High Spatial Resolution of the ferroelectric domain structure by Confocal Raman Microscopy coupled whit Atomic Force Microscopy

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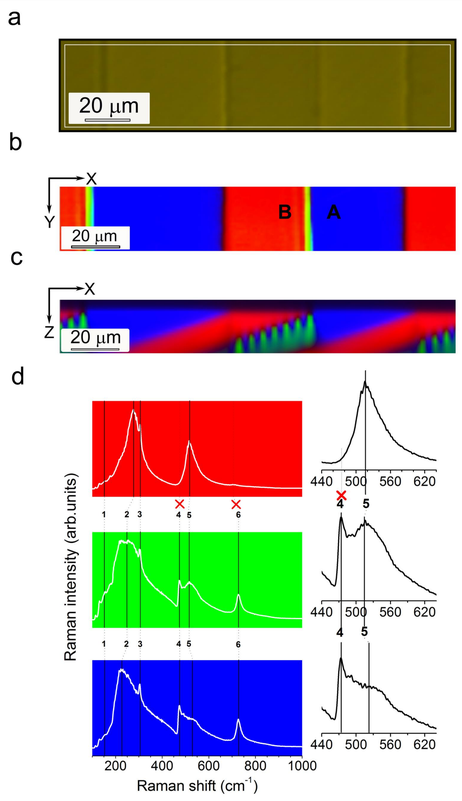
In order to investigate the structure and distribution of ferroelectric domains, a number of techniques have been usually applied, among them, scanning probe microscopy, environmental scanning microscopy, polarized light microscopy, transmission electron microscopy, atomic force microscopy and lately, scanning electron microscopy in the backscattered mode. In contrast to spectroscopic methods, the above mentioned techniques yield no or very limited chemical information. For complex domain structure, the purely topographic information is not sufficient to understand the distribution of all domains within a ceramic material. Different attempts have been made to combine the high spatial resolution of scanning probe microscopy with chemical information provided by spectroscopic techniques. Methods based on micro Raman spectroscopy give the possibility to study at a local scale the structural deformations of perovskites, which are induced both by the tilting of BO_6 octahedra and by the cationic displacements. In this contribution we present and discusses the ferroelectric domain structure existing in different lead-free piezoceramics, such as (K,Na)NbO_3 (KNN), $Bi_4Ti_3O_{12}$ (BIT), $BaTiO_3$ (BT), and in single crystals ($BaTiO_3$), studied by Confocal Raman Microscopy (CRM) coupled with Atomic Force Microscopy.

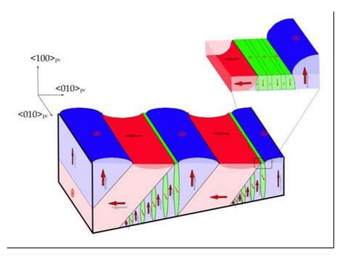
$BaTiO_3$ (BTO) single crystal



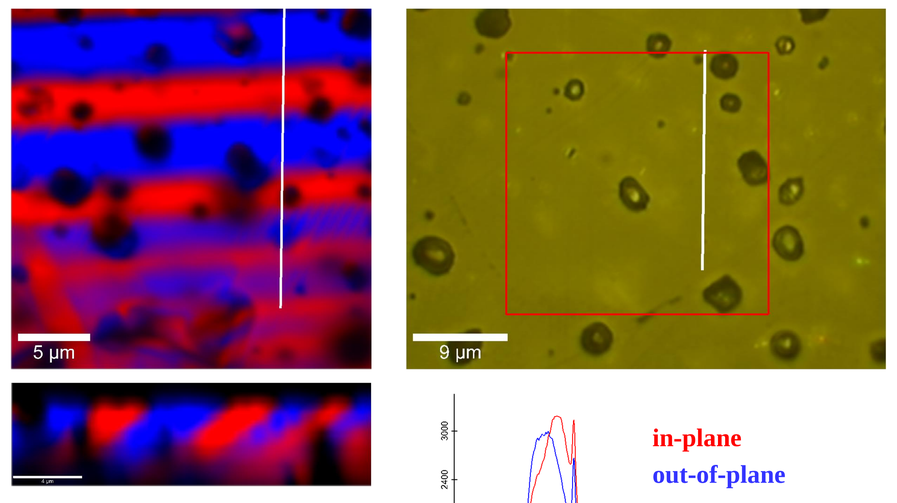
Mapping of the domain structure of the through Confocal Raman spectroscopy: (a) optical image of the A-plane of the BTO single crystal. Raman colour maps showing the distribution of the different ferroelectric domains in the planar-section **(b)** and in the cross-section **(c)** represented as a rectangle area in (a). The Raman spectra in the planar section were collected at a plane located below the surface of the sample (~ 2 μm). The Raman image resulted from mapping the different single Raman spectra collected in each pixel. Raman spectra having same spectral shift for the Raman modes were colour identified. The intensity of the colour correlated with the Raman intensity. **(d)** Raman spectrum of BTO indicating its active modes depending to the ferroelectric domains kind of the BTO. Main Raman spectra corresponding associated with different colours. The inserts show magnified Raman spectra, ascribed to the **4** and **5** Raman modes, respectively.

Table S1. Raman modes and their mode symmetry assignments in tetragonal $BaTiO_3$ single crystal.

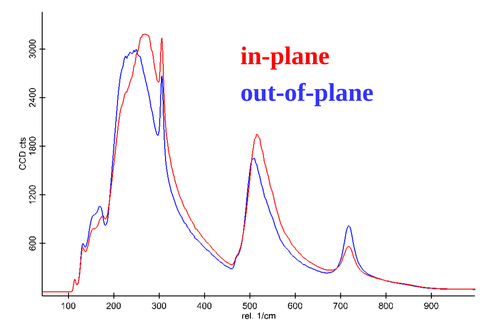
Raman Shift (cm^{-1})	Symmetry	Abbreviated number
36	E (TO)	**1**
170	A_1 (TO)	
180	E (TO_2), E (LO)	
185	A_1 (LO)	
270	A_1 (TO_2)	**2**
305	E (TO_3 + LO_2)	**3**
305	B_1	
463	E (LO_3)	**4**
475	A_1 (LO_2)	
486	E (TO_4)	
518	E (TO_5)	**5**
520	A_1 (TO_3)	
715	E (LO_4)	**6**
720	A_1 (LO_3)	



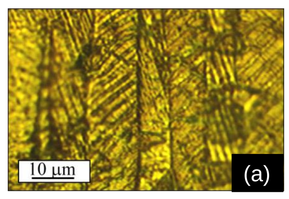
$BaTiO_3$ (BTO) ceramic

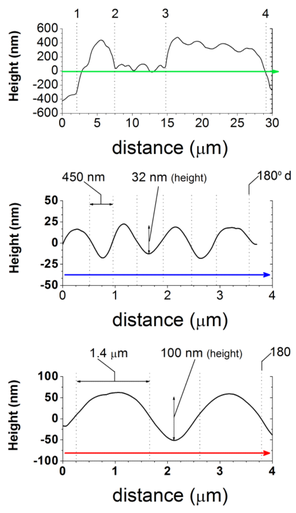


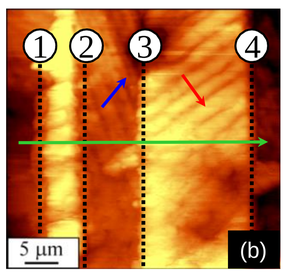
We have found a very similar domain structure in $BaTiO_3$ ceramics that in single crystal, configured by adjacent striped domains with c-axis oriented in-plane or out-of-plane.



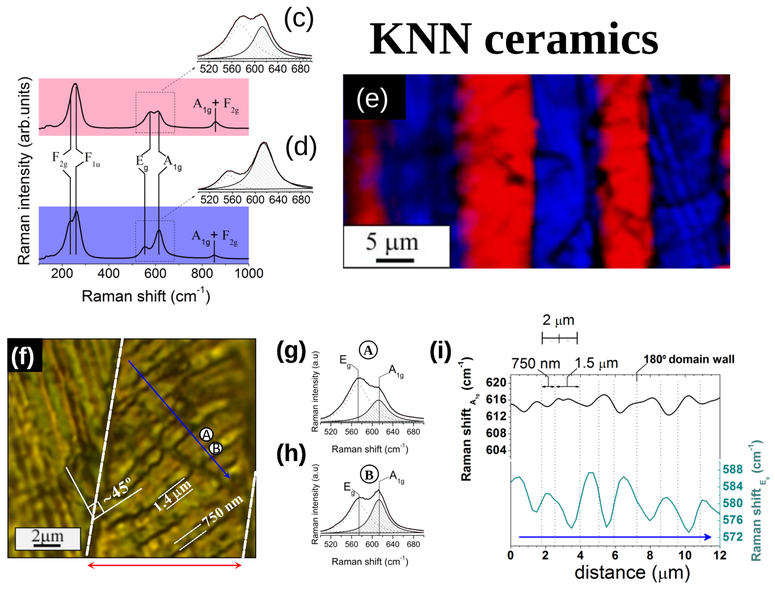
KNN ceramics







Optical (a) and AFM (b) images of a KNN ceramic **after the chemical etch** showing the domain structure. (c and d) Average Raman spectra of adjacent striped domains separated by a 90º domain wall. These spectra are fitted to the sum of two Lorentzian peaks, ascribed to the E_g and A_{1g} Raman modes, respectively. (e) Raman map of domain structure of the KNN exhibiting clear differences between average spectra of adjacent striped domains separated by a 90º domain wall.



(f-i) *Characterization of the 180º domain walls by confocal Raman spectroscopy*: (f) OM image of two domains separated by a 90º domain wall. (g and h) Magnified Raman spectra and Lorentzian fits of domain structure corresponding to the points labelled A and B in the image shown in (f). (i) Evolution of the A_{1g} and E_g modes which were measured following the blue arrow marked in (f) across the 180º domain walls.

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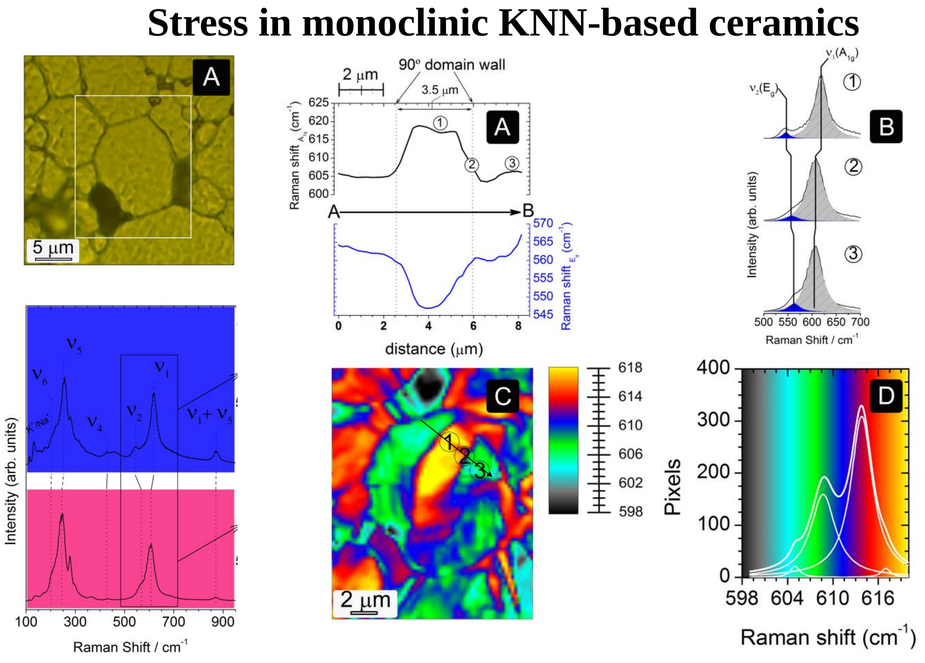
Stress in monoclinic KNN-based ceramics



(A) Optical images **after the thermal etch** (A) Evolution of the Raman shift of A_{1g} and E_g modes, which were measured following the black arrow in (C). (B) Magnified Raman spectra corresponding to the points labelled 1, 2 and 3 fitted to the sum of two Lorentzian peaks, ascribed to the E_g and A_{1g} Raman modes. (C) Colour coded map showing the Raman shift corresponding to the A_{1g} mode. (D) Statistical analysis of the number of spectra corresponding to different Raman shift values of the A_{1g} mode.

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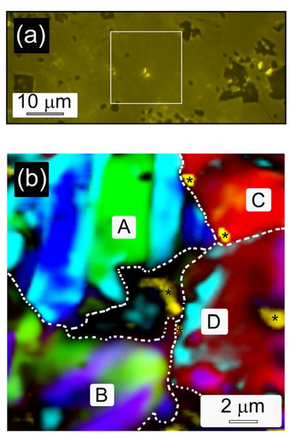

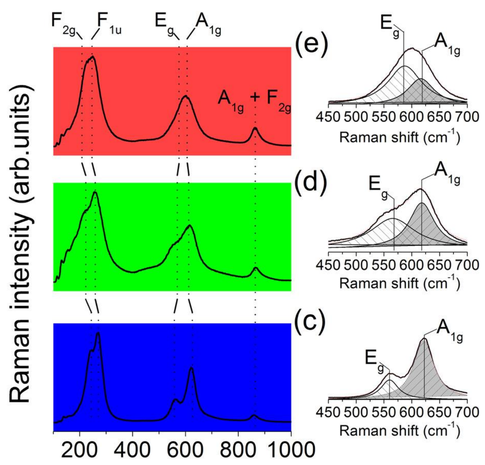

(KNL)Co-NTS ceramics: samples without any thermal or chemical etching . The regions delimited by bright dotted lines and marked as A, B, C, and D represented four different grains. In addition, a secondary phase in yellow was signalled with an asterisk (*) .

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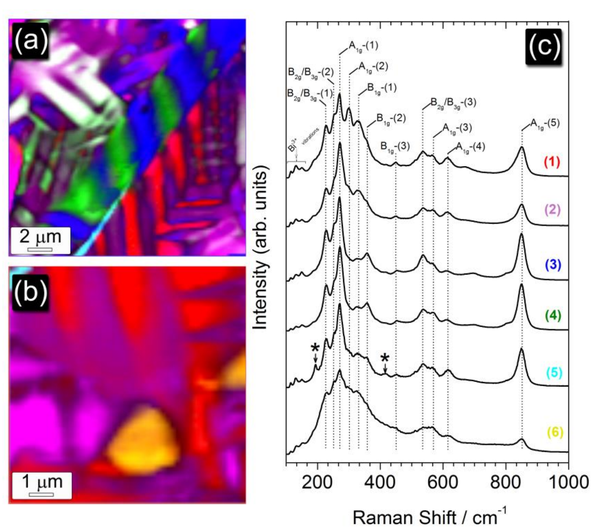
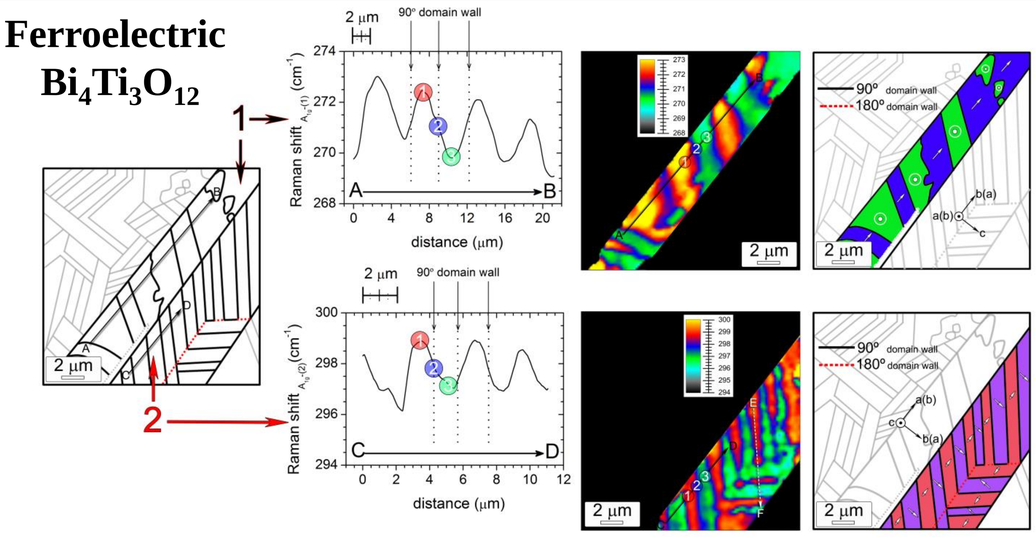


Raman image of domain structure of BIT (a) and BIT Ti-rich (b) ceramic, with a striped 90º domain structure in the biggest grains in addition with a needle-like domain structure in the smallest ones.

Ferroelectric $Bi_4Ti_3O_{12}$



Stress distribution in BIT ceramic grains. The colored images represent the displacement on the Raman Shift of the modes centered in 271 and 297 cm^{-1} respectively, which are related with the stress. The variation of the Raman shift along two lines (A-B, C-D) drawn in each grain is also shown. The crystal orientations within the grains are identified in the right image.