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Effect of Heat Treatment on the Ultrasonic Attenuation in Mn-Ferrites

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Abstract. The acoustic losses in single crystals of manganese ferrites were studied in the temperature range from 180 to 650 K by applying longitudinal vibrations of 150 kHz. Loss peaks were observed at 232 and 537 K with activation energies of 0.3 and 0.8 eV, respectively. The first loss peak at 232 K is regarded as a stress-induced relaxation of electrons between two and three-valent ions. The second peak at 537 K is ascribed to the exchange motion of iron cations and their vacancies on octahedral sites. Heat treatments at 300 and 600°C affect the oxygen stoichiometry and distribution of cations between octahedral and tetrahedral sites which results in the changes of the loss peaks magnitudes.

1. INTRODUCTION

In our previous paper the classification of the magnetic and acoustic relaxation processes were suggested [1]. It appeared that many phenomena have a common origin. Namely, relaxations at low temperatures and with low activation energies were assigned to electronic processes occurring mostly between two and three valent iron ions. Relaxesations at high temperatures and possessing larger activation energies are due to the exchange of cations with their neighbouring vacancies.

To get more information about the processes occurring in the intermediate temperature and energy range the acoustic loss and Young’s moduli of three single crystal samples out of the manganese ferrite spinel system were investigated.

2. EXPERIMENT

Specimens for acoustic measurements were prepared from single crystal rods of the \( \text{Mn}_x\text{Fe}_{3-x}\text{O}_4 \) \((x=0.82, 1.0 \text{ and } 1.1)\) spinel series grown by arc-image floating-zone melting as described elsewhere [2]. After the growth process the crystals were additionally heat-treated in controlled atmospheres to improve oxygen stoichiometry and mechanical properties.

From the single crystal rods rectangular bars of approximate dimensions of 2.5 x 2.5 x 20 mm\(^3\) along the main crystallographic axes \(<100>\), \(<110>\) or \(<111>\) were cut. Corresponding \((100), (110)\) and \((211)\) faces were finely polished and etched by HCl solution to a depth of about 10 μm in order to remove the outermost damaged surfaces.

Acoustic losses and Young’s moduli were measured by a composite-bar resonator [3] which was mounted in a metal chamber evacuated to 10\(^{-7}\) torr. Measurements in the temperature range from 180 to 650 K were carried out in a liquid nitrogen cryostat using longitudinal vibrations mainly at 149 kHz with a strain amplitude of 10\(^{-4}\). Both the mechanical stress and the external dc magnetic field up to 600 Oe were applied parallel to the longest edge of the specimen.

3. RESULTS

The representative temperature dependencies of the acoustic loss and the Young’s modulus for the as grown samples are shown in Fig. 1 a). Two clear loss peaks accompanied with dips in the Young’s modulus are found at 232 and 537 K for \(<110>\) and \(<111>\) oriented specimens. No anomalies in \(<100>\) oriented samples were found in agreement with earlier results [3-4]. The high temperature loss peak possessed a nonsymmetrical shape (open symbols) which became symmetrical (closed symbols) upon the application of the external magnetic field. The nonsymmetrical contribution extends from about 380 K up to 545 K, the latter temperature coinciding with the Curie temperature of the \( \text{Mn}_{0.82}\text{Fe}_{1.18}\text{O}_4 \) sample. Similar measurements at two other resonant frequencies (130 and 201 kHz) showed a temperature shifts of the peak’s maxima so that the pre-exponential factor \( \tau_0 \) and the activation energy \( \epsilon \) in the Arrhenius relation \( \tau = \tau_0 \exp(\epsilon/kT) \) could be determined as 10\(^{-13}\) sec and 0.3 eV for the low-temperature peak and 3x10\(^{-14}\) sec and 0.8 eV for the high-temperature one, respectively. A plot of the low temperature peak for all the as grown samples is seen in the inset of Fig. 1 a).

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Three kinds of heat treatments were carried out with the specimens in order to change the oxygen stoichiometry and to achieve a different distribution of cations among tetrahedral and octahedral positions [5]:
(1) heating at 600°C in air for 1 hour followed by quenching to room temperature,
(2) heating at 300°C in air for 1 week followed by quenching to room temperature,
(3) heating at 600°C in nitrogen for 1 hour and slow-cooling to room temperature.
The influence of the heat treatment procedures on sample x=1.1 are demonstrated in Fig. 1 b). All measurements are made in an applied magnetic field of 600 Oe and only minor changes can be detected with the air treatments (1) and (2) of the sample. On the other hand, a significant decrease of the high temperature peak and a small increase of the low temperature peak is found on reduction of the sample by treatment (3) in nitrogen atmosphere. The effect of the heat treatment upon the low temperature peak for sample MnFe₂O₄ is shown in the inset of Fig. 1 b).

Comparing the present results with those of as-grown samples we can conclude that changes of the distribution of cations (difference between treatments (1) and (2)) hardly influence the acoustic loss of the samples. Treatments in reducing atmosphere (3) decrease magnitude of the high-temperature peak and slightly increase magnitude of the low-temperature peak.

4. DISCUSSION

To discuss the results we recall to our early paper [1]. The first loss peak at 232 K is regarded as a stress-induced relaxation of electrons between two and three-valent manganese and iron ions. The second peak at 537 K is ascribed to the interchange of iron cations and vacancies on octahedral sites. Heat treatments in the temperature range from 300 to 600°C were shown to affect the distribution of cations between octahedral and tetrahedral sites [5]. Moreover, the heat treatment in nitrogen decreases the concentration of cation vacancies on octahedral sites.

From Fig. 1 it follows that the reduction of the oxidation state (treatment (3)) has much larger influence on the acoustic losses than the changes in the degree of inversion of the samples (treatments (1) and (2)). A significant decrease of the magnitude and narrowing of the high temperature peak after reduction (3) support the idea that the relaxation processes connected with this peak are due to the cation - vacancy exchange.

A slight increase of the low temperature peak with samples x=1 and 1.1 and its absence for x=0.82 are in accord with the early idea that the processes involved are connected with the simultaneous presence of two valent iron and three valent manganese ions forming pairs in octahedral sites. For x=1 a number of such "free" pairs attains a maximum. The number of pairs decreases with rising manganese content x due to a decrease of two valent octahedral ions, probably present as Mn⁺

A sharp decrease of this effect below x=1.0 (and its total absence in x=0.82 sample) results from the "blocking" effect of the abundant Fe²⁺ for these compositions that prevent reorientation of the octahedral iron-manganese "pairs".

References