The Influence of Mechanochemical Activation and Thermal Treatment on Magnetic Properties of the BaTiO$_3$-Fe$_x$O$_y$ Powder Mixture

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Abstract:

Powder mixture of 50 mass % of barium titanate (BaTiO$_3$) and 50 mass % of iron (Fe) was prepared by solid-state reaction technique, i.e. ball milled in air for 60 min, 80 min, 100 min, 120 min and 150 min. During mechanochemical activation it was observed the iron powder transitsion to iron oxides. Depending on the activation time the content of iron oxides FeO, Fe$_2$O$_3$ and Fe$_3$O$_4$ varies. Simultaneously, with the content change of the activated system, magnetic properties change as well. The XRD analysis of milled samples shown that as the activation time increase, the iron oxide percentage increases to, whereby the percentage of BaTiO$_3$ in a total sample mass decreases. The percentage of iron oxides and BaTiO$_3$ in annealed samples changes depending on annealing temperature. The thermomagnetic measurements performed by Faraday method shown that the powder mixture milled for 100 minutes exhibit maximum magnetization prior to annealing. The increase of magnetization maximum was observed after annealing at 540 ^{o}C with all milled samples, and at room temperature it has enhancement from 10 % to 22 % depending on the activation time. The samples milled for 100 min and 150 min and then sintered at 1200 ^{o}C exhibit magnetoelectric properties

Keywords: *BaTiO$_3$-Fe$_x$O$_y$ powder mixture, Mechanochemical activation, Thermomagnetic properties**, Magnetoelectric properties.*

1. Introduction

Correlation of magnetic and electric phenomena brings together few effects that attracted considerably research attention in last decade (magnetoresistance MR [1-3], magnetoimpedance MI [4-6] and dc Joule heating [7-9]). Denoted effects were investigated with the aim to evaluate potential of amorphous or nanocrystalline ferromagnetic alloys as materials for different applications [10-12]. Very interesting combination of amorphous ribbon with piezofiber laminates [13, 14] involves magnetoelectric (ME) composites as a new generation of multifunctional materials. Wang et al. [13] presented Metglas/PMN-PT fiber

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laminates as an excellent ME composite for low noise sensor of ultralow magnetic field (at frequency f = 1 Hz).

Magnetoelectric coupling effect (usually recognized as a combination of ferromagnetism and ferroelectricity) make multiferroic Fe doped $BaTiO_3$ (BTO) ceramics as a promising material for sensor application (for instance magnetic field sensor). Lin et al. were reported the highest room temperature saturation magnetization for $Ba(Ti_{0.93}Fe_{0.07})O_3$ (BTFO) ceramics prepared by solid-state reaction [15]. The transition metal (M) codoped BTO ceramics (Fe/M, M=Cr, Mn, Ni) prepared by grinding of powder mixture also exhibit ferromagnetism at room temperature [16]. Recently, it was shown that the influence of thermal treatments for the Fe-implanted BTO films was followed with decrease of coercivity and enhancement of magnetization [17, 18]. Mechanical activation is well established preparation route for barium-titanate [19] and magnesium titanate (MTO) [20] based electroceramics.

In this study mechanical activation of BTFO powder mixture (with the same starting mass quantity of Fe and BTO) was followed with investigation of magnetic properties dependence vs. milling time interval and annealing temperature.

2. Experimental

The initial powder was the mechanical mixture of 50 mass % of Fe and 50 mass % of $BaTiO_3$. The powder mixture was activated in planetary ball mill (Retsch PM 400) for 60 min, 80 min, 100 min, 120 min and 150 min at 300 rev/min. During the activation in the air atmosphere the iron powder oxidized, while the mass percent of the iron oxides Fe_xO_y and $BaTiO_3$ in the powder mixture was changed. X-ray diffraction (XRD: Bruker AXS D8 with Cu-K_α radiation, λ= 0.154 nm) was used to analyze phase structure of the investigated samples. Mass percent have been calculated by full width of the peak at half maximum (FWHM method) by means of EVA 9.0 program. XRD analysis was performed for the powder mixtures activated for 80 min, (sample A), 100 min (sample B), 120 min (sample C) and for 150 min (sample D). Powder samples were pressed by 500 MPa in disc shaped samples with 8 mm in diameter.

Succesive heating runs, followed with 30 min. annealing at temperatures of 360 ^{o}C, 440 ^{o}C, 540 ^{o}C and 640 ^{o}C were performed in air atmosphere.

Thermomagnetic measurements in air atmosphere were conducted by Faraday method that presumes the influence of non-homogenic magnetic field on magnetic sample during heating [11]. The measurement sensitivity of the magnetic force was 10^{-6} N in the applied magnetic field with intensity of H_{app} = 9.6 kA/m. Sintering was performed at 1200 ^{o}C during 1hour in air atmosphere.

3. Results and discussion
3.1. X-ray diffraction analysis

XRD patterns of the powder mixture activated for 80 min, 100 min, 120 min and 150 min are shown in Fig. 1.

The analysis of results shown in Fig. 1 indicates that the increase in activation time of the powder is followed with increase of broadening of peaks in diffraction pattern while intensities of peaks decrease. Therefore, the mechanical activation of the powder causes the comminution of the powder particles and generation of defected powder structure.
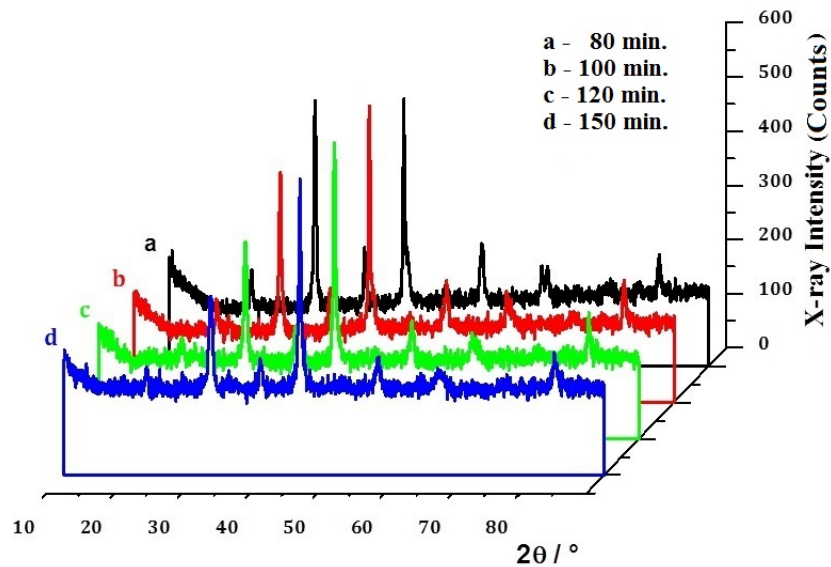
Fig. 1. X-ray diffraction patterns of the powder mixture milled during:
a)   80 min (sample A), b) 100 min (sample B), c) 120 min (sample C) and d) 150 min
b)   (sample D).

Simultaneously, during the powder activation process in the air atmosphere, iron oxides Fe_xO_y emerged and their content changes with milling time, as it is shown in Fig. 2.
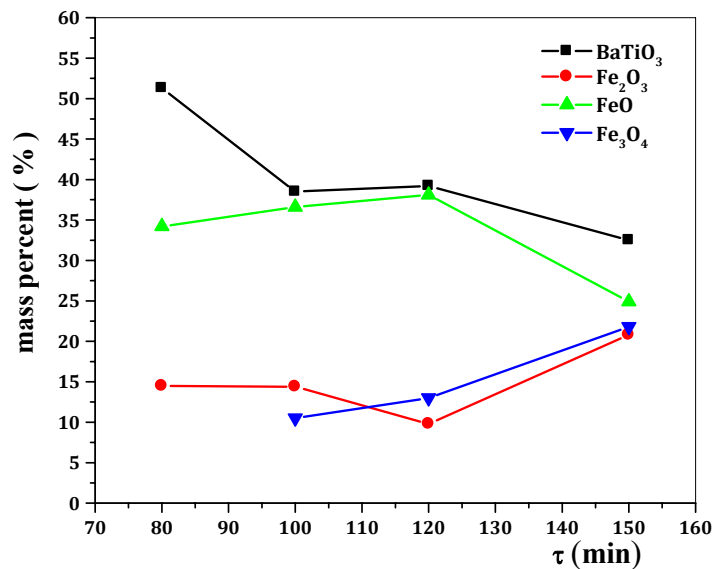

Fig. 2. The changes of the mass percent of $BaTiO_3$ and Fe_xO_y with milling time.
The lines are a guide to the eye.

The results shown in Fig. 2 indicate that the magnetite (Fe_3O_4) in the powder mixture occur only after the activation time interval of 100 min. With further increase in the milling time from 100 min to 120 min a part of Fe_2O_3 transits into Fe_3O_4, while the mass percent of FeO and $BaTiO_3$ slightly changes. During the activation time of 120 min and 150 min, FeO partially transits into Fe_2O_3 and Fe_3O_4 whose content significantly increases, while FeO and $BaTiO_3$ in the total mass decreases.

The contents of powders A, B, C and D are shown in the Table I.

Tab. I The contents of the powder samples prepared by different milling time.

Powder	Milling time (min)	$BaTiO_3$ %	FeO %	Fe_2O_3 %	Fe_3O_4 %
A	80	51.3	34.2	14.5	0
B	100	38.5	36.6	14.4	10.5
C	120	39.2	38	9.8	13
D	150	32.5	24.9	20.8	21.8

X-ray patterns of the powder mixture samples milled for 150 min (as-prepared (sample D), annealed at 440 ^{o}C and at 640 ^{o}C) are shown in Fig. 3.
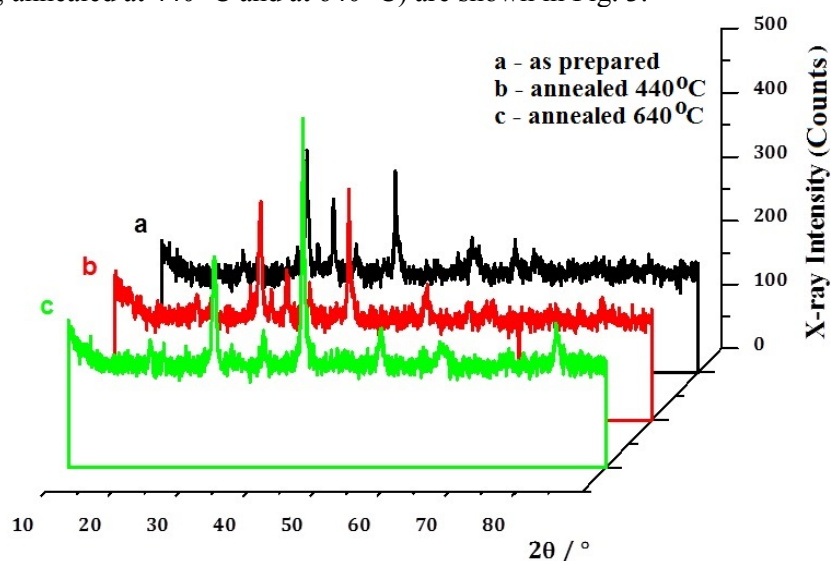
Fig. 3. X-ray diffraction patterns of the powder mixture samples milled for 150 min: a) as-prepared (sample D), b) annealed at 440 ^{o}C, c) annelaed at 640 ^{o}C.
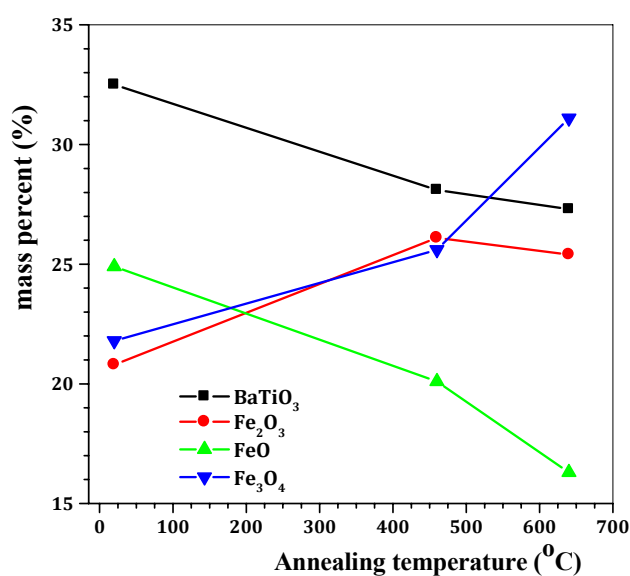

Fig 4. The changes of mass percent of $BaTiO_3$ and Fe_xO_y with annealing temperature (sample D milled during 150 min). The lines are a guide to the eye.

The results presented in Fig. 3 show that the increase of annealing temperature is followed with decrease of broadening of the peaks, as well as increase of intensity. Simultaneously, the changes in composition of samples were observed and given in Fig. 4.

The results presented in Fig. 4 shows that the content of oxides Fe_2O_3 and Fe_3O_4 increases, while the content of FeO decreases with annealing temperature increase.

3.2. Results of thermomagnetic measurements

Experimentally obtained temperature dependences of normalized magnetic permeability during sucessive heating runs of the powder mixture samples (milled for 60 min, 80 min, 100 min, 120 min and 150 min) are shown in Figures 5, 6, 7, 8 and 9 respectively.
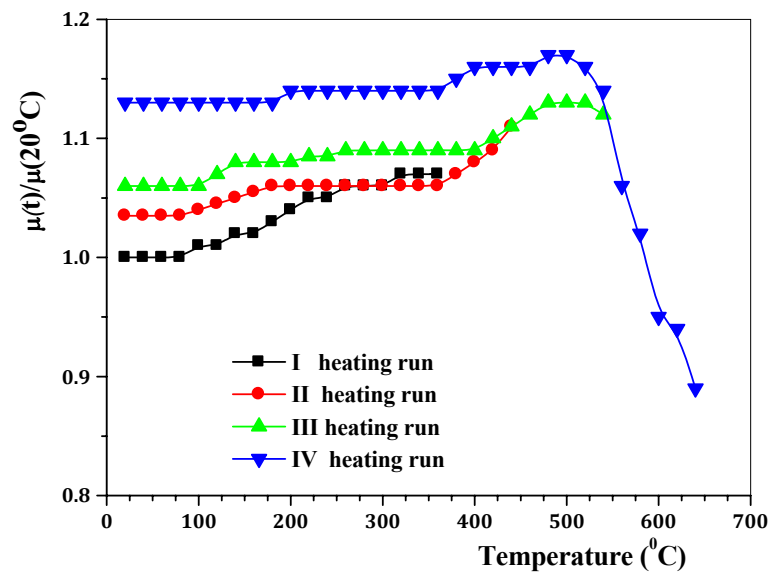

Fig. 5. Temperature dependence of the normalized magnetic permeability of the pressed powder mixture milled for 60 min.
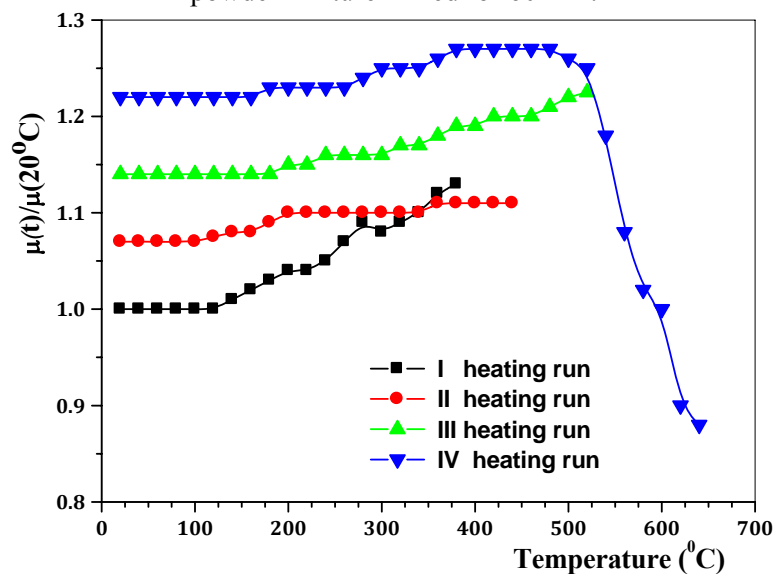

Fig. 6. Temperature dependence of the normalized magnetic permeability of the pressed powder mixture A (milled for 80 min).
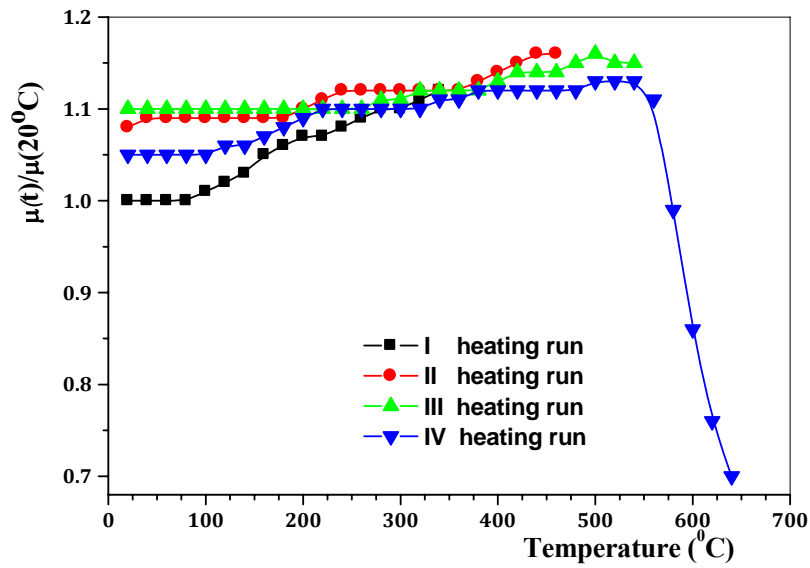
Fig. 7. Temperature dependence of the normalized magnetic permeability of the pressed powder mixture B (milled for 100 min).
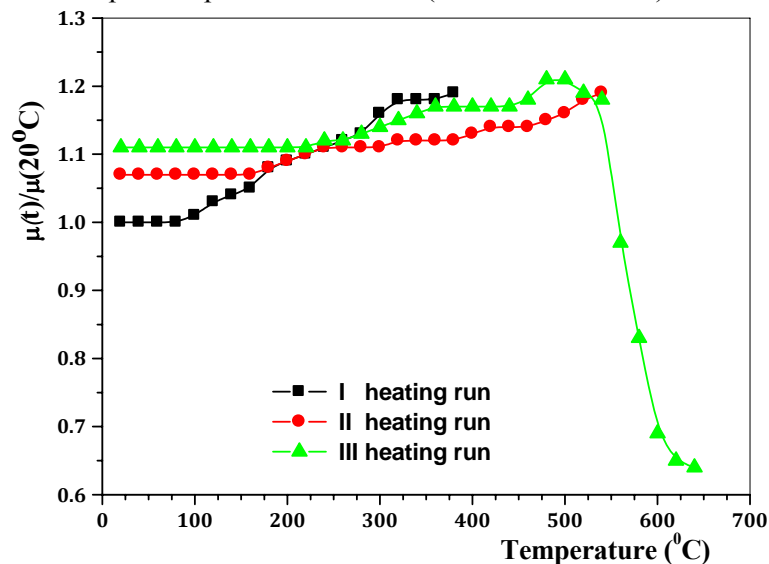

Fig. 8. Temperature dependence of the normalized magnetic permeability of the pressed powder mixture C (milled for 120 min).

The analysis of the results shown in Fig. 5 to 9 indicates that the magnetic permeability of all samples during the annealing increases till the temperature of about 500 °C.

Curie temperature of the samples A, B, and C is about 570 °C, whereas for the sample D it increases and is about 600 °C. The increase in Curie temperature of the sample D (milled for 150 min), is caused by more stable powder structure obtained during previous annealing. The internal energy of the longest activated powder (150 min) is increased, which enable structural rearrangement during thermal treatments and it is followed by increase in Curie temperature.
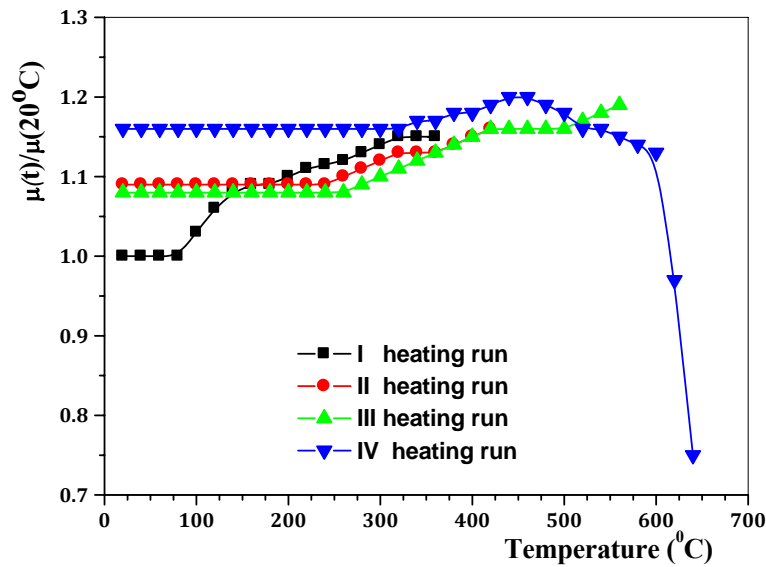
Fig. 9. Temperature dependence of the normalized magnetic permeability of the pressed powder mixture D (milled for 150 min).

The dependence of magnetization (after thermal treatments) vs. annealing temperature for different milling time interval is shown in Fig. 10. The results of the measurements shown in Fig. 10 indicate that the maximum magnetization of all samples is attained after annealing at 540 ^{o}C. The increase in magnetization upon the annealing at 540 ^{o}C is caused by the structural relaxation process of the powder mixture.
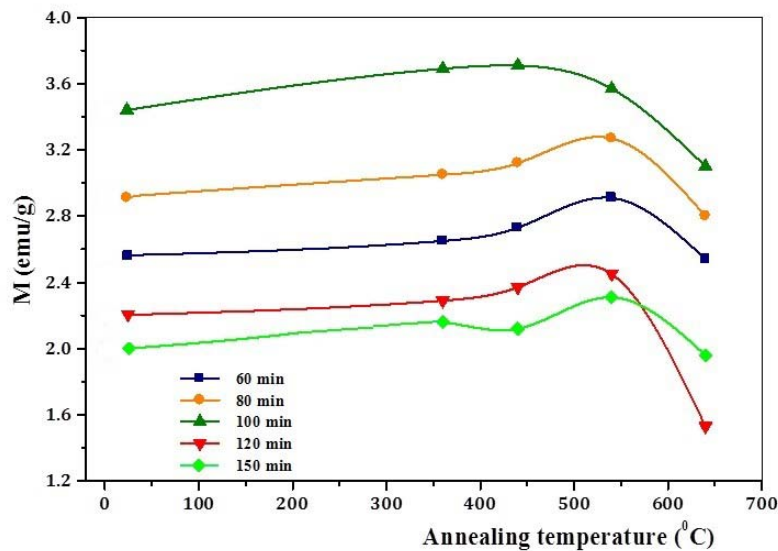

Fig. 10. The dependence of magnetization (at room temperature) vs. annealing temperature for all milled samples.

The XRD analysis showed that during the activation, structural defects and mechanical microstrains are generated in powder mixture. This defects and microstrains act as a magnetic domain wall pinning centers and reduces their movement. Annihilation of defects and mechanical microstrains under thermal treatment improve the mobility of magnetic domain walls. Simultaneously, structural relaxation process enable better overlapping of electron 3d and 4s orbits of iron atoms. Therefore, the structural relaxation process during thermal treatement causes the increase of magnetization.

The diagram on Fig. 11 shows dependence of maximum magnetization (measured at room temperature) before and after annealing up at 540 ^{o}C vs. activation time interval. The results shown in Fig. 11 indicate that the maximum magnetization before and after annealing has the sample of powder mixture activated for 100 min, being M_0 = 3.42 emu/g before and M' = 3.57 emu/g after annealing .
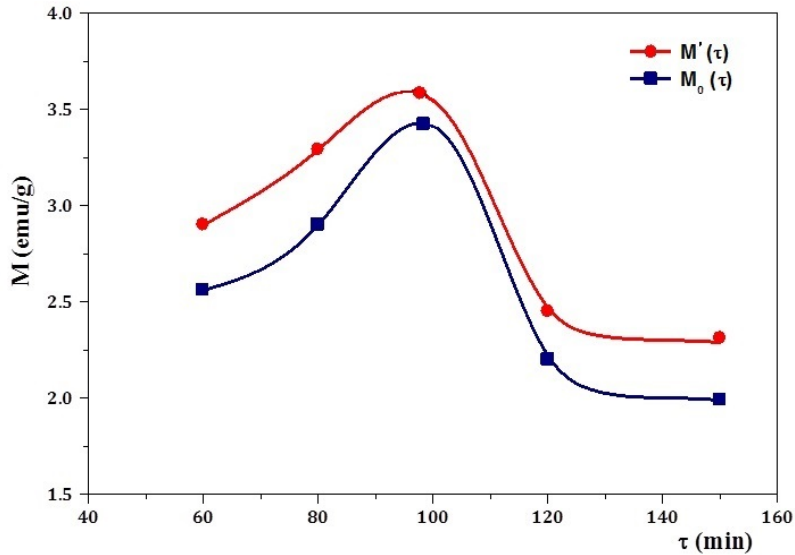

Fig. 11. Dependence of the maximum magnetization (measured at room temperature) before (M_0) and after (M') annealing at 540 ^{o}C vs. activation time.

This result can be explained by $FeO \cdot Fe_2O_3$ magnetite spinel structure, i.e. by exchange interaction of Fe^{3+} ion in tetrahedral (A) and octahedral (B) positions.

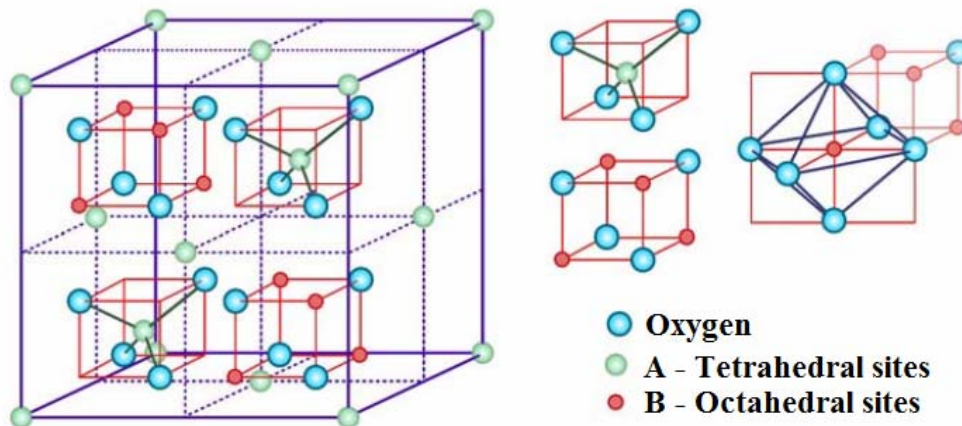**Fig. 12.** The magnetite spinel structure $FeO \cdot Fe_2O_3$ [21].

The exchange interactions (AA, AB and BB) favour anti-parallel orientation of the spins connected by interraction. The magnetic moments of magnetite $FeO \cdot Fe_2O_3$ is presented on Fig. 12. Feri (Fe^{3+}) ions are with the 5/2 spin state and zero orbital momentum. Therefore, every Fe^{3+} ion should contrubute with five Bohr magneton$s$ ($5\mu_B$) to the saturation momentum. Fero (Fe^{2+}) ions have spin 2 and should contribute with $4\mu_B$, while neglecting residual - orbital momentum. However, AB interaction is the strongest, meaning that in order to have all A spins anti-parallel to B spins, all A spins are inter-parallel as well as all B spins. Hence, the total contrubution of feri (Fe^{3+}) ions to magnetization due to exchange interraction

of Fe^{3+} ions in tetrahedral positions with Fe^{3+} ions in octahedral positions (AB) is practically annuled.

Therefore, magnetic moment of magnetite $FeO \cdot Fe_2O_3$ is generated only from Fe^{2+} ions embedded in octahedral (B) positions. After 100 minute activation of initial as-prepared powder, the percentage of Fe^{2+} ions in the powder reaches the maximum, which causes maximum magnetization. By increasing the activation time interval ($\tau > 100$ min), the percentage of Fe^{2+} ions in the activated powder decreases, which causes the decrease in magnetization of the pressed samples.

The diagram on the Fig. 13 shows the dependence of the normalized magnetic permeability of the samples B (100 min) and D (150 min) sintered at temperature of 1200 ^{o}C within one hour.
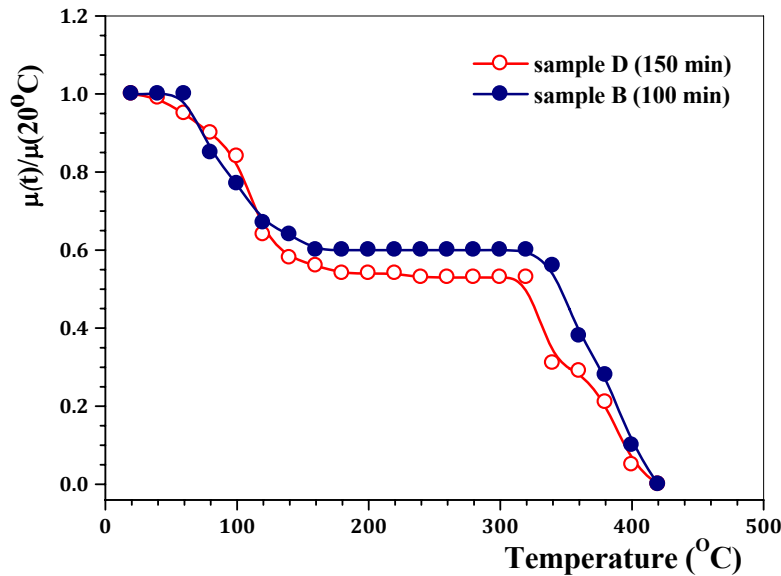

Fig. 13. The dependence of normalized magnetic permeability over the temperature of the samples activated for 100 min and 150 min with following sintering at 1200 ^{o}C.

The analysis of the experimental results shown in Fig. 13 indicates two significant decrease in magnetic permeability of the samples B and D. The first decrease in magnetic permeability of about 45% occurs at ferroelectric Curie temperature range of barium-titanate phase (from 60 ^{o}C to 130 ^{o}C). The second decrease is in the temperature range betweeen 320 ^{o}C do 400 ^{o}C, that is the ferromagnetic Curie temperature of the sample. With further heating over 400 ^{o}C the investigated samples exhibit non-feromagnetic properties. This behaviour is in very well accordance with results of Xu et al. [22] for Fe-doped $BaTiO_3$ ceramics prepared also by solid state reaction method. They reported ferroelectric-paraelectric transition at $T_{FE} = $ 365 K (92 ^{o}C) for $BaTi_{0.95}Fe_{0.05}O_{3-}$ ceramics, as well as ferromagnetic-paramagnetic transition $T_{FM} = 680$ K (403 ^{o}C), for preheated, presintered and finally sintered samples at 1300 K (1027 ^{o}C). Recently, Deka et al. [23] examined $BaTi_{1-x}Fe_xO_3$ ceramics and observed the decrease of T_{FE} with increase of iron content (from 390 K (x=0) to 312 K (x=2)), as well as $T_{FM} = 462$ K (189 ^{o}C). Hou et al. [24] have reported $T_{FM} = 580$ K (303 ^{o}C) for Fe:BTO film (obtained by pulsed laser deposition) implanted with Fe ions as well as distinct change in magnetization at $T_{FE} = 457$ K (184 ^{o}C) as an evidence of coupling effect of ferromagnetism and ferroelectricity. Therefore, it can be concluded that the iron content in BTFO ceramics strongly affected both T_{FE} and T_{FM} temperatures. Analysis of the curves on Fig. 13 shows coupling between the ferroelectric and ferromagnetic order parameters.

4. Conclusion

Mechanical activation of BTFO powder mixture (with the same starting mass powders of Fe and BTO) was investigated over milling time and annealing temperature. The content of obtained BTFO powder mixture depends on the activation time.

It has been shown that with the increasing of activation time interval, the content of iron oxides FeO, Fe_2O_3 and Fe_3O_4 significantly changes. The magnetic properties of investigated samples obtained from pressed powder mixture were in direct coorelation with the presence of different iron oxides Fe_xO_y and their inter-relation.

The XRD analysis of the powder mixture activated for 80 min, 100 min, 120 min and 150 min showed that the increase in activation time interval is followed with the increase of involved structural defects and mechanical microstrains. Therefore, different magnetic properties were observed with activated samples. The process of structural relaxation proceeds during annealing treatment and enhancement of magnetic permeability were attained with all samples.

It has been shown that the maximum increase in magnetic permeability, at room temperature, is achieved upon the annealing to the temperatrure of 540 ^{o}C, when the structural relaxation process is finished. The maximum magnetization before and after annealing has the sample obtained from pressed powder mixture activated for 100 min, being $M_0 =$ 3.42 $\dfrac{emu}{g}$ before and M' = 3.57 $\dfrac{emu}{g}$ after the annealing. This is probably the result of high percentage of Fe^{2+} ions in the powder mixture activated for 100 min. The samples milled for 100 min and 150 min and then sintered at 1200 ^{o}C exhibit magnetoelectric properties which depends on iron oxides content.

Acknowledgements

5. References

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Садржај: *У раду су испитивана својства BaTiO₃-FeₓOᵧ смеше прахова добијене механохемијском активацијом у трајању од 60, 80, 100, 120 и 150 минута. Узорци за испитивање су добијени изостатичким пресовањем. Током млевења једнаких маса баријум титаната и гвожђа на ваздуху, одиграва се оксидација гвожђа и појава оксида FeO, Fe₂O₃ и Fe₃O₄ чији садржај зависи од дужине трајања млевења. Рендгеноступтурном анализом је показан пораст садржаја оксида гвожђа и смањење садржаја баријум титаната. Одгревањима на више различитих температура до максималне температуре од око 640 ᴼC остварена је релаксација структуре праћена повећањем вредности магнетизације механохемијски активиране смеше прахова. Након термичких третмана регистровано је повећање вредности нормализоване пермеабилности од око 10 % до 22 %. Синтеровањем на температури од 1200 ᴼC добија се изражен магнетоелектрични ефекат код узорака млевених 100 мин. и 150 мин.*
Кључне речи: *BaTiO₃-FeₓOᵧ смеша прахова, механохемијска активација, термомагнетна својства, магнетоелектрична својства.*