaller cation substitution for the larger cation causes the interplanar spacing to decrease in agreement with Vigard's law. A small percentage of the dopants enters the material interstitially. Because of the large increase of the interplanar spacings from Mg- to Sr-substitution and their further increase for Ba-substitution of La, partially exceeding that of pure La-ferrite, our results were in full agreement with previous investigators [9–11] that most of the Mg^{2+}, Sr^{2+} and Ba^{2+} substituents enter the ferrite lattices by substitution. Careful matching of the present XRD data with those of the ASTM-XRD cards clearly indicates that all the present substituted ferrite samples belong to a distorted orthorhombic perovskite crystal system [12] having the space group ($Pdnm$ D_{2h}^{16}). Besides, a common feature for all diffractograms is a noticeable broadening (see Fig. 1). This could be explainable on the basis of some kind of induced lattice defect as a result of substituting lanthanum with alkaline earth oxides of variable ionic radius.

Figure 2 and Table 2 include differential thermal analysis data for the substituted La-ferrites. It can easily be seen that the sample of Sr-substituted La-ferrite possesses higher thermal stability than the other alkaline earth-substituted ferrites. The very weak, broad exothermic peak observed in all samples at around 50–150°C is most probably due to the heat capacity and/or some kind of slight internal changes in the crystalline lattice. This is in accordance with the previous concluded by Chiranjeevi Rao [13] from his physico-chemical studies on other materials.

From thermogravimetric analysis data (TGA), no weight loss or gain could be detected for all samples up to 800°C. This indicates that the present ferrite materials possess high thermal stability in the investigated temperature range. Alternatively, the weak exothermic peaks appearing in the DTA curves (Fig. 2) at 222, 280, 355 and 400°C for Mg-substituted La-ferrite as well as the observed weak exothermic peak at 301°C for

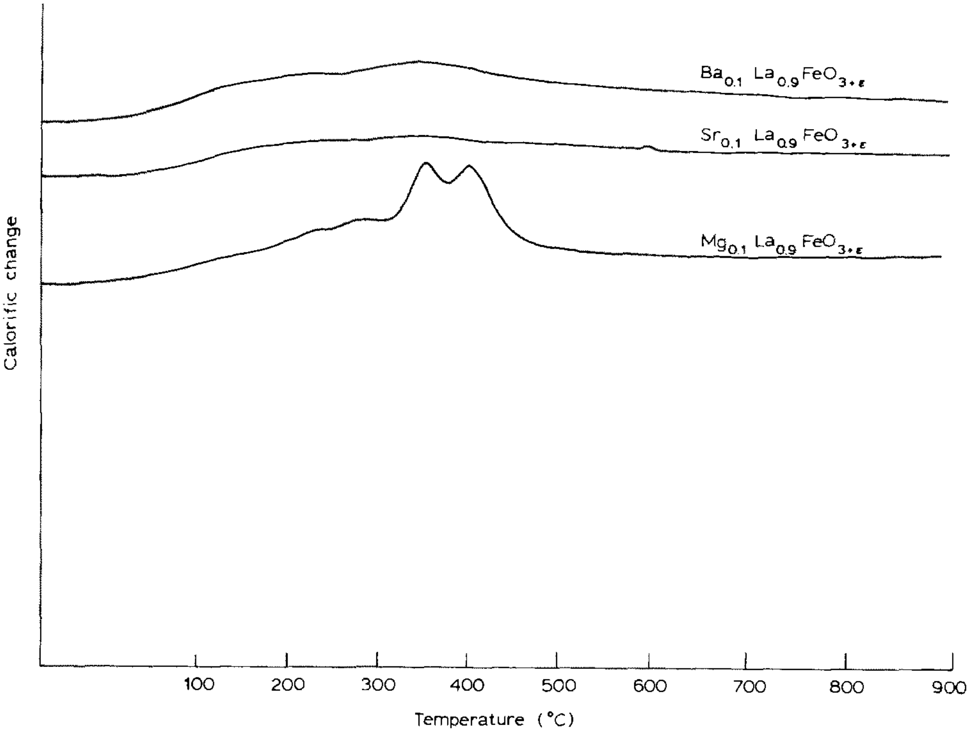

Fig. 2. Differential thermal analysis (DTA) of the substituted ferrite series.

Ba-substituted La-ferrite are proved to be due to some kind of lattice rearrangements and/or lattice imperfections as caused by the diffusion of oxygen vacancies in interstitial lattice sites. This is in conformity with the present XRD results and those from a previous deduction of similar materials [14]. This, in turn, may affect the final ratio of Fe^{4+}/Fe^{3+} which always

TABLE 2

Differential thermal analysis data (DTA) of the alkaline earth-substituted La-ferrites

Material	Temperature (°C)			Characerization
	Stable zone	Exothermic change	Endothermic change	
$Mg_{0.1}La_{0.9}FeO_{3-\epsilon}$	18–210	222	–	broad
		280	–	broad
		355	–	weak
		400	–	weak
$Sr_{0.1}La_{0.9}FeO_{3-\epsilon}$	18–900	–	–	very stable
$Ba_{0.1}La_{0.9}FeO_{3-\epsilon}$	18–240	301	–	very broad

TABLE 3

Values of bulk density, specific gravity and percentage sintering of the alkaline earth-substituted La-ferrites

Material	Specific gravity (gm cm^{-3})	Bulk density (gm cm^{-3})	Percentage sintering	Ionic radii of alkaline earth element (Å)
$Mg_{0.1}La_{0.9}FeO_{3-\epsilon}$	4.100	3.770	92	0.65
$Sr_{0.1}La_{0.9}FeO_{3-\epsilon}$	4.510	4.280	95	1.13
$Ba_{0.1}La_{0.9}FeO_{3-\epsilon}$	5.040	4.890	97	1.35

plays an important role in the electric conduction and its attendent activation energy.

Table 3 and Fig. 3 represent the variation of the true density (specific gravity) and bulk density of the prepared ferrites as functions of ionic radii of the alkaline earth elements. It is clear that both straight-line curves have general trend in common: the bulk and true densities increase with increasing ionic radii of the alkaline earth elements in a straight-line relationship. This behaviour could be attributed to the increased atomic weight and sintering parameter in the same direction (see Table 1). The very high bulk density obtained for test samples reaching 97% of the corresponding true density indicates the attainment of well-sintered ferrite bodies of high sinterability. Further evidence for this deduction is the translucent bright appearance of the alkaline earth-substituted ferrite bodies obtained.

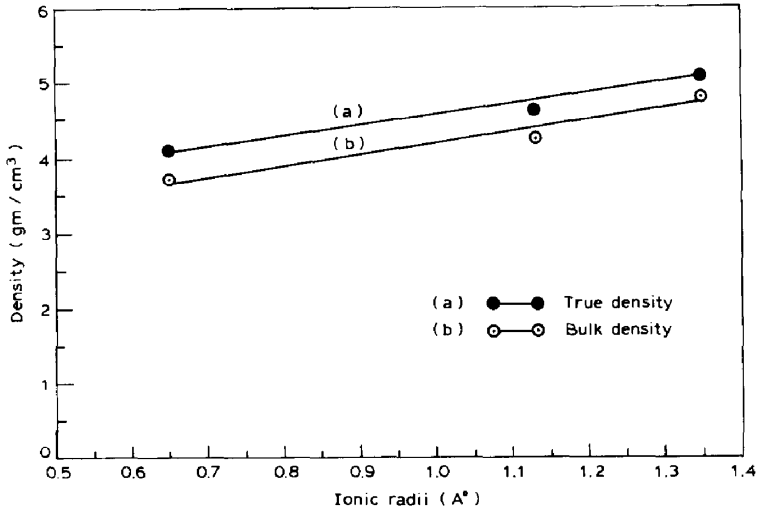

Fig. 3. Variation of (a) specific gravity and (b) bulk density with ionic radii of alkaline earth elements in the substituted ferrite series.

CONCLUSIONS

Results of X-ray diffraction measurements (XRD), true and bulk density measurements proved the attainment of well-sintered ferrite bodies and the propagation of lattice imperfections together with the diffusion of oxygen vacancies as a result of alkaline earth interactions with the La-ferrite lattice.

Results of thermogravimetric analysis (TGA) revealed the high thermal stability of the ferrite samples investigated.

Differential thermal analysis (DTA) data revealed the highest thermal stability for the Sr-substituted La-ferrite sample.

Finally, best quality La-ferrites having high thermal stability and a good sintering parameter (percentage sintering) could be obtained by partial substitution of lanthanum in the ferrite lattice with alkaline earth elements, in particular with strontium. This can most probably be ascribed to a ferrimagnetic → paramagnetic phase transition and/or to the increased Fe^{4+}/Fe^{3+} ratio, as induced by oxygen vacancy diffusion in the ferrite lattices.

Accordingly, the large thermal stability acquired, particularly for Sr-substituted La-ferrites, could plausibly be correlated with the increased bond strength. A relationship which is of course a result of the interaction of alkaline earth substituents with lanthanum ferrite lattice and which are useful for ferrite applications in the electronic industry and engineering.

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