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A NEW TYPE OF POTASSIUM NIOBATE CRYSTAL: UTILIZING THE POTASSIUM SITES (PREPRINT)

Dean R. Evans

Hardened Materials Branch
Survivability and Sensor Materials Division

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MATERIALS AND MANUFACTURING DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

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*//Signature//

DEAN R. EVANS, Ph.D.
Agile Filters Project
Exploratory Development
Hardened Materials Branch

//Signature//

MARK S. FORTE, Acting Chief
Hardened Materials Branch
Survivability and Sensor Materials Division

//Signature//

TIM J. SCHUMACHER, Chief
Survivability and Sensor Materials Division

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D.R. Evans (AFRL/MLPJ)
J. Carns (General Dynamics Information Technology, Inc.)
M.A. Saleh (UES, Inc.)
G. Cook (Universal Technology Corporation)
S.A. Basun (A.F. loffe Physico-Technical Institute)
J.M. Seim and G.J. Mizell (VLOC)

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Hardened Materials Branch (AFRL/MLPJ)
Survivability and Sensor Materials Division
Materials and Manufacturing Directorate
Wright-Patterson Air Force Base, OH 45433-7750
Air Force Materiel Command, United States Air Force

General Dynamics Information Technology, Inc.
5100 Springfield Pike, Suite 509
Dayton, OH 45431

UES, Inc.
4401 Dayton-Xenia Road,
Dayton, OH 45432

Universal Technology Corporation
1270 North Fairfield Road
Dayton, OH 45432

A.F. loffe Physico-Technical Institute
St. Petersburg, Russia

VLOC
New Port Richey, FL

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Materials and Manufacturing Directorate
Wright-Patterson Air Force Base, OH 45433-7750
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14. ABSTRACT
• Darker regions (perturbed Fe – FeNb near a AgK) in the crystal exhibit strong contra-directional-TBC.
• There is a similar affect for interchanging NiNb for FeNb and RbK for AgK. AuK should work as well, but there's no evidence yet.
• The presence of Ag changes the local environment, perturbing the other impurities (i.e. Oh-), and the phonon/Raman modes are strongly affected.
Abstract concluded on reverse side

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14. ABSTRACT (concluded)

- Ag was then purposely used as a codopant $KNbO_3$:Fe, Ag and is responsible for:
  - An enhanced visible/OH- absorption
  - A stronger PV field
  - The strong affect on the Raman scatter
  - A possible increase in trap density (undetermined)
- Codoping with Ag is better than Rb in terms of speed, there's no significant difference in AOD.
- Singly doped Ag and unperturbed Fe are hole conducting, whereas perturbed Fe is electron conducting.

A New Type of Potassium Niobate Crystal; Utilizing the Potassium Sites

D. R. Evans J. L. Carns, M. A. Saleh, and G. Cook
Air Force Research Laboratory
Materials and Manufacturing Directorate
Wright-Patterson Air Force Base, OH

S. A. Basun
A. F. Ioffe Physico-Technical Institute
St. Petersburg, Russia

J. M. Seim and G. J. Mizell
VLOC
New Port Richey, FL

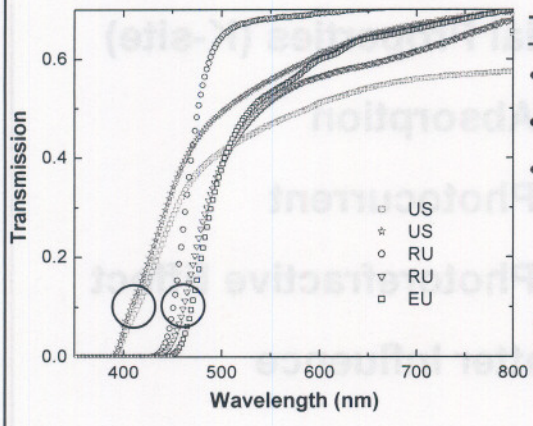
Outline

- Motivation/Background
- Modified Material Properties (K-site)
  - Enhanced Absorption
  - Enhanced Photocurrent
  - Enhanced Photorefractive Effect
  - Raman Scatter Influence
- Summary

Motivation

- Some $KNbO_3$ crystals, from different growers, have few regions that allow efficient counter-propagating TBC.
- What is the difference between spots that couple and those that don't?
- Can we control the growth process to give homogeneous materials (in terms of TBC)?

Large Shifts in Band Edges
(Dependent of Crystal Origin)



Three thoughts:

- Different composition (K/Nb)
- Different starting mat'ls
- Post growth issues

- Starting mat'ls are unknown
- Growth procedures unknown
- Poling procedures known for 2 of 3 growers

Motivation

- Small regions, particularly near the edges, exhibit strong counter-propagating TBC efficiencies.
- We hypothesized that the enhanced TBC was due to contamination from the post-growth poling process (electrodes).
- A series of codoped $KNbO_3$:Fe,Ag crystals were grown with different concentrations of Ag.

Crystals used in this study:

1000 ppm Fe; 1000 ppm Ag

1000 ppm Fe; 5000 ppm Ag

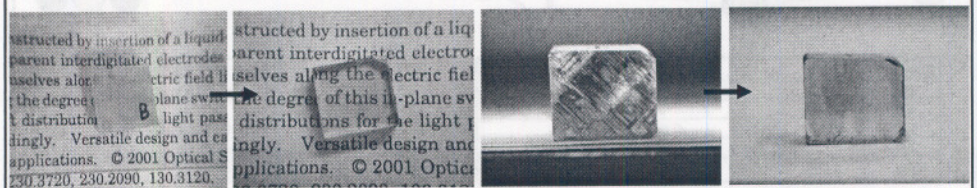
1000 ppm Fe; 10,000 ppm Ag

10,000 ppm Ag

Domain Poling

- Growth complicated by two solid phase changes:
  - -Material starts as cubic
  - -Becomes tetragonal at 435°C
  - -Orthorhombic below 225°C
- Internal stresses from phase changes create multiple domains and twins
- Poling is required to create a single domain crystal

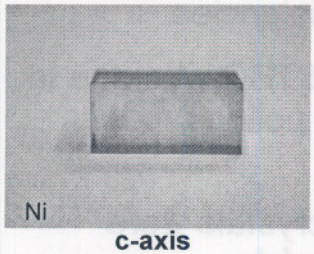
Without poling, multiple random domains, i.e. sign of the electro-optic coeff. changes throughout the crystal – no/weak coupling



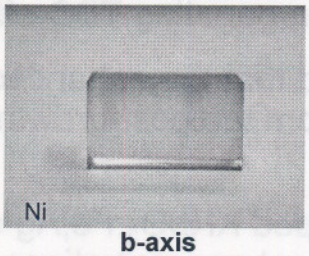
Before Poling | After Poling | Before Poling | After Poling

Unintentional/Intentional Codopants

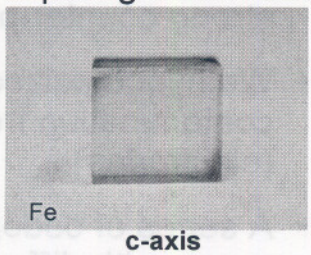
Assumed contamination from diffusion of poling electrodes



c-axis

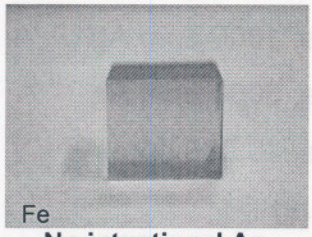


b-axis

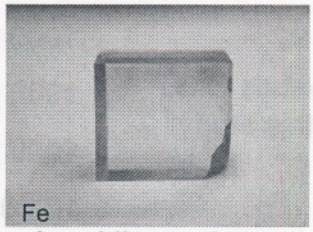


c-axis

Intentionally singly/doubly doped (in the melt) crystals

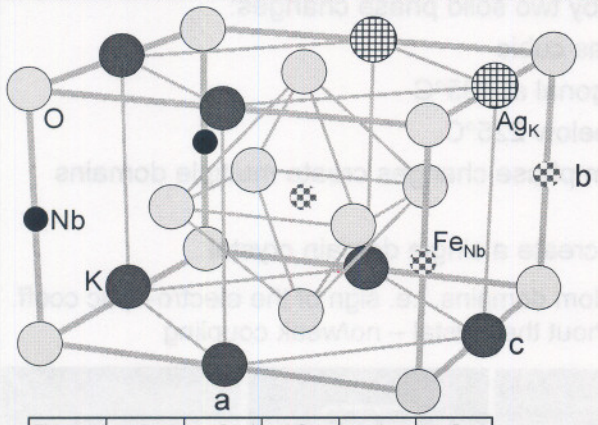


No intentional Ag

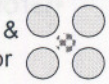


Ag adding to the melt

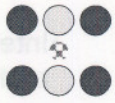
$KNbO_3$ Lattice Structure



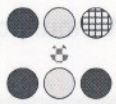
Fe with an O near & next near neighbor



Fe with a K next near neighbor



Fe with an Ag next near neighbor



Element	+1	+2	+3	+4	+5
K	1.33				
Nb				0.74	0.69
Fe		0.74	0.64		
Ni		0.69			
Ag	1.26	0.89			

Fe_{Nb} and Ni_{Nb} are interchangeable

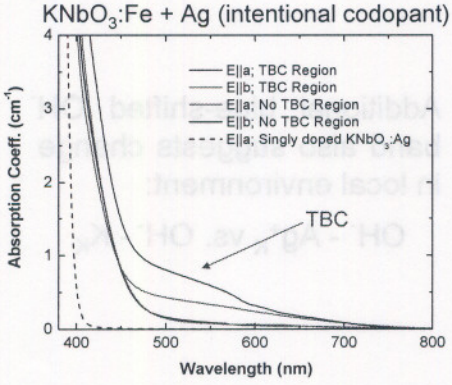
Ag_K and Rb_K are interchangeable

Schematic above does not reflect the distorted lattice

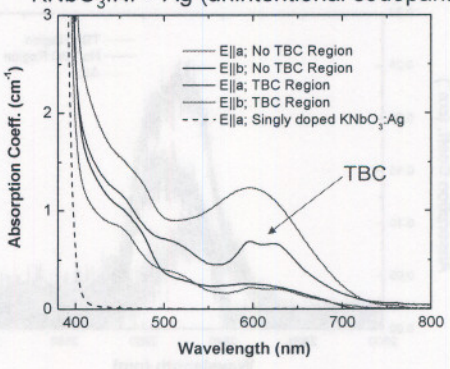
B. Zysset, et al., J. Opt. Soc. Am. B **9**, (1992) 380, and K. G. Deshmukh et al., J. Phys. D: Appl. Phys. **4**, (1971) 124.

Absorption Spectra
(Visible Region)

$KNbO_3$:Fe + Ag (intentional codopant)



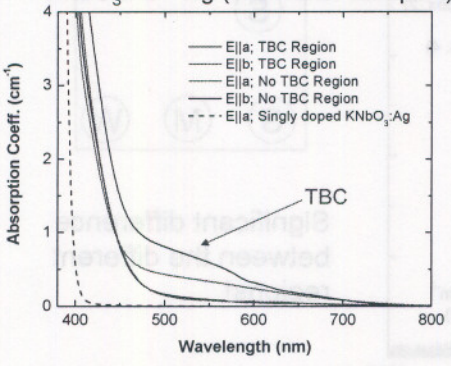
$KNbO_3$:Ni + Ag (unintentional codopant)



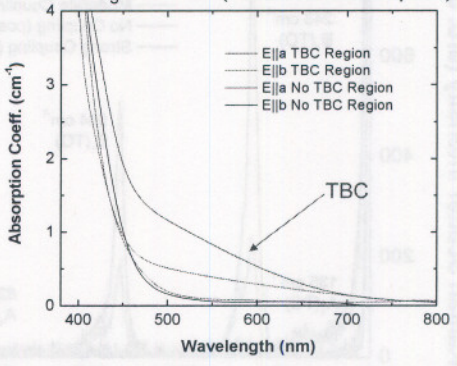
In our geometry: TBC requires light polarized in the ac-plane

Absorption Spectra
(Visible Region)

$KNbO_3$:Fe + Ag (intentional codopant)



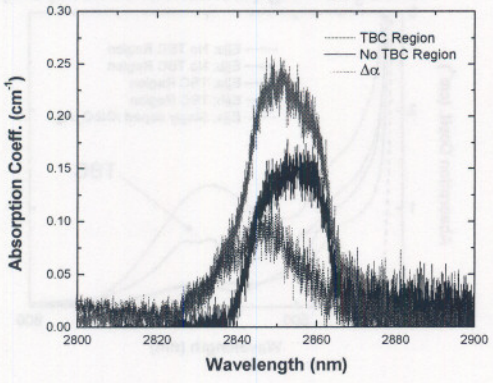
$KNbO_3$:Fe + Rb (intentional codopant)



In our geometry: TBC requires light polarized in the ac-plane

Absorption Spectra
(OH^- Feature)

$KNbO_3$:Fe,Ag

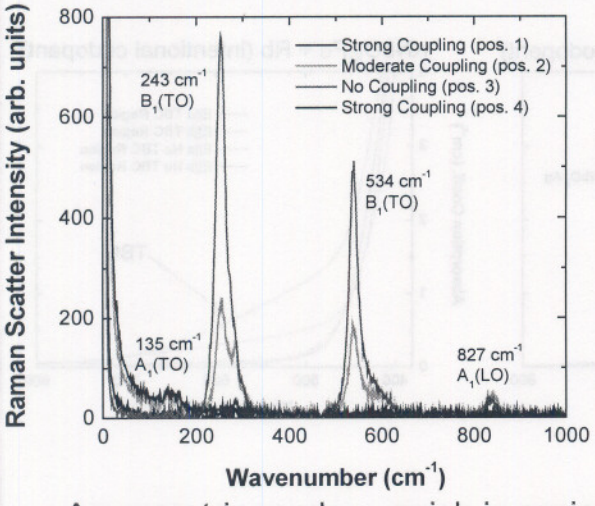


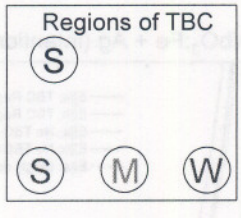
Additional blue-shifted OH^- band also suggests change in local environment:

$OH^- - Ag^+_K$ vs. $OH^- - K_K$

Light polarized in the ac-plane; E||a (TBC geometry)

Raman Scatter
(Asymmetric Modes)



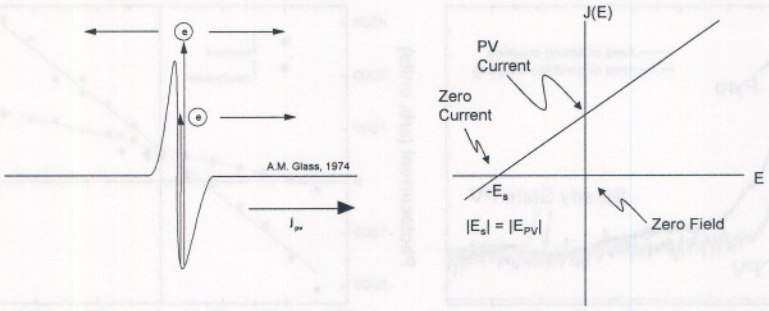


Significant difference between the different regions!

Asymmetric modes vanish in regions of strong coupling

[1]D. G. Bozinis and J. P. Hurrell, Phys. Rev. B **13,** 3109 (1976).

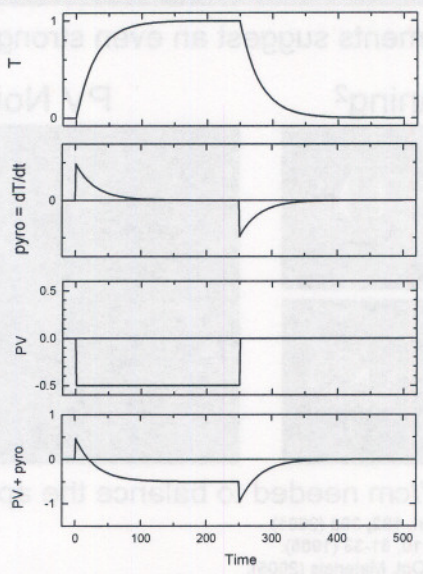
Photovoltaic Effect



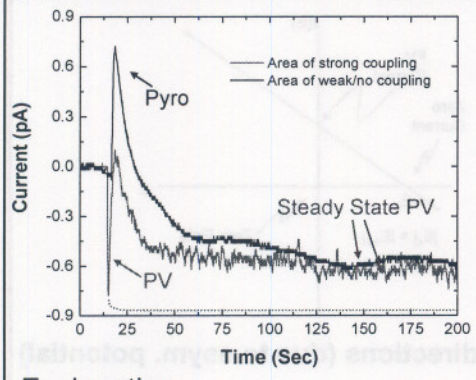
- PV field drives the electron in one directions (due to asym. potential)
- Applying an external E-field will oppose the current flow.
- At $-E_S$ the photocurrent will equal zero, the effects of the PV and ext. E-field cancel out.

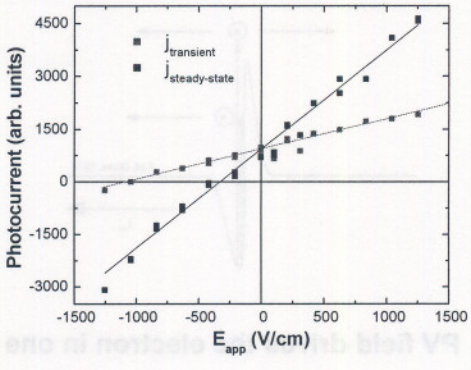
A. M. Glass, et al., Appl. Phys. Lett. **25,** 233 (1974).

Pyroelectric vs. Photovoltaic



Photovoltaic and Pryoelectric Current Measurements





Explanation –
Initially, the PV current is strong, but:

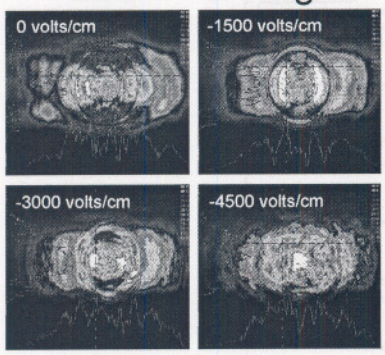
1) is inhibited by pyroelectric current in strong-TBC region ($Fe_{Nb} \rightarrow Ag_K$)

2) is decreased as the space-charge field forms (i.e. large intensity gradient between front and rear of crystal

Optical Photovoltaic Measurements[1]

Optical measurements suggest an even stronger PV field:

Beam Fanning[2]



PV Noise[3,4]

Estimate 15-20kV/cm needed to balance the apparent PV field

1. G. Cook, et al., Opt. Commun. **192,** 393 (2001).
2. S. Odoulov, et al., Opt. Lett. 10, 31-33 (1985).
3. D. R. Evans, et al., in press Opt. Materials (2005).
4. D. R. Evans, et al., IEEE J. Quantum. Elec. 38, 1661 (2002).

Trap Density
(Another Possibility)

- Theory[1] suggest PV fields (~20 kV/cm) alone, may not be enough to account for such large a photorefractive gain (TBC efficiency).
- The TBC efficiency (SCF) will also be strongly dependent on the trap density.
- An increase in trap density due to the incorporation of Ag would increase the space-charge field.

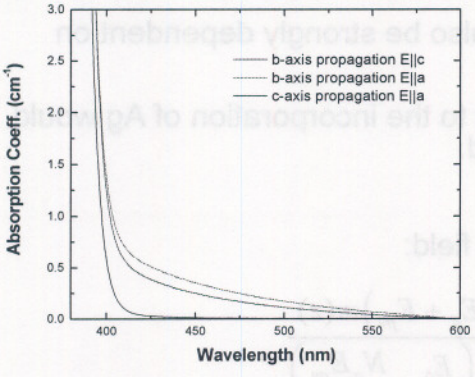
Steady-state the space-charge field:

$$E_{sc}(z) = \frac{-\left(E_0 + iE_d + E_{pv}\right)m(z)}{1 + \frac{E_d}{E_q} - i\left(\frac{E_0}{E_q} + \frac{N_a E_{pv}}{N_d E_q}\right)}$$

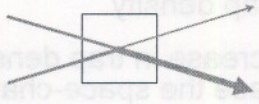
1. G. Cook, et al., Opt. Commun. **192,** 393 (2001).

Two-Beam Coupling Results

Co-directional TBC in $KNbO_3$:Ag



Co-propagate along b, k||c, E ⊥a

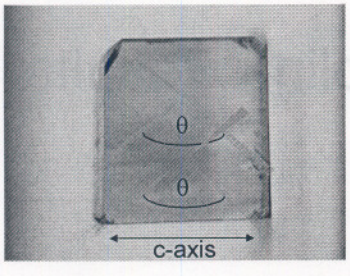


$\Delta OD = 0.08$

$I_{pump} = I_{signal}$

Hole Conductivity

$KNbO_3$:Fe
(Ag diffused in during poling)



Unperturbed Fe region –
Hole conductivity slow
Small gain

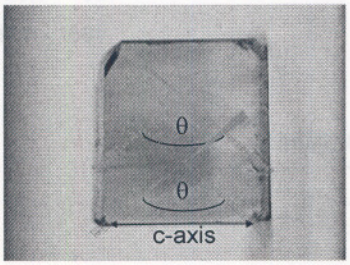
Perturbed Fe region –
Electron conductivity fast
Large gain

$\Delta OD_{Fe} = 0.15$

$\Delta OD_{Fe'} = 0.35$

i.e. Γ direction changes

$KNbO_3$:Fe
(Ag diffused in during poling)



Perturbed Fe region –
Electron conductivity fast
Large gain

Unperturbed Fe region –
Hole conductivity slow
Small gain

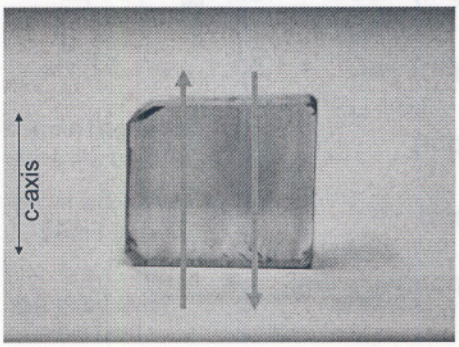
$\Delta OD_{Fe} = 0.15$

$\Delta OD_{Fe'} = 0.35$

i.e. Γ direction changes

$\theta = 20°$

$KNbO_3$:Fe
(Ag diffused in during poling)



Unperturbed Fe region –
hole conductivity

Perturbed Fe region –
electron conductivity

i.e. Γ direction changes
No bipolar transport

20° - 1.536 μm

180° - 121 nm

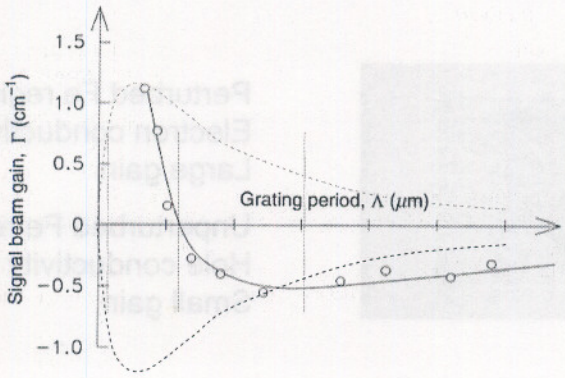
$\Delta OD_1 = 0.77$, $t_{1/e} = 28$ ms

$\Delta OD_2 = 1.5$, $t_{1/e} = 392$ μs

5 mW, f/20

Measurement for the "To-Do" List

Diffusion rates for holes and electrons are different.



20° - 1.536 μm

180° - 121 nm

Two-wave mixing gain as a function of grating period. Eg. anomalous $BaTiO_3$ the cross over point at $\Lambda = 0.6$ μm

*L. Solymar, D. J. Webb and A. Grunnet-Jepsen, *The Physics and Applications of Photorefractive Materials*, Oxford Series in Imaging Science, vol. 11, Clarendon Press, Oxford, 1996.

Performance of Doped $KNbO_3$

- $KNbO_3$:Fe,Ag (1000/10000 ppm) $\Delta OD = 1.52$; $t_{1/e} = 784$ μs
- $KNbO_3$:Fe,Rb (1000/10000 ppm) $\Delta OD = 1.53$; $t_{1/e} = 1.52$ ms
- $KNbO_3$:Fe,Au (1000/10000 ppm) X We don't know if Fe,Au will work
- $KNbO_3$:Ni,Ag (1000/10000 ppm) X We know Ni,Ag and Fe,Ag
- $KNbO_3$:Fe,Ag (1000/100000 ppm) X This one should have been the best ever

We should retry $KNbO_3$:Fe,Ag (1000/100000 ppm) and $KNbO_3$:Fe,Au (1000/10000 ppm)

Mysteries?

Doping $KNbO_3$ with:

Ag – hole conductivity

Fe – hole conductivity,
but…

Fe,Ag (perturbed Fe) – electron conductivity?

In $KNbO_3$:Ag – what is the acceptor?

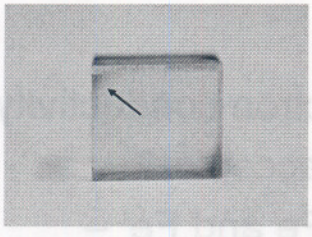
Same question for $KNbO_3$:Fe and Fe' –
is it Fe^{3+} of some other species?

Summary

- Darker regions (perturbed Fe – Fe_{Nb} near a Ag_K) in the crystal exhibit strong contra-dir.-TBC.
- There is a similar affect for interchanging Ni_{Nb} for Fe_{Nb} and Rb_K for Ag_K. Au_K should work as well, but there's no evidence yet.
- The presence of Ag changes the local environment, perturbing the other impurities (i.e. OH^-), and the phonon/Raman modes are strongly affected.
- Ag was then purposely used as a codopant $KNbO_3$:Fe,Ag and is responsible for:
  - a stronger space-charge field
  - an enhanced visible/OH^- absorption
  - a stronger PV field
  - the strong affect on the Raman scatter
  - a possible increase in trap density (undetermined)
- Codoping with Ag is better than Rb in terms of speed, there's no significant difference in ΔOD.
- Singly doped Ag and unperturbed Fe are hole conducting, whereas perturbed Fe and is electron conducting.

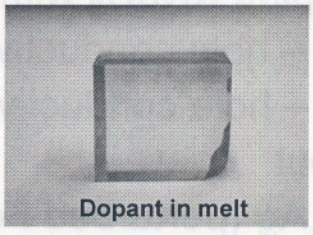
Ag Codoping Status
(Where We Are at the Moment)

Started with a small mystery region in several crystals

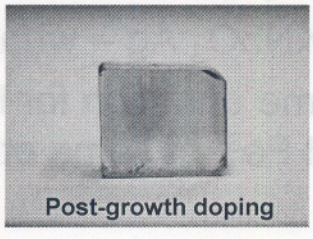


Assumed post-growth doping

Current status



Dopant in melt



Post-growth doping