LANTHANUM-SUBSTITUTED BARIUM HEXAFERRITES

I. N. Frantsevich and L. N. Tul'chinskii

The development of a new type of semiconductor device, namely, ferrite thermistors [1, 2], has created a demand for magnetic oxide materials possessing any predetermined conductivity. Such materials may be formulated on the base of both soft and hard magnetic ferrites, in particular barium hexaferrites (BHF) with additions designed to regulate their electrical conductivity.

The reason for the choice of small additions of oxides of the rare-earth elements (REE) is that magnetization intensity, being an additive property, is hardly affected by such additions, whereas electrical conductivity changes by several orders of magnitude.

Replacing barium by lanthanum according to the equation

\[
\text{Ba}^{2+} + \text{Fe}^{3+} \xrightarrow{\text{La}} \text{La}^{3+} + \text{Fe}^{2+},
\]

with the formation of the hexaferrite

\[
\text{Ba}_{1-x}\text{La}_x\text{Fe}_{12}\text{O}_{19},
\]

where \(x\) is the degree of substitution, leads to the formation of N-type carriers, whose number would be expected to be uniquely related to the amount of lanthanum added.

In the preparation of BHF, use is made of reagents and auxiliary products containing a small quantity of oxides of alkali metals. Thus, the permissible concentration of oxides of alkali metals is \(0.1\%\) in ferric oxide of the "pure for analysis" grade and \(0.5\%\) in polyvinyl alcohol [3, 4], which is used as a plasticizer. These oxides form a compound with a hexagonal structure of the type

\[
\text{AFe}_{11}\text{O}_{17}
\]

(where \(A\) is an alkali metal), which is a compensated antiferromagnetic.

When lanthanum oxide is added at high temperatures, a compound of the type

\[
(\text{ALa})_{0.5}\text{Fe}_{12}\text{O}_{19},
\]

is formed, whose magnetic properties are, as has been shown in [5], analogous to those of BHF.

Since the magnetic moment of an \(\text{Fe}^{2+}\) ion is \(4 \mu_B\), in the presence of large lanthanum additions \((x = 0.5)\) the magnitude of the AB-reaction between the magnetic sublattices in BHF will be extremely small, which will give rise to the formation of the compensated antiferromagnetic

\[
(\text{BaLa})_{0.5}\text{Fe}_{12}\text{O}_{19}.
\]

Small lanthanum additions leading to the appearance of \(\text{Fe}^{2+}\) ions statistically distributed throughout the whole specimen volume do not appreciably reduce the AB-reaction, and it is therefore possible to preserve the magnetic parameters of the unalloyed material whilst substantially raising its electrical conductivity. The influence of oxides of other REE on the properties of BHF is lined with electronic structure characteristics, possible valency states, and the existence of an orbital magnetic moment. According to Summergrad and Banks [5], hexaferrites with Pr, Nd, Sm, and Gd at room temperature are weakly magnetic.

Fig. 1. Compensation coil for magnetic intensity determination: a) general view; 
b) electric circuit.

Fig. 2. Dependence of density of lanthanum-substituted hexaferrites on degree of 
substitution.

Fig. 3. Effect of density on properties of 
lanthanum-substituted hexaferrites.

Deschamp and Bertaut [6] have shown that, when the Ba$^{2+}$ 
on is replaced by REE ions, the lattice parameters are 
not greatly reduced in spite of a significant difference in 
ionic radii. Apart from a substitution according to Eq. (1), 
the following reaction is said to be possible [6]: 

$$3\text{Ba}^{2+} \rightarrow 2\text{La}^{3+},$$

(6)

with the formation of vacancies. The correctness of this 
hypothesis can be verified by measurements of electrical 
and magnetic parameters.

Since the maximum magnetic energy of BHF prepared 
from technical reagents is attained, according to [7-9], 
when there is a slight deviation from the stoichiometric 
composition, experiments were conducted on specimens 
with compositions corresponding to the formula:

$$(\text{BaO})_{1-x}(\text{La}_2\text{O}_3)_{x/2}\cdot 5.6\text{Fe}_2\text{O}_3$$

(7)
in the range $0 \leq x \leq 0.12$.

Lanthanum was added to a prepared mixture of ferric 
oxide and barium carbonate in the form of an aqueous so-
lution of its nitride, which helped to distribute it uniformly 
throughout the charge volume. The charge was mixed for 
1 h in a 6-liter vibratory mill at a charge:water:ball ratio 
of 1:1:10 (the charge weight was 700 g). Ferritization 
was carried out in compacts for 6 h at 1300°C and was 
followed by wet vibratory milling for 4 h, as a result of 
which particles with a mean size of about 1 µ were ob-
tained. Specimens compacted under a pressure of 3.5 tons/
$c m^2$ were sintered in air at 1180-1300°C for 3 h, after which 
they were furnace-cooled.

The demagnetization curves of specimens were plotted 
using the strong-field permeameter of a U541 apparatus. 
The specimen was placed in the single-turn coil, which was 
rigidly attached to a compensating coil of the same section, 
but wound in the opposite direction (Fig. 1). Magnetization 
intensity was determined by individual measurements with 
an F-18 microwebermeter. The field in the specimen was 
measured with an instrument provided with a small Hall 
sensor [10].