EFFECTS OF TEMPERATURE AND NON-STOICHIOMETRY ON THE ELECTRICAL CONDUCTIVITY OF SOME RELATED PEROVSKITE FERRITES

M.M. ABOU SEKKINA *

Chemistry Department, Faculty of Science, Tanta University, Tanta (Egypt)

M.A. EWAIDA, M.M.F. SABRY and R.M. EL-BAHNASAWY

Al-Monoufia University, Shibin El-Kom, Al-Monoufia (Egypt)

K.A. EL-ZEWEIL

National Research Centre (NRC), Dokki, Cairo (Egypt)

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ABSTRACT

Several samples of di-lead ferrites as well as various alkaline earth and lanthanum partially substituted lead ferrites have been prepared and identified. Comprehensive measurements of true density, bulk density and the temperature dependence of electrical conductivity were undertaken on these samples.

Density measurements indicated the attainment of well-sintered ferrite bodies for all samples prepared. Conductivity measurements proved the semiconducting character of materials investigated. At relatively low temperatures, some samples show inversion from the electronic to ionic conduction mechanism as well as metallic conduction mechanism. The extent of lead substitution by alkaline earth elements can be used as a rapid tool for controlling the desired semiconducting parameters during ferrite synthesis. Finally, best quality di-lead ferrite semiconductors were obtained by lead substitution by alkaline earths. This has been explained in detail and correlated with the induced ferrimagnetic → paramagnetic phase inversion as a result of substitution interaction.

INTRODUCTION

This study is of interest due to the great application of ferrites in microwave devices such as isolators, switches, circurators and gyrators. The co-existance of different oxidation states of transition elements occurs naturally in minerals and ores, and is frequently induced synthetically during the preparation of solid state catalytic compounds and ferromagnetic materials

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* Author to whom all correspondence should be addressed.

[1]. The crystal structure of $Ca_2Fe_2O_5$, dicalcium ferrite, can be easily derived from the cubic perovskite structure AMO_3. The ordering of oxygen vacancies in $A_2M_2O_5$, 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 (MO_6) octahedra and (MO_4) tetrahedra [2]. The correlation of both structures has suggested a general model for the $A_2M_2O_{6-x}$ phases of intermediate composition ($0 < x < 1$), which predicts a succession of perovskite like sheets of (MO_6) octahedra separated by one sheet formed by parallel chains of (MO_4) tetrahedra [3,4]. The exact ratio between the number of octahedra and tetrahedra in such a structure is $((2 - x)/x)$. Grenier et al. [5] prepared and measured the specific gravity of $Pb_2Fe_2O_5$ at room temperature giving a value of 8.32 ± 0.02 g cm^{-3}. Such phases have been actually observed in several $\{AMO_3–Ca_2Fe_2O_5\}$ systems (A=Ca, Sr, Ba, Y, La, Gd; M=Ti, Fe, Ga).

The electrical and optical properties of some stoichiometric perovskite structure materials have been studied [6,7]. Recently, Abou Sekkina and Aiad [8] studied the semiconductor and spectral properties of lanthanum modified di-lead ferrites.

This report is aimed at evaluating the effects of various substitutions in ferrite lattices on the temperature dependence of DC electrical conductivity, with an attempt to evaluate the optimum preparative conditions for ferrite electronic industries for good semiconducting parameters.

EXPERIMENTAL

Material synthesis and preparation

Several samples were prepared; $Pb_2Fe_2O_5$ and the three systems $(Pb_{2-x}Ca_xFe_2O_5)$, $(Pb_{2-x}Sr_xFe_2O_5)$ and $(Pb_{2-x}La_xFe_2O_5)$. The starting materials, of analytical grade (BDH), were $PbCO_3$, $Fe_2(NO_3)_3 \cdot 9$ H_2O, La_2O_3, $CaCO_3$, $SrCO_3$, HNO_3 and bidistilled water. In each case, the procedure involves co-precipitation of the corresponding hydroxide, gentle evaporation on a sand bath at 140°C and firing at 550°C for 30 days. This was carried out on the basis of a method given by Mountvala and Ravitz [9] with major modification. The products were pulverized, ground, compressed into cylindrical pellets at 400 kg cm^{-2} and sintered at 500°C for two hours. The prepared materials were then subjected to X-ray diffraction analysis and density measurements and compared with those prepared by other methods; see Berger and Pawlek [10].

Specific gravity (true density) measurements

The prepared ferrites were finely ground using an agate mortar. The room temperature (20°C) true density (g cm^{-3}) was estimated for the ground

materials as a function of x. This was undertaken using a pycnometer (thermostated at 20°C) with bidistilled water as a medium and under vacuum (10^{-2} mm Hg).

Bulk density (apparent) measurements

Following sintering, bulk density was measured using the mercury balance as described by Clark and White [11] and used by Abou Sekkina with some modification [12].

DC electrical conductivity measurements

This was performed using the two probe technique under vacuum and 616 B-Keithley electrometer (U.S.A.). The circuit and mode of measurements used are very similar to those previously described [13].

Measurements were made at both room and elevated temperatures up to $\cong 500$ K and the readings were taken three times at 15 min after each temperature equilibration, the circuit used was well shielded with copper.

In all of the above measurements the readings were taken three times and in each case reliable data were obtained.

RESULTS AND DISCUSSION

Table 1 and Figs. 1 and 2 show the variation of specific gravity as well as bulk density for materials prepared as a function of Ca-, Sr- and La-substitution of Pb in di-lead ferrites.

From Table 1 and Figs. 1 and 2 it can be seen that the ratios of bulk density: true density ranged from 97–87%, 97–93% and 97–96% for Ca-, Sr-, and La-substitution, respectively. This high ratio together with the trans-
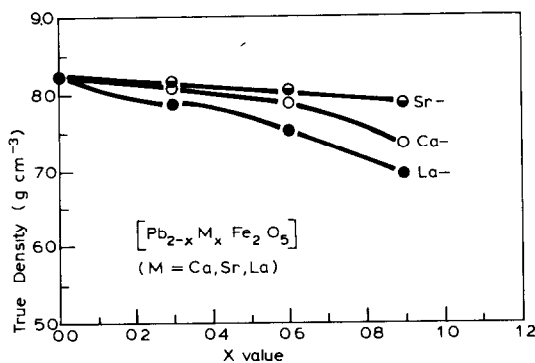

Fig. 1. Variation of true density (g cm^{-3}) as a function of x value.

TABLE 1

The variation of true density and bulk density (g cm^{-3}) as a function of Ca-, Sr-, and La-substitution of Pb in di-lead ferrites

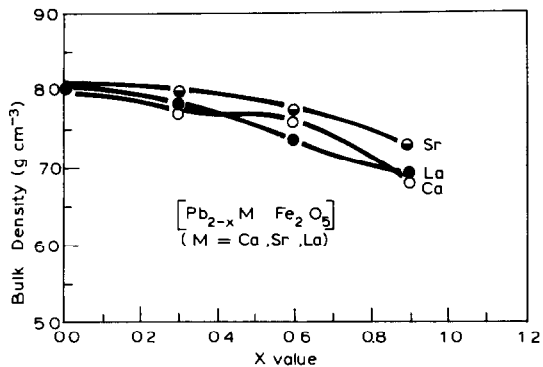| x value	Ca-substitution			Sr-substitution			La-substitution		
	Formula	Density		Formula	Density		Formula	Density	
		True	Bulk		True	Bulk		True	Bulk
0.0	$Pb_2Fe_2O_5$	8.25	8.0	$Pb_2Fe_2O_5$	8.25	8.0	$Pb_2Fe_2O_5$	8.25	8.0
0.3	$Pb_{1.7}Ca_{0.3}Fe_2O_5$	8.10	7.73	$Pb_{1.7}Sr_{0.3}Fe_2O_5$	8.15	7.96	$Pb_{1.7}La_{0.3}Fe_2O_5$	7.90	7.87
0.6	$Pb_{1.4}Ca_{0.6}Fe_2O_5$	7.93	7.61	$Pb_{1.4}Sr_{0.6}Fe_2O_5$	8.0	7.70	$Pb_{1.4}La_{0.6}Fe_2O_5$	7.54	7.35
0.9	$Pb_{1.1}Ca_{0.9}Fe_2O_5$	7.32	6.84	$Pb_{1.1}Sr_{0.9}Fe_2O_5$	7.81	7.30	$Pb_{1.1}La_{0.9}Fe_2O_5$	7.00	6.90

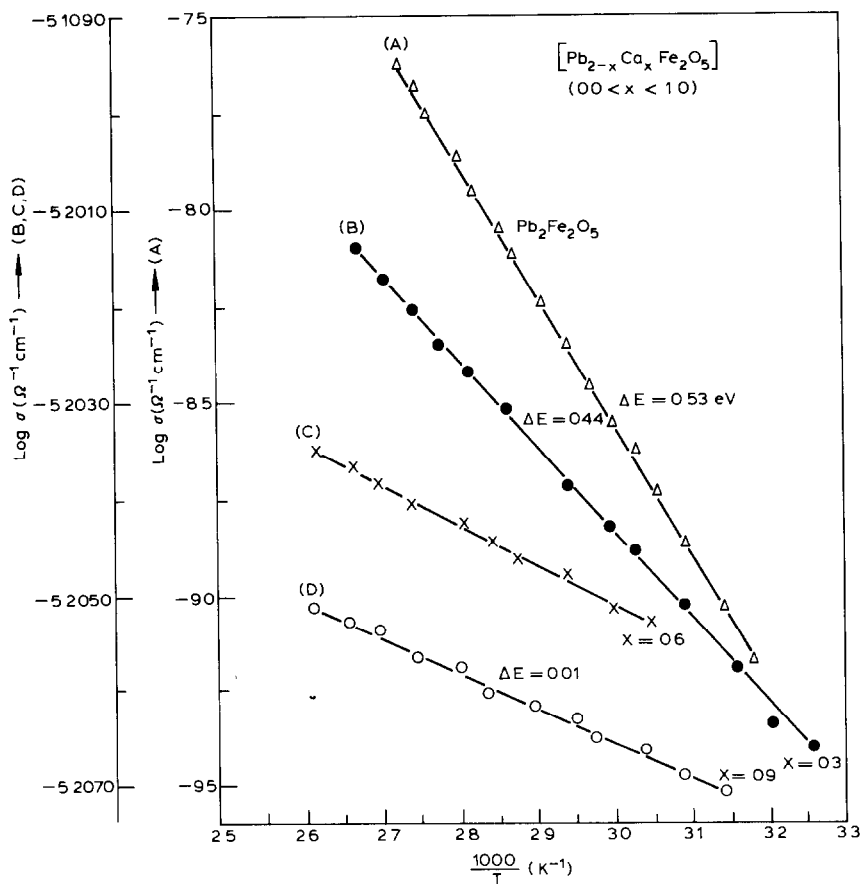Fig. 2. Variation of bulk density (g cm^{-3}) as a function of x value.

Fig. 3. A schematic illustration of the temperature dependence of electrical conductivity for Ca-substituted di-lead ferrites at various x values.

lucent bright appearance, confirms the presence of well-sintered ferrite bodies. All curves (Figs. 1 and 2) have a general trend in common, namely a decrease in both true density and bulk density as a function of substitution. This is most probably correlated with the induced lattice imperfections which lead to the formation of defective crystal lattices. The magnitude of lattice imperfection was found to vary depending on the difference between ionic radii as well as atomic weights of lead and the substituent element.

Figures 3–5 represent the plots of log σ vs. $(1000/T\,\text{K}^{-1})$ for the systems $(Pb_{2-x}Ca_xFe_2O_5)$, $(Pb_{2-x}Sr_xFe_2O_5)$ and $(Pb_{2-x}La_xFe_2O_5)$, respectively. Since there is a positive temperature coefficient of electrical conductivity $(d\sigma/dT)$ on at least a portion (Fig. 3, curve C) of each curve, all of the investigated materials are semiconductors.

The conductivity varies exponentially with temperature according to the well known relation [14]
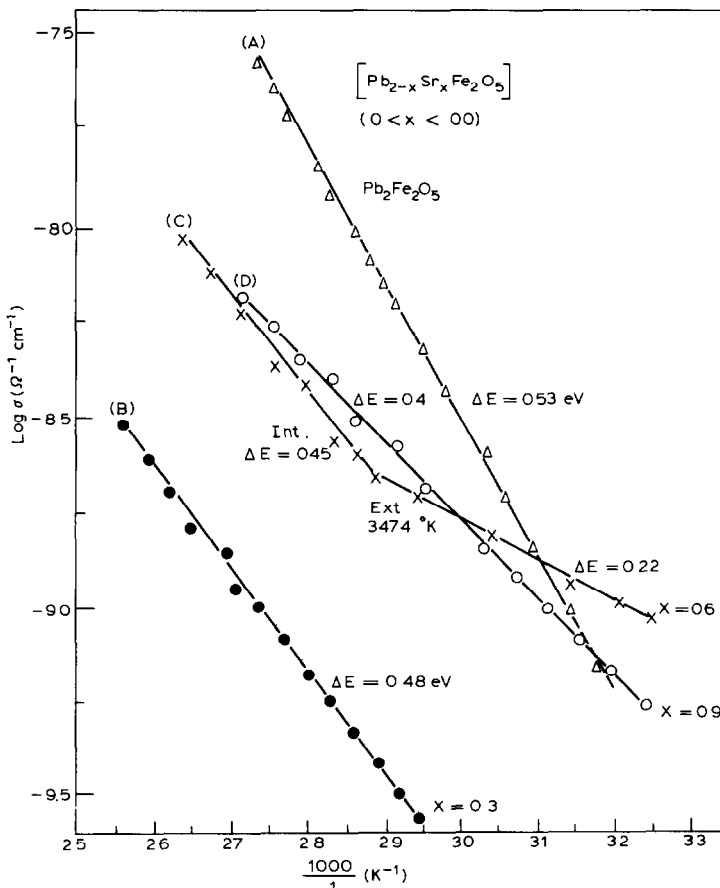
$$\sigma = \sigma_0 e^{-\Delta E/KT}$$

Fig. 4. Variation of electrical conductivity for Sr-substituted di-lead ferrites at various x values.
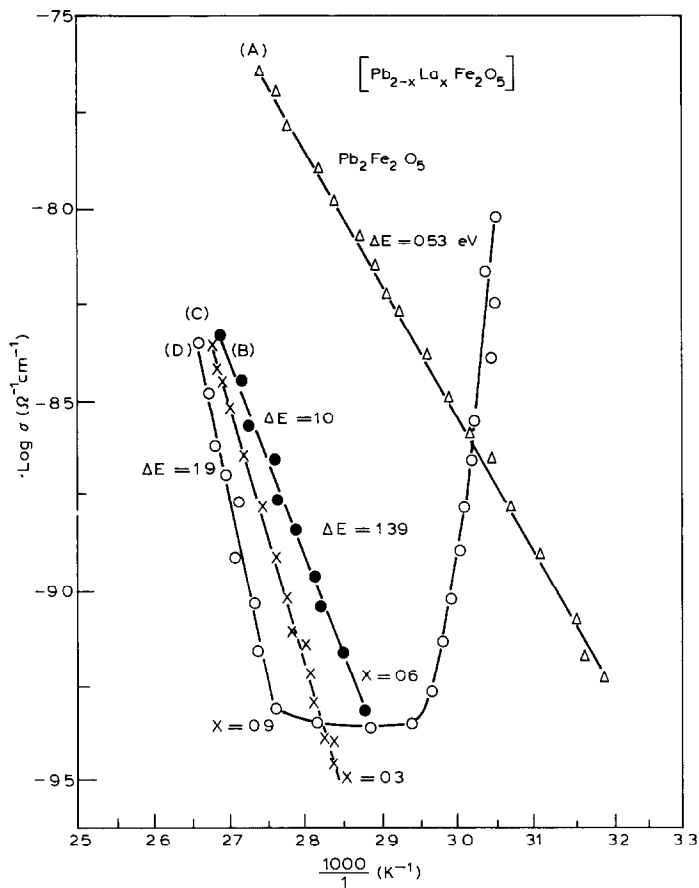
Fig. 5. The temperature dependence of electrical conductivity for La-substituted di-lead ferrites at different x values.

The relatively slight response of σ with temperature involves ΔE values which can be interpreted by a simple single band model in most cases.

The ΔE values are calculated (Table 2) and assumed to correspond to the activation energies of defect mobilities.

From Table 2, it can be easily seen that the activation energies are considerably decreased as a function of lead substitution by alkaline earth (Ca or Sr) elements. This could be explained by the decrease in bond strength and increased lattice imperfections or lattice defects in the same direction. Another contribution to the decreased activation energies and its attendant increased electrical conductivity is the non-stoichiometry effect, that is, the Fe^{4+}/Fe^{3+} ratio [14].

Figure 4, curve C represents the temperature dependence of electrical conductivity of $Pb_{1.4}Sr_{0.6}Fe_2O_5$. The relationship shows two straight line portions with a change in slope at 347.2 K. Calculating the activation energies for the two straight line portions gives values of 0.22 eV and 0.45 eV

TABLE 2

Values of the obtained activation energies (eV) for the Ca-, Sr-, and La-substituted di-lead ferrites

Ca- subst. di-lead ferrites		Sr- subst. di-lead ferrites		La-subst. di-lead ferrites	
Formula	ΔE (eV)	Formula	ΔE (eV)	Formula	ΔE (eV)
$Pb_2Fe_2O_5$	0.53	$Pb_2Fe_2O_5$	0.53	$Pb_2Fe_2O_5$	0.53
$Pb_{1.7}Ca_{0.3}Fe_2O_5$	0.44	$Pb_{1.7}Sr_{0.3}Fe_2O_5$	0.48	$Pb_{1.7}La_{0.3}Fe_2O_5$	1.39
$Pb_{1.4}Ca_{0.6}Fe_2O_5$	0.16	$Pb_{1.4}Sr_{0.6}Fe_2O_5$	0.22/0.45	$Pb_{1.4}La_{0.6}Fe_2O_5$	1.00
$Pb_{1.1}Ca_{0.9}Fe_2O_5$	0.14	$Pb_{1.1}Sr_{0.9}Fe_2O_5$	0.40	$Pb_{1.1}La_{0.9}Fe_2O_5$	1.90

for the low and high temperature straight line portions, respectively. Since the activation energy for conduction is doubled on going from the low temperature to the high temperature zone, the abrupt change in the slope could be explained by the transition from the electronic conduction mechanism (low temperature region) to the ionic conduction mechanism (high temperature region).

Figure 5, curve D represents the temperature dependence of electrical conductivity of $Pb_{1.1}La_{0.9}Fe_2O_{5+3}$ and displays the metallic conduction mechanism in the relatively low temperature region. This anomaly is most probably correlated with the existence of minute amounts of metallic lead evaporated and condensed on the grain surface during the thermal preparation and sintering techniques. At high temperatures all lead impurities are completely ionized, allowing the semiconducting conduction mechanism to take place. This view is further supported by the more severe preparative conditions of this sample than for the others.

However, at elevated temperatures, the creation of lattice defects may take place exponentially via the Frenkel and/or Schottky mechanisms, as follows

$$n = Ne^{-W/2KT}$$

where n is the number of the formed defects, N is the number of possible defects, W is the activation energy for defects, which is very high for the case of Frenkel defects, K is the normal gas constant and T is the absolute temperature. Since the creation of new lattice defects varies exponentially with temperature rise, it may also increase exponentially with an increase in the molar ratio of additives (degree or extent of substitution) (see Figs. 3 and 4).

In ferrites, the transition from the ordered ferrimagnetic state to the paramagnetic state is accompanied by changes in various physical properties. The activation energy for electrical conductivity has been found to be smaller in the ferrimagnetic region than in the paramagnetic region [15–17]. Therefore, we may attribute the increased electrical conductivities and their attendant decreased activation energies for conduction, as a function of
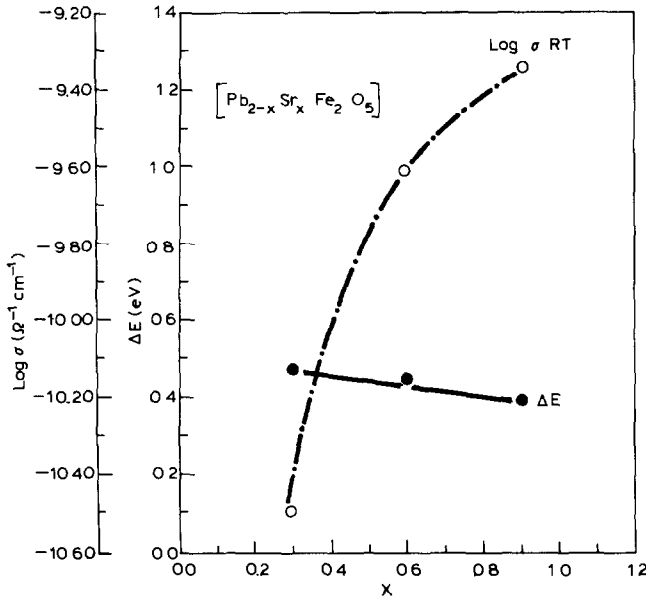
Fig. 6. Variation of both room temperature electrical conductivity ($\log \sigma_{RT}$) and activation energy for conduction (ΔE) as a function of x value for Sr-substituted di-lead ferrites.

alkaline earth substitution in di-lead ferrites to the transition of the ferrites present from the ordered ferrimagnetic ferrites to the disordered para-magnetic ferrites.

Finally, in di-lead ferrites, substitution of lead with the alkaline earth elements (Ca or Sr) can be used as a tool controlling the final obtained electrical conductivities and their attendant activation energies to the desired values.
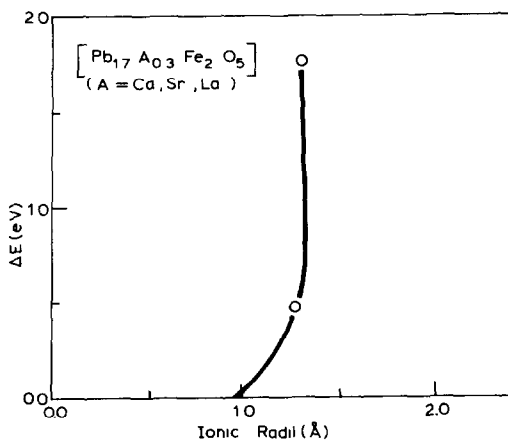

Fig. 7. Variation of activation energy for conduction (ΔE) as a function of ionic radii of various substituents in di-lead ferrites.

Figure 6 shows the variation of electrical conductivity (log σ_{RT}) and activation energy for conduction as a function of lead substitution with Sr. It can be easily seen that the electrical conductivity increases and the activation energy for conduction decreases as a function of Pb-substitution by Sr. This could be explained on the aforementioned basis by being correlated with ferrimagnetic → paramagnetic phase transition [16,17].

Figure 7 shows the variation of activation energy for conduction (ΔE) as a function of ionic radius of the substituent element. It can be noted that the activation energy for conduction is directly proportional to the ionic radius of the substituent element. Since we are concerned with the ionic conduction mechanism, this could be ascribed to the decreased ionic mobility resulting from the increase in ionic radii.

CONCLUSIONS

Results of true and bulk density measurements indicate the attainment of well-sintered ferrite bodies and propagation of lattice imperfections as a function of substitution. Conductivity measurements prove the semiconducting conduction mechanism of all materials investigated. With special regard to alkaline earth partially substituted lead in di-lead ferrite lattices, the extent of substitution could find a useful application in controlling the obtained semiconducting parameters to the desired qualifications.

Finally, best quality di-lead ferrites having low activation energies and relatively high electrical conductivity could be obtained by partial substitution of lead with alkaline earth elements. This is most probably correlated with ferrimagnetic → paramagnetic phase transition and/or the increased Fe^{4+}/Fe^{3+} ratio.

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