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as of 13-Mar-2023

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STEM Degrees: **STEM Participants:**

Major Goals: The Army Research Office awarded North Carolina Central University $600,000 to acquire an advanced instrument referred to as the Integrated Optical Nanoprobe (ION). The goal is to provide scientists from all categories of STEM departments and their collaborators with the most advanced tool for characterizing various materials and nanomaterials at the nanoscale and in the time domain. The instrument also offer opportunity to train minority students in using research instruments for their research.
The purchase included a one-year warranty, required support service, and training. The university received on-campus training consisting of two 4-day sessions and one 2-day off-campus advanced training session. The catalog price for the instrument is $900,000, but the university received an exceptional discount of $300,000 from WITec.
The equipment was further augmented with two attachments using other funding. The first attachment is a cryogenic optical stage that cools and heats the sample during characterization, and the second is an optical hot stage with variable ambient gas for processing materials during characterization.
The objective of this project is to establish state-of-the-art analytical techniques for submicron and nanoscale characterization of semiconductors, piezoelectric and ferroelectric nanomaterials, as well as composite polymer materials. Due to the optical nanoprobe technology, this instrument is also suitable for analyzing biomaterials. Some of the techniques offer a resolution of 50 picoseconds, making it possible to resolve processes in real-time. The ION is a unique instrument that can be customized to build new functionalities.
The ION is based on the WITec alpha300RAS Near-field Optical Microscopy, which features three continuous wave (CW) lasers and one pulsed laser, three spectrometers equipped with high-resolution spectral cameras, a fast data acquisition system with additional channels for customized measurements, and advanced scanning software. Furthermore, the ION's capabilities have been augmented with two Linkram cryogenic stages, costing $28,000 on a NNSA sponsored project, title: Nuclear Security Advanced Manufacturing enhanced with Machine Learning (NSAM-ML). The stages will allow for cryogenic measurements starting from LN2 temperature and in-situ characterization of material phase transforms during thermal cycling from RT-1500°C. The PI plans to add more functionalities to the instrument, both from the manufacturer and in-house development.
This advanced research instrument supports several funded projects, including the NSAM-ML, three NSF Excellence in Research projects, and the NSF PREM project. The ION also facilitates collaboration with other universities, particularly the PI's partners at ECSU, and provides training for undergraduate and graduate students

conducting research projects for their thesis. Overall, the ION is an excellent asset for the university and its research endeavors.

Accomplishments: For this project we essentially have carried:

1) Research on various projects. The work is described in the uploaded document: Research Done,Karoui,NCCU. pdf

2) Training on the instrument. This is described in the section Training

3) Collaboration with partners in other universities (Elizabeth City State University). Scientist from ECSU have attended the training and have used the instrument to analyze their samples

4) Submitted several research papers to conferences.

5) journal papers are being prepared and will be submitted.

Training Opportunities: The acquired instrument is a custom-made system based on the WITec alpha300R Confocal Raman Microscope with 3 Excitation Lasers combining scanning probe setup (SPM), atomic force microcopy (AFM), scanning near-field optical microscopy (SNOM), time resolved Photoluminescence (PL), scanning fluorescence spectroscopy, Kelvin Scanning Probe (KSP), Conductive AFM, and Magnetic Imaging. The apparatus will be in fact delivered with a set of fourteen (14) measurement techniques. While these techniques are completely different from each other, as they can be operated independently, they remain coupled in space and time. Because of the complexity of the measurements, the fundamental concepts on which these nanaoscale and time resolved measurements are based, various trainings were offered to the users: undrgraduate and graduate students, postdoctoral scienctis and faculties. The trainings were detailed to enable both undergraduates and graduate students carrying out effectively their research projects and without damaging the instruments.
The organized trainings and participated individuals in measurements are:

a) Senior Scientists and Postdocs. Advanced training at the WITec Academy during 2 days.
- Abdennaceur Karoui
- Fouzia Sahtout
- Afzal Akram

b) On-campus training sessions

1. Senior Scientists and Postdocs who
- Abdennaceur Karoui
- Milledge Gaolin
- Fouzia Sahtout
- Afzal Akram

2. Undergraduates
- Nixon W. Ogoi
- Brianna Simone O’Briant
- Brandon Ma
- Naasir Smalls
- Kristen Hauser

3. Graduate students
- Oluwatoyin Ruth Atikekeresola
- Godwin Smart
- Ayobami Abiodun Taiwo
- Joseph Nduka
- Oluwatobiloba P Aiyewunmi
- Precious Anavberokhai

4. Others (Senior scientists Collaborators from Elizabeth City State University)
- Bijandra Kumar
- Baleeswaraiah Muchharla

Another cohort of students are being prepared for more training in the summer.

Results Dissemination: Conference papers:

1. Fozia Sahtout , Abdennaceur, Karoui , Branislav Vlahovic , Bijandra Kumar , Baleeswaraiah Muchharla, Characterization of Carbon Nanotube Film Structure, Mechanical and Optical, Properties for Flexible Sensors, accepted for presentation at the MRS Spring Meeting April 2023, San-Francisco, USA.

2. O. Atikekeresola, Fazli Akram, Fozia Sahtout,Abdennaceur Karoui, Branislav Vlahovic , Structural and Ferroelectric Properties of the Bi1/2(Na0.78K0.22)1/2TiO3 Ceramics, submitted to MRS Spring Meeting, San-Francisco 2023.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Abdennaceur Karoui
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Co PD/PI
Participant: Branislav Vlahovic
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Partners

,

RPPR Final Report

as of 13-Mar-2023

I certify that the information in the report is complete and accurate:
Signature: Abdennaceur Karoui
Signature Date: 3/10/23   9:02PM

Research Carried out using the New Instrument

In the following we discuss some of the research done with the acquired instrument.

1) Raman Spectroscopy Analysis of Carbon Nanotube Film Structure for Flexible Sensors

F. Sahtout[a], A. Karoui[a], B. Vlahovic[a], B. Kumar[b], B. Muchharla[b]

High sensitivity flexible sensors of few molecules require nanoscale and atomic studies of base materials. Confocal 2D Raman spectroscopy with 532 nm and 1064 nm excitation wavelengths, Atomic Force Field (AFM), Scanning Electron Microscopy (SEM-EDS) to analyze carbon nanotubes (CNTs) film vibrational spectrum and structure.

The SEM, AFM and confocal Raman 2D scanned images shows CNT film forming a random network with CNTs as the major component; the nanotubes laying horizontally on the surface of a substrate and forming bundles in several areas.

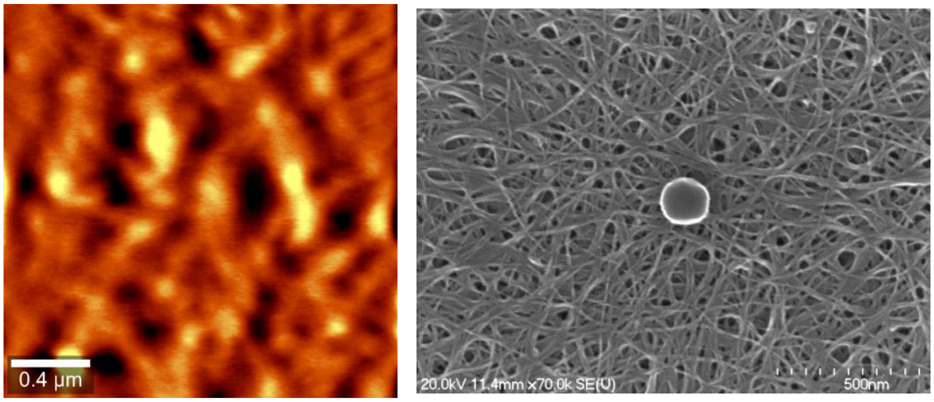
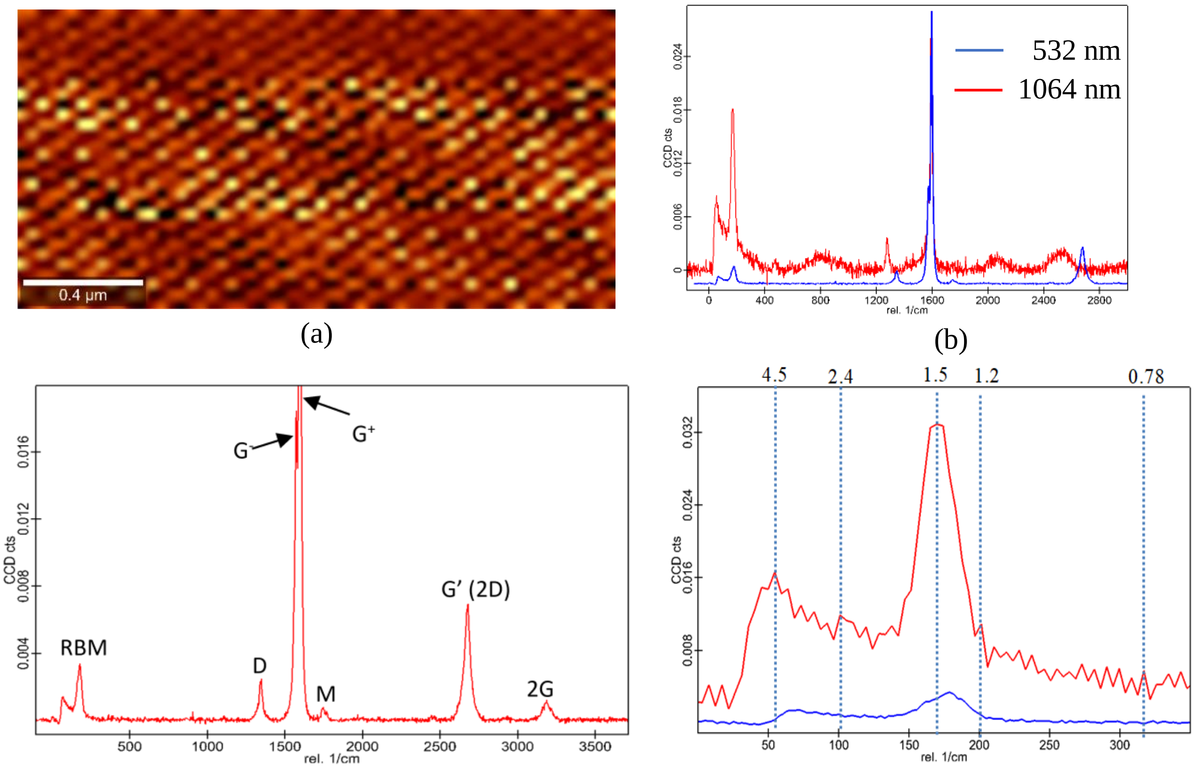


Figure 1: AFM and SEM images of CNTs film. Scan on a 2µm x 2µm area.

Confocal Raman spectrum exhibits five bands, RBM (Radial Breathing Mode), D band, G$^+$ and G$^-$ bands, and G' (2D) band. The RBM characteristic of carbon nanotubes is in the lower frequency range 50-350 cm^{-1} and its peaks position ω_{RBM} (cm^{-1}) have the following relationship with the CNT diameter d(nm): $d\ (nm) = {}^{248}/_{\omega_{RBM}}$.[1] The RBM-band can have contributions from several tubes simultaneously in resonance with the laser photon frequency. The IR excitation wavelength gave stronger in intensity RBM which allowed us to assess precisely the diameter range of the CNTs which range from 0.78 nm to 6 nm and the most common having a diameter ~ 1.5 nm corresponding to the RBM peak with higher intensity. This is in agreement with the sizes observed in SEM and AFM images. RBM is observed only when Single Walled CNTs (SWCNTs) are present[1], meaning that the CNT film contains mainly SWCNTs.

Three Raman bands are observed in the 1300-1750 cm^{-1} region. The D band at 1342 cm^{-1} (532nm excitation wavelength) identifies disordered sp$_2$ carbon network. This band shifts to 1283 cm^{-1} when the 1064nm wavelength is used. The known G band around 1590 cm^{-1} in graphene splits into two bands for CNTs, G$^-$ transverse wave mode (TO) at 1574 cm^{-1} and G$^+$ longitudinal (LO) wave mode at 1595 cm^{-1}. The G band derived from the in-plane vibration of the six-membered ring common to carbon-based substances. G$^+$ mode always appears regardless of the diameter of the carbon nanotube, while G$^-$ mode changes in inverse proportion to the square of the diameter.



(a) (b)

(c) (d)

Figure 2: (a) 2D Confocal Raman Scan; (b) Raman Spectra, 532 and 1064 nm excitations and (c) Vibration modes; (d) RBM zoomed-in with CNT diameter values (nm) at the top corresponding to each frequency.

The CNTs present in the layer are semiconducting carbon nanotubes because of the sharpness of the G band, which would be much broader if it was metallic due to the Kohn anomaly effect observed in metallic nanotubes· The spectrum from the 532nm laser excitation exhibits several additional double resonance Raman modes[2] weak in intensity. The M band appeared at 1750 cm^{-1} is interpreted as an overtone mode of the out-of-plane TO phonon modes (oTO). G’ band with peak at 2672 cm^{-1} (2566 cm^{-1} when using 1064 cm^{-1} laser) is an overtone of D mode. The G’ peak is related to the Raman scattering due to a vibrational mode characterized by the breathing of six carbons pertaining to a hexagon in the hexagonal lattice of graphene. The 2G mode with peak at 3180 cm^{-1} is an overtone of G mode and involves also two phonons.

2) Structural and Ferroelectric Properties of the Bi1/2(Na0.78K0.22)1/2TiO3 Ceramics

Oluwatoyin Atikekeresola, F. Akram, F. Sahtout, A. Karoui, B. Vlahovic

The development and design of piezoelectric ceramics with good energy conversion efficiency are the fundamental requirements for advanced energy-harvesting devices. However, lead (Pb)-free piezoelectric materials have been proposed to be an alternative to lead-based (Pb[Zr, Ti]O$_3$) due to their eco-friendly properties and have been extensively used in transducers, sensors, and actuators. The Pb-free ferroelectric $Bi_{1/2}(Na_{0.78}K_{0.22})_{1/2}TiO_3$ (BNKT) material was synthesized by a conventional solid-state reaction method (CSSR). The crystal structure, Raman, microstructure, and ferroelectric properties of the sample were studied in detail. The XRD pattern demonstrates the coexistence of the tetragonal dominant phase and the pseudo-cubic minor phase. Confocal Raman measurements were carried out at room temperature using 532 nm laser excitation and a frequency range of 70 cm^{-1} to 2000 cm^{-1}. The 2D Raman scan exhibits four components (I, II, III, and IV), which indicate the existence of different phases. The component-I shows a pure tetragonal phase for BNKT material with four active modes (I_1, I_2, I_3, and I_4) from 90 cm^{-1} to 900 cm^{-1}. The Raman active mode I_1, I_2, I_3, and I_4 is associated with *A*-site cation vibrations (Na-O, K-O, Bi-

O bonds), Ti-O bond vibrations, TiO_6 octahedra vibrations, and A1 (LO) and E (LO) overlapping bands, respectively. The component-II demonstrates a pseudo-cubic phase for the BNKT materials, and more splitting in the *A*-site was observed. Components III and IV are related to the vibration modes of sodium titanate and potassium titanate formed from the remaining Na+, Ti^{4+} and K^+ ions after BNKT perovskite phase crystallization. The SEM images show a well-dense microstructure with no noticeable pores detected as well as definite grains observed. The samples exhibited the ferroelectric polarization response with noticeable maximum polarization (P_{max}), remnant polarization (P_{rem}), and coercive field (E_c) of 38 $\mu C/cm^2$, 28 $\mu C/cm^2$, and 27 kV/cm, respectively. The research provides an idea for the synthesis of BNKT-modified ceramics for advanced ferroelectric and piezoelectric applications.

3) Characterization of Multiferroic NiFe2O4/BaTiO3 Ceramic Powder by Raman Spectroscopy

F. Sahtout, A. Karoui, B. Vlahovic, V. Pavlovich

a) Introduction

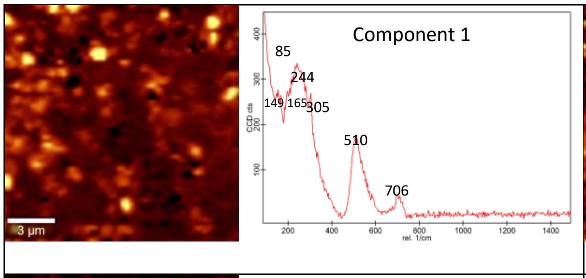
Multiferroic materials attract much research interest because of their fundamental physical properties and potential applications[1,2,3,4,5], such as magnetic probes, transducers, novel actuators and sensors. These materials possess simultaneously magnetic and electric moments, have elastic orders, and display a magnetoelectric coupling, in which the electric polarization or permittivity can be modified by an applied magnetic field, or a magnetic moment can be induced by an electric field[1,4]. For multiferroic material it is not just important to possess multiple ferroic abilities, but also it is crucial to achieve significant coupling interaction between them, defined as magnetoelectric effect[1,2,3,5]. Here we report on the characterization of multiferroic ceramic powder, namely $NiFe_2O_4/BaTiO_3$ by mean of Raman spectroscopy. The nanopowders were synthesized by thermal decomposition method. Raman measurements were performed as well as 2D imaging chemical characterization using the Confocal Raman (in the WITec alpha 300 RS new instrument) and 532 nm laser excitation.

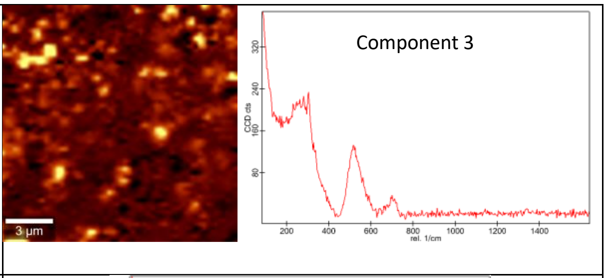
b) Raman Spectroscopy of NiFe2O4-BaTiO3 multiferroic composites

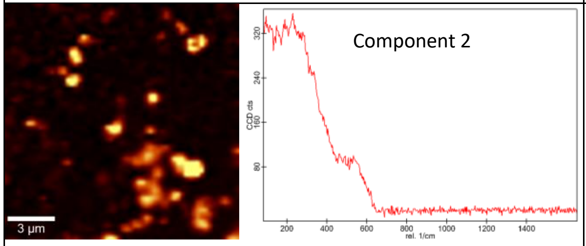
Figure *3* shows Raman spectra for each chemical component and 2D chemical composition images for $NiFe_2O_4$-$BaTiO_3$ powder. The powder was glued on a Si substrate and formed a thin film, which was then polished to prevent light scattering. The area scanned is 15µm x 15µm. The covered spectral range is from 70 cm^{-1} to 2000 cm^{-1}. The powder exhibits five Raman active components (
Figure *3*a-1e), each belonging to a different Raman spectrum.

We found that the Raman exhibits the spectrum of the ferroelectric alloy $BaTiO_3$ and the magnetic alloy $NiFe_2O_4$ this infers that the two compounds coexist in the powder as two separate components of the materials. Therefore, the powder is a composite of two nanocrystalline phases, $BaTiO_3$ and $NiFe_2O_4$, respectively, that form interfaces with each other. They do not form a core–shell structure as initially thought.

The spectrum of the tested material shows that the powder was synthesized as a pure tetragonal phase; and due to fabrication conditions, it ended-up with a cubic structure. This in agreement with the fact that at room temperature $BaTiO_3$ is tetragonal and has $C4v$ symmetry (P4*mm* space group), while no Raman-active mode is predicted for the cubic phase (*Pm*3*m* space group).


3 µm
Component 1
85
244
149
165
305
510
706
CCD cts
400
300
200
100
200
400
600
800
1000
1200
1400
rel. 1/cm


3 µm
Component 3
CCD cts
320
240
160
80
200
400
600
800
1000
1200
1400
rel. 1/cm


3 µm
Component 2
CCD cts
320
240
160
80
200
400
600
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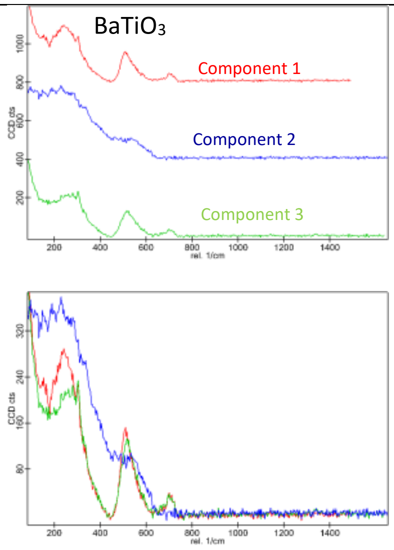
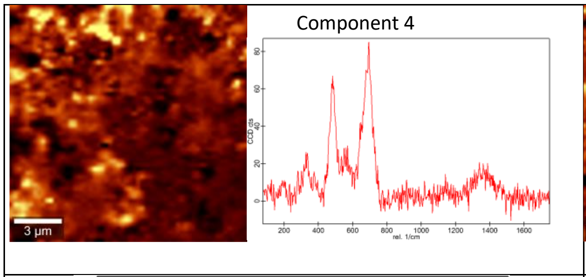
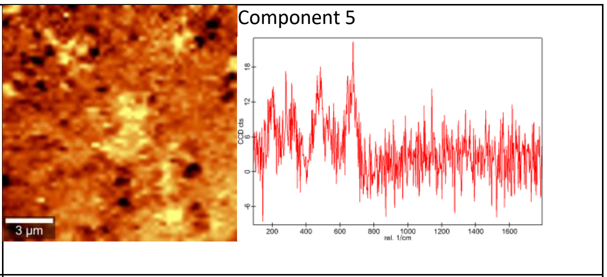
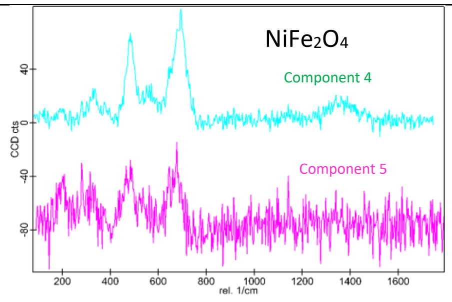
1000
1200
1400
rel. 1/cm


BaTiO3
Component 1
Component 2
Component 3
CCD cts
1000
800
600
400
200
200
400
600
800
1000
1200
1400
rel. 1/cm
CCD cts
320
240
160
80
200
400
600
800
1000
1200
1400
rel. 1/cm


3 µm
Component 4
CCD cts
80
60
40
20
0
200
400
600
800
1000
1200
1400
1600
rel. 1/cm


3 µm
Component 5
CCD cts
18
12
6
0
-6
200
400
600
800
1000
1200
1400
1600
rel. 1/cm


NiFe2O4
Component 4
Component 5
CCD cts
40
0
-40
-80
200
400
600
800
1000
1200
1400
1600
rel. 1/cm

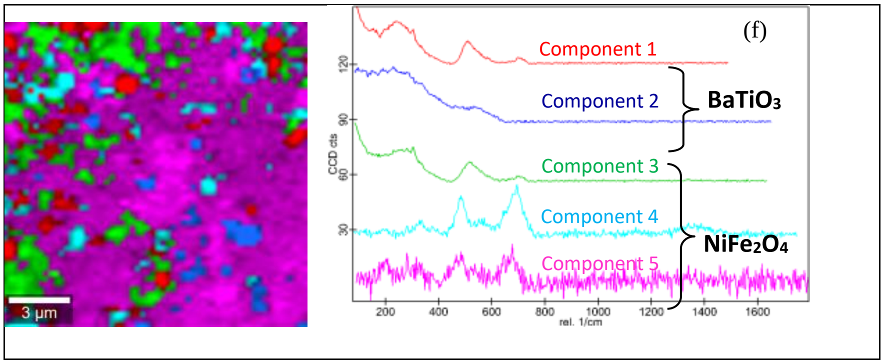


Figure 3: Raman measurement of $NiFe_2O_4/BaTiO_3$ (M21 Polished on Si).

Raman $BaTiO_3$ unit cell contains 5 atoms, leading to 15 vibrational modes. Excluding 3 acoustic modes, there are 12 optical modes. According to the group theory analysis 12 optical vibrational modes of $BaTiO_3$ can be represented as follows: 3*A*1(R, IR)+*B*1(R)+4*E*(R, IR), where R and IR denote Raman and IR modes, respectively, while *A*1 and *B*1 denote the non-degeneracy modes, *E* denotes the double degeneracy modes. If we consider double degeneracy mode *E* as one mode, the $BaTiO_3$ optical vibrational modes include 8 Raman active modes (3*A*1, 1*B*1, 4*E*) and 7 IR active modes (3*A*1, 4*E*). In addition, another *A*1 mode and a double degenerate *E* mode constitute the acoustic modes of $BaTiO_3$.
$BaTiO_3$ has uneven baseline and broad peaks. In component 1-2, one of the soft *E* mode at 85 cm^{-1} of the tetragonal $BaTiO_3$ affects the baseline of the spectrum. In the non-centrosymmetric P4*mm* space group, the polar modes (*A*1 and *E*) can be split into transverse optical (TO) modes and longitudinal optical (LO) mode[6], which may be the reason the peaks are wide. In component 1, the broad peaks at 244 cm^{-1}, and an asymmetric peak at 510 cm^{-1} are assigned to the fundamental TO phonon mode of A1 and E symmetry. The peak at 149 cm^{-1} is assigned to A1 symmetry and the peak at 165 cm^{-1} to E. The peak at 305 cm^{-1} is assigned to the [B1, E(TO+LO)] mode, indicating the asymmetry of TiO_6 octahedra with $BaTiO_3$ structure. This peak decreases in component 2 and 3 of $BaTiO_3$. The peak at 706 cm^{-1} is related to [A1(LO), E(LO)] and disappears in component 2 indicating the presence of a different structure of $BaTiO_3$. Indeed, as observed by XRD analysis[7], pseudo cubic state or low tetragonal distortion may be expected in titanate phase, which explains the weak Raman response of barium titanate component 2 and at a lesser extent component 3.

Trevorite $NiFe_2O_4$ nickel iron oxide mineral belongs to the spinel group AB_2X_4 which crystallize in the cubic crystal system. Group theory predicts five Raman active modes ($A_{1g} + E_g + 3F_{2g}$) for the spinel group with symmetry Fd3m, and all these modes were observed clearly in the Raman spectra in Figure *3* c, e and h. In the cubic ferrites, the strongest modes 693 cm^{-1} correspond to symmetric stretching of oxygen in tetrahedral AO_4 groups, and can be considered as A_g symmetry. E_g at about 329 cm^{-1} is due to symmetric bending of oxygen with respect to cation in tetrahedral surrounding. $F_{2g}^{(1)}$ at 190 cm^{-1}, is due to translational movement of the whole tetrahedron. $F_{2g}^{(2)}$ at 482 cm^{-1}, $F_{2g}^{(3)}$ at 562 cm^{-1} correspond to the vibrations of octahedral group: $F_{2g}^{(2)}$ is due to asymmetric stretching of O and $F_{2g}^{(3)}$ is caused by asymmetric bending of O.

c) Further Work

We will investigate the properties of $Ni_{0.5}Zn_{0.5}Fe_2O_4/BaTiO_3$ and $ZnFe_2O_4/BaTiO_3$ multi-ferroic powders using Raman spectroscopy, as well as these materials sintered at 1150°C and 1300°C.

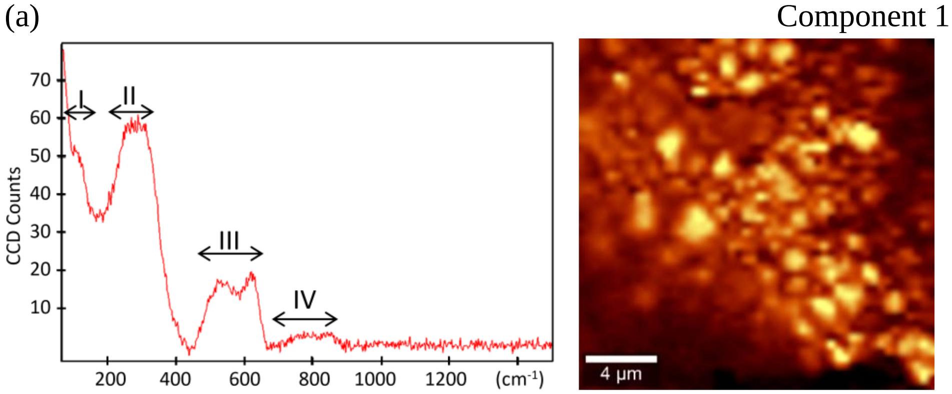
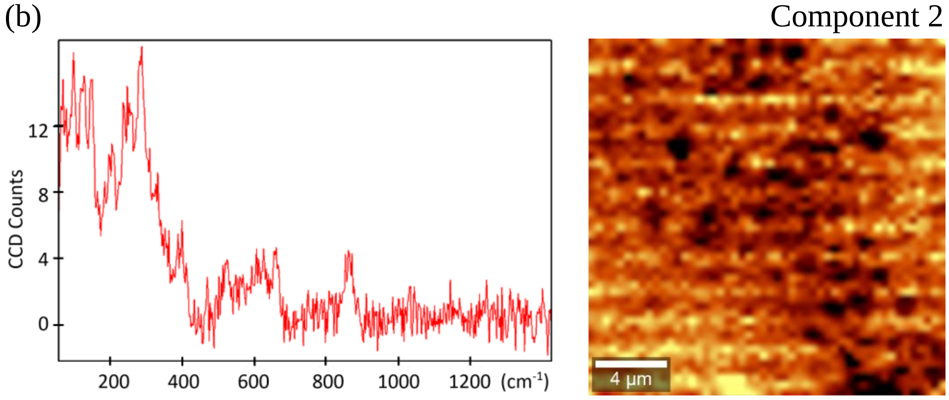
4) Raman Spectroscopy of Piezoelectric $Bi_{0.5}(Na_{0.78}K_{0.22})_{0.5}TiO_3$ Ceramics

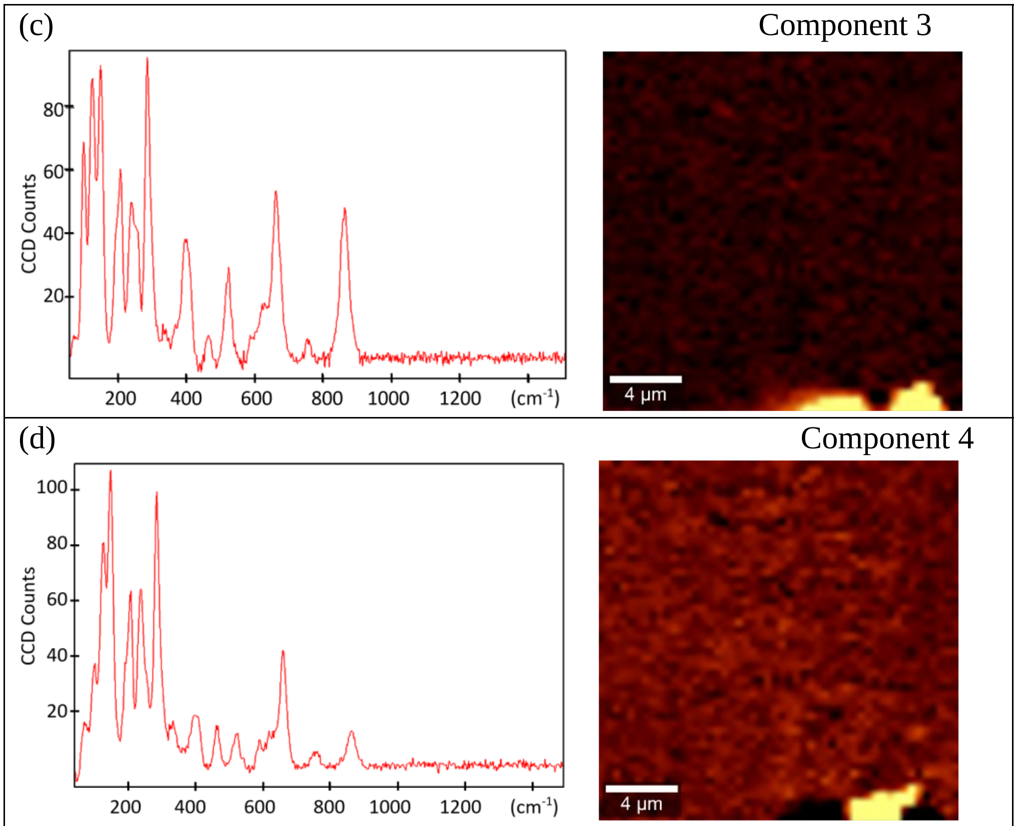
F. Sahtout, A. Karoui

We report on the characterization of piezoelectric ceramic particles $Bi_{0.5}(Na_{0.78}K_{0.22})_{0.5}TiO_3$ by means of Raman Spectroscopy, using the Confocal Raman (of the WITec alpha 300 RS instrument) done with a 532 nm laser excitation. The measured Raman data allowed us to obtain 2D chemical maps that unravel clusters of particles with variable composition.

Figure 3 shows Raman spectra for each chemical component and 2D chemical composition images for $Bi_{0.5}(Na_{0.78}K_{0.22})_{0.5}TiO_3$ ceramic. The area scanned is 20 µm x 20 µm. The Raman measurements were carried out at room temperature. The frequency-covered range is from 70 cm^{-1} to 2000 cm^{-1}. Four components were detected in the scanned area, see Figure 4**,** each one corresponding to a Raman spectrum.

$Bi_{0.5}(Na_{0.78}K_{0.22})_{0.5}TiO_3$ spectrum shows that the ceramic was synthesized in a pure tetragonal phase. This in agreement the fact that at room temperature $Bi_{0.5}(Na_{0.78}K_{0.22})_{0.5}TiO_3$ is tetragonal and has *C*4*v* symmetry (P4*mm* space group). Tetragonal symmetry gives 15 Raman-active modes (3A1 + 3B1 + 2B2 + 7E) in the irreducible representations including 3 acoustic modes.[8]

(a) Component 1 	Tetragonal P4mm I: <200 cm^{-1} Na-O, K-O, Bi-O bonds II: 200-400 cm^{-1} Ti-O bonds III: 450-695 cm^{-1} TiO_6 IV: >700 cm^{-1} LO bands overlapping.
(b) Component 2 	Pseudo cubic pm$\bar{3}$m



Combination of the 4 compositional components

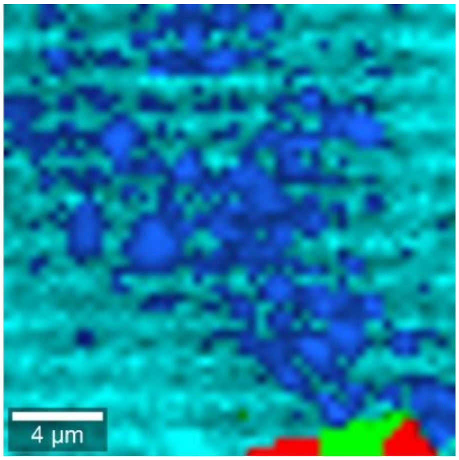


Figure 4: Confocal Raman measurement of $Bi_{0.5}(Na_{0.78}K_{0.22})_{0.5}TiO_3$ ceramic

Figure 4 **(a)** shows the vibrational spectra $Bi_{0.5}(Na_{0.78}K_{0.22})_{0.5}TiO_3$. The Raman vibrational spectra can be divided in four regions I, II, III, and IV; these are mapped across the scanned area of the material.

I: Vibrational map for wavenumbers below 200 cm^{-1}. High intensity regions are due to vibration of perovskite A-site involving Bi, Na and K cations, involving the Na-O, K-O, Bi-O bonds.

II: Vibrational map for the 200-400 cm^{-1} range, which is associated with the Ti-O bonds.

III: Frequency region 450 – 695 cm^{-1}, which is related to the vibration of the TiO_6 octahedron. We propose for this range a superposition of longitudinal optical (LO) and transverse optical (TO) mode, because of the A1 character for that vibration.

IV: The high-frequency region greater than 700 cm^{-1} has been linked to A1 (longitudinal optical mode) and E (longitudinal optical) overlapping bands.

Figure 4 **(b)** (component 2) is also the Raman spectrum for $Bi_{0.5}(Na_{0.78}K_{0.22})_{0.5}TiO_3$, but with splitting of the modes especially vibration of perovskite A-site (Still under investigation).

Figure 3(c, d) component 3 (c) and Figure 4 (d) component 4 are related to the vibration modes of sodium titanate and potassium titanate. After BNKT perovskite phase crystallization, the residual melt is significantly Bi^{3+} deficient, the remained ions Na^+, Ti^{4+} and K^+ reacted to form $Na_2Ti_6O_{13}$ and $Na_2Ti_3O_7$ [9]; $K_2Ti_8O_{17}$ and $K_2Ti_6O_{13}$.

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