Co-doping of Lead-free $Bi_{1/2}Na_{1/2}TiO_3$ (BNT) - $Bi_{1/2}K_{1/2}TiO_3$ (BKT) -based Piezoceramics

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Why Doping / Co-doping?

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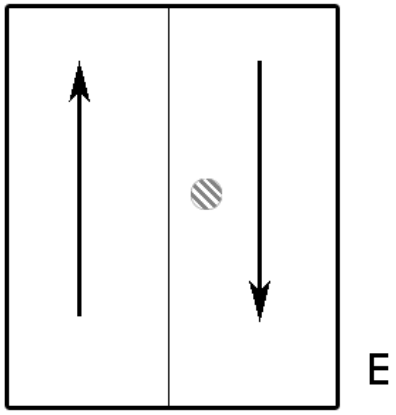
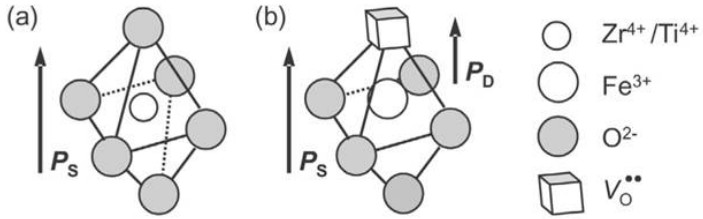
In-fluen-ces

Acceptor doping, *e.g.*: $Mn_2O_3 \rightarrow 2Mn'_{Ti,Zr} + V_{\ddot{O}} + 3O_O^X$

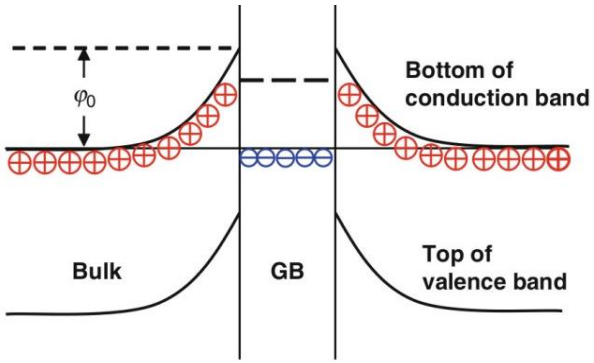
Donor doping, *e.g.*: $Nb_2O_5 + PbO \rightarrow 2Nb_{Ti,Zr}^{\cdot} + V''_{Pb}$

- **Domain walls**
- **Defect dipoles**
- **Schottky barriers**





Erdem, E. et al., IEEE Trans. Ultras. Ferroel. Freq. Control 55, 1061-1068 (2008)



Cao, W., Disorder and Strain-Induced Complexity in Funct. Mater. Vol. 148, Ch. 7, 113-134 (Springer Berlin, 2012)

What are Possible Applications?

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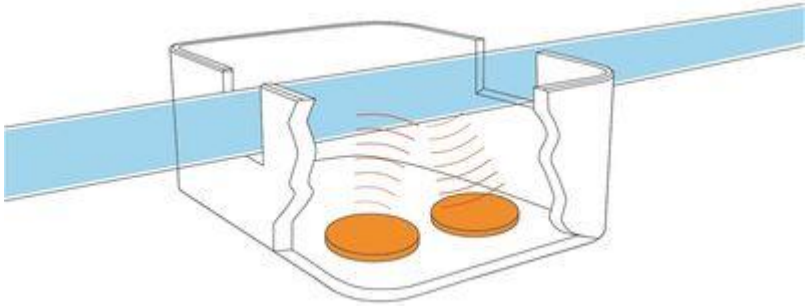
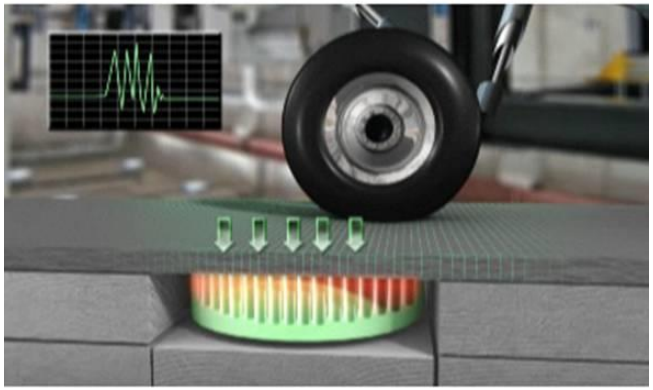
Piezoelectric flow meters



Nano-positioning

Energy harvesting



High power applications

Compositions / Synthesis / XRD Characterization

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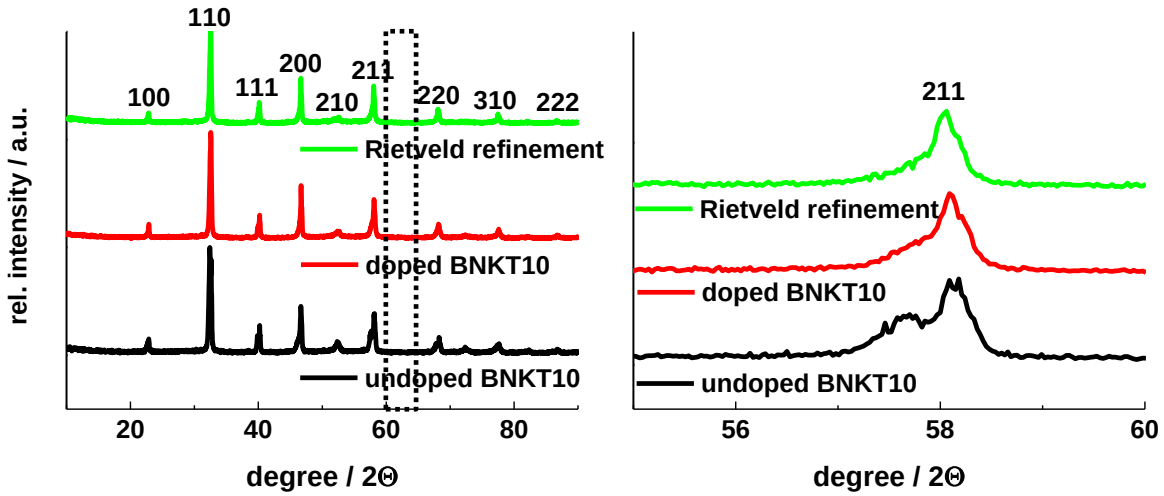
$Bi_{0.5}(Na_{(1-x)}K_x)_{0.5}Ti_{0.995}Cu_yV_{(0.005-y)}O_3$, BNKT20 + excess V_2O_5

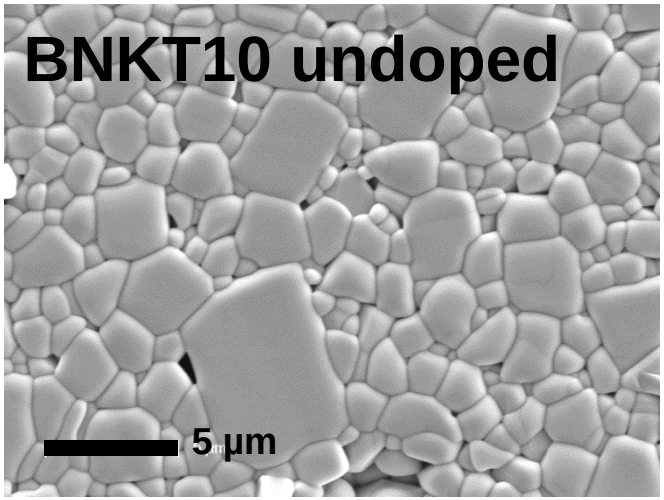
$Bi_{0.5}(Na_{(1-x)}K_x)_{0.5}Ti_{1-y}(Mn,V,Cu,Mo,Al)_y\,O_3$

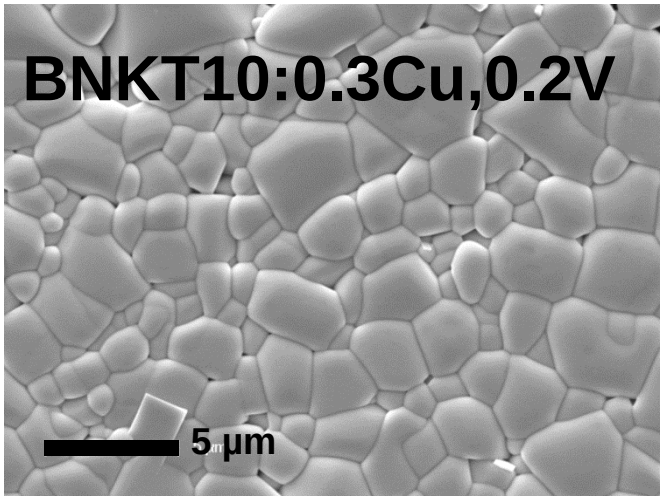
mixing + milling 12h in ethanol → calcining 800 - 900 °C → milling 12h in ethanol → uniaxial+ isostatic at 350 MPa → sintering 1080 - 1150 °C



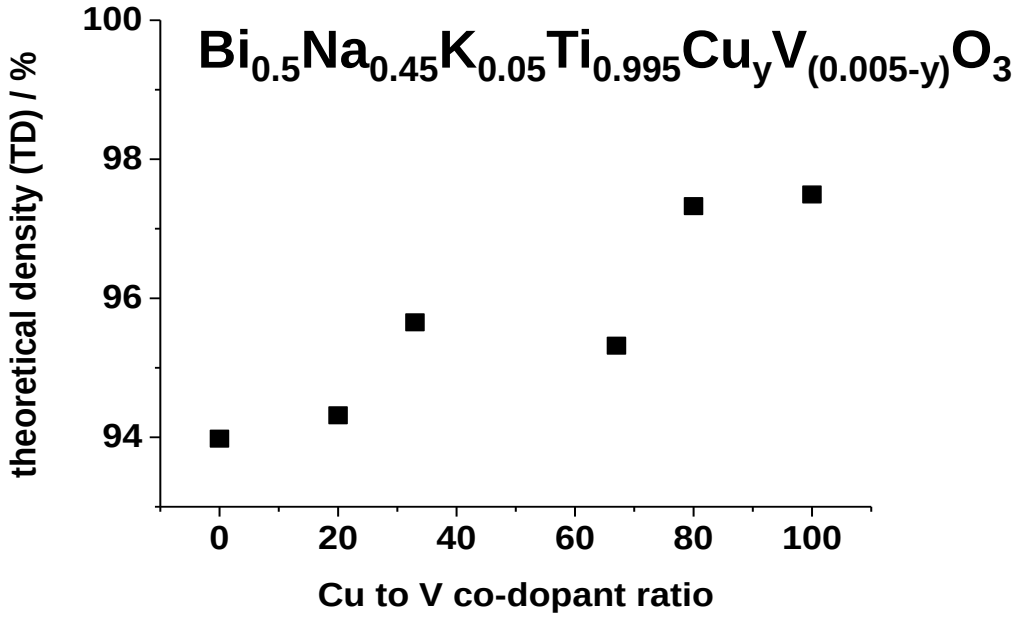
- **Solid state sythesis**
- **Less rhombohedral character upon (co-)doping**

SEM Investigation / Density

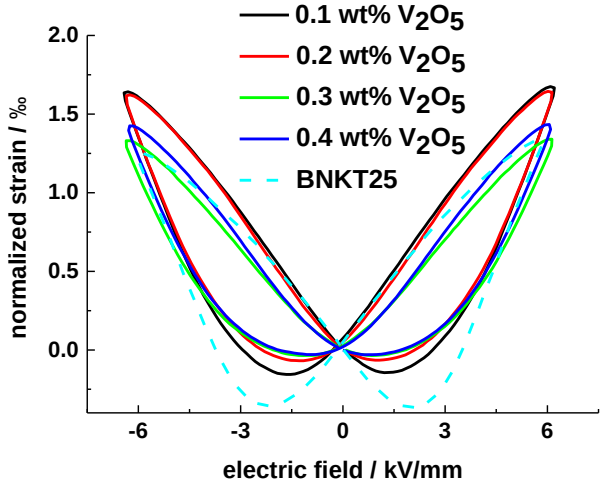


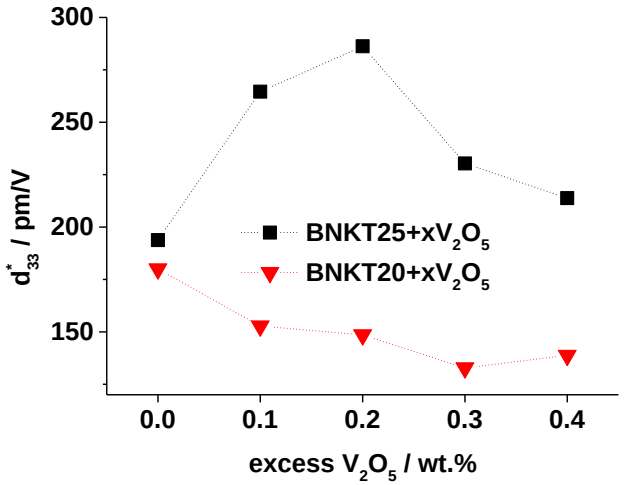


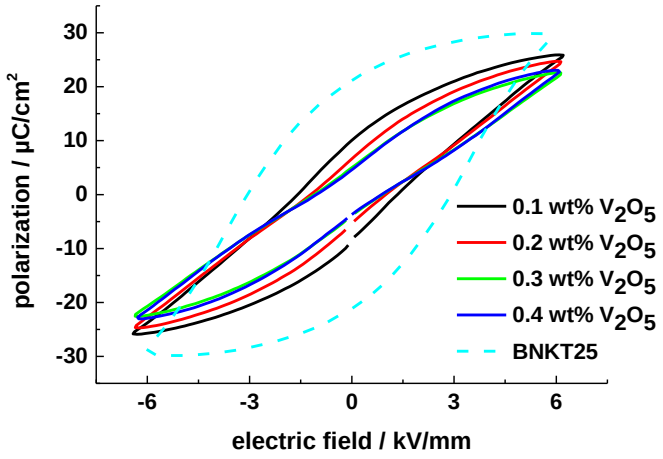
- More homogeneous size distribution of doped BNKT10
- %TD increases with Cu-content

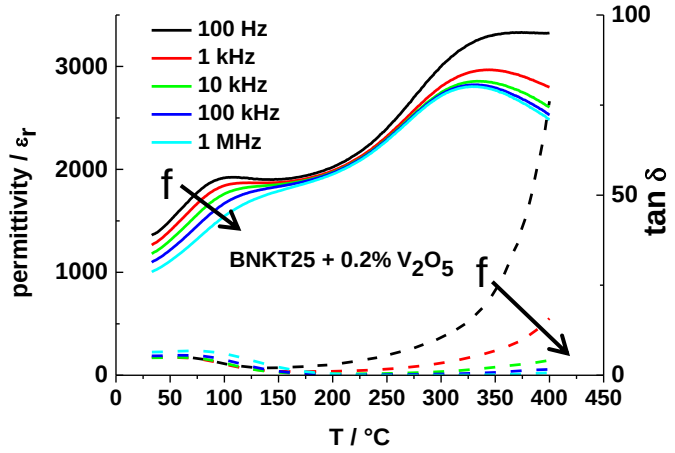


Excess Doping of BNKT20 and BNKT25 with V_2O_5









- **Pinching of P-E loop**
- **Strain increase for BNKT25**
- **$T_{f\text{-}r}$ lowered and broadened**
- **Frequency dispersion**

(Co)-doping V + Cu Overview

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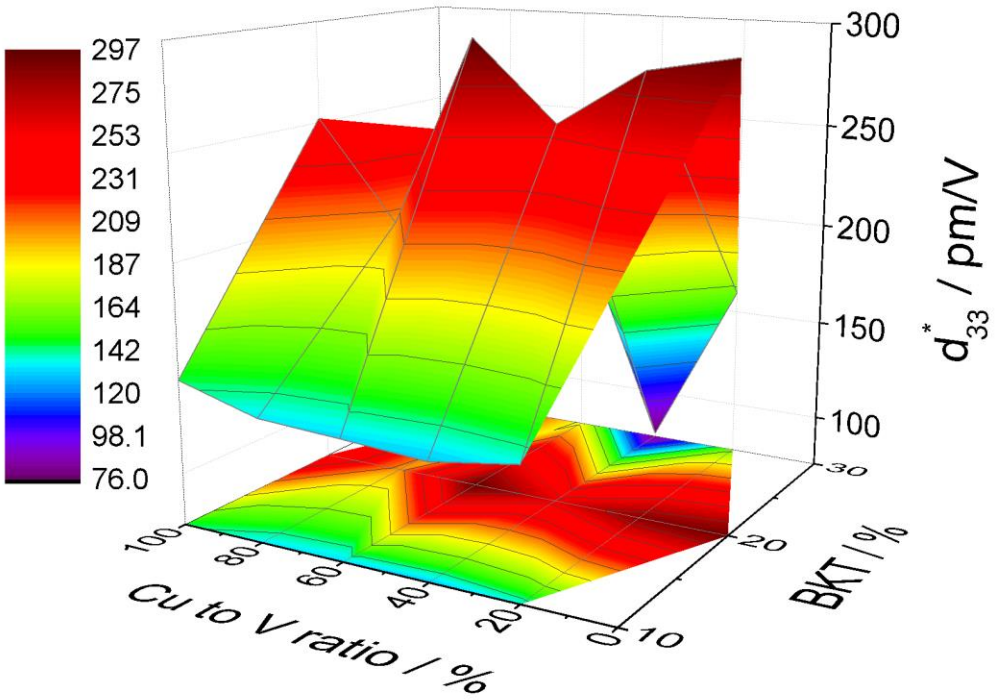
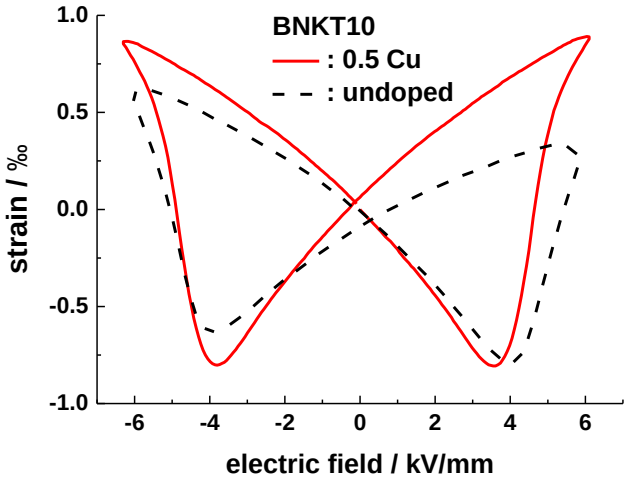
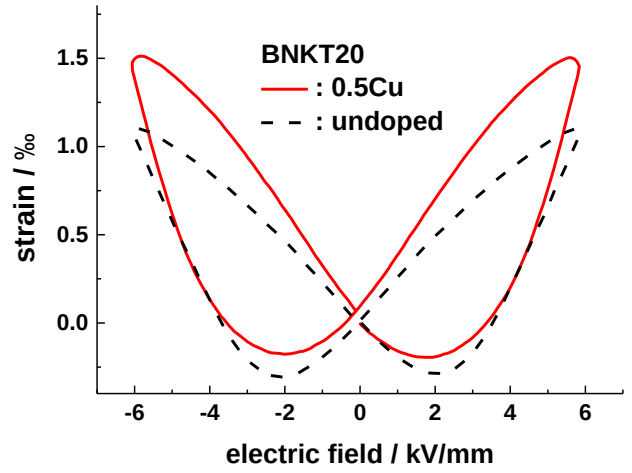
- **High strain at MPB + some tetragonal compositions**







(Co)-doping V + Cu Overview

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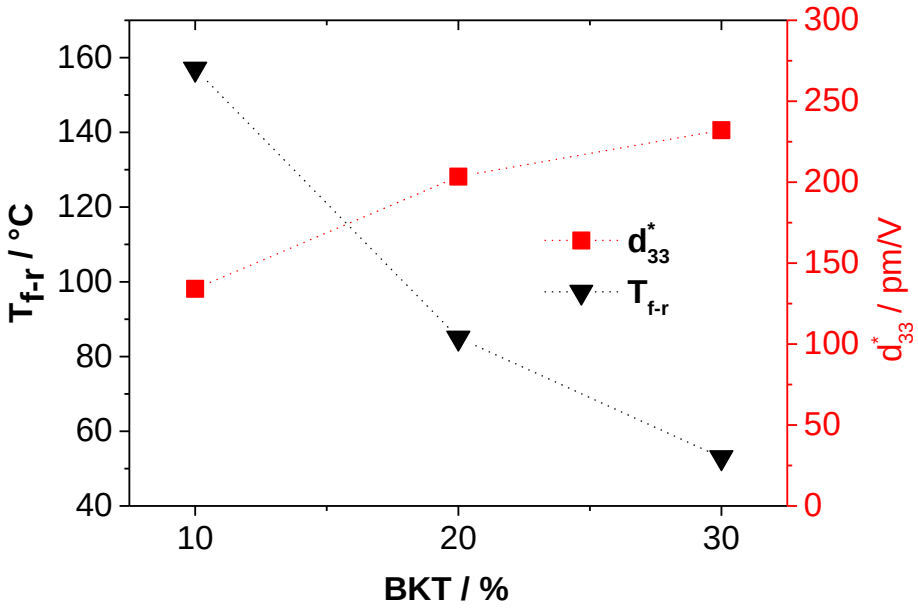
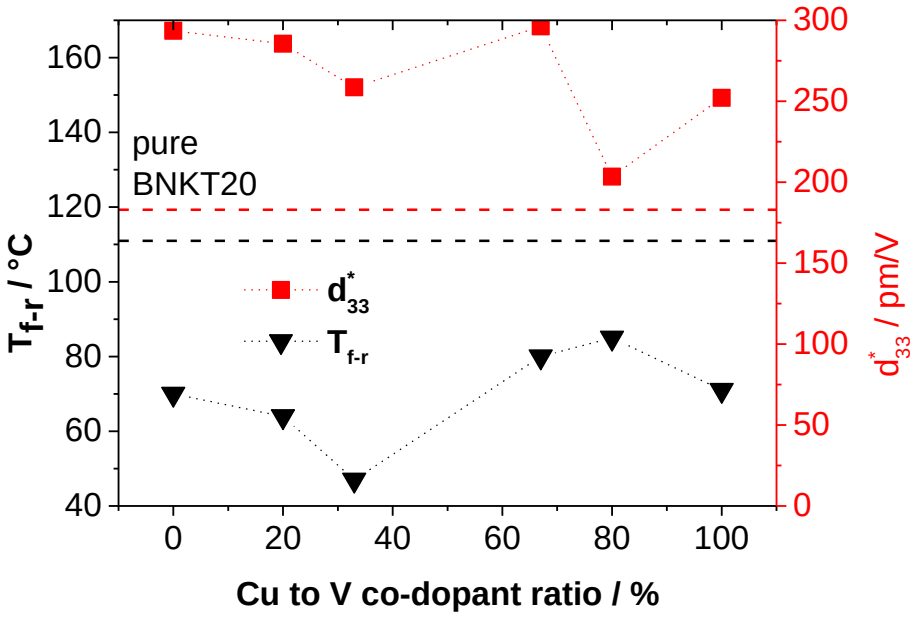
0.4Cu,0.1V fixed, BKT varied



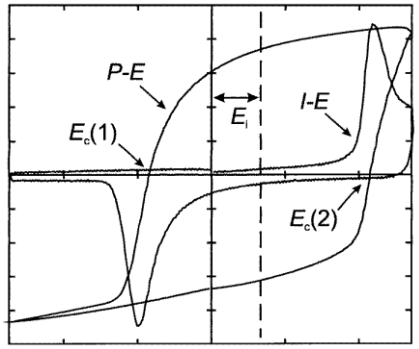
BKT fixed to 20 %, Cu to V ratio varied



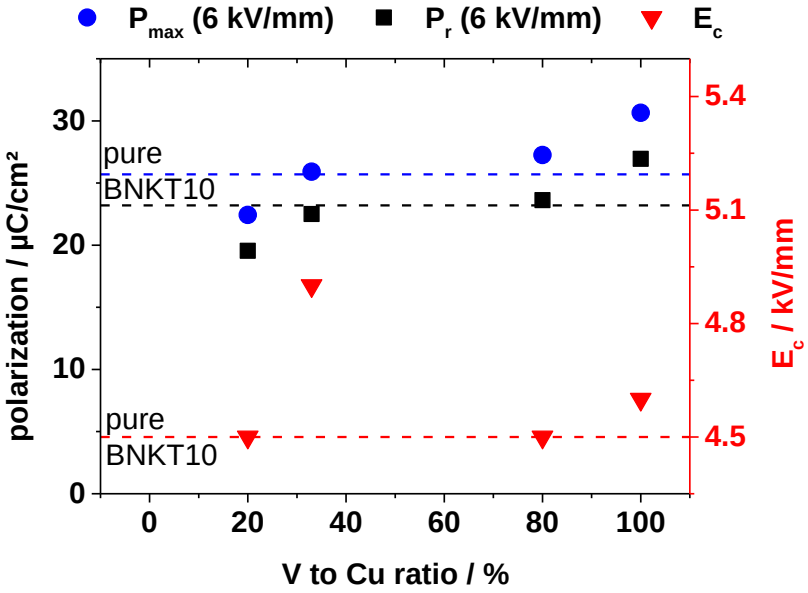
- T_{f-r} lowered with BKT content; d^*_{33} rises
- d^*_{33} generally higher due to co-doping

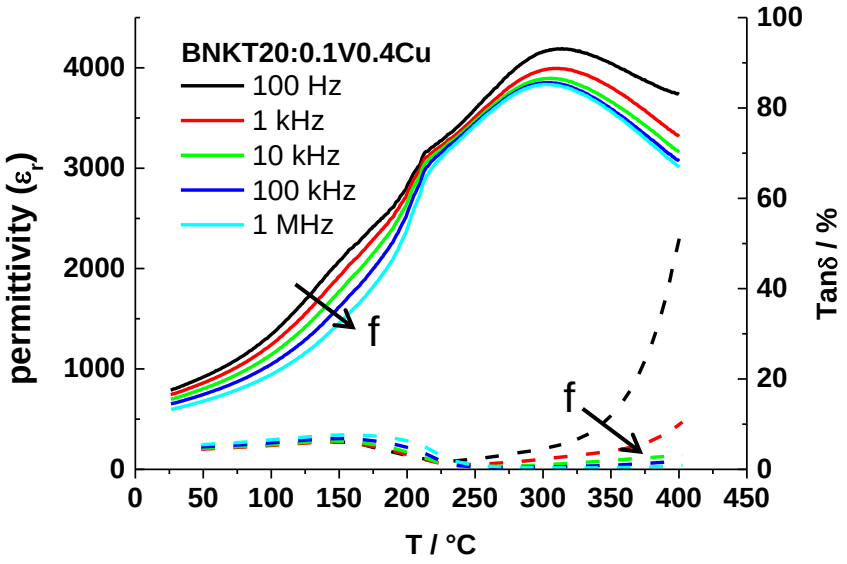
(Co)-doping BNKT10

Hall, D. A. *et al.*, Journal of Physics: Condensed Matter 10, 9129 (1998).



- **BNKT10 based samples → no bias field**
- **PZT or BT → bias field upon doping**





Resonance Measurements (Co-)doped BNKT10

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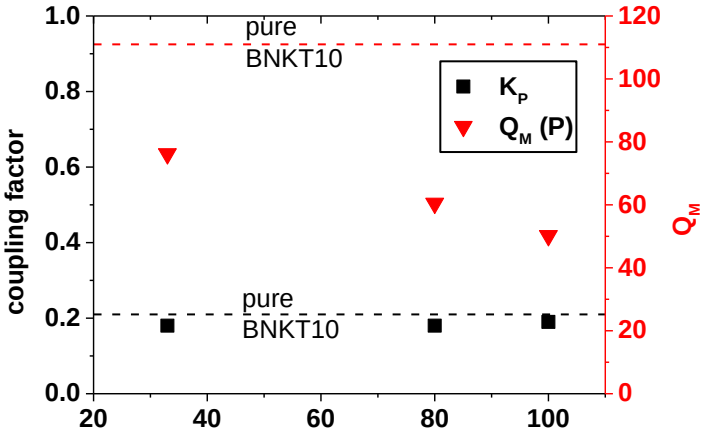
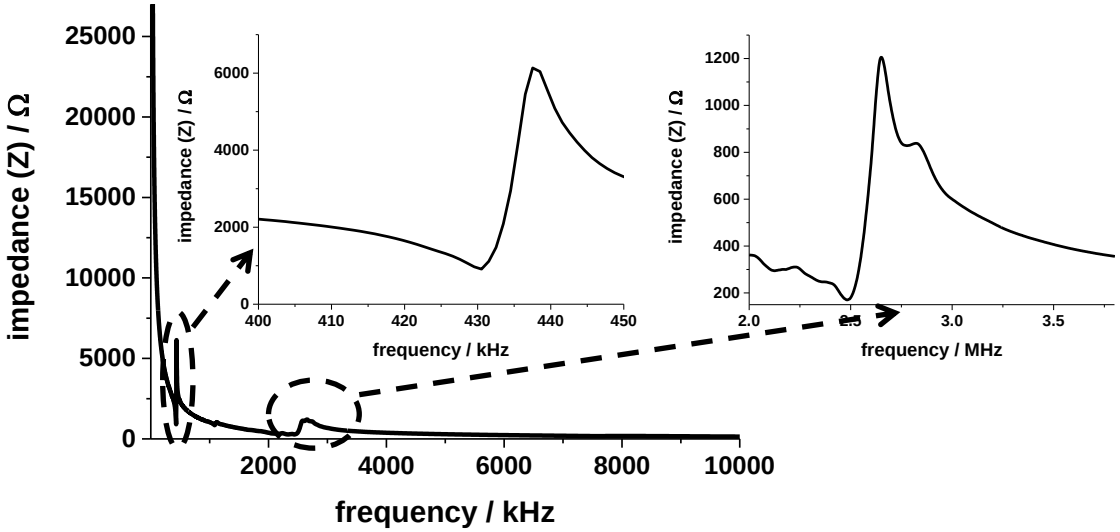
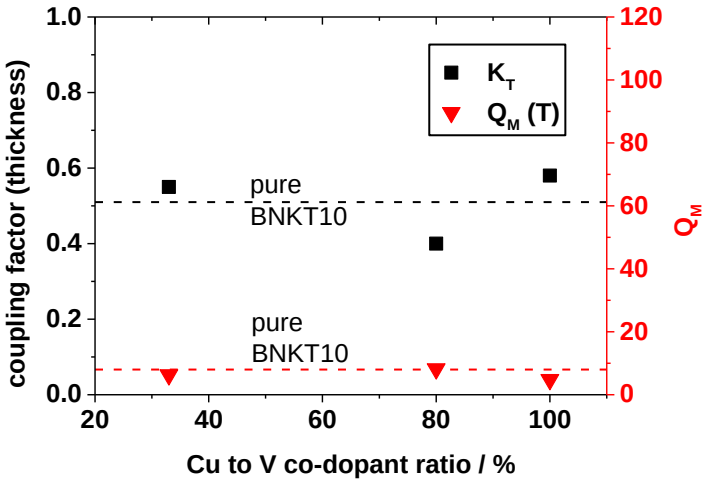
- $Q_{M\ (planar)}$ decreased by Cu
- High (up to 0.58) thickness mode coupling (Q_M around 5)

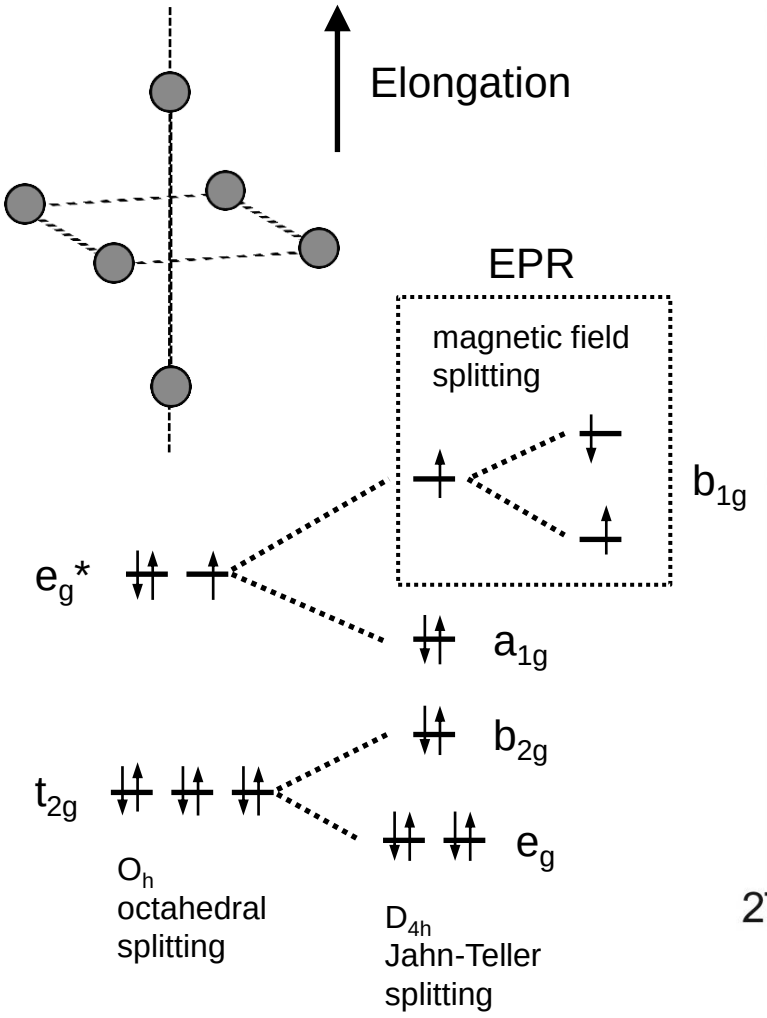


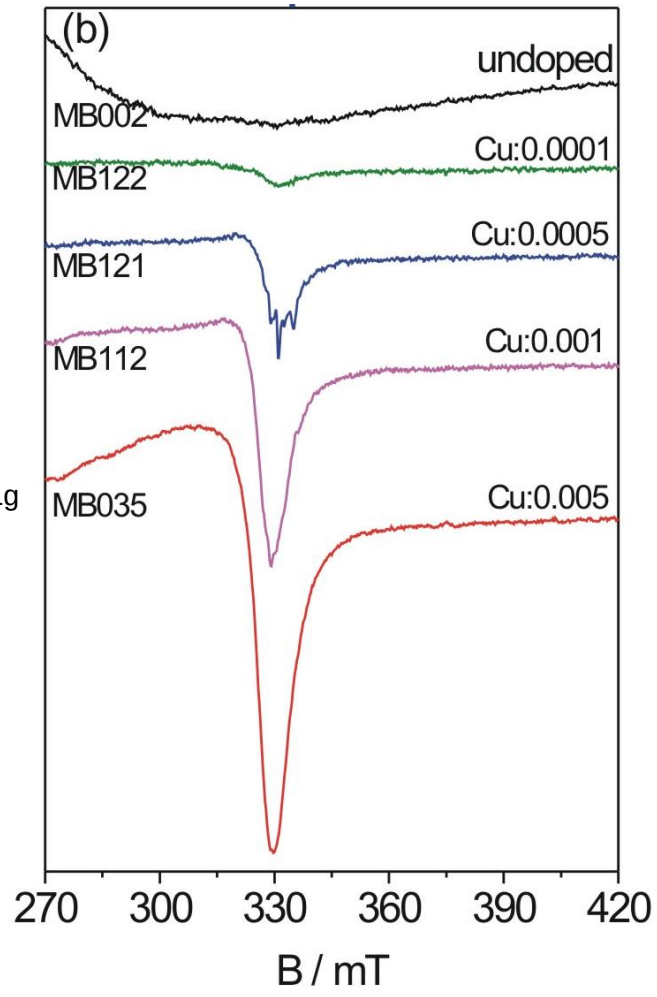
BNKT10:0.5Cu





Electron Paramagnetic Resonance (Co-)doped BNKT10





X-band EPR of Cu-doped BNKT10

- **Peak broadening**
- **Cu^{2+} at grain boundaries / above solubility limit**

Electron Paramagnetic Resonance (Co-)doped BNKT10

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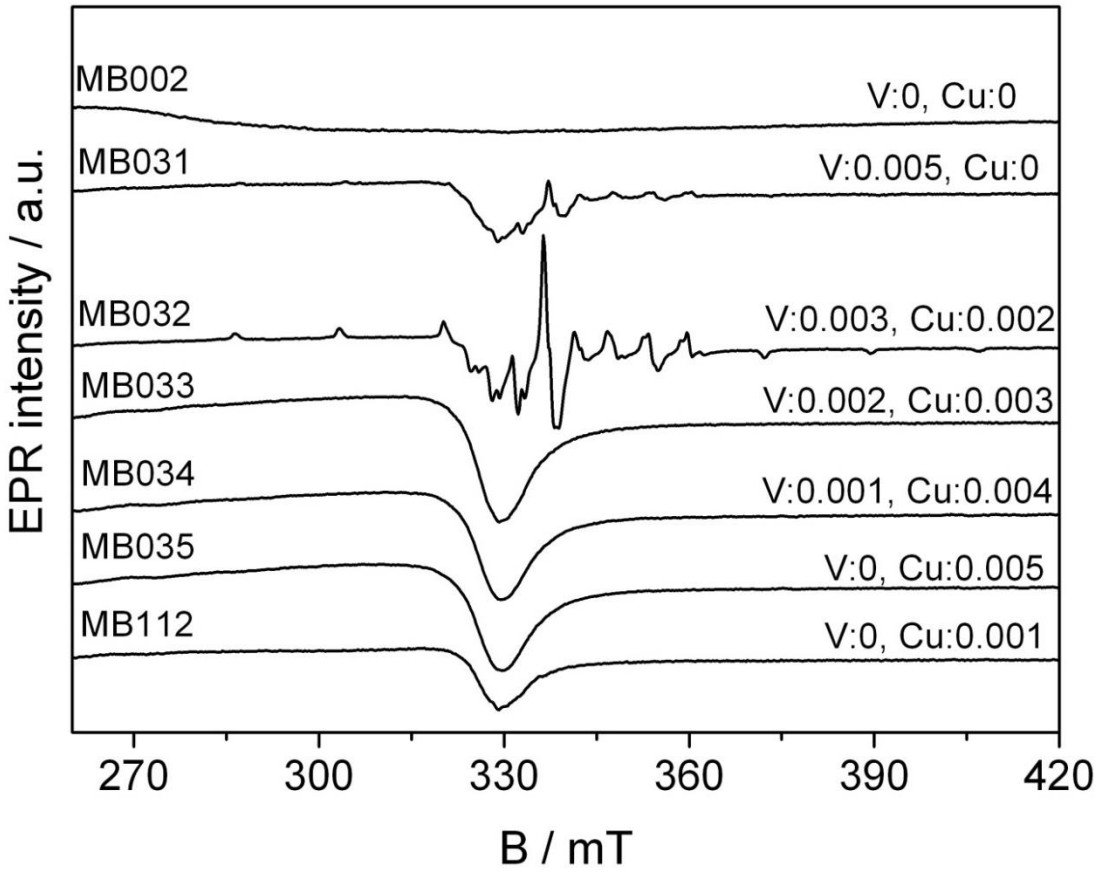
X-band EPR of sintered samples



$$CuO \overset{TiO_2}{\rightarrow} Cu''_{Ti} + V_{\ddot{O}}$$

$$\left(V_2O_5 \overset{TiO_2}{\rightarrow} 2V_{\dot{T}i} + V'''_{Bi} \;/\; V'_{Na,K} \right)$$

$$V_2O_5 \overset{TiO_2}{\rightarrow} 2V^{X}_{Ti} \;\; !$$

- **V incorporated as V^{4+}**
- **Cu-V-ratio influences V-oxidation state**

Summary / Conclusions

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- **Co-doping at rhombohedral site of MPB (BNKT10)**
  - **Butterfly-type strain curve, high K_T, P_r, P_{max}, E_c and T_{f-r}**
  - **Transducers, high power applications**
- **Co-doping at MPB (BNKT20) / excess doping**
  - **Polarization loop pinching, high S_{max}, low E_c, relatively low T_{f-r}**
  - **Actuator applications**
- **Vanadium state V^{5+}? / V^{4+}; Cu^{2+} at grain boundaries**

Thank you

for your attention!

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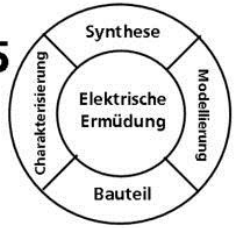
SFB 595



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