

Change in Magnetization of the Fe/Pb/Zr/BaTiO₃ System Driven by Time of Mechanochemical Activation and Thermal Treatment

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Abstract: Mixtures of high purity powders of 50 mass % Fe, 4 mass % Pb, 3 mass % Zr and 43 mass % BaTiO₃ were activated in a rotary ball mill for durations ranging from 30 min to 300 min. Samples were then pressed and sintered in the air atmosphere for 2 hours at 1200 °C. It was observed that the pressing alone, i.e. without sintering, led to a decrease of magnetization in all of the samples, with the process of sintering decreasing it further, with the most dramatic drop of 90.11 % belonging to the sample activated for 150 min. Samples activated for 90 min, 180 min and 300 min were subjected to subsequent cycles of heating to Curie temperature of 345.26 °C, then cooling to 25 °C, in the applied magnetic field of 20 kA m⁻¹, where an increase of magnetization in all of the samples was observed, with the biggest increase in magnetization of 198.56 % observed for the sample activated for 300 min.

Keywords: doped barium titanate; thermomagnetic properties; mechanochemical activation; sintering

1. INTRODUCTION

For many decades, in solid-state science a class of materials known as perovskites has been occupying a central place in manifold research endeavours [1]. By virtue of their structure generalized as ABX₃ (Figure 1) where the large A cation occupies the body center, 12-coordinate position [2], perovskites doped with various elements continue to raise scientific interest demonstrating functional properties such as multiferroicity, ferroelectricity, piezoelectricity and superconductivity, among others.

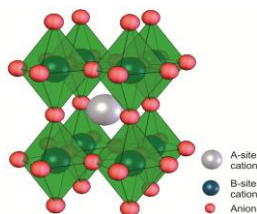


Figure 1. The cubic ABO₃ perovskite structure [3]

Of all the perovskites, barium titanate (BaTiO₃) has been one of the most investigated, due to the innate ability to accommodate into its structure a large number of dopants that yield interesting and, albeit in principle, *a priori* tailored properties. Novel development of practical applications of such systems range from high-power energy storage systems [4, 5] to sophisticated multifunctional

sensors [6], highly stable WORM (Write-Once-Read-Many times) resistive memories [7] and so forth.

In this paper main focus is on the influence of mechanochemical activation time and the thermal treatment on magnetization of the Fe/Pb/Zr/BaTiO₃ system with preordained mass % composition of its constituents, hoping to contribute to the fundamental understanding of the processes that could benefit aforementioned applications.

2. EXPERIMENTAL

High purity powders of iron, lead, zirconium and barium titanate (Aldrich, St. Louis, MO, p.a. 99.99 %, 99.999 %, 99.99 % and 99 %, respectively) of 50 mass % Fe, 4 mass % Pb, 3 mass % Zr and 43 mass % BaTiO₃ were mixed and activated in a rotary ZrO₂ ball mill (Retsch PM 400) with rotation speed of 400 rpm for durations ranging from 30 min to 300 min. Samples were then pressed using the pressure of 500 MPa and sintered in the air atmosphere for 2 hours at 1200 °C. Modified Faraday method [8, 9] was used to realize thermomagnetic measurements with laboratory balance sensitivity of 10⁻⁷ kg and 20 kA m⁻¹ of externally applied magnetic field at the location point of the sample. Experimental results were analyzed utilizing suitable software tools [10, 11].

3. RESULTS AND DISCUSSION

Since the investigated Fe/Pb/Zr/BaTiO₃ system is of fixed composition, time of mechanochemical activation predominantly affects the behavior of magnetization, prior to pressing and sintering. This was monitored using the equation

$$M = \Delta m \cdot g / m_s \quad (1)$$

where magnetization *M* is expressed as a function of the sample weight change, $\Delta m \cdot g$, caused by the external magnetic field. Here 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 the standard acceleration due to gravity ($\sim 9.80665 \text{ m s}^{-2}$).

Figure 2 shows the change in magnetization due to pressing and subsequent sintering of initial powdery samples in regard to the time of mechanochemical activation, with the applied magnetic field of 20 kA m⁻¹ and at the room temperature (before the thermal treatment).

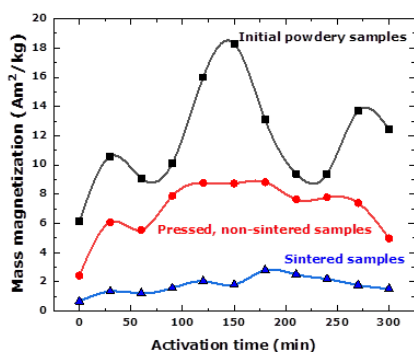


Figure 2. Influence of pressing and the following sintering on the magnetization of initial powdery samples

A noticeable decrease can be seen in the value of magnetization of pressed non-sintered samples from Figure 2, as well as sintered ones compared to the initial powders, for all activation times, with the most dramatic decrease in magnetization of 90.11 % shown by the sample activated for 150 min (Table 1). Iron dominantly contributes to the magnetization of the system both because of the starting amount of 50 mass %, as well as of its largest nuclear magnetic dipole moment of 1.22 μN [12] at the room temperature compared to the ones of lead and zirconium.

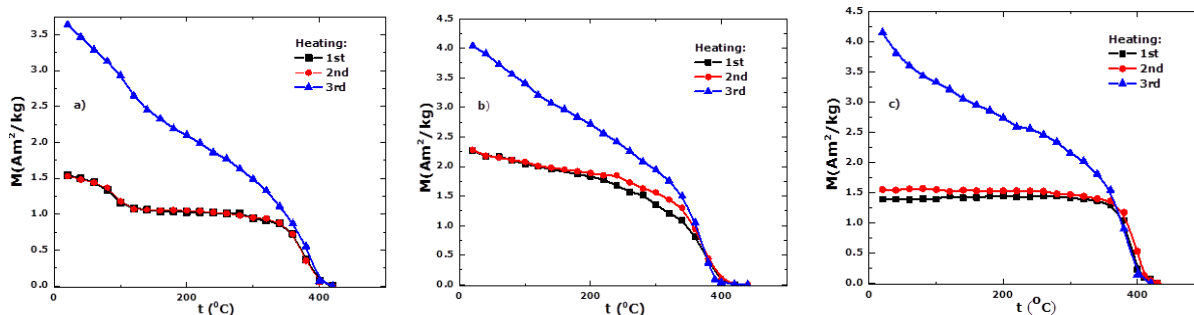


Figure 3. Magnetization in an applied field of 20 kA m⁻¹ as a function of successive heating and cooling for the sintered sample activated for: a) 90 min; b) 180 min and c) 300 min

Table 1. Decrease in magnetization of the initial powdery samples after the pressing and sintering processes.

Activation time (min)	Magnetization (A m ² kg ⁻¹)		
	Initial	After pressing	After sintering
0	6.13	2.43	0.67
30	10.60	6.09	1.35
60	9.10	5.56	1.22
90	10.10	7.88	1.58
120	16.00	8.78	2.05
150	18.30	8.74	1.81
180	13.10	8.83	2.80
210	9.40	7.65	2.51
240	9.40	7.78	2.20
270	13.68	7.41	1.78
300	12.43	4.97	1.53

During the sintering (in an air atmosphere), iron enters the structure of the barium titanate lattice in the form of Fe²⁺ and Fe³⁺ ions, most likely replacing Ti⁴⁺ ions, but also Ti³⁺ and Ti²⁺ ions on the surface of crystallites. The potential of Fe-Ti substitution becomes even more apparent by comparing their intrinsic properties such as the same atomic radius of 156 pm, complementary oxidation states of +2 and +3, as well as comparable electronegativity of 1.83 for Fe and 1.62 for Ti. Sintering of samples involves pressing and thermal treatment during which the applied pressure and temperature in an oxygen (air) atmosphere affect the system not only in the sense of incorporation of Fe into the BaTiO₃ structure, but also of removal, i.e. evaporation of certain newly formed species such as lead and iron oxides, PbO and Fe₃O₄, in that order [13]. According to the defective dipole model [14], the incorporated iron effectively immobilizes its immediate chemical environment by reducing the mobility of neighboring dipoles, whereby new, more magnetically inert domains are formed.

Therefore, the observed decrease in magnetization can be explained by the superposition of all the above-mentioned processes, whereby the question of saturating the system with iron naturally arises, since the initial composition was 50 mass % Fe, 4 mass % Pb, 3 mass % Zr and 43 mass % BaTiO₃. Sintered samples that were activated for durations of 90 min, 180 min and 300 min were subjected to three successive cycles of heating to 420 °C and then cooling to room temperature of 25 °C (Fig. 3).

It is noticeable that under the thermal treatment, magnetization follows comparable paths in all of the three samples.

Magnetization of the sample activated for 90 min begins to drop almost from the beginning of the first heating and the initial value of $1.54 \text{ A m}^2 \text{ kg}^{-1}$, reaching plateau at approximately $160 \text{ }^\circ\text{C}$ and retaining the value of about $1.03 \text{ A m}^2 \text{ kg}^{-1}$ until the Curie temperature of $345.26 \text{ }^\circ\text{C}$ is reached, when it steeply decreases to zero. The said drop at the beginning could be attributed to the phase transition the system undergoes thus changing its crystallinity. At the Curie temperature, thermal energy absorbed by the system becomes dominant and the system shifts from being ferromagnetic to paramagnetic [15]. During the second heating, magnetization follows almost identical path, starting with the value of $1.54 \text{ A m}^2 \text{ kg}^{-1}$. The second cooling however leads to an increased magnetization of $3.64 \text{ A m}^2 \text{ kg}^{-1}$ (Table 2). During the third heating, magnetization constantly decreases, with the aforementioned drop still visible albeit less pronounced.

Table 2. Change in magnetization of the sintered samples activated for 90 min, 180 min and 300 min, caused by the thermal treatment.

Activation time (min)	Magnetization ($\text{A m}^2 \text{ kg}^{-1}$)	
	Before the 1st heating (initial)	Before the 3rd heating (after the 2nd cooling)
90	1.54	3.64
180	2.27	4.04
300	1.39	4.15

In comparison to the sample activated for 90 min, magnetization of the sample activated for 180 min exhibits similar trend, the main difference being the diminishing of the initial drop. Starting from a value of $2.27 \text{ A m}^2 \text{ kg}^{-1}$, the magnetization gradually decreases, manifesting sharp decline once the same Curie temperature is reached. The second heating then cooling leads to an overall increase and the value of $4.04 \text{ A m}^2 \text{ kg}^{-1}$.

Magnetization of the sample activated for 300 min shows complete disappearance of the drop, nigh on maintaining its initial plateau value of $1.39 \text{ A m}^2 \text{ kg}^{-1}$ until the Curie temperature shared with the previous two samples activated for 90 min and 180 min is reached. The second cooling elevates the magnetization up to $4.15 \text{ A m}^2 \text{ kg}^{-1}$, the highest net increase of 198.56 % amongst the selected samples.

4. CONCLUSION

Ongoing development of practical applications of perovskites, namely barium titanate doped with various elements, continues to attract attention of

researchers worldwide. Fe/Pb/Zr/BaTiO₃ samples with 50 mass % Fe, 4 mass % Pb, 3 mass % Zr and 43 mass % BaTiO₃ were mechanochemically activated for time intervals ranging from 30 min to 300 min, then pressed and sintered at $1200 \text{ }^\circ\text{C}$. Pressing, as well as sintering that followed, decreases magnetization of all of the initial powdery samples, with the most pronounced decrease of 90.11 % belonging to the sample activated for 150 min. Magnetization of the sintered samples activated for 90 min, 180 min and 300 min, subjected to three successive cycles of heating to $420 \text{ }^\circ\text{C}$ and then cooling to room temperature, displayed comparable behavior and transition from ferromagnetic to paramagnetic phase at the Curie temperature of $345.26 \text{ }^\circ\text{C}$. After the second heating then cooling, the biggest increase in magnetization of 198.56 % showed the sample activated for 300 min.

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