Preparation of a pH Sensor with Mg-doped BST-oxide gate and dielectric characteristics of Sensor Structure under Ultrashort Electron Beam Irradiation

Norayr Martirosyan

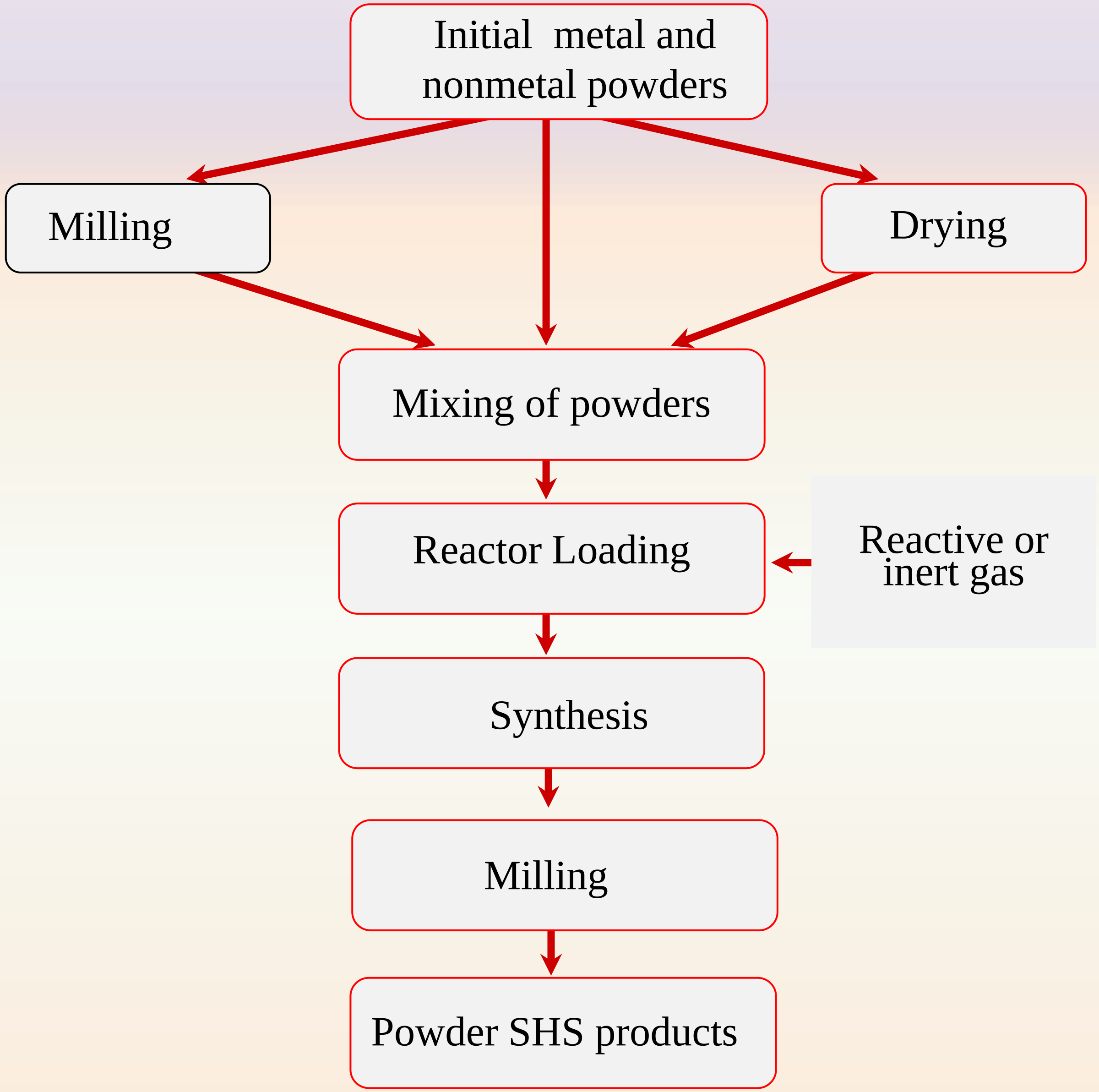
CANDLE, 0040 Yerevan, Armenia

E-mail: n_martirosyan@asls.candle.am ; Tel.: +374 99 993349

Topics

- SHS of $Ba_{0.8}Sr_{0.2}Mg_{0.1}Ti_{0.9}O_3$ Compound
- Properties of BST Based Capacitive Field-effect pH Sensors
- Dielectric characteristics of nanofilm Pt/Ba0.8Sr0.2Mg0.1Ti0.9O3/Pt structure under electron beam irradiation

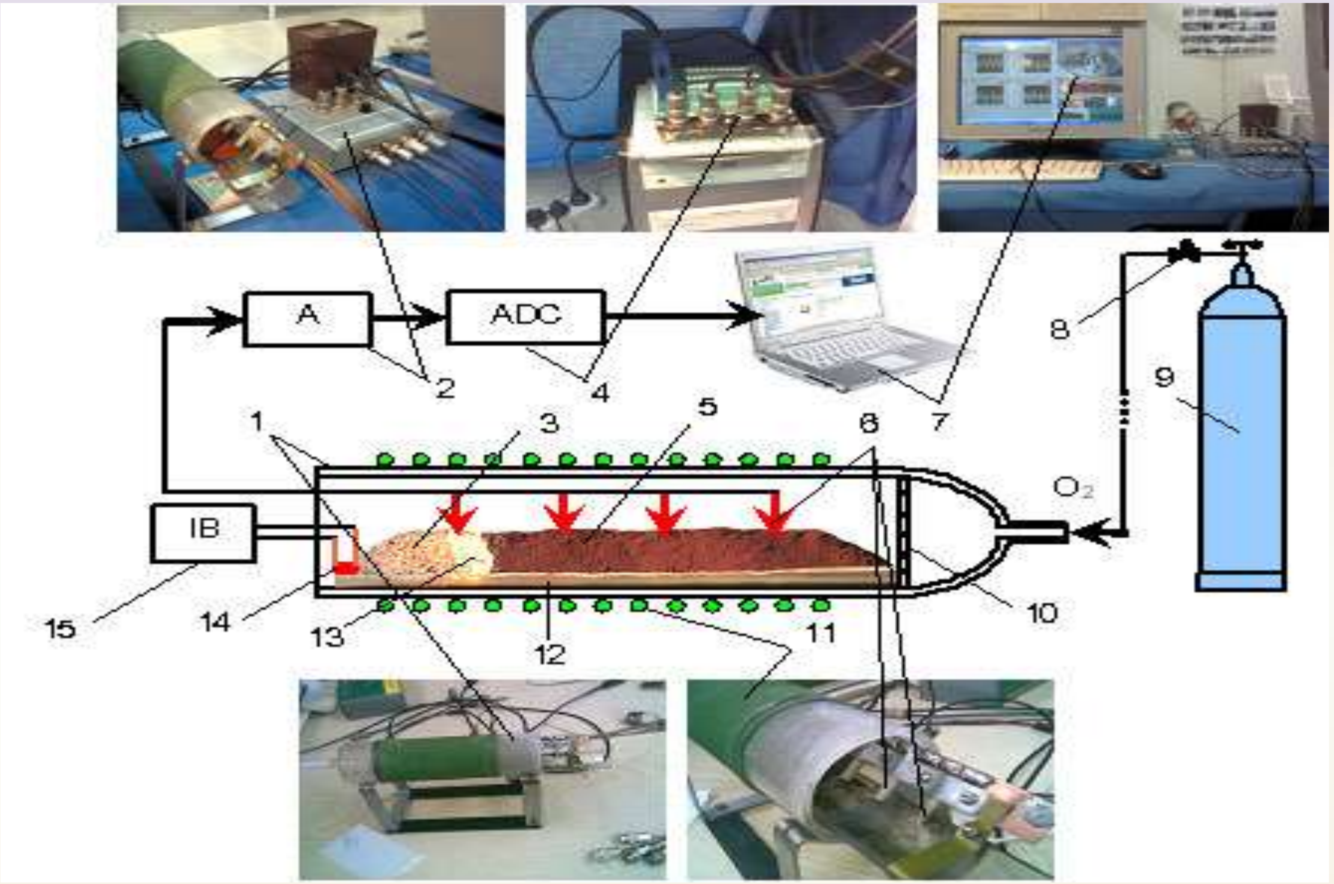
SHS Powder Production Technology



The technological scheme of powder production includes the following operations:

- preparation of a green mixture;
- milling, drying of components;
- mixing;
- filling of a reactor with a green mixture and gases;
- synthesis after a short–time thermal initiation;
- subsequent processing of synthesized products;
- milling, drying.

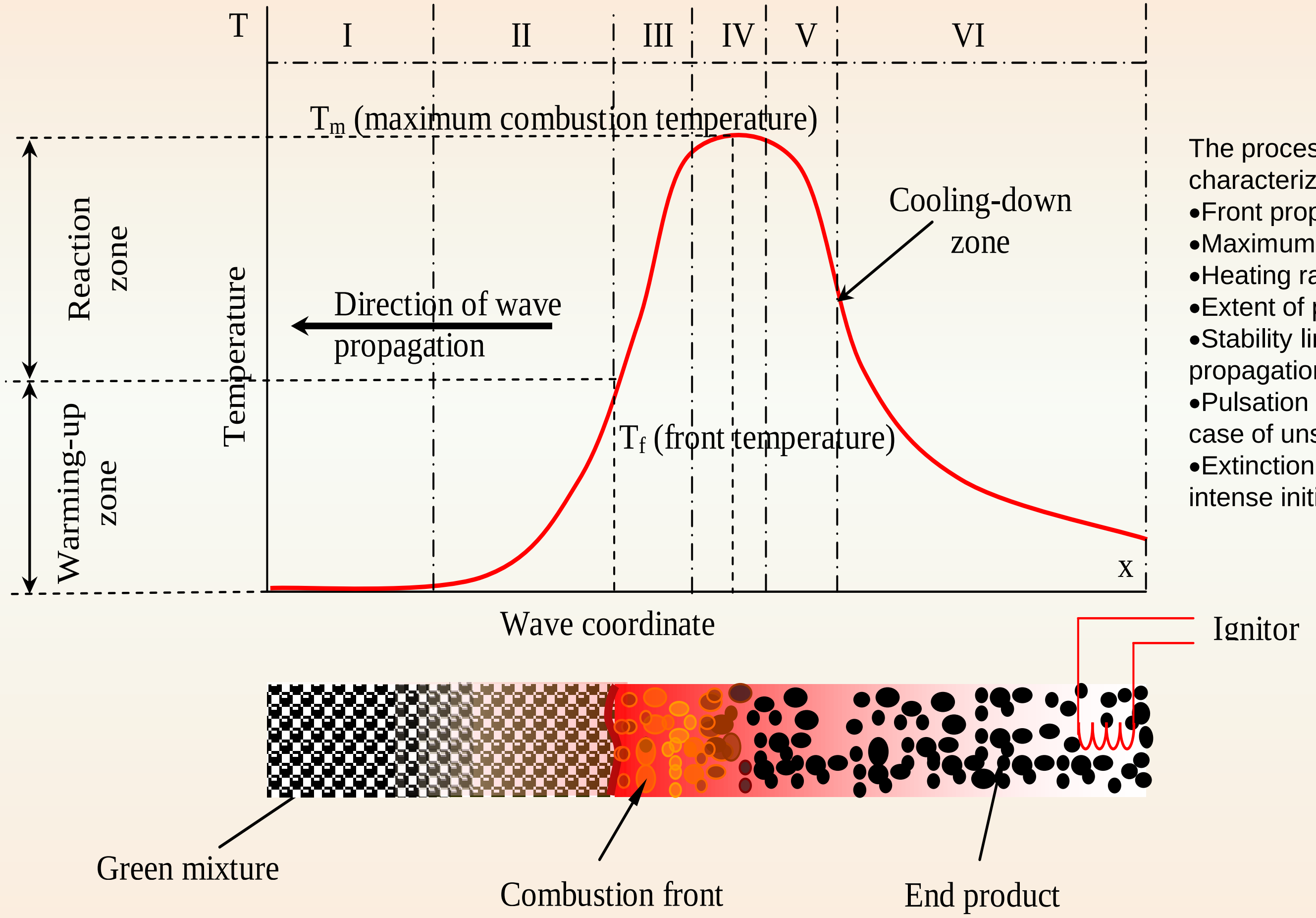
Experimental SHS Reactor



1. Quartz tube; 2. low noise amplifier; 3. end product; 4. analog-digital convertor; 5. green mixture; 6. thermocouples; 7. PC; 8. oxygen flow controller; 9. oxygen; 10. quartz mesh; 11. heater; 12. thermoresistant boat; 13. combustion front; 14. wolfram ignitor; 15. ignition block.

Temperature Distribution Along Combustion Front Propagation

I-green mixture; II-warming-up zone; III-metal oxidation zone; IV-active oxidation of metal and formation of the intermediated; V-zone of secondary chemical interactions between intermediates and formation of final product; VI-cooling-down zone.



The process of wave propagation is characterized by:

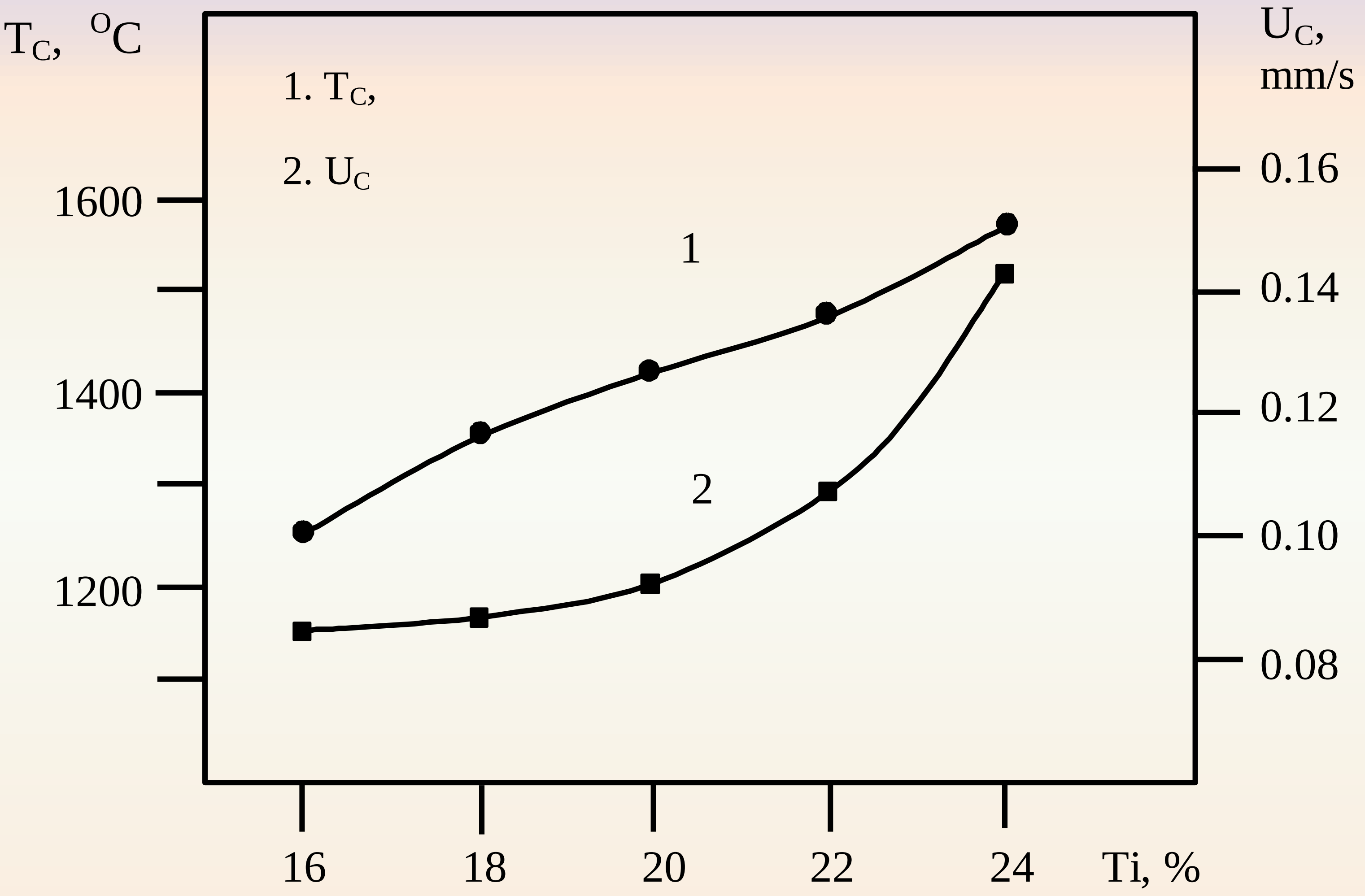
- Front propagation (burning) velocity.
- Maximum combustion temperature.
- Heating rate in the combustion front.
- Extent of phase/structure transformation.
- Stability limit (steady or unsteady wave propagation) .
- Pulsation frequency, hot spot velocity, etc. (in case of unsteady combustion).
- Extinction limit (no combustion even upon intense initiation).

The Synthesis were Done According to the Following Chemical Schemes

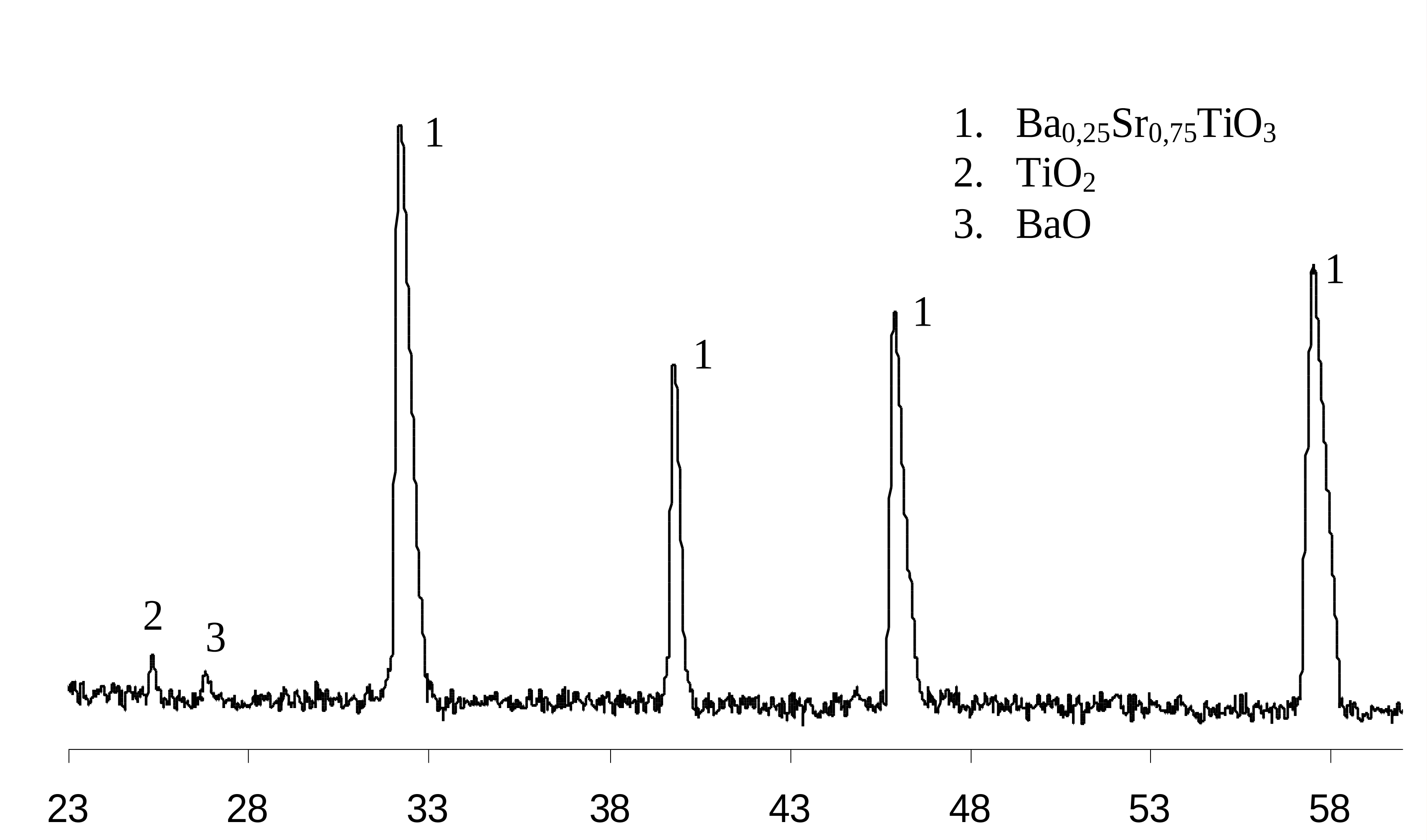
- $yMgO + x\mathrm{BaO_2} + [1\text{-}y][(1\text{-}k)\mathrm{TiO_2} + k\mathrm{Ti}] + (1\text{-}x)\mathrm{SrCO_3} + \mathrm{O_2} \rightarrow \mathrm{Ba_xSr_{1\text{-}x}Mg_yTi_{1\text{-}y}O_3}$

- $x\mathrm{BaO_2} + (1\text{-}k)\mathrm{TiO_2} + k\mathrm{Ti} + (1\text{-}x)\mathrm{SrCO_3} + \mathrm{O2} \rightarrow \mathrm{Ba_xSr_{1\text{-}x}TiO_3}$

Combustion temperature (T_c) and velocity (U_c) *vs.* amount of combustible (Ti) in the initial mixture



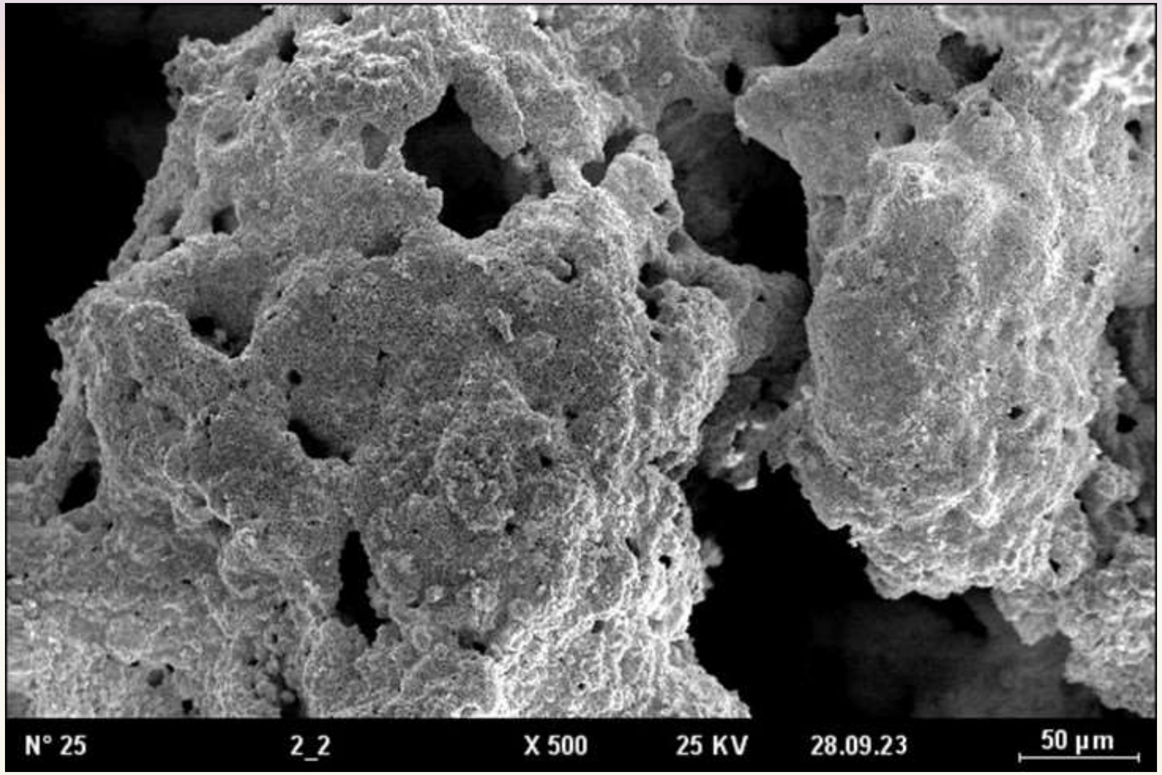
XRD patterns of BSTO powder



SEM images of Mg doped $Ba_{0.8}Sr_{0.2}TiO_3$ compositions after SHS

a)k=0.4; b)k=0.6.

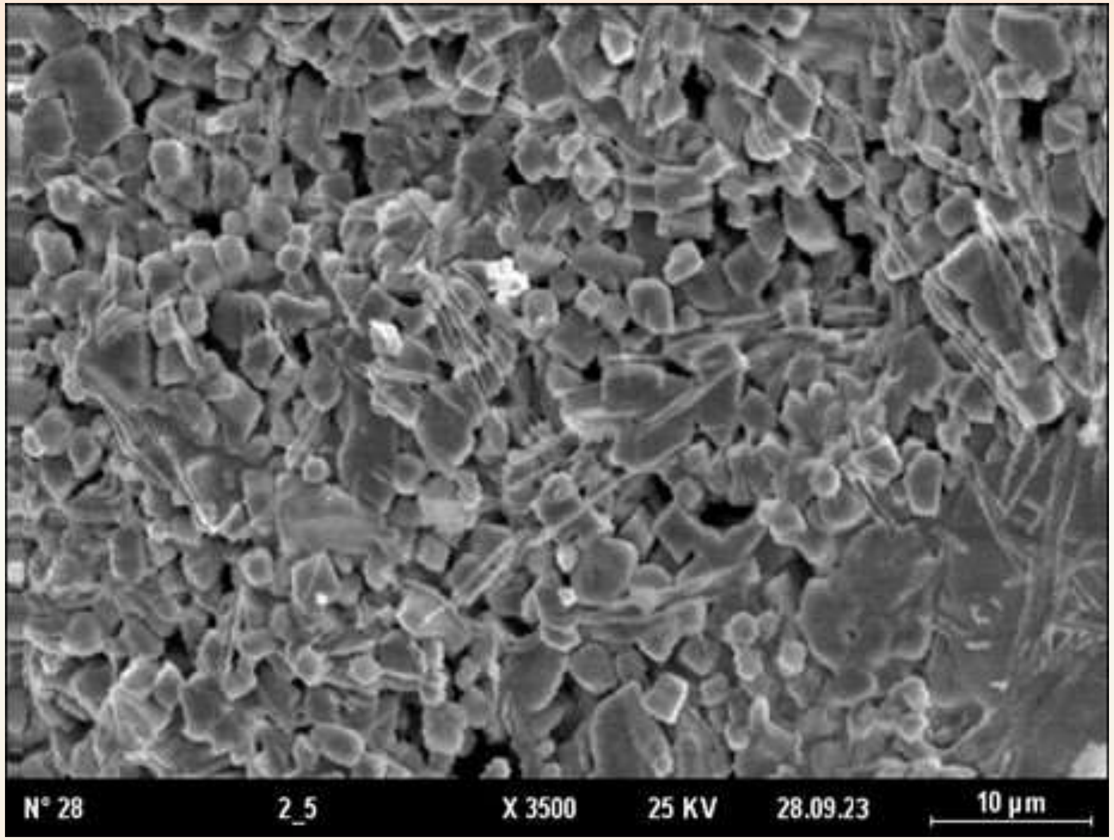
a)



b)

SEM images after grinding by PULVERISETTE 6 planetary ball mill

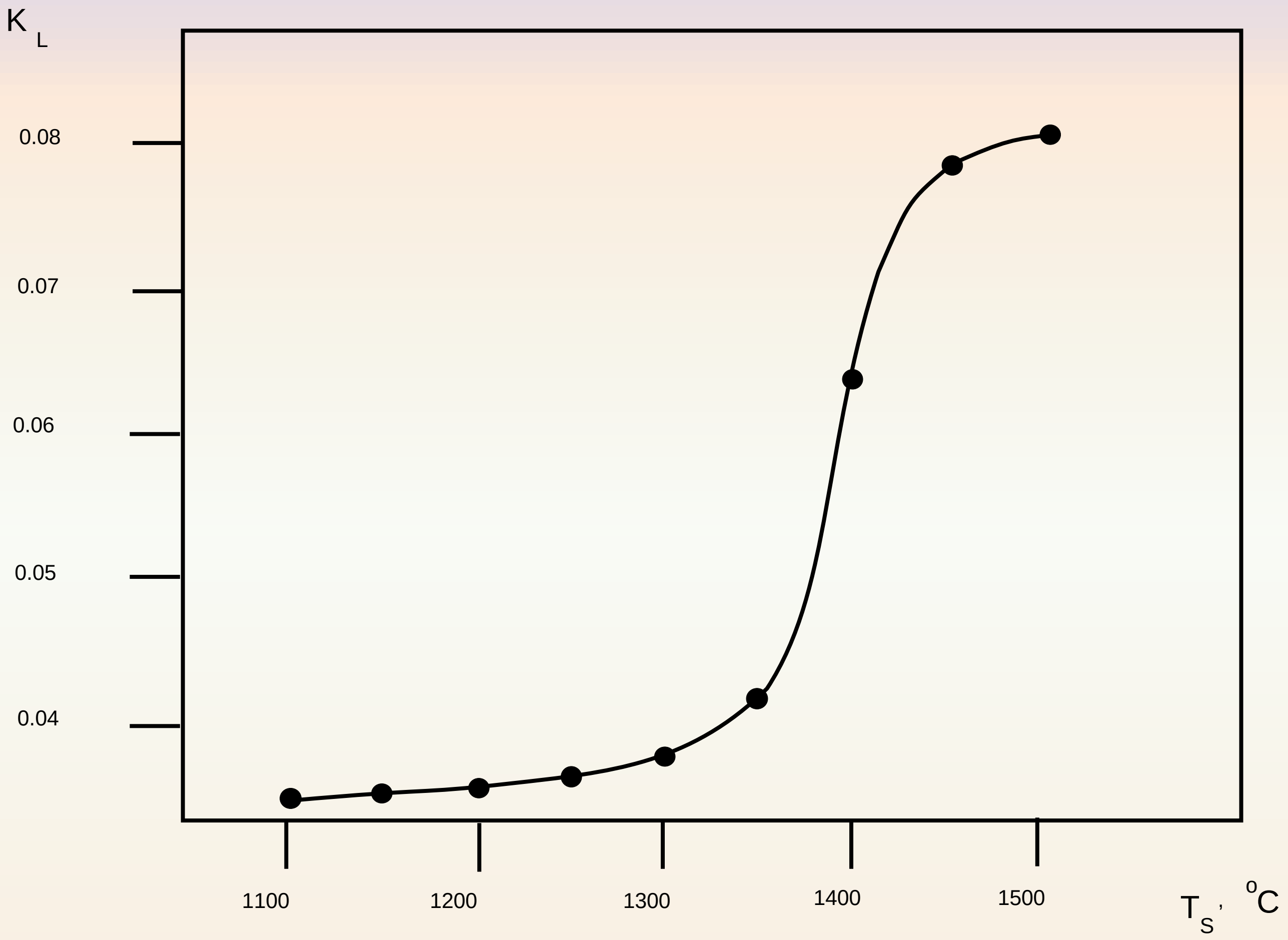
The milling duration is a)- 6 hours, b)- 11 hours.



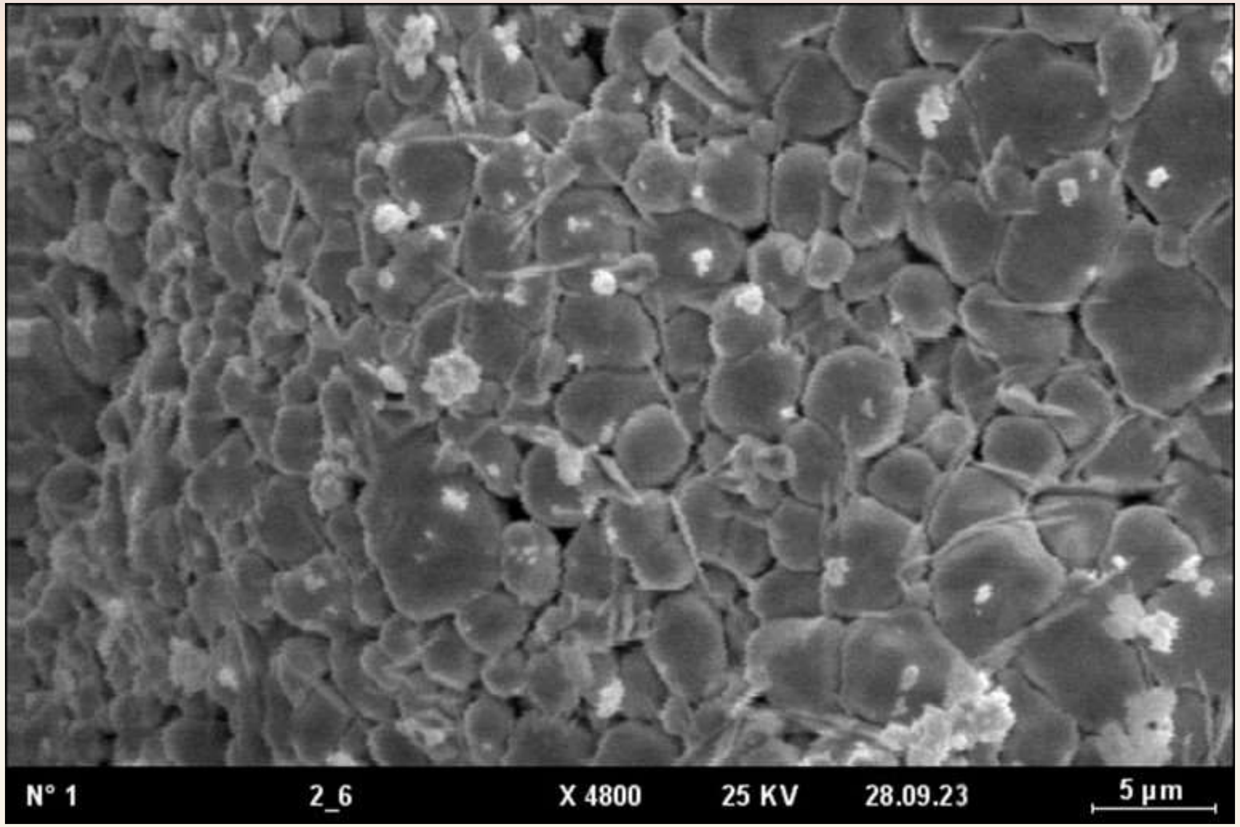
a)

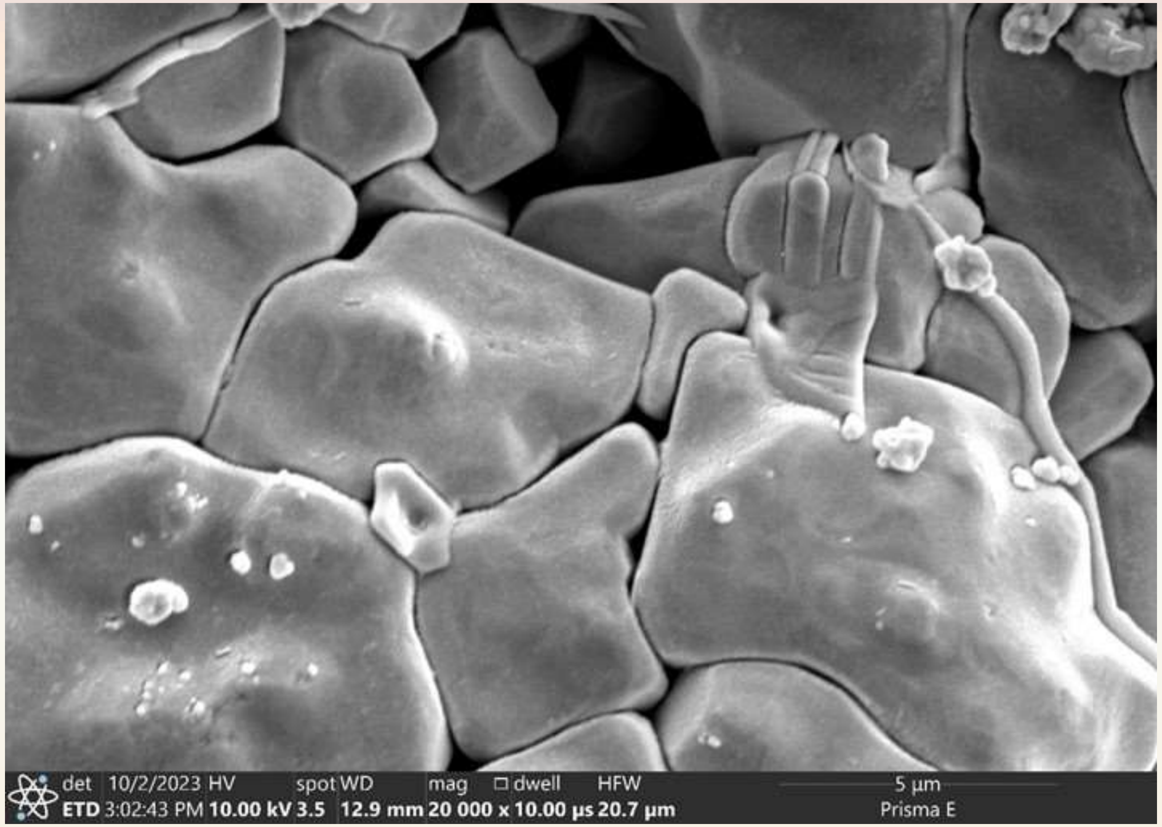
b)

Linear shrinkage factor of $Ba_{0.25}Sr_{0.75}TiO_3$ ceramic samples vs. sintering temperature

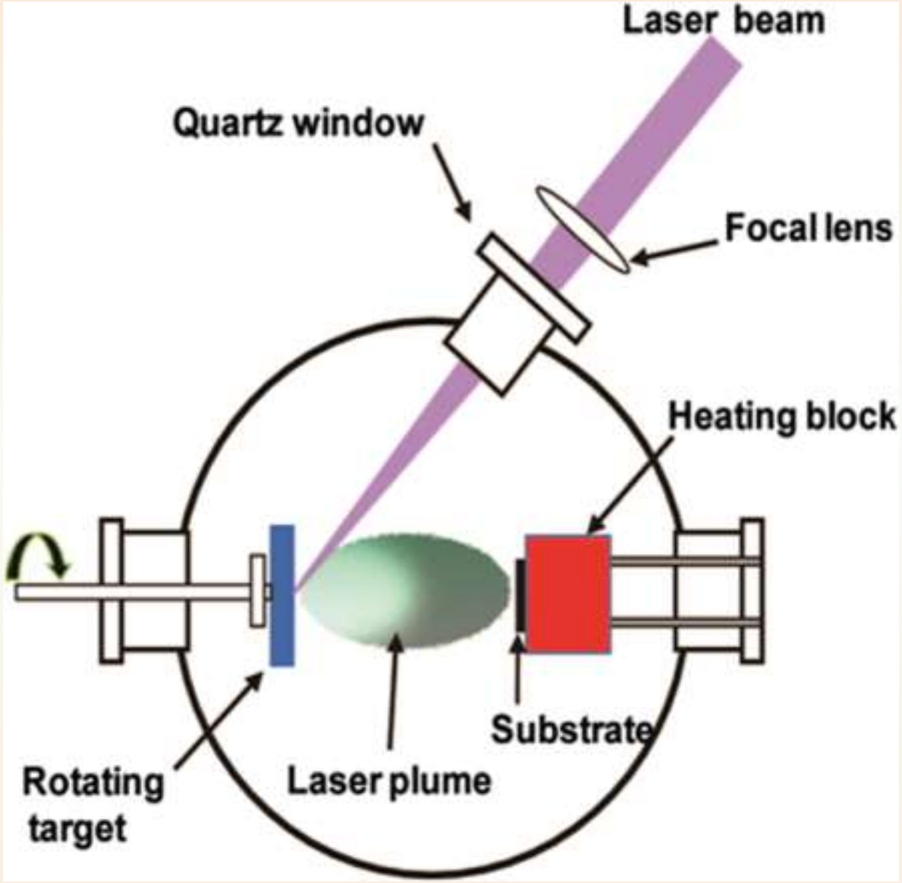


SEM image of $Ba_{0.25}Sr_{0.75}TiO_3$



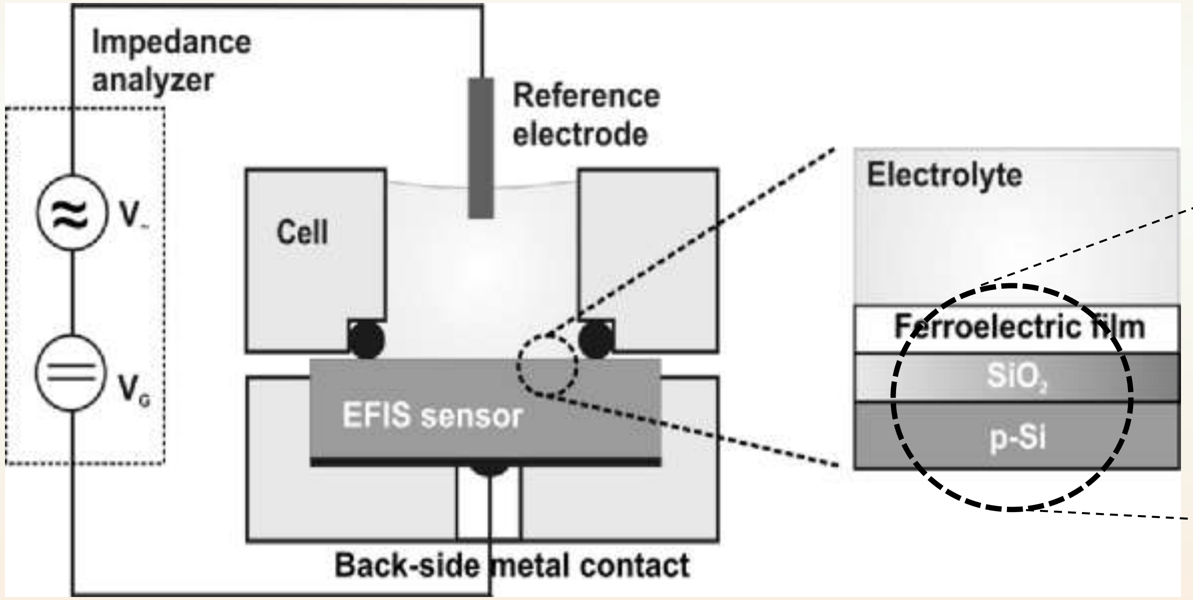


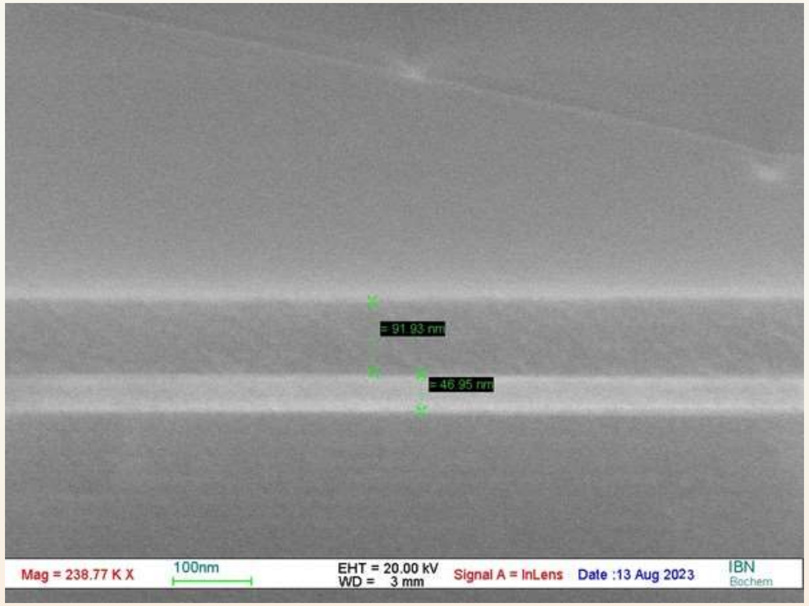
PLD of Mg doped $Ba_{0.8}Sr_{0.2}TiO_3$ on a silicon substrate (p-Si, ρ = 1000 Ωcm)



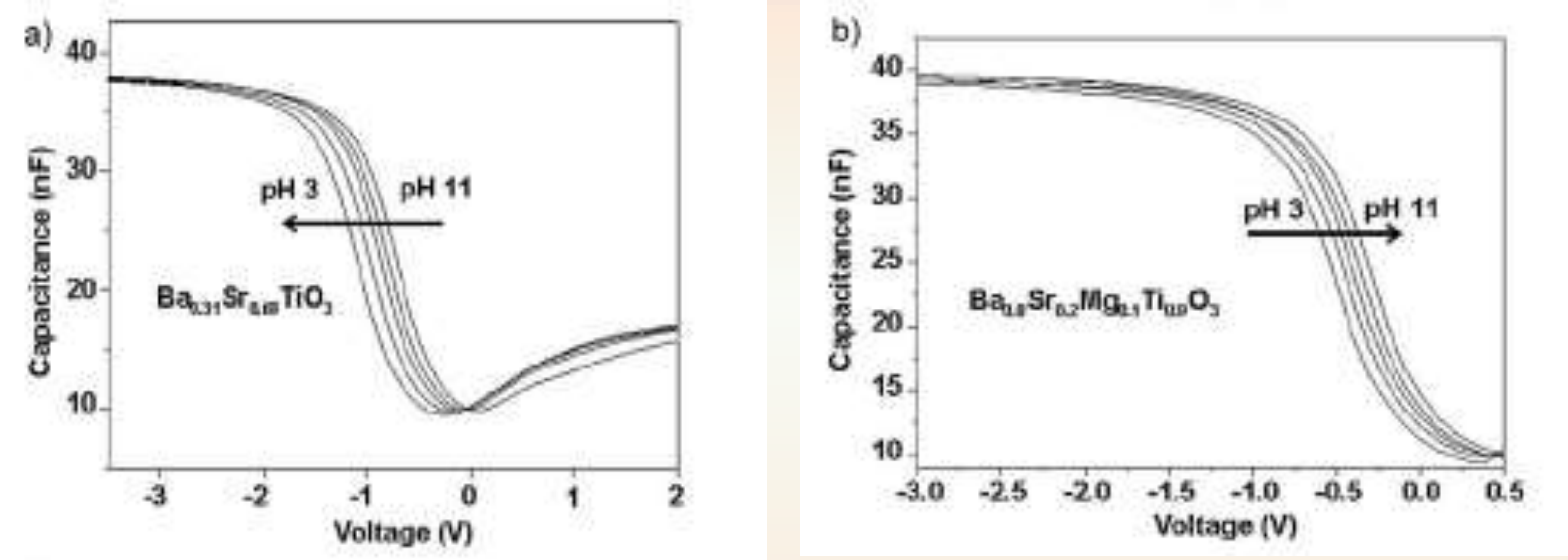
- Oxygen flow 30 mL/min, pressure $2x10^{-3}$ mbar;
- KrF-excimer laser (Lambda LPX305) with a pulse width of 20 ns ;
- Pulse energy of approximately 1J per pulse;
- Energy density of 2.5 Jcm^{-2} ;
- Repetition rate of 10 Hz;
- Deposition time of 100 s.

BST Based Capacitive Field-effect pH Sensors

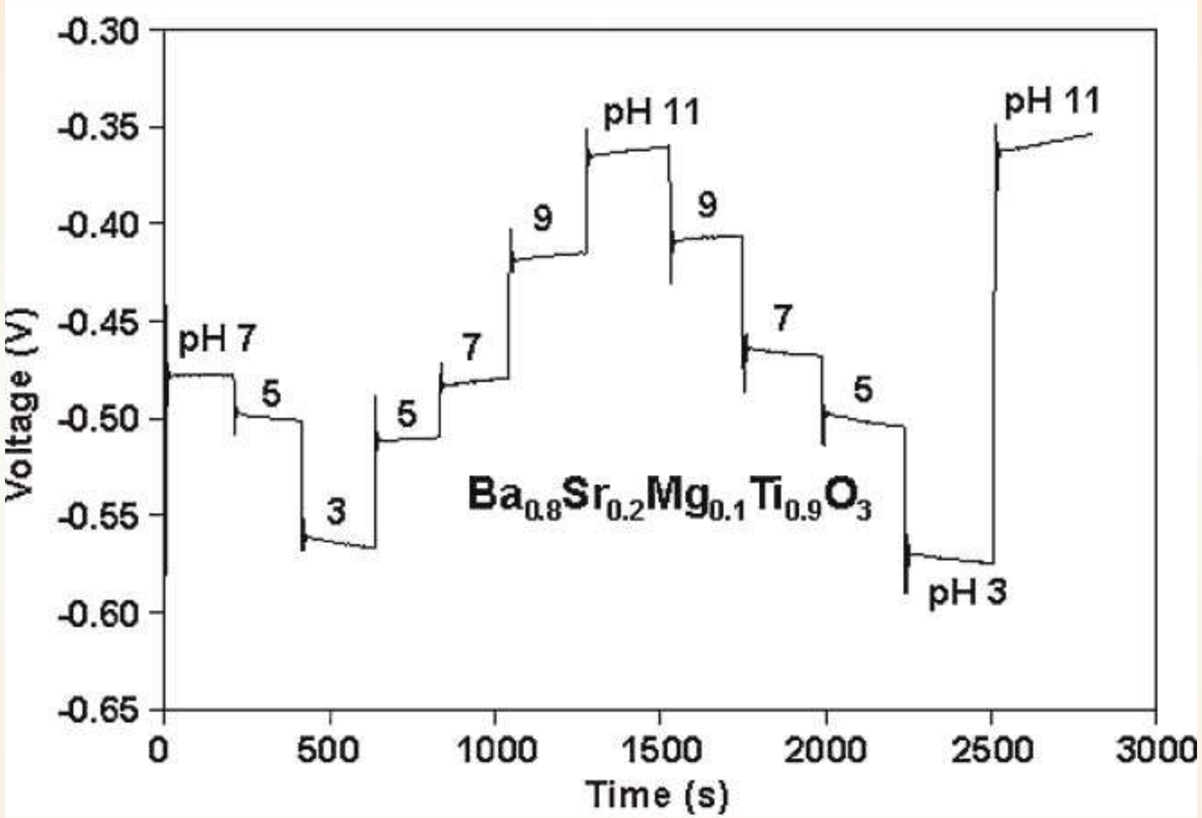


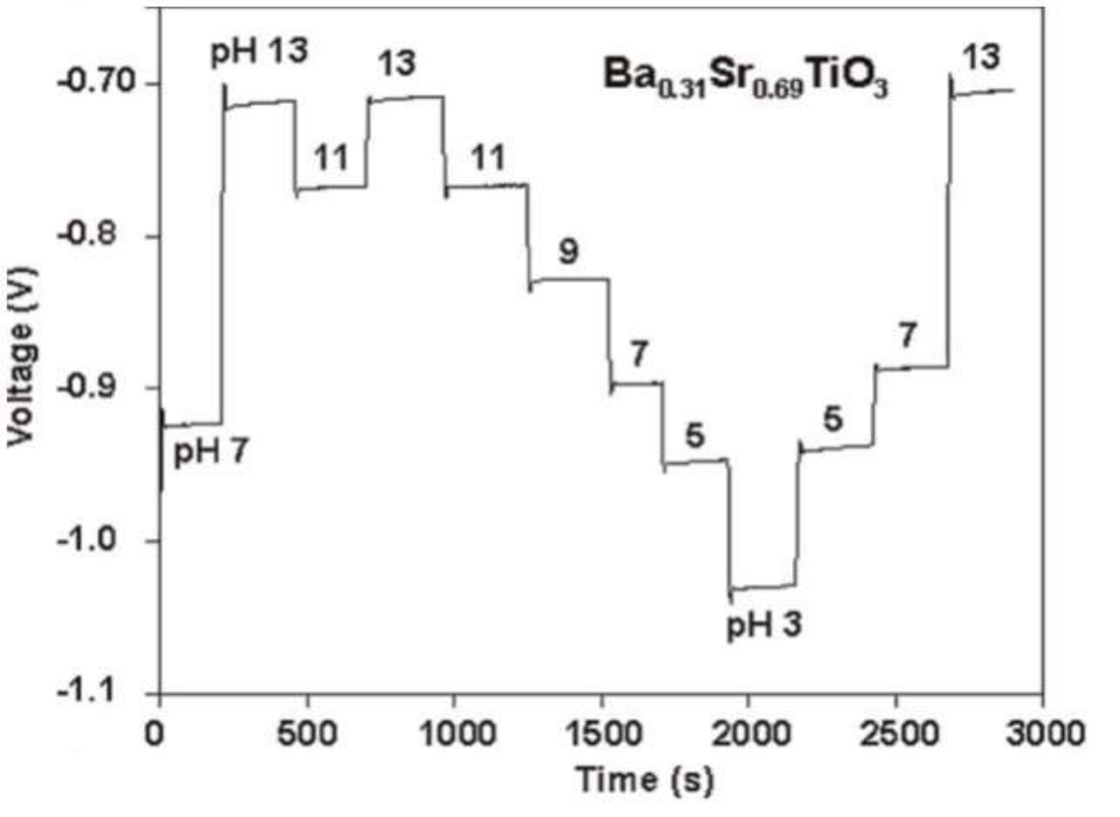


C-V Curves for BST-based Field-Effect Sensors



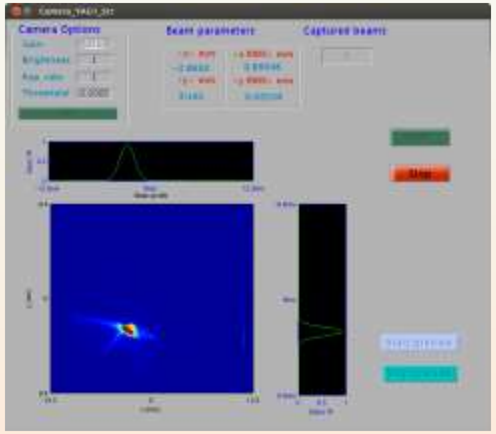
ConCap response of an EBSTIS sensor with $Ba_{0.31}Sr_{0.69}TiO_3$ and $Ba_{0.8}Sr_{0.2}Mg_{0.1}Ti_{0.9}O_3$ film recorded in buffer solutions of different pH values

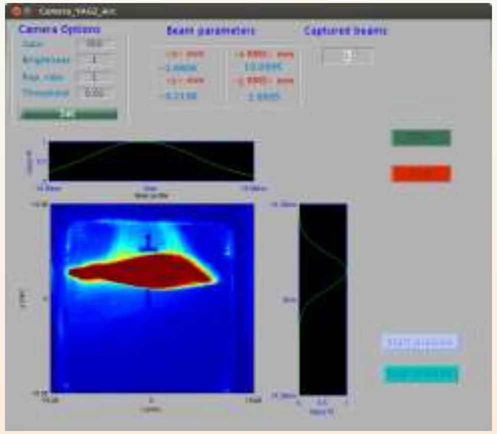




AREAL machine parameters for Electron Beam Irradiation of $Ba_{0.8}Sr_{0.2}Mg_{0.1}Ti_{0.9}O_3$

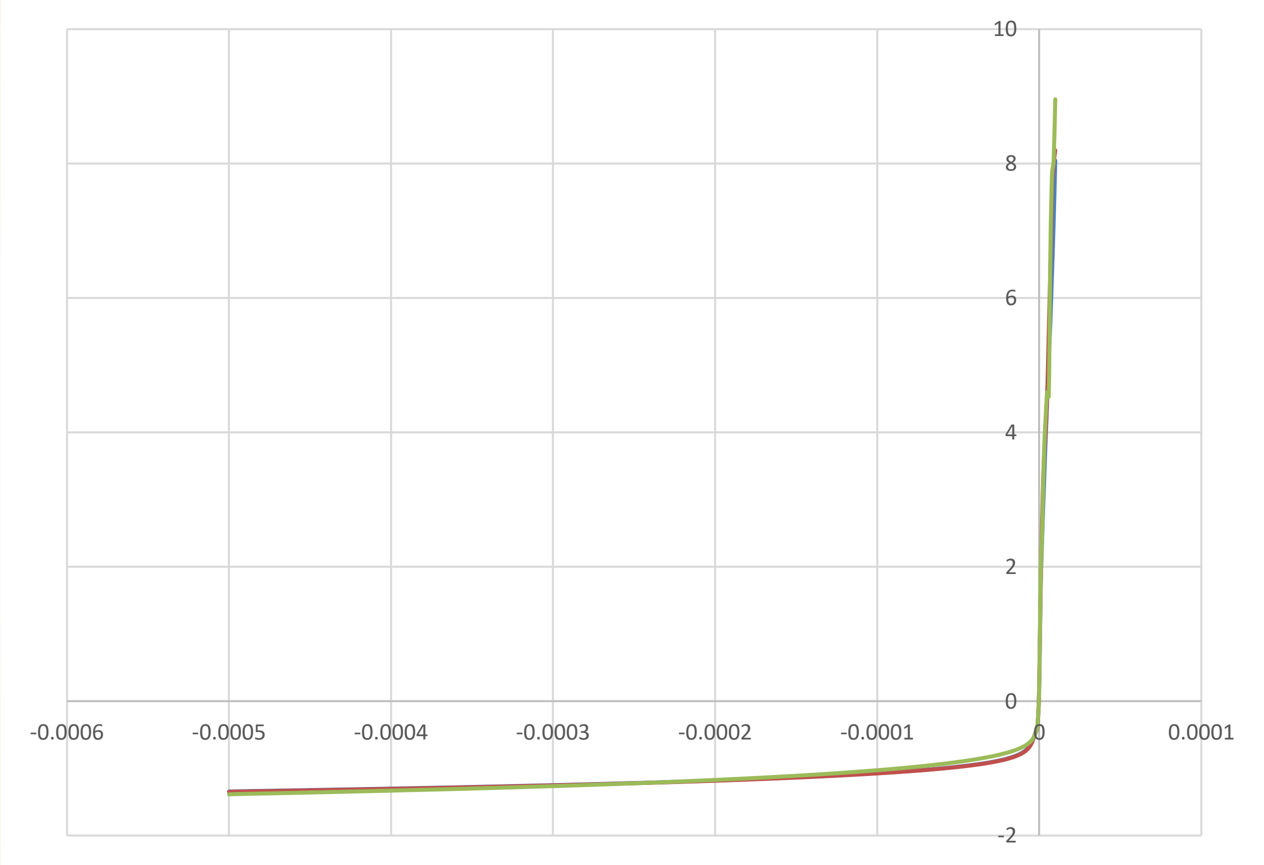
RF System			
RF High Voltage	[kV]	133	
RF High Voltage (Peak Power)	[dBm]	-4.58	Power meter on Gun
RF Phase	[deg]	-38	
Pulse Repetition Rate	[Hz]	12	
Magnets			
Solenoid Current	[A / V]	9.8/46	
Dipole Current	[A / V]	4.2/9	
Corrector Magnet (X | Y)	[A / V]	2.91/8	
Beam Parameters			
Beam Charge (FC-IN / FC-OUT)	[pC]	300/50	30 (absorbed by sample)
Beam Energy spectrometer	[MeV]	3.6	
Laser System			
Laser pulse duration	[ps]	0.5	
Time		1 hour	
Beam Profile @ YAG 1 (straight screen)		***Beam profile @ spectrometer E=3.7 MeV***	

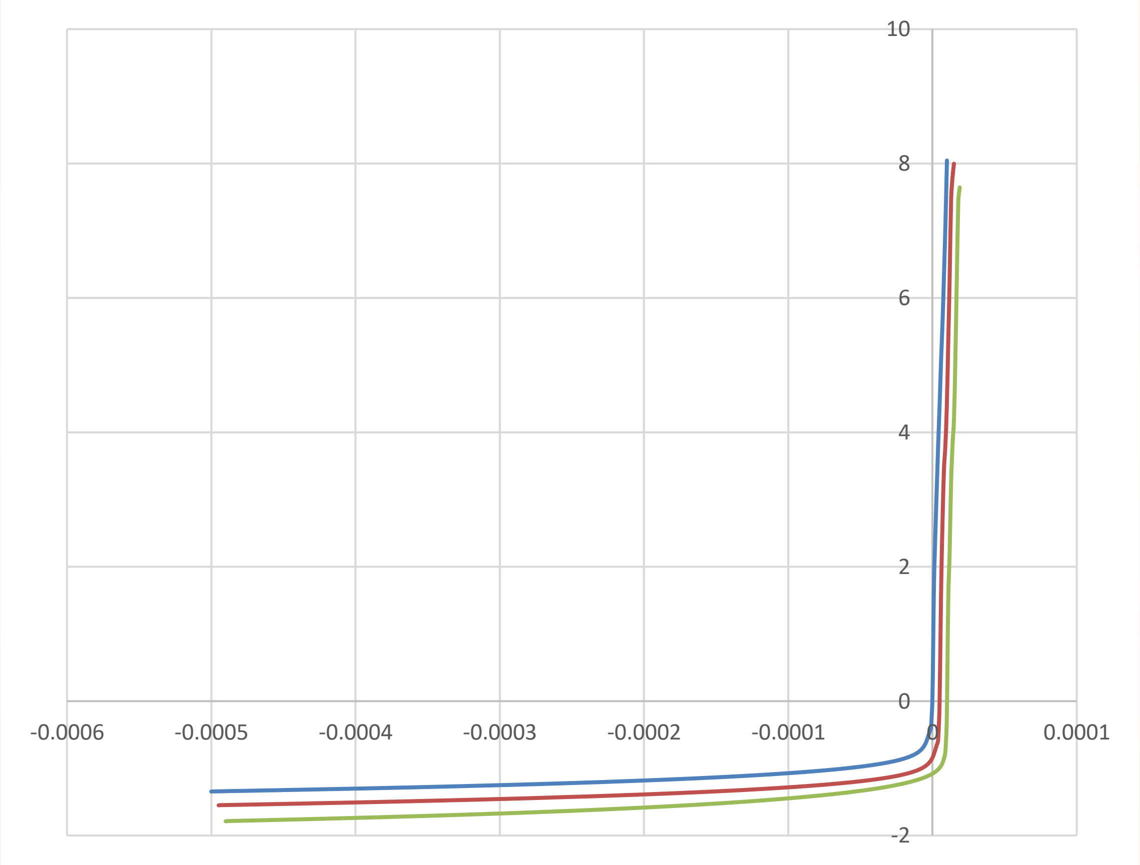




V-I Characteristics of $Ba_{0.8}Sr_{0.2}Mg_{0.1}Ti_{0.9}O_3$

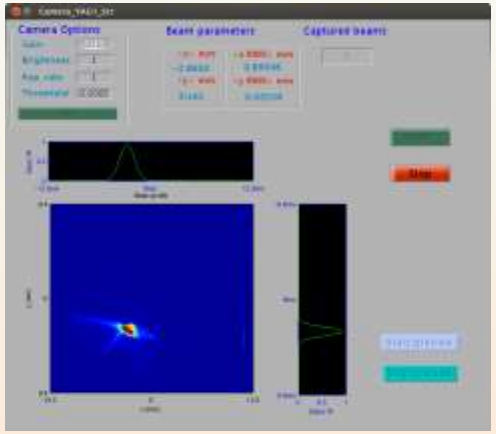
Before Irradiation — After 1st Irradiation — After 2nd Irradiation

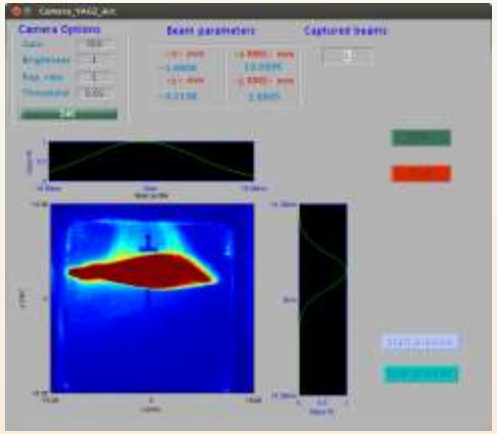




AREAL machine parameters for Electron Beam Irradiation of $Ba_{0.31}Sr_{0.69}TiO_3$

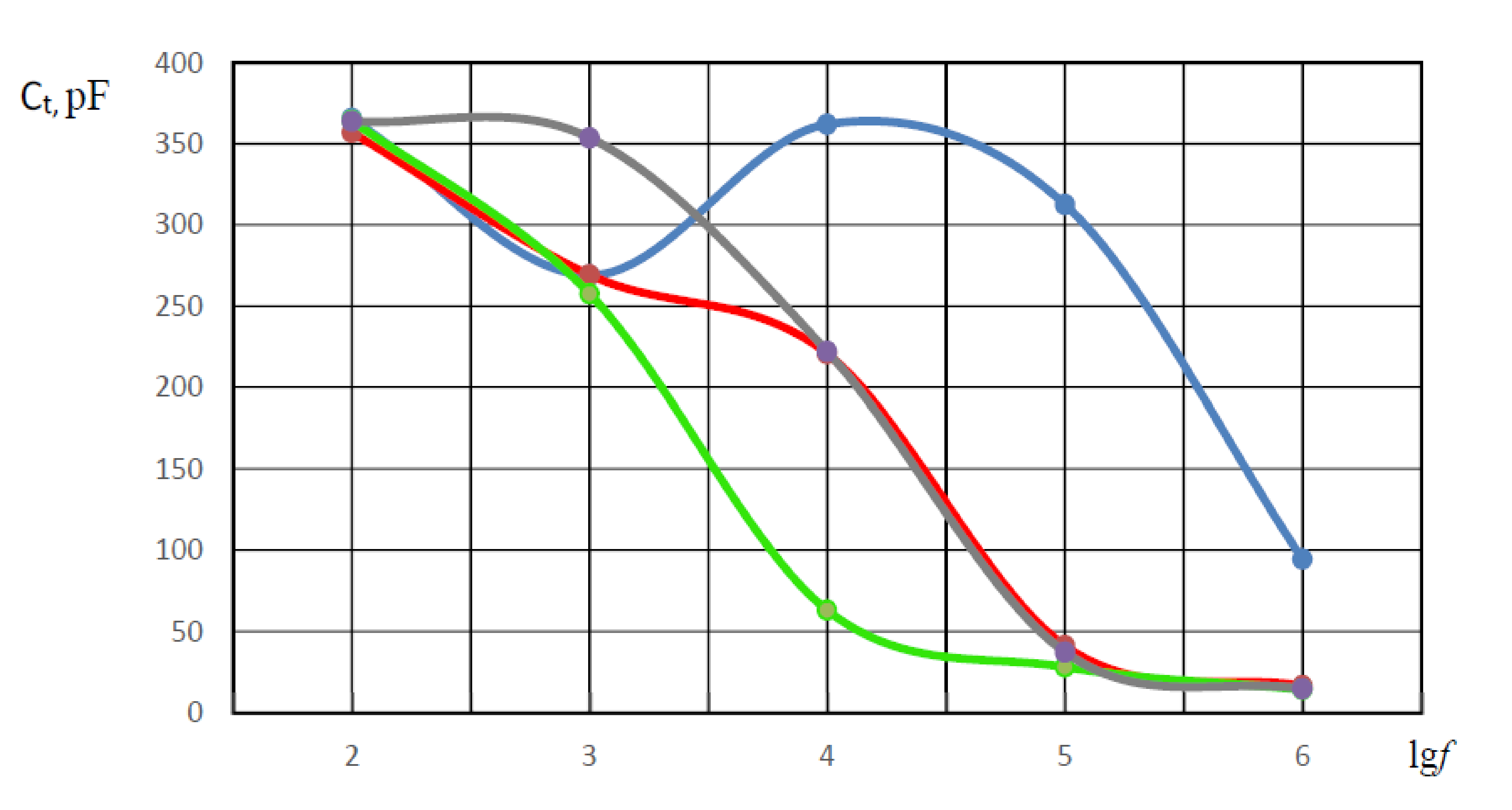
RF System			
RF High Voltage	[kV]	132	
RF High Voltage (Peak Power)	[dBm]	-4.02	Power meter on Gun
RF Phase	[deg]	-38	
Pulse Repetition Rate	[Hz]	12	
Magnets			
Solenoid Current	[A / V]	9.6/45	
Dipole Current	[A / V]	4.2/9	
Corrector Magnet (X | Y)	[A / V]	2.91/8	
Beam Parameters			
Beam Charge (FC-IN / FC-OUT)	[pC]	255/53	30 (absorbed by sample)
Beam Energy spectrometer	[MeV]	3.7	
Laser System			
Laser pulse duration	[ps]	0.5	
Time		1 hour	
Beam Profile @ YAG 1 (straight screen)		*Beam profile @ spectrometer E=3.7 MeV*	





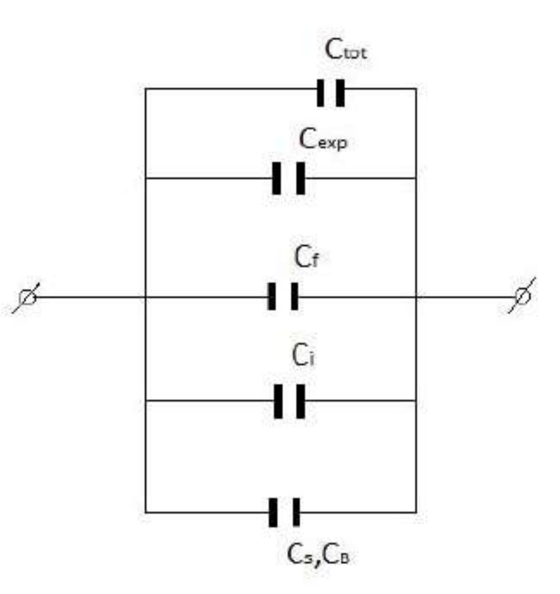
The C–f dependences of the examined structure

Before-blue line; after the first irradiation-red;
after the second irradiation-green; after the third irradiation-purple.



The calculation of ε_f *of the examined structures*

Equivalent circuits of the examined structures



The total (measured) capacitance of the structure:

$$C_{t_o t} = (n-1) l \cdot C_1$$

n is the amount of fingers, l is the length of the fingers.

$$C_1 = \frac{\varepsilon_o \varepsilon_f}{2} \cdot \frac{K[(1-k^2)^{1/2}]}{K(k)} = \frac{\varepsilon_o \varepsilon_f K(k^1)}{2 \cdot K(k)} ,$$

$K(k)$is the complete elliptic integral of the fins t kind with modules of k.

$$k = \cos\left(\frac{\pi}{2} \cdot \frac{w}{w+S}\right).$$

The capacitance of the equivalent circuit of structure:

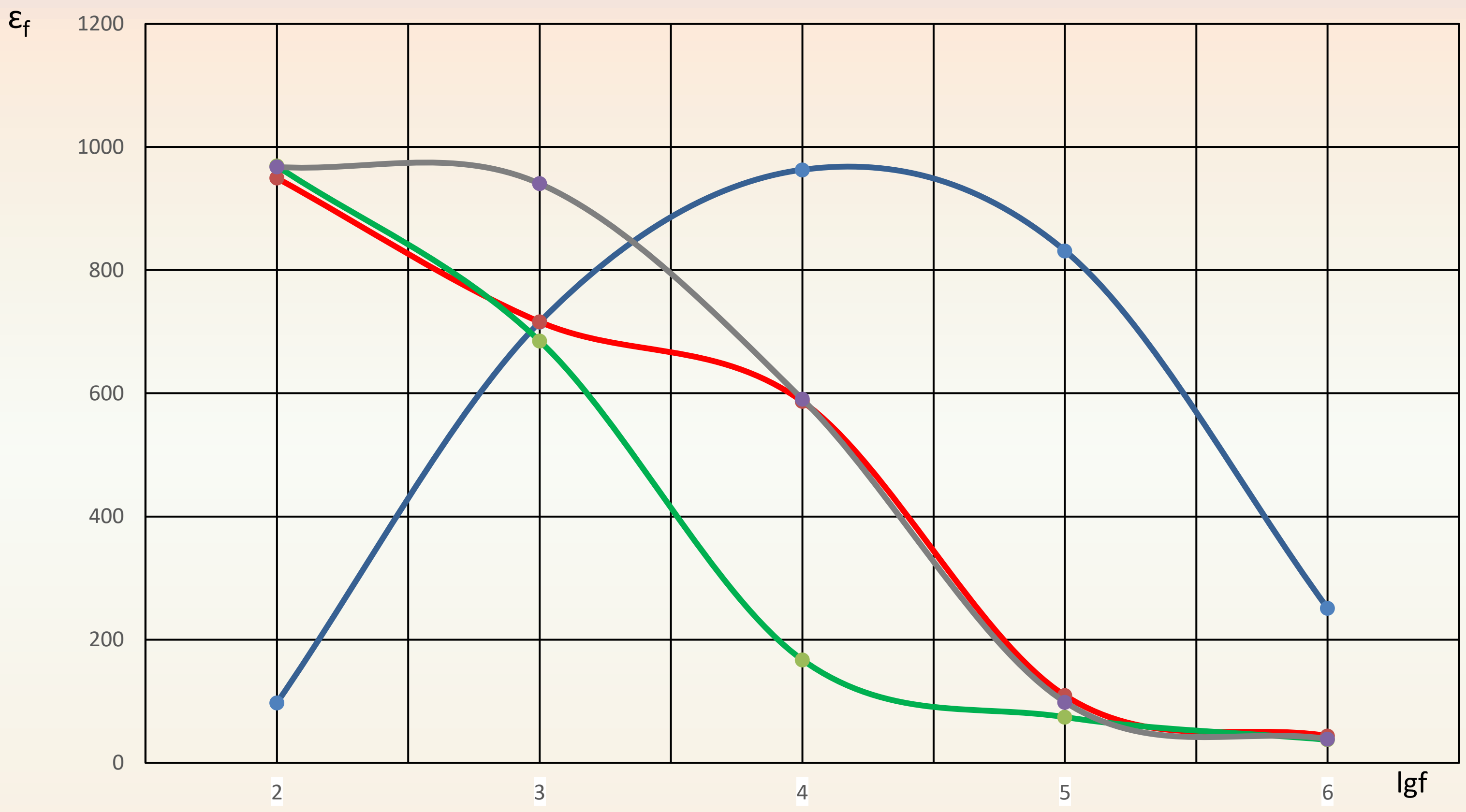
$C_{t_o t} = C_s + C_\beta + C_f + C_{exp} + C_i$,

where C_s is the capacitance of the substrate(pS_i), C_β is the parasitic capacitance between P_t electrodes (fingers), C_f is the capacitance of ferroelectric film, C_{exp} is the capacitance of the measurement set-up, C_i is the insulator lager (SiO_2) capacitance. The numerical calculations of C_i, C_β is shows, that its value about two order less than that the C_f and ignoring also the C_s , C_β and C_{exp}, we used the approximation of:

$$\varepsilon_f \cong \frac{2C_{t_o t}}{\varepsilon_o \cdot l \cdot (n-1)} \cdot \frac{K(k)}{K(k^1)}$$

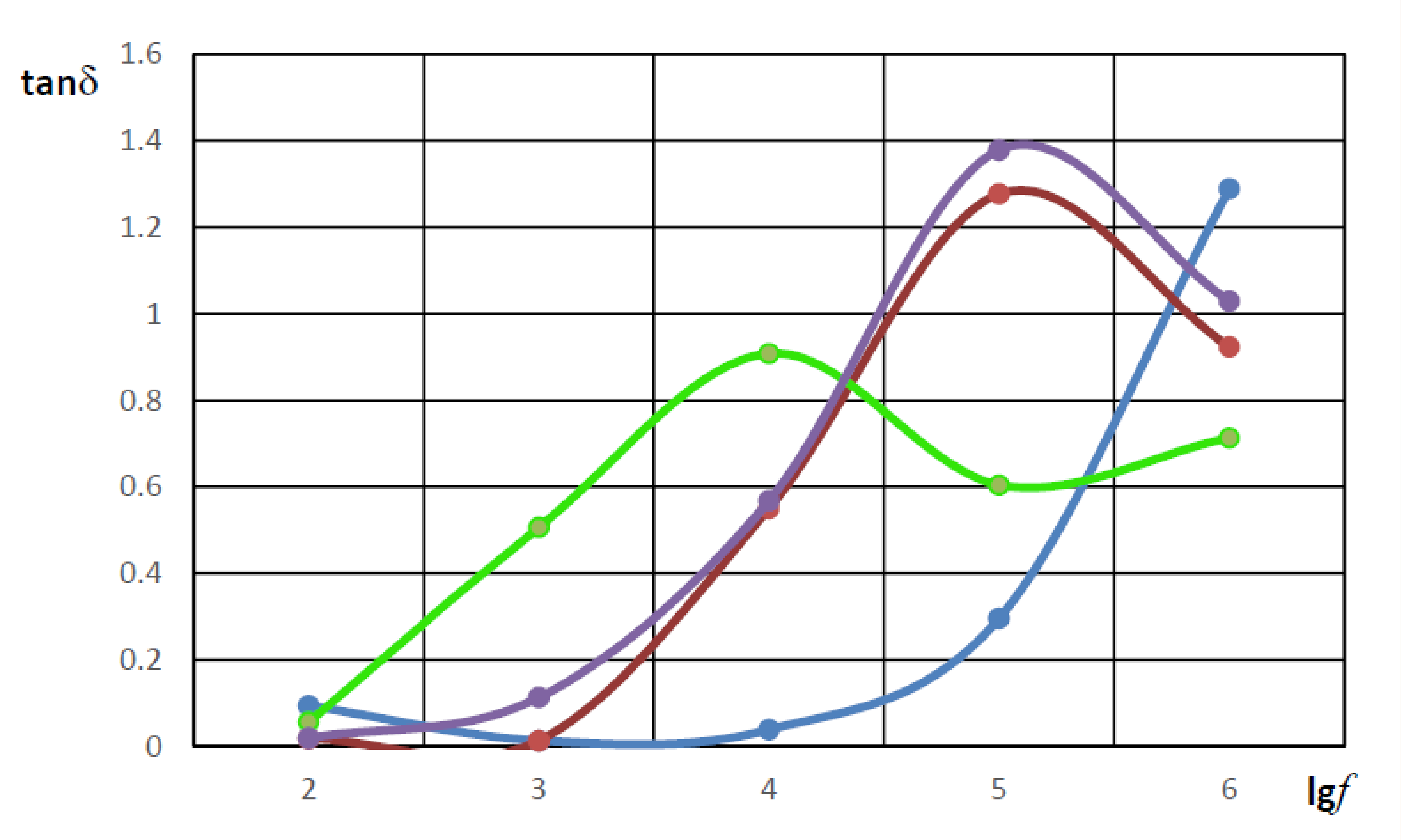
The ε_f –f dependences of the examined structures

Before-blue line; after the first irradiation-red; after the second irradiation-green; after the third irradiation-purple.



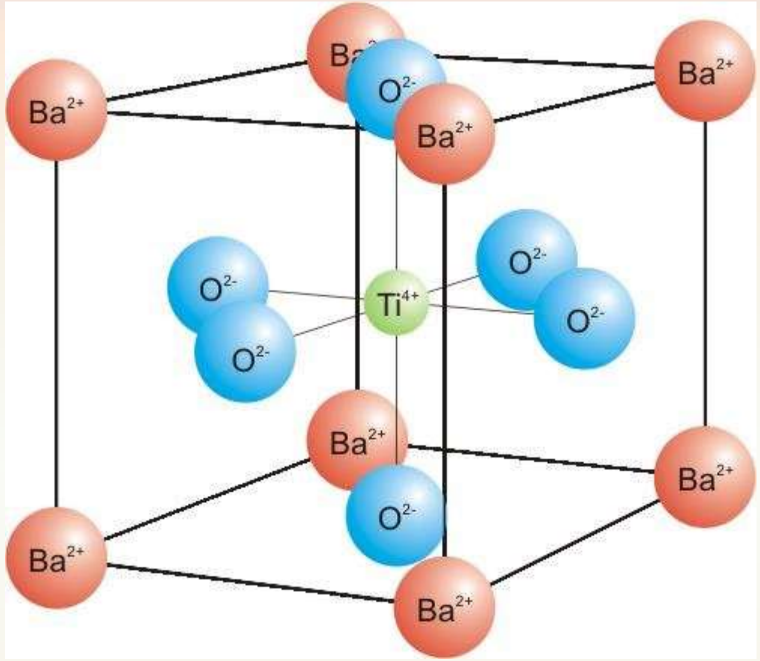
The tanδ–f dependences of the examined structures

Before-blue line; after the first irradiation-red;
after the second irradiation-green; after the third irradiation-purple.

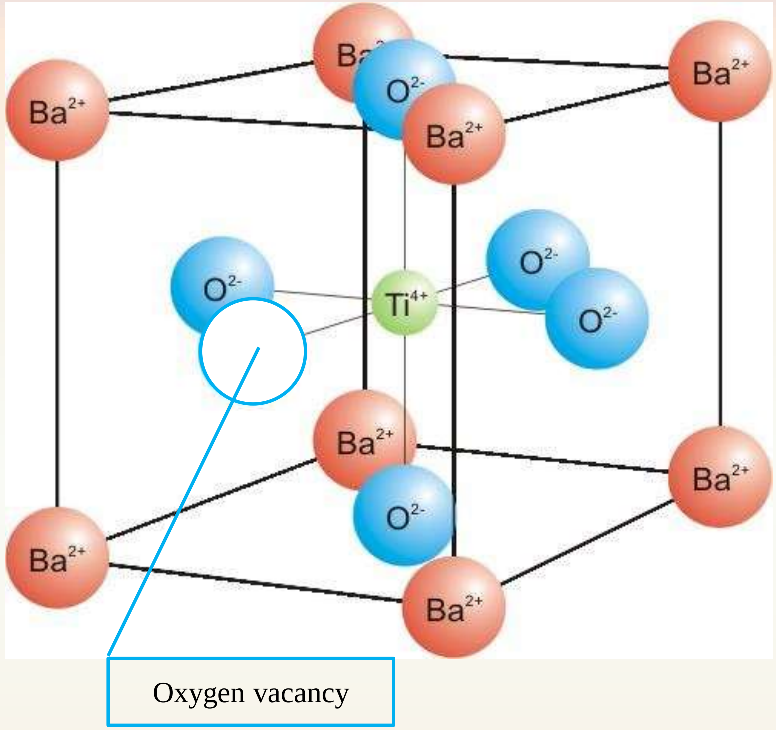


Formation of oxygen vacancy

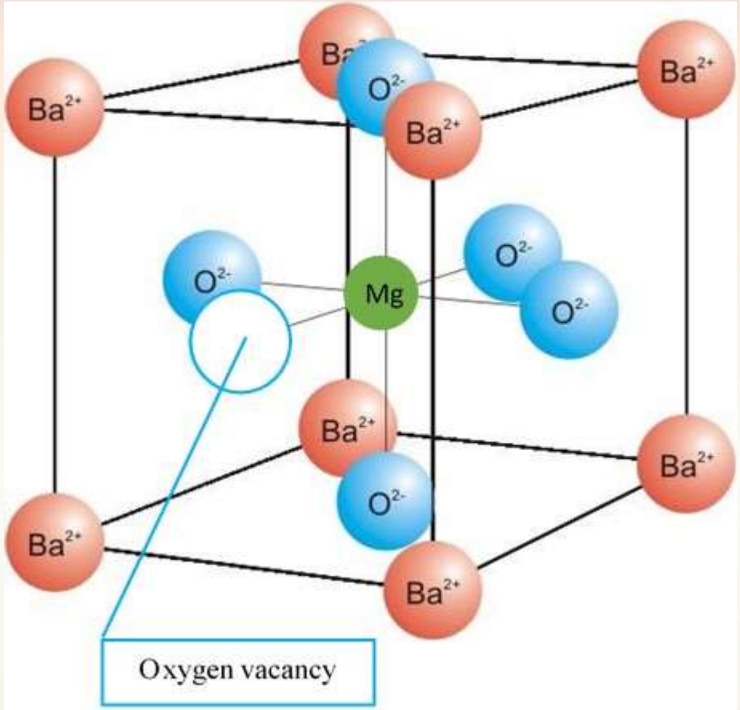
Before Irradiation of $Ba_{0.31}Sr_{0.69}TiO_3$



After Irradiation of $Ba_{0.31}Sr_{0.69}TiO_3$



$Ba_{0.8}Sr_{0.2}Mg_{0.1}Ti_{0.9}O_3$



SUMMARY AND CONCLUSION

- It is established that the threshold value for k is 0.5 (if K=0) and for K is 0.25 (if k=0), only at greater values of k and K, the process can proceed under the self-sustaining mode.
- The phase structure investigation shows no other phases when the amount of combustible was about 10% (where Fe-8%, Ti-2%).
- As a result of calculations and series of experiments, it is determined that optimal grinding regimes and conditions are as follows: the volume relationship of the charge (material to be milled) and milling bodies/balls should be 1/4…1/3; acetone has to be used as a milling medium to form a freely flowing cream. Efficient milling is obtained when the volume of acetone is between 100 and 200% of the volume of the charge. The quantity of the grinding body/ball has been taken 70% of pots volume. The milling body/ball were of 4...8 mm in size (the largest diameter being of the order of a tenth of the diameter of the pot). The rate of the rotation (ωd) of the base disk is 400…600 rev/min. The milling duration is 7 hours.
- BF–BT based pellets are sintered between 700 °C and 1000 °C in an electric furnace and air atmosphere for 2 hours under controlled heating/cooling rates of 2.5 °C/min.
- The dependence for linear shrinkage factor and gas-penetrability of the samples vs. sintering temperature indicates that intensive sintering begins with 880 °C, and the maximum density of the samples is practically obtained at 950 °C.
- The tunability factors ($\varepsilon(0)/\varepsilon(E)$ and $\mu(0)/\mu(E)$) for dielectric and magnetic permeability of BFO-BST are in the range of 1.22-1.27 and 1.18-1.19 respectively at 60 KV/cm biasing field.
- The change of dielectric constant and tangens losses is a result of oxygen vacancy formation during irradiation.

Thank You