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Dielectric ceramic and nanopowders of holmium-doped $BaTiO_3$ prepared by sol-gel combustion

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Aim: Investigation of the structure and dielectric properties of derived $Ba_{0.97}Ho_{0.03}TiO_3$ ceramics prepared by sol-gel combustion

Sol-gel synthesis of $Ba_{0.97}Ho_{0.03}TiO_3$

Synthesis conditions

- Ba precursor: barium acetate $Ba(CH_3CO_2)_2$
- Ti precursor: titanium (IV) isopropoxide $Ti(OC_3H_7)_4$
- Ho precursor: holmium oxide Ho_2O_3
- Sol aq. 1M $Ba(CH_3CO_2)_2$
- Holmium oxide disolved in H_2O+HNO_3
- Peroxo-citrate complex of titanium isopropoxide:
  - titanium (IV) isopropoxide;
  - nitric acid;
  - citric acid;
  - hydrogen peroxide;
  - water.
  - Molar ratio citric acid:metal cations = 2.5:1
- Molar ratio citrate:nitrate (CA/NO_3^-) =1.3.
- pH: 5; (ammonium hydroxide).
- Refluxing temperature: ~75°C
- Dry gel temperature: 100 °C
- Firing temperature of the gel to obtain $Ba_{0.97}Ho_{0.03}TiO_3$: 1100 °C
- Sintering temperature to obtain BT-$Ho_{0.03}$ ceramic: 1350 °C, 2h.

Microstructures analysis

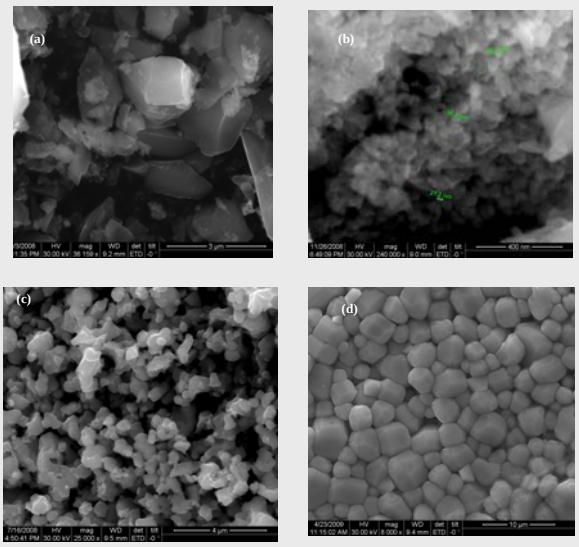


Fig.1. SEM images of BT-$Ho_{0.03}$ precursor gel dried at 100 °C (a), fired at 700 °C (b) and 1100 °C (c) and, ceramic sintered at 1350 °C, 2h in air (d). Average grains size: 30 nm (b), 250 nm (c) and 2 μm (d)

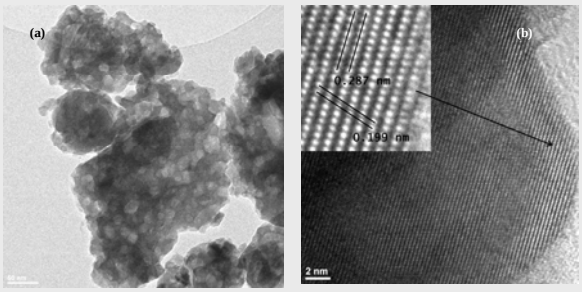
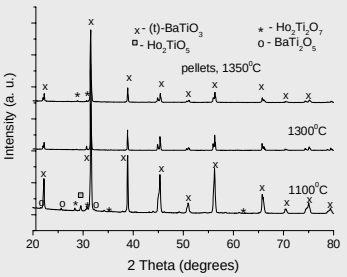


Fig.2. TEM and HR-TEM micrographs of the (Ba,Ho)TiO_3 gel heated at 700 °C

Structure analysis



X-ray diffraction analysis results

- $Ba_{0.97}Ho_{0.03}TiO_3$ cryst. on the t-$BaTiO_3$ lattice, $BaTi_2O_5$, Ho_2TiO_5 and $Ho_2Ti_2O_5$, at 700-1100 °C (powder);
- $Ba_{0.97}Ho_{0.03}TiO_3$ cryst. on the t-$BaTiO_3$ lattice, and $Ho_2Ti_2O_5$, at 1300 °C (powder);
- $Ba_{0.97}Ho_{0.03}TiO_3$ cryst. on the t-$BaTiO_3$ lattice, and $Ho_2Ti_2O_5$, at 1350 °C (ceramic).

Fig.3. XRD patterns of sol-gel processed (Ba, Ho)TiO_3 powder, heated at 1100 and 1300 °C and, ceramic sintered at 1350 °C

Electrical properties

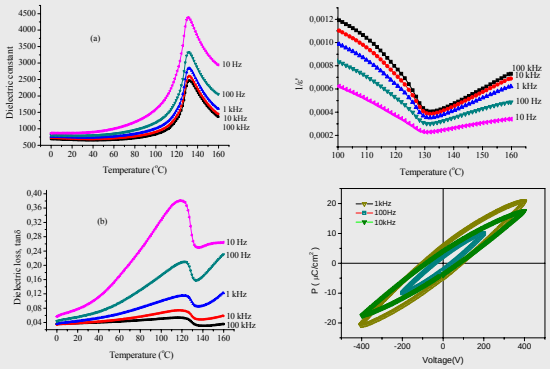


Fig.4. Variation of dielectric constant and dielectric loss of BT-$Ho_{0.03}$ ceramics with temperature and frequency

Tab.1. Temperature coefficient of capacitance (TCC) measured at 100 Hz and 1 kHz for (Ba,Ho)TiO_3 ceramic

$Ba_{0.97}Ho_{0.03}TiO_3$	f=100Hz	TCC	f=1 kHz	TCC
T_{rel}=303.94 °C	C_{RT} =62 pF		C_{RT} =52 pF	
T_1=273.15 °C	C_1= 63 pF	TCC_1=5.38·10^{-4}	C_1= 56 pF	TCC_1=2.56·10^{-3}
T_2=333.76 °C	C_2=68 pF	TCC_2= –3.31·10^{-3}	C_2=53 pF	TCC_2= –6.41·10^{-4}
		TCC= –1.33·10^{-3}		TCC=0.96·10^{-3}

Table 2. Tc and T_0 obtained from the slope of 1/ε′ vs T plot at various frequencies for $Ba_{0.97}Ho_{0.03}TiO_3$ ceramic

Frequency	10 Hz	100 Hz	1 kHz	10 kHz	100 kHz
Curie temperature Tc (°C)	132	132	132	132	132
Curie-Weiss Temperature T_0 (°C)	102	107	110	111	112

Conclusions

- Powder of $BaTiO_3$ doped with 3 mol% Ho, consisting of $Ba_{0.97}Ho_{0.03}TiO_3$ as main phase was obtained by heating the precursor gel at 700 °C.
- The as-prepared powder is composed of particles with agglomerated structures; the average size of the crystallites was 30 nm.
- The XRD patterns of the powders and sintered BT-$BT_{0.03}$ ceramics indicated a material composed of $Ba_{0.97}Ho_{0.03}TiO_3$ crystallized on the tetragonal-$BaTiO_3$ lattice, and traces of $Ho_2Ti_2O_5$.
- The BT-$Ho_{0.03}$ ceramics prepared by sol-gel auto-combustion, presented good dielectric properties.

References

[1] M. Cernea, G. Montanari, C. Galassi and A. Costa: Synthesis of La and Nb doped PZT powder by the gel-combustion method, Nanotechnology, 17, 1731 (2006).

[2] M. Cernea, E. Andronescu, R. Radu, F. Fochi, C. Galassi, "Sol-gel synthesis and characterization of $BaTiO_3$ doped-$(Bi_{1/2}Na_{1/2})TiO_3$ piezoelectric ceramics", Journal of Alloys and Compound Materials, 490 (2010) 690-694.