

Activation Time Dependent Magnetization of the Fe/BaTiO₃ System with Varying Constituent Mass Ratios

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Abstract: Powdery mixtures of Fe and BaTiO₃ with mass ratios of 10% Fe, 20% Fe, 30% Fe, 50% Fe, 60% Fe and 70% Fe were activated in a planetary ball mill for times ranging from 30 min to 300 min. Activated powders were pressed, then sintered for 2 h at 1200 °C. Depending on the activation time, the system changes its chemical composition. It has been experimentally observed that the magnetization of sintered samples rises with the increase of iron in the initial powders. For each sample, two measurements of the magnetization dependency on the activation time were made: the first measurement at room temperature and the second measurement after the heating to Curie temperature and subsequent cooling in the applied magnetic field of 50 kA m⁻¹. The most pronounced increase of mass magnetization before and after the thermal treatment shows the sample with minimal content of iron (10%), with the magnetization of 2.78 A m² kg⁻¹ (compared to 1.10 A m² kg⁻¹ at room temperature) which is a net increase of ~152.7%. Further increase of the activation time of initial powders leads to a decrease of magnetization of all sintered samples.

Keywords: barium titanate; iron doping; thermomagnetic properties; mechanochemical activation; sintering.

1. INTRODUCTION

Barium titanate is a well known perovskite with a structure that allows for accommodation of numerous different dopants and, consequently, modification of its functional properties in accordance with the desired results of a research. Investigated intensively since the mid-twentieth century because of its intrinsic properties such as piezoelectricity, ferroelectricity, superconductivity, multiferroicity and others, perovskites have become even more prominent in regard to possible practical applications in data storage industry [1].

Considering the ever growing amount of information in contemporary, digital age we live in, the necessity of their physical storage in the form of microscopic magnetic domains within the suitable material, it becomes clear why this is the case.

Development of technology has always rested on research efforts toward the creation of novel materials that possess coveted, controllable properties.

The latter is of great importance for the class of materials known as multiferroics. Multiferroicity, which entails manifestation of more than one of the ferroic features (ferroelectricity [2], ferromagnetism [3] and ferroelasticity [4]) in the same material, is seldom achievable in nature. In her renowned paper [5] from 2000, while considering conditions requisite for simultaneous occurrence of both ferroelectricity and ferromagnetism in certain A-B-O₃ systems, Spaldin concluded that the cause of this are d-electrons of transition metal which, despite being of fundamental importance for magnetism, suppress tendency toward ferroelectric distortion of cation inside of oxygen octahedron (Figure 1).

The question of what can give rise to ferroelectric - ferromagnetic coexistence in a material provoked the scientific community to search for answers and, by virtue of needed experimental technics already present, the race could commence [6].

Nearly two decades later, the quest for functional multiferroic magnetoelectrics [7] is still equally alive and dynamic. In this paper, we give our modest contribution to multiferroics research by

studying the influence of time of mechanochemical activation on magnetization of perovskite Fe/BaTiO₃ system with varying mass ratios of constituents.

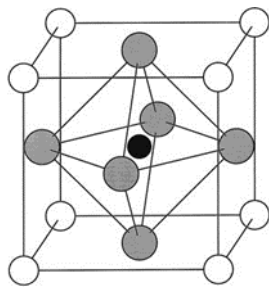


Figure 1. Cubic perovskite A-B-O₃ structure. Small B - cation (black) is in the center of octahedron comprised of oxygen anions (grey). Large A - cations (white) are situated in corners of the unit cell [5].

Observing the evolution of magnetization guided by change of these two parameters (time of activation and the amount of doped iron), we determined the mass ratio of constituents in initial powders as well as the activation time in terms of maximum magnetization increase after the heating to Curie temperature and cooling in the applied magnetic field.

2. EXPERIMENTAL

Powders of iron (Aldrich, St. Louis, MO, p.a. 99.99%) and barium titanate (Aldrich, St. Louis, MO, p.a. 99%) were mechanically mixed with mass ratios of 10% Fe, 20% Fe, 30% Fe, 50% Fe, 60% Fe and 70% Fe.

These initial powders were activated in a planetary ZrO₂ ball mill (Retsch PM 400) for duration of 30 min, 60 min, 90 min, 120 min, 150 min, 180 min, 210 min, 240 min, 270 min and 300 min, in the air atmosphere with rotation speed of 400 rpm. After the milling, samples were pressed into tablets under the pressure of 500 MPa and then sintered for 2h at temperature of 1200 °C.

Thermomagnetic measurements were performed by modified Faraday method (Figure 2) [8] in the temperature interval from 293 K – 873 K at a heating rate of 10 K/min, in an argon atmosphere. The applied magnetic field intensity at the point where the sample was positioned was 50 kAm⁻¹, whereas the field gradient was dH/dz = 4·10⁻⁹ Am⁻¹m⁻¹. The sensitivity of the laboratory balance (Sartorius 2462) was 10⁻⁷ kg.

Analytical and graphical scrutiny of experimental results were performed using appropriate software solutions [9, 10].

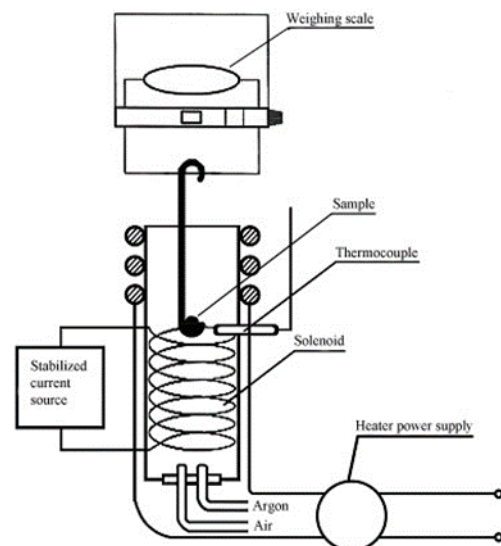


Figure 2. Schematics of the apparatus used for thermomagnetic measurements. Force that acts upon thermally regulated sample during its insertion into the magnetic field, equals by intensity to $F = \Delta m \cdot g$, where Δm is the difference in masses of a given sample outside the magnetic field and inside the field.

3. RESULTS AND DISCUSSION

Mechanochemical activation of initial mixed powders affects the content of iron and its oxide forms, given that, according to conditions of the experiment and the amount of energy that the system absorbs during activation, Fe could transition from wustite, hematite or magnetite configuration into BaTiO₃ (BTO) matrix. Site of incorporation of iron (and, withal, of other dopants, primarily belonging to the transition metals group) into BTO lattice is determined mainly by relevant ionic radii [11], i.e. ones which are involved in the process of incorporation. It is known that iron, predominantly as Fe³⁺, can embed itself on site of Ti⁴⁺ ion within the oxygen octahedron cage [12]. The experiment validates the thesis that the activation time plays a significant role in these affairs (Figure 3). Evolution of magnetization in all of the samples exhibits a similar pattern: with the activation time increasing, magnetization rises as well to a certain maximum value within the 90 min ≤ τ ≤ 120 min interval after which it follows a more or less pronounced decline. Longer milling decreases the average crystallite grain size and initial powders are becoming finer.

From the relation:

$$M = \frac{\Delta m \cdot g}{m_s} \quad (1)$$

magnetization value M could be monitored as a function of the observed change in weight of a sample $\Delta m \cdot g$, when the field is applied. In equation (1) Δm is the apparent change in mass of the sample, m_s is the mass of a measured sample without the applied field and g is standard gravity constant ($\sim 9.80665 \text{ ms}^{-2}$).

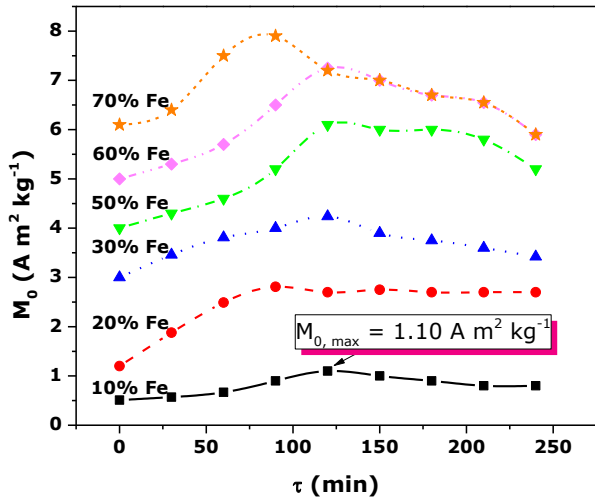


Figure 3. Change in the magnetization of samples with different initial content of iron, caused by an increase in the time of mechanochemical activation (τ), without the applied magnetic field and at room temperature (before the thermal treatment).

Notwithstanding, it is noticeable that for each sample there exists some critical value of the average size of crystallite (determined by the time of activation), after which coalescence of grains into larger agglomerates could occur, leading to decrease of magnetization due to randomization and reorienting of local magnetic moments.

Activation gives rise to defects as well as microstrain in the structural lattice – these factors influence the mobility of the Bloch wall [13] between magnetic domains, effectively reducing it (in addition, results of X-ray diffractometry obtained from the complementary Fe/BaTiO₃ (BFTO) systems [14, 15] seem to support this).

During the heating, defects and microstrain vanish and the system relaxes its structure, increasing the mobility of the walls between magnetic domains, leading to an increase in the total magnetization of samples. The magnetization maxima shift towards higher activation times and are found to be in the $120 \text{ min} \leq \tau \leq 180 \text{ min}$ interval (Figure 4).

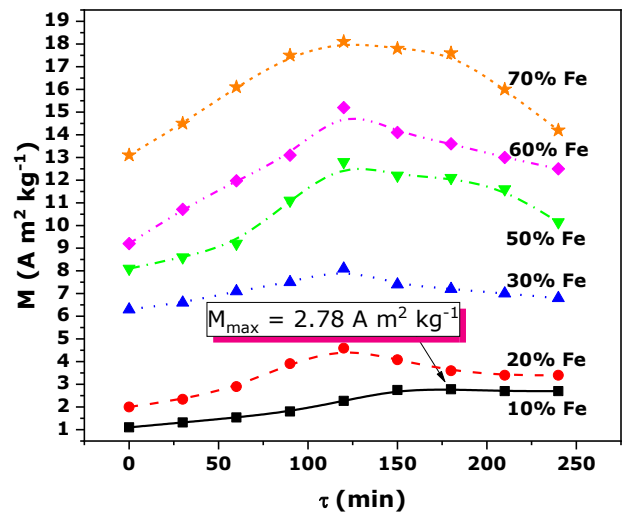


Figure 4. Magnetization of samples with different initial content of iron after the thermal treatment (heating to Curie temperature [15] and subsequent cooling to room temperature in the applied magnetic field of 50 kA m^{-1}) depending on time of mechanochemical activation (τ).

Figure 5 shows that increasing the content of iron in the initial powder affects the growth of magnetization at room temperature. Growth is even more noticeable after the thermal treatment and an increase in the difference between maxima of magnetization measured before and after the thermal treatment is observed, with the rise of iron content in the system (Table 1), but this growth is not monotonous.

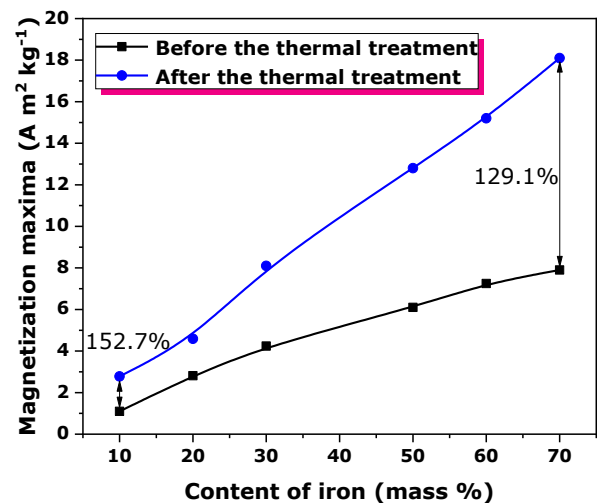


Figure 5. Maximum magnetization values of samples with different content of iron, before and after the heating to Curie temperature and cooling in the applied field of 50 kA m^{-1} .

Table 1. Influence of the content of iron in initial powders on the difference in increase of mass magnetization before and after the thermal treatment.

Fe content (mass %)	$M_{\max} - M_{0,\max}$ (%)
10	152.7
20	63.3
30	91.0
50	109.8
60	109.7
70	129.1

The greatest difference in the increase of mass magnetization is shown by the sample with the lowest content of iron (10%). Such a small amount of iron available leads to a more efficient distribution and incorporation into a BTO structure compared to, for example, a sample containing 70% of iron (see Figure 5). The excess of Fe ions can interfere with their migration into the grains due to their available free surface being limited. Further increase in the content of iron saturates the system and drives the growth of magnetization.

Although the incorporation of Fe^{3+} ions is predominant, flexibility of the BTO lattice allows for accommodation of iron ions with different valences, which can interact with each other twofold: via the mechanism of exchange of nearest neighbours (antiferromagnetic interaction) and the mechanism of alteration of next nearest neighbours (ferromagnetic interaction) [16-18].

Moreover, Apostolova et al. reminded us of empirical findings that clearly indicate the presence of incorporated Fe^{4+} ion [19]. Ferromagnetic $\text{Fe}^{4+}-\text{O}^{2-}-\text{Fe}^{4+}$ interaction is dominant in comparison with antiferromagnetic $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{4+}$ and $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ interactions, which incipiently explains the increase in magnetization [20, 21] in all of the samples. Magnetization increase, induced by the rise of iron content in the system, can be fairly well described by the function shown in Figure 6.

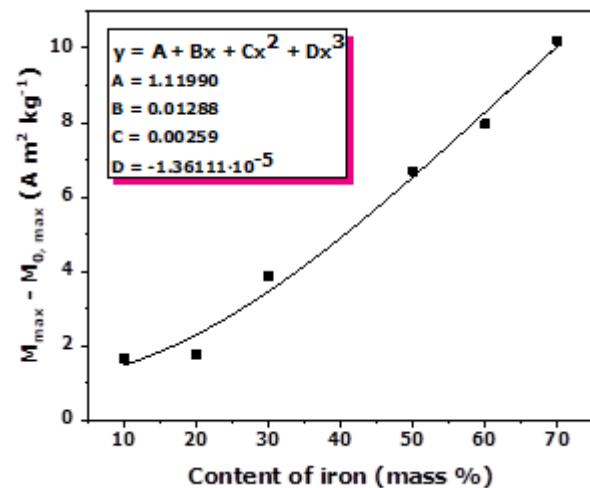


Figure 6. Difference in maximum values of mass magnetization of samples depending on the content of iron. Increase of the difference follows a polynomial function.

4. CONCLUSION

Flexible, perovskite nature of barium titanate structure permits incorporation of a large number of different dopants, which alters its functional properties, including magnetization. Mixtures of Fe and BaTiO_3 powders with mass ratios of 10% Fe, 20% Fe, 30% Fe, 50% Fe, 60% Fe and 70% Fe were activated in a planetary ball mill for time intervals ranging from 30 min to 300 min. Activated powders were pressed, then sintered for 2 h at a temperature of 1200 °C. Duration of mechanochemical activation changes the chemical composition of the system. As the activation time increases, the magnetization rises to a certain maximum and then decreases, which is directly related to the change in crystallite size in the examined samples.

Activation gives rise to defects and microstrain in the structural lattice that reduce the mobility of walls between magnetic domains. Heating relaxes the BFTO structure, with defects and microstrain disappearing and the total magnetization of samples increases. The content of iron affects magnetization and the largest difference in mass magnetization increase of ~152.7% is shown by the sample with the lowest iron content of 10%. Superposition of various mechanisms of Fe ion exchange could explain the observed increase in magnetization, which is well described by a polynomial type function $y = A + Bx + Cx^2 + Dx^3$, where A, B, C and D are constants.

Overall, magnetization of the Fe/ BaTiO_3 system is determined by the complex influence of time of mechanochemical activation coupled with the presence of iron in the initial powders, with grain size as a parameter of paramount importance.

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