PROGRAMMA DI RICERCA STM

The Candidate: Robert C Pullar

Candidate's Institution: Department of Materials and Ceramic Engineering / CICECO, University of Aveiro, Aveiro 3810-193, Portugal.

Qualification: PhD Level: Investigador (Researcher)

Host Department: CNR-ISTEC National Research Council - Institute of Science and Technology for Ceramics, I-48018 Faenza (RA), Italy

Proposer Dr. Carmen Galassi Head of the Group "Processes and materials for electromechanic applications"

Visit performed from November 9, 2014 to November 23, 2014

Title of programme: Development of novel magnetoelectric / multiferroic ceramic composites

Final report

Summary

During the visit Dr. Pullar gave two talks and participated to the planning of the joint research and to experimental work performed to produce new materials or to characterize samples carried from his Laboratory.

The focus was on the preparation of ceramic samples starting from the side phases, ferrite and ferroelectric material to produce a number of composite and test the densification, reaction etc, after the heat treatment at the sintering temperature.

On a selected composition preliminary milling was performed prior to mixing with the ferroelectric phase. On a selection of the sintered samples XRD analysis was performed and the dielectric and ferroelectric properties were tested. The experimental work and data analysis were performed with the contribution of Ioana Ciuchi (PhD student), Pietro Galizia (PhD student) and Claudio Capiani (Technician).

Samples Made at Faenza CNR-ISTEC Nov 2014 STM grant

Powders used:

SrZ made by UA from solid state route – very coarse powder.

High energy ball milled (Fritzch) in ISTEC at 400 RPM in zirconia pot with 5 mm zirconia balls in ethanol for 4 hours – about 10 μm afterwards. (50 g powder, 50 g ethanol, 500 g balls). XRD confirms this to still be a good Sr-Z sample after milling.

Other powders used: **Sr-M** citrate, **Sr-Z2** citrate, **Ba-Z** citrate from UA.

$Ba_{0.75}Sr_{0.25}M$ (**BS-M**) calcined at 1000 °C / 24 h from ISTEC.
is $Ba_xSr_{1-x}Fe_{12}O_{19}$ (x = 0.05, 0.15, 0.25, 0.35) – this would be x = 0.75.

BNBT – $(BiNa)_{0.94}Ba_{0.06}TiO_3$ calcined at 800 °C (500 if made from citrate gel) from ISTEC

Pure ceramic samples:
Pellets in 12 mm die, uniaxial pressing a 120 MPa, then isostatic pressing at 250 MPa.
Sintered at 5 °C / min up, 2 h dwell, natural cooling.
Samples surrounded by BNBT powder to prevent Na loss via evaporation.

BNBT	$(BiNa)_{0.94}Ba_{0.06}TiO_3$	1200 °C
BS-M	$Ba_{0.75}Sr_{0.25}Fe_{12}O_{19}$	1200 °C
Sr-M	$SrFe_{12}O_{19}$ citrate	1200 °C
Sr-Z	$Sr_3Co_2Fe_{24}O_{41}$ solid state	1200 °C

Composites
All weight %.
Ball milled with 5 mm & 3 mm zirconia balls in ethanol for 24 hours to mix.
Pellets in 12 mm die, uniaxial pressing a 120 MPa, then isostatic pressing at 250 MPa.
Sintered at 1200 °C x 2 h (heating rate at 150 °C/h). 5 °C / min up, , natural cooling.
The samples were placed on Pt-coated alumina and sintered in a bismuth-sodium-saturated enclosure obtained by placing an alumina cup upside down over the samples. BNBT pack was placed around the samples to ensure Bi-Na saturation throughout the sintering procedure. Additional BNBT pack was used to seal the rim of the cup.

BB25	25% BSM + 75% BNBT	1200 °C
BB50	25% BSM + 75% BNBT	1200 °C
BB75	25% BSM + 75% BNBT	1200 °C
SB25	25% SrM + 75% BNBT	1200 °C
SB50	25% SrM + 75% BNBT	1200 °C
SB75	25% SrM + 75% BNBT	1200 °C
SZB50	50% SrZ + 50% BNBT	1200 °C
BZB50	50% BaZ + 50% BNBT	1200 °C
SZB502	50% SrZ2 + 50% BNBT	1200 °C

Samples fired at 1200 °C on platinum coated alumina melted / evaporated

Samples Measured at Faenza CNR-ISTEC Nov 2014 STM grant

Samples brought from UA:

All were uniaxially pressed at 100 MPa, then any cold isostatic pressing was at 200 MPa.
Heating rates were 5 °C / min, dwell times 2 h, natural cooling, fired in air.
BaM = $BaFe_{12}O_{19}$, SrM = $SrFe_{12}O_{19}$, BaZ = $Ba_3Co_2Fe_{24}O_{41}$, SrZ = $Sr_3Co_2Fe_{24}O_{41}$.
BT = $BaTiO_3$, KNN = $K_{0.5}Na_{0.5}NbO_3$.

1.	BaM:Ti 1%	1000 °C	solid state	unixaial press
2.	BaM:Ti 5%	1000 °C	solid state	unixaial press
3.	BaM:C 1%	1000 °C	solid state	unixaial press
4.	BaM:C 5%	1000 °C	solid state	unixaial press
5.	BaM:Pig 4 1%	1000 °C	solid state	unixaial press
6.	BaM:Pig 4 5%	1000 °C	solid state	unixaial press
7.	BaM-BT 80-20	1200 °C	solid state	isostatic press
8.	BaZ-BT 70-30	1200 °C	solid state	isostatic press
9.	SrM-BT 70-30	1200 °C	solid state	isostatic press
10.	SrZ-BT 70-30	1200 °C	solid state	isostatic press
11.	SrM-BT 90-10	1200 °C	citrate	isostatic press
12.	BaM-BT 80-20	1200 °C	citrate	isostatic press
13.	BaZ-BT 70-30	1200 °C	citrate	isostatic press
14.	BaM-KNN 90-10	1200 °C	citrate	isostatic press
15.	SrZ-KNN 90-10	1200 °C	citrate	isostatic press
16.	BaM-KNN 90-10	1200 °C	coprecipitated	isostatic press
17.	BaZ-KNN 80-20	1200 °C	copreciptiated	isostatic press
18.	BaZ-KNN 70-30	1200 °C	coprecipitated	isostatic press

Samples 7-13 were parallel polished to 0.5 mm height with Rob's patented Parallel Washer Polisher (PWP©), coated with silver paint dried at room temp.

Work to be carried out in future

The plan is to continue the collaboration by performing further experimental work to complete the activity started during the visit, as follows:

BNBT composites

As a partial reaction occurred in the first test, a further densification trial will be performed by sintering at only 1000 °C for a starting point.

Pure SrZ

We will press some pellets and sinter pure SrZ at 1180-1200 °C in air, to see what the optimum temperature is.

We will measure ferroelectric & piezoelectric loops of 7-15, and also SrZ. We will also try to apply magnetic fields to test for ME coupling. If we can measure capacitance/permittivity/dielectric losses over frequency ranges that will be carried out, and we will also attempt to modulate permittivity/capacitance with magnetic fields as well.

We will submit a joint abstract for EMF2015 in Porto.

Given talks:

Environmentally Sustainable Multifunctional Ceramics and Nanomaterials

Robert C. Pullar, D. M. Tobaldi, C. Piccirillo, P. Marques, J. Amaral, P. M. L. Castro, M. M. Pintado, M. F. Silva, I. Braga da Cruz, R. Jorge, S. I. A. Pereira, A. P. G. C. Marques, D. Campos, W. Hajjaji, M. P. Seabra, J. A. Labrincha

Magnetoelectric and Multiferroic Hexagonal Ferrite Ceramics and Composites

Robert C. Pullar, D. Karpinski, I. Bdikin, P. Marques, M. Medeiros, E. Selezneva, A. Kholkin, J. Amaral

The Host

Carmen Galassi

The Visitor

Robert Pullar

Faenza, November 21st, 2014