Non-Contact Methods of Measuring Stresses in High Temperature Materials

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Everyone talks about the weather..

but nobody does anything about it

Mark Twain

(Samuel Clemens)

*Everyone talks about **stresses**…….*
but nobody does anything about them

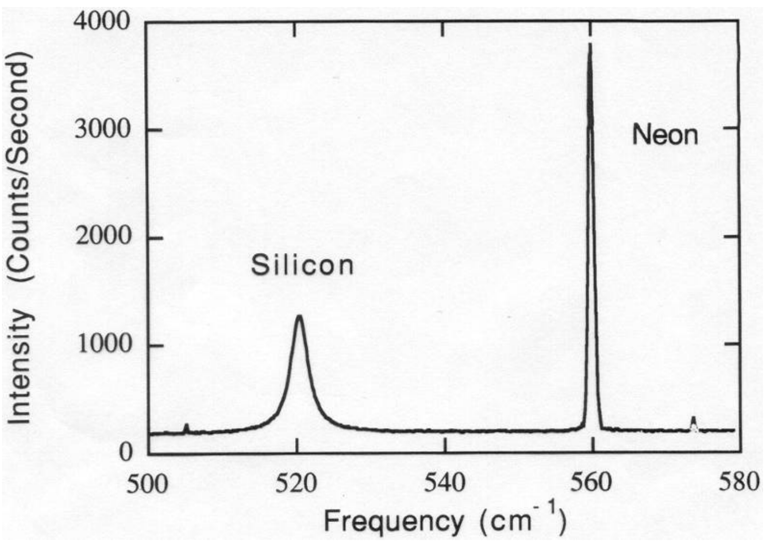
Outline

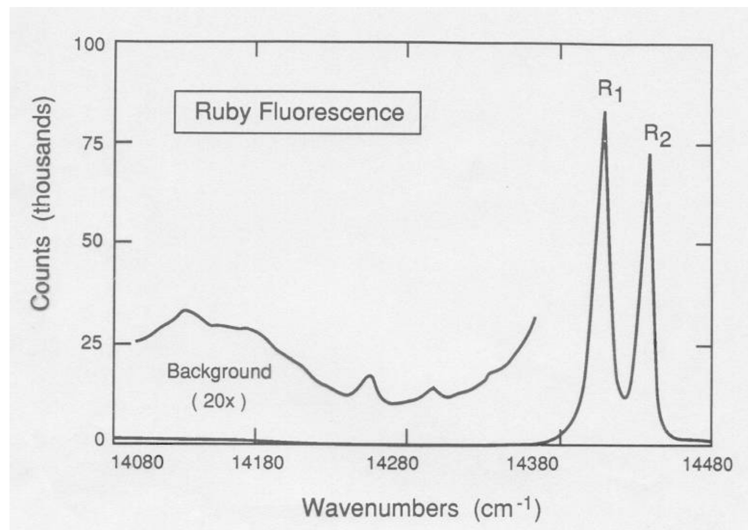
- Introduction to Cr^{3+} based luminescence and piezospectroscopy (luminescence and Raman).
- Phase transformations during the growth of alumina by thermal oxidation
- Latest developments on piezospectroscopy
- Modes of strain energy relief in oxide films and coatings
- Wrinkling, wrinkling kinetics leading to oxide film failure
- Buckling and buckle growth
- Conditions for spalling by the growth of buckles
- Large scale buckling
- Rumpling
- Monitoring damage evolution in TBCs by piezospectroscopy
- Summary

Principal Types of Piezospectroscopy

Vibrational piezospectroscopy –
Raman piezospectroscopy

Luminescence piezospectroscopy

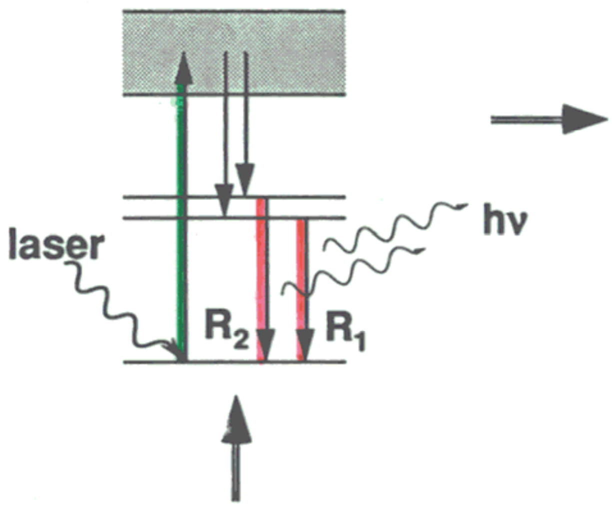


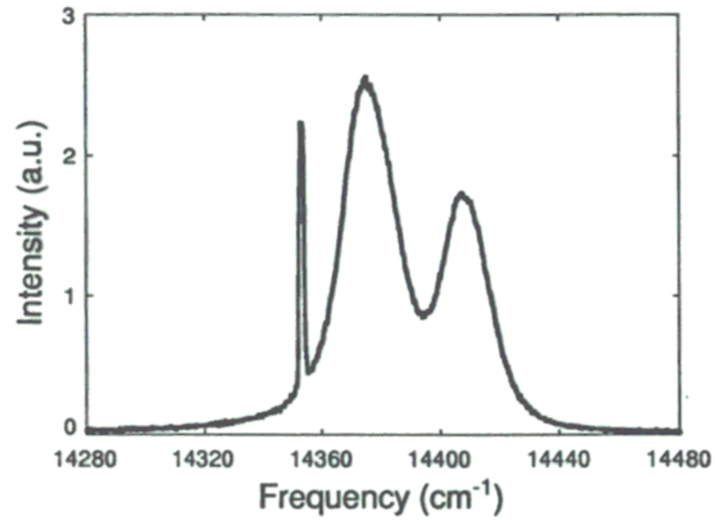


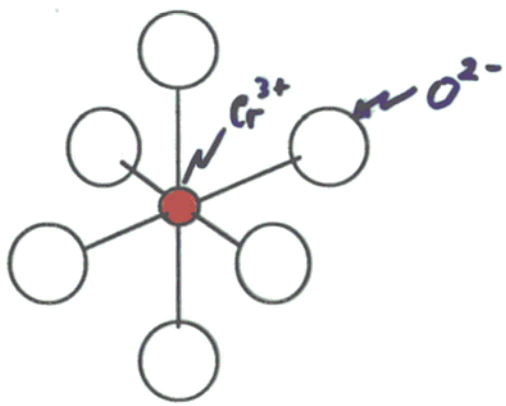
Single crystal silicon

Sapphire containing Cr dopant

Physical Basis of Luminescence Piezospectroscopy: Synopsis







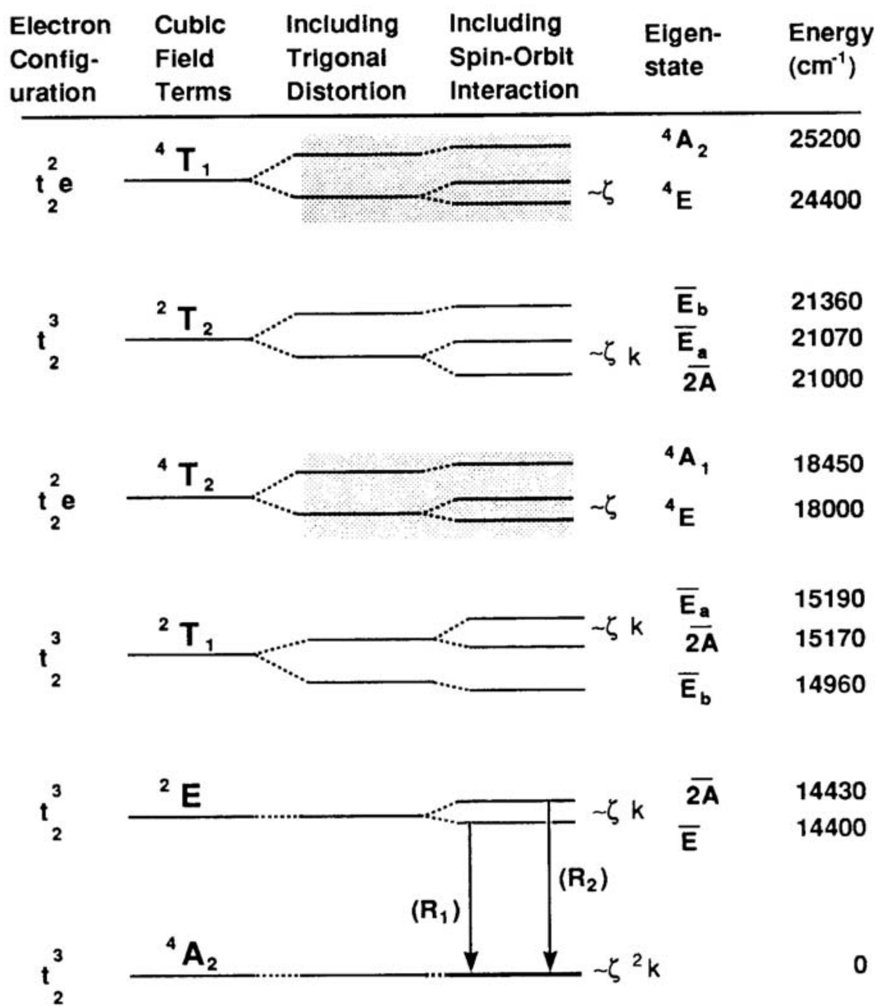
Octahedral coordination of Cr^{3+}

$$\Delta\nu = \Pi_{ij}\,\sigma_{ij}^{c} = \Pi_{ij}\,a_{ki}a_{lj}\sigma_{kl}$$

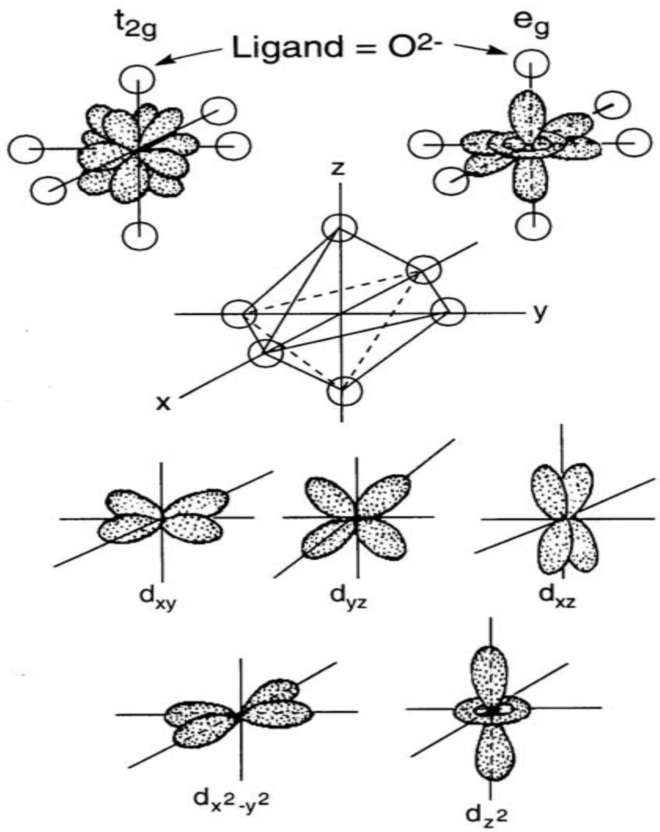
$$\Pi = \begin{bmatrix} \Pi_a & 0 & 0 \\ 0 & \Pi_m & 0 \\ 0 & 0 & \Pi_c \end{bmatrix}$$

Piezospectroscopy Relation

Electronic Transitions of *d* ^{3} Electrons

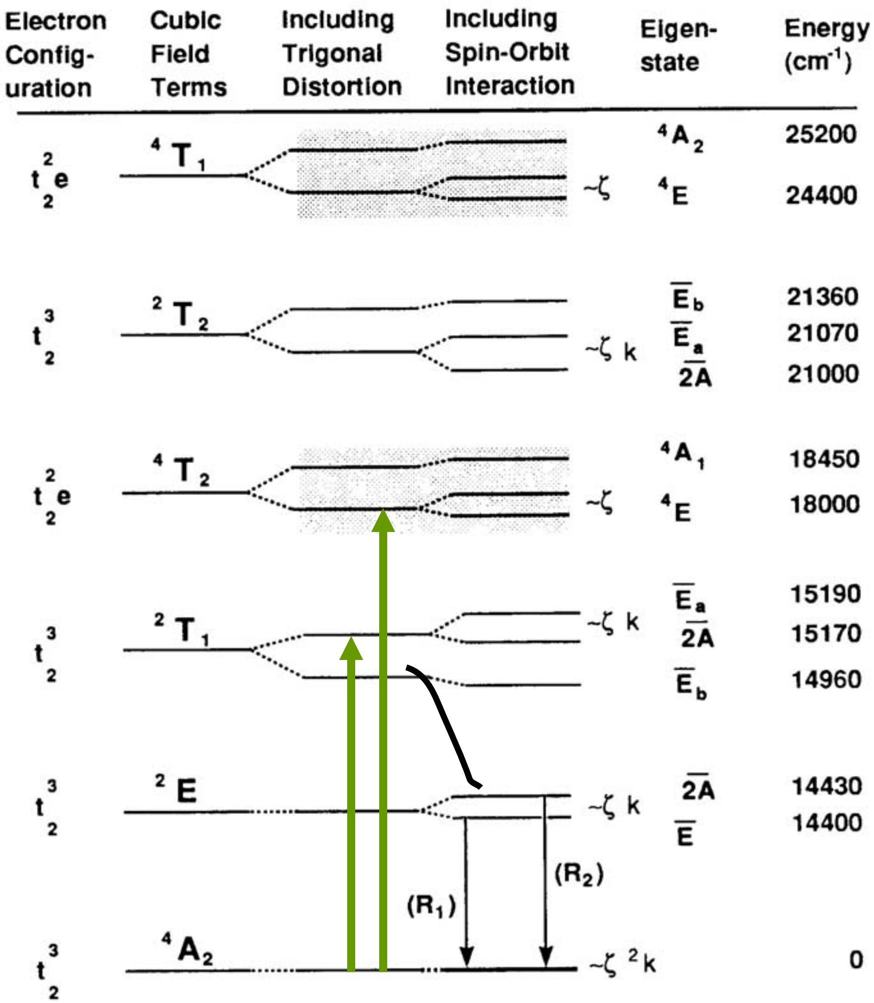


Ambient pressure transitions in the visible

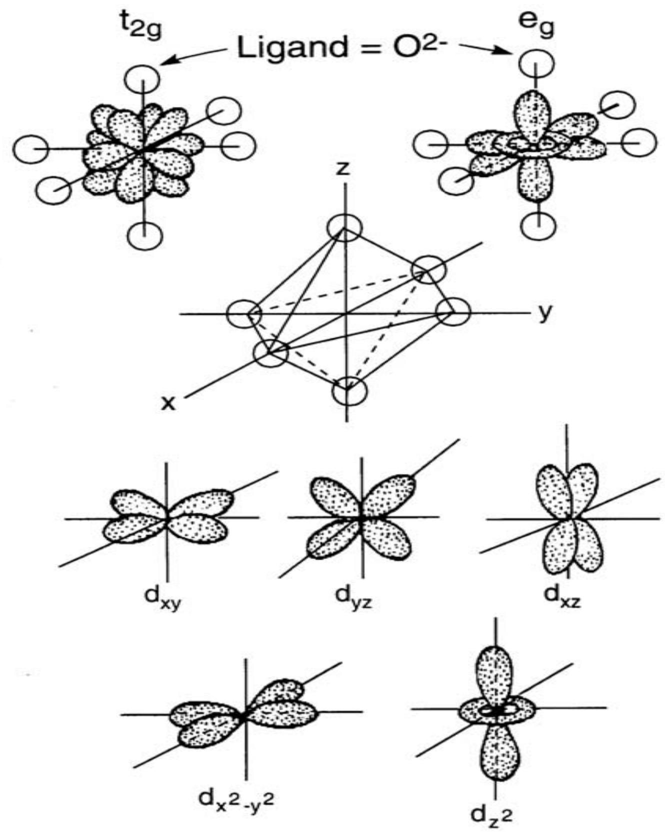


Strain alters ligand length and hence local potential on the electrons.

Electronic Transitions of *d* ³ Electrons



Ambient pressure transitions in the visible



Strain alters ligand length and hence local potential on the electrons.

Cr^{3+} Piezospectroscopy in Sapphire

In crystal coordinates, frequency shift, $\Delta\nu$, is related to stress:

$$\Delta\nu = \Pi_{ij}\,\sigma_{ij}^{c} + \Lambda_{ijkl}\,\sigma_{ij}^{c}\,\sigma_{kl}^{c}$$

where Π_{ij} are the piezo-spectroscopic coefficients.

Point symmetry of Cr^{3+} ion in sapphire imposes condition:

$$\Pi_{11} = \Pi_{22} = \Pi_{a} \quad : \quad \Pi_{33} = \Pi_{c}$$

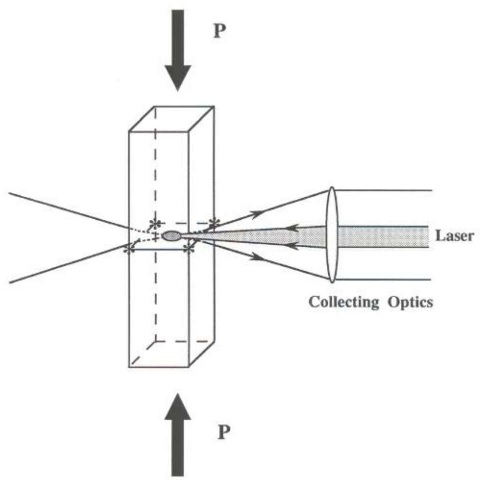
<u>R1 Line</u>:

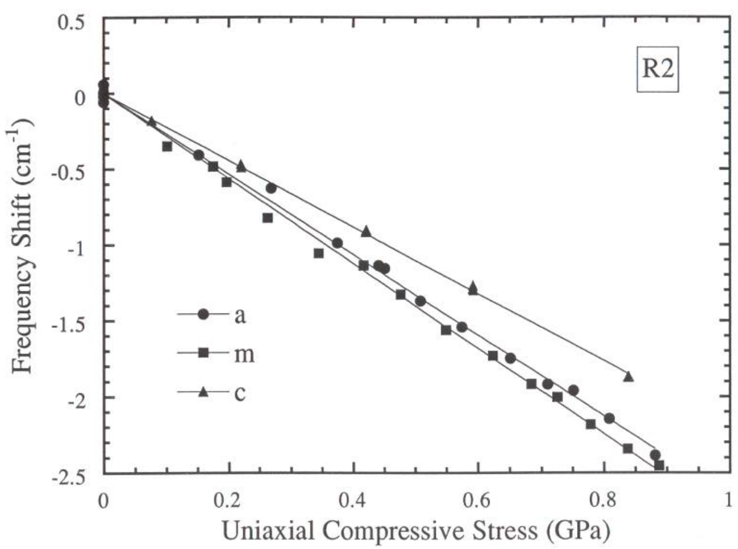
$$\Pi_{ij} = \begin{pmatrix} 2.56 & 0 & 0 \\ 0 & 3.50 & 0 \\ 0 & 0 & 1.53 \end{pmatrix} \quad cm^{-1}/GPa$$

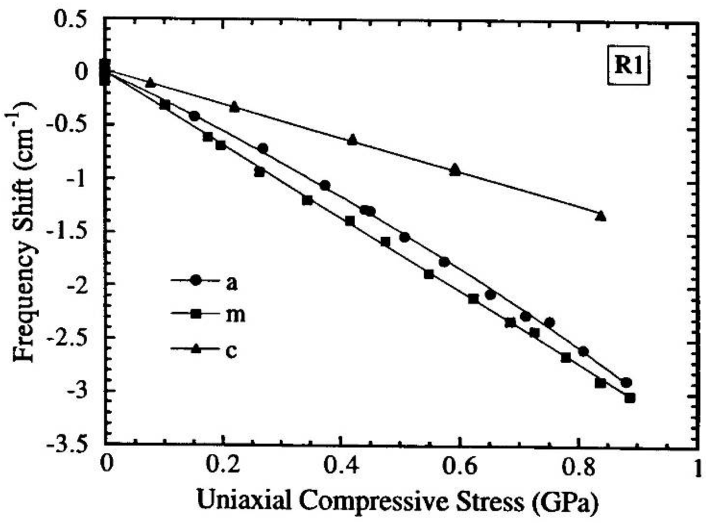
<u>R2 Line:</u>

$$\Pi_{ij} = \begin{pmatrix} 2.65 & 0 & 0 \\ 0 & 2.80 & 0 \\ 0 & 0 & 2.16 \end{pmatrix} \quad cm^{-1}/GPa$$

Calibration of piezo-spectroscopy coefficients







Piezospectroscopic Coefficients for R lines

	Π_{11}	Π_{22}	Π_{33} (cm^{-1}/GPa)	$\Pi_{11}+\Pi_{22}+\Pi_{33}$
R1	2.56 *	3.50	1.53	7.59
R2	2.65	2.80	2.16	7.61

* Parabolic fitting $\Lambda_{1111}=-0.8$ cm^{-1}/GPa^2

Analysis for General Orientation

- In Crystal Structure Coordinates, x'_i $\quad \Delta\nu = \pi_{ij}\ \sigma'_{ij}$
- Point Symmetry of Al_2O_3 (D_{3d}) $\quad \pi_{11} = \pi_{22} \neq \pi_{33}$

$$\pi_{ij} = O \quad \delta_{ij} \neq 1$$

- Deformation Frame Coodinates, x_i
- Transformation matrix a_{ij}, thus $\quad x_i = a_{ij}\ x'_j$
- Thus, stress in crystal structure coordinates

$$\sigma'_{ij} = a_{ik}\, a_{jl}\, \sigma_{kl}$$

- In general case

$$\Delta\nu = \pi_{11}(\sigma_{11} + \sigma_{22} + \sigma_{33}) + (\pi_{33} - \pi_{11})\,(a_{31}^2\,\sigma_{11} + a_{32}^2\,\sigma_{22} + a_{33}^2\,\sigma_{33}$$

$$+ 2\,(\pi_{33} - \pi_{11})\,(a_{31}\,a_{32}\,\sigma_{12} + a_{31}\,a_{33}\sigma_{13} + a_{32}\,a_{33}\,\sigma_{23})$$

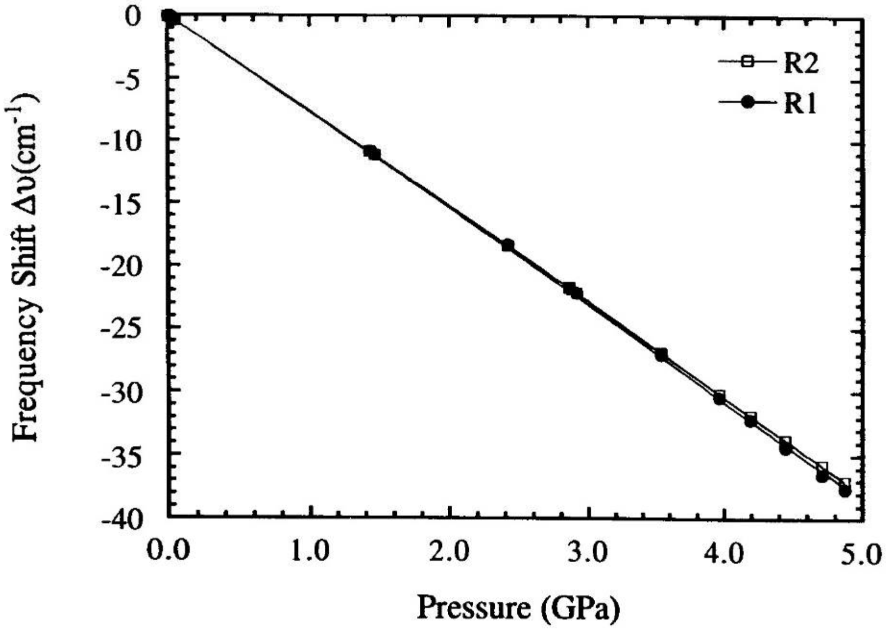
- Pure Hydrostatic stress

$$\Delta\nu = (2\pi_{11} + \pi_{33})\,P$$

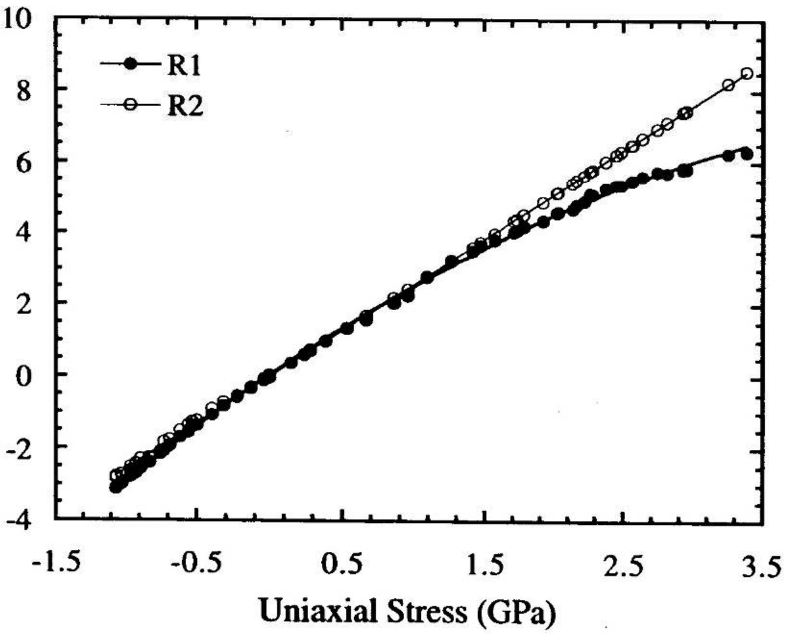
Calibration for polycrystalline, randomly oriented alumina

$$\sigma^*_{ij} = a_{ik} a_{jl} \sigma_{kl} \qquad \overline{\Delta\upsilon} = \iiint P(\theta, \phi, \psi) \Delta\upsilon \, d\theta \, d\phi \, d\psi$$

$$\overline{\Delta\upsilon} = \frac{1}{3}(\Pi_{11} + \Pi_{22} + \Pi_{33})(\sigma_{11} + \sigma_{22} + \sigma_{33})$$

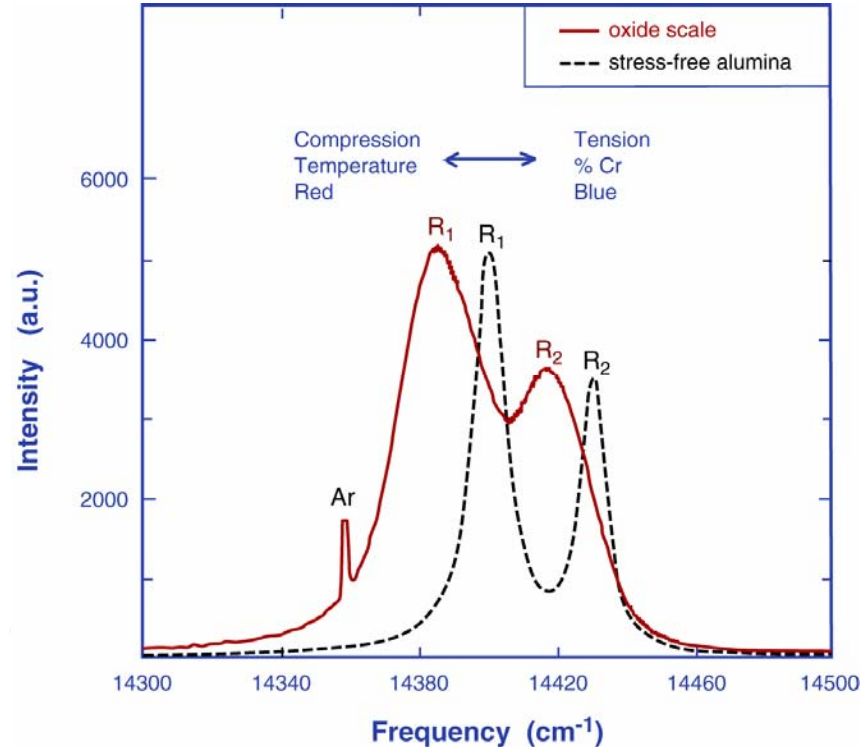


Hydrostatic stress



Uniaxial Compression to tension

Summary of Luminescence Shifts



Piezospectroscopic Shift:

$$\Delta\nu = \Pi_{ij}\,\sigma^{*}_{ij} + \Lambda_{ijkl}\,\sigma^{*}_{ij}\,\sigma^{*}_{kl}$$

(For polycrystalline alumina: $\Delta\nu = (\Pi_{11} + \Pi_{22} + \Pi_{33})\langle\sigma_{11} + \sigma_{22} + \sigma_{33}\rangle$)

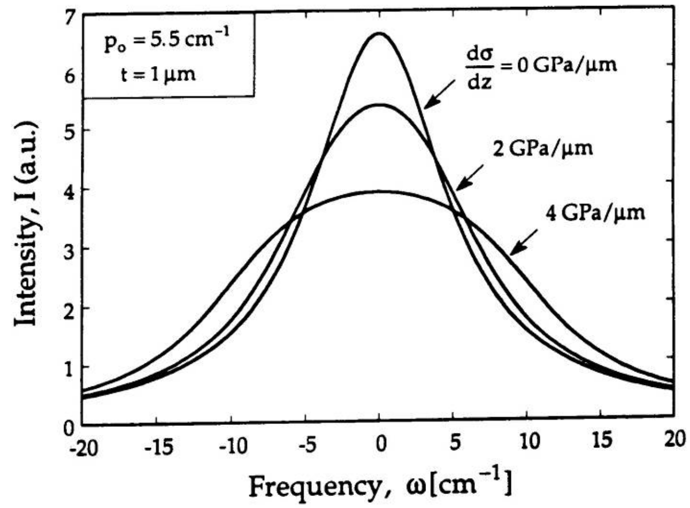
Temperature Shifts:

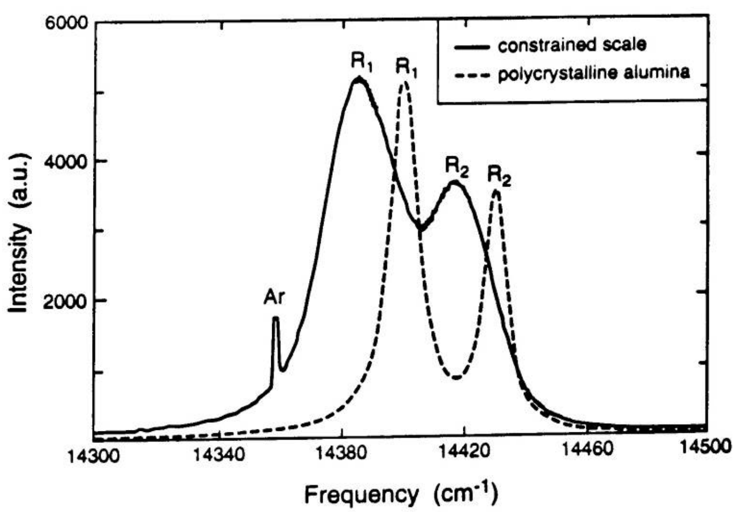
$$\nu(T) = \nu(T_o) + \alpha(T - T_o) \qquad \alpha_{R1} = -0.144 \qquad \alpha_{R2} = -0.134 \quad cm^{-1}/C$$

Concentration Shift:

$$\nu(\%Cr) = \nu_o + \ 0.99\, a/o\ Cr \qquad cm^{-1}$$

Effect of Stress Gradient



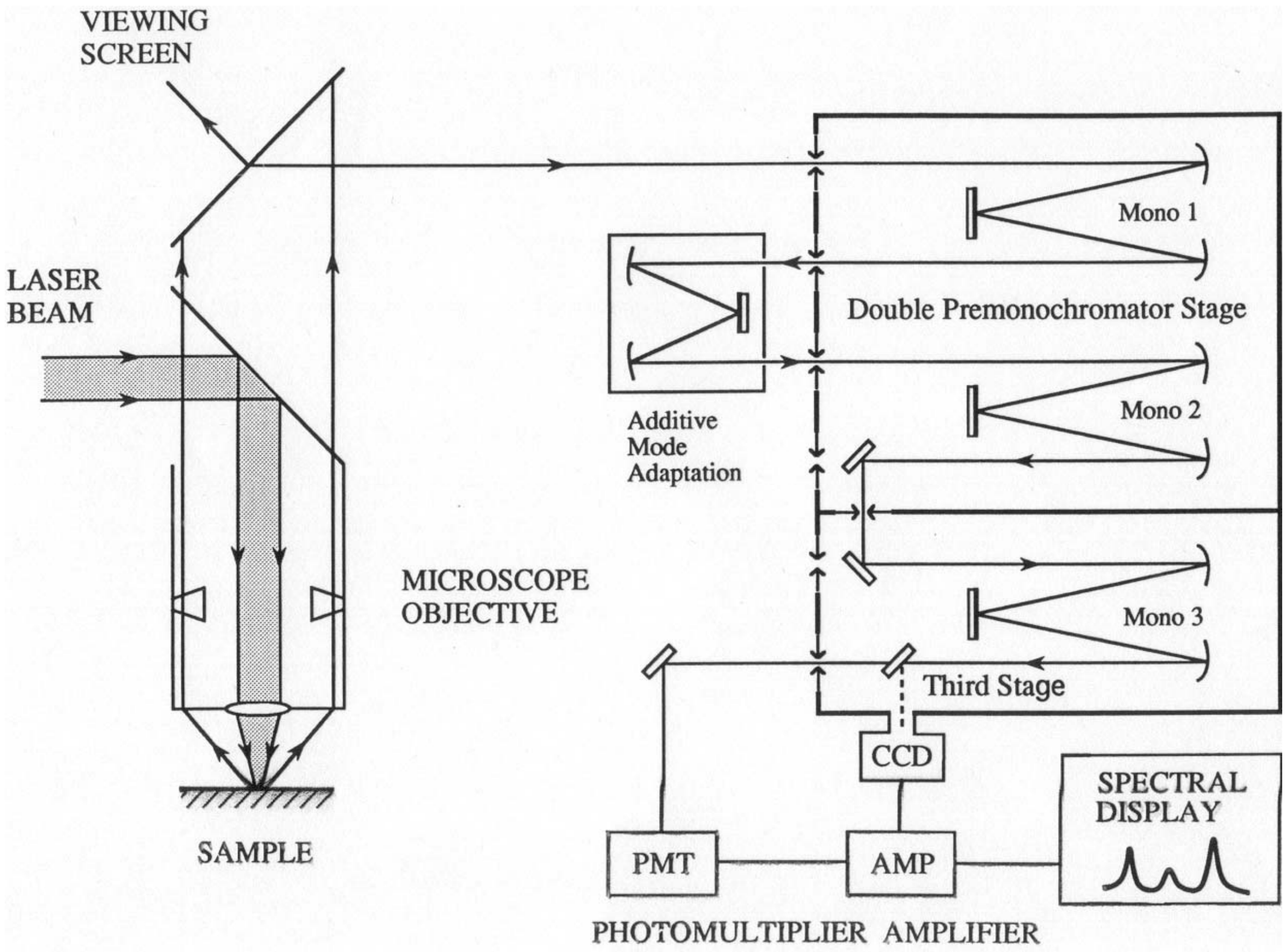


Stress gradient causes peak broadening

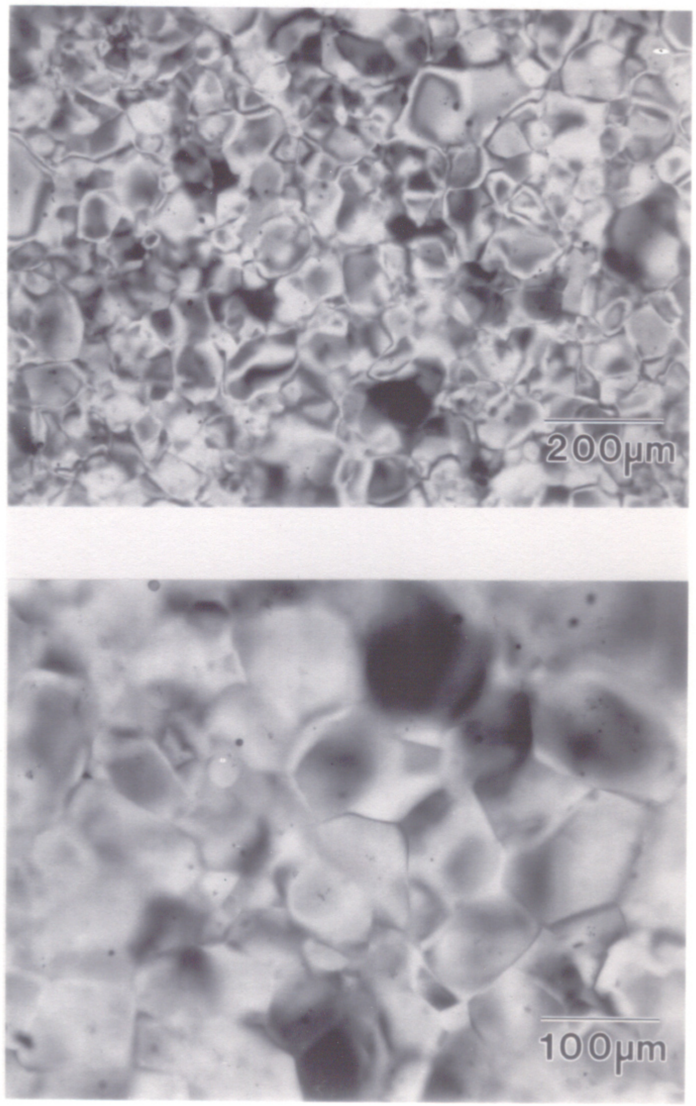
$$\frac{d\sigma}{dz} = \frac{3}{t\Pi_{ii}}\sqrt{\left(w^2 - w_o^2\right)}$$

Lipkin and Clarke, Oxidation of Metals (1995)

Optical Microprobe Configuration



Internal Stress Distribution in Polycrystalline Alumina

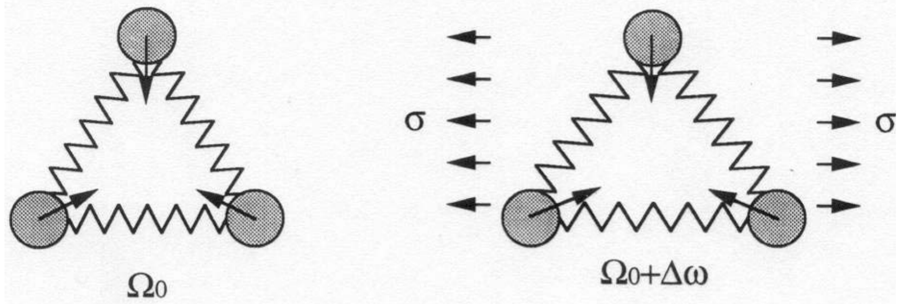


Observation in transmitted light through cross-polarizers of alumna.

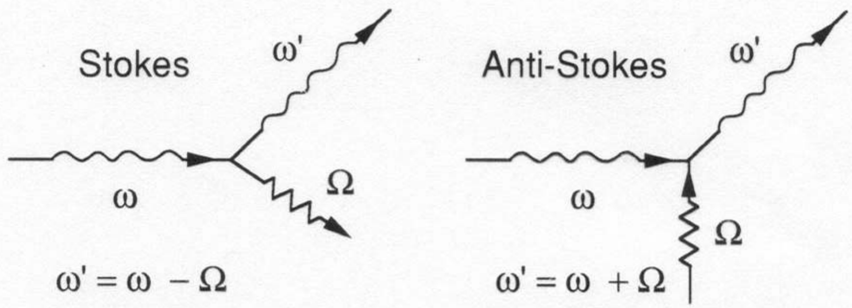
Variation in stress made visible through the piezo-optical effect.

Raman Piezospectroscopy

Raman Piezospectroscopy



Normal Vibration Modes

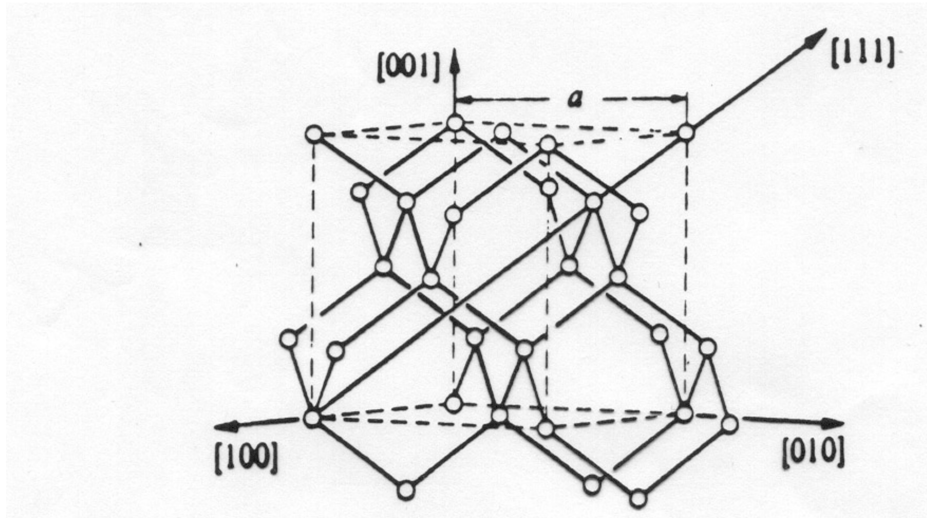


Raman Process

Intensity Ratio

$$\frac{I_{AS}}{I_S} = \left(\frac{\omega+\Omega}{\omega-\Omega}\right)^3 \frac{(\Sigma/\alpha)_{AS}}{(\Sigma/\alpha)_S} \exp\left(-\frac{\hbar\Omega}{k_B T}\right)$$

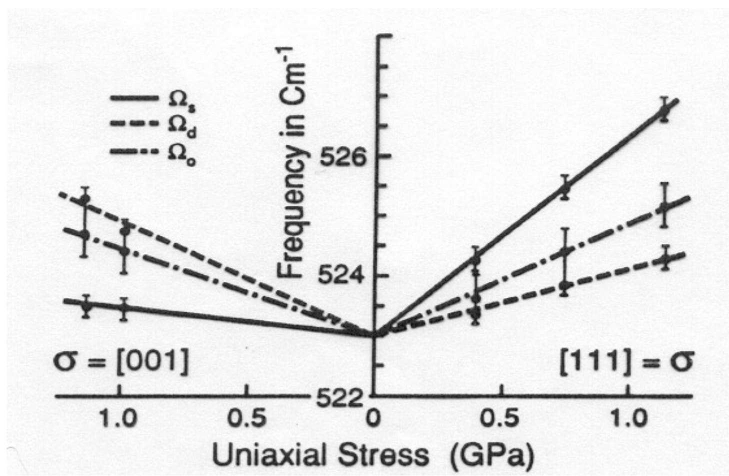
Raman Piezospectroscopy of Silicon



Active vibrational modes

Transverse Optical --- TO1 along [100], TO2 along [010]

Longitudinal Optical – LO along [001]



Raman Piezospectroscopy

1. Strain-free c-Si Polarizability tensor

$$\underset{\text{TO}_1}{\mathbf{R}_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}} \qquad \underset{\text{TO}_2}{\mathbf{R}_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}} \qquad \underset{\text{LO}}{\mathbf{R}_3 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}}$$

Scattering efficiency

$$S = A\sum_j |\mathbf{e}_j \cdot \mathbf{R}_j \cdot \mathbf{e}_s|^2$$

Raman line frequency $\nu_0 = 520$ Rcm^{-1}

2. In the presence of a strain ε_{ij}

$$\begin{vmatrix} p\varepsilon_{XX} + q(\varepsilon_{YY} + \varepsilon_{ZZ}) - \lambda & 2r\varepsilon_{XY} & 2r\varepsilon_{XZ} \\ 2r\varepsilon_{XY} & p\varepsilon_{YY} + q(\varepsilon_{XX} + \varepsilon_{ZZ}) - \lambda & 2r\varepsilon_{YZ} \\ 2r\varepsilon_{ZX} & 2r\varepsilon_{ZY} & p\varepsilon_{ZZ} + q(\varepsilon_{XX} + \varepsilon_{YY}) - \lambda \end{vmatrix} = 0$$

Eigenvalues $\lambda_{ij} = \nu_i^2 - \nu_0^2$, i= 1,2,3

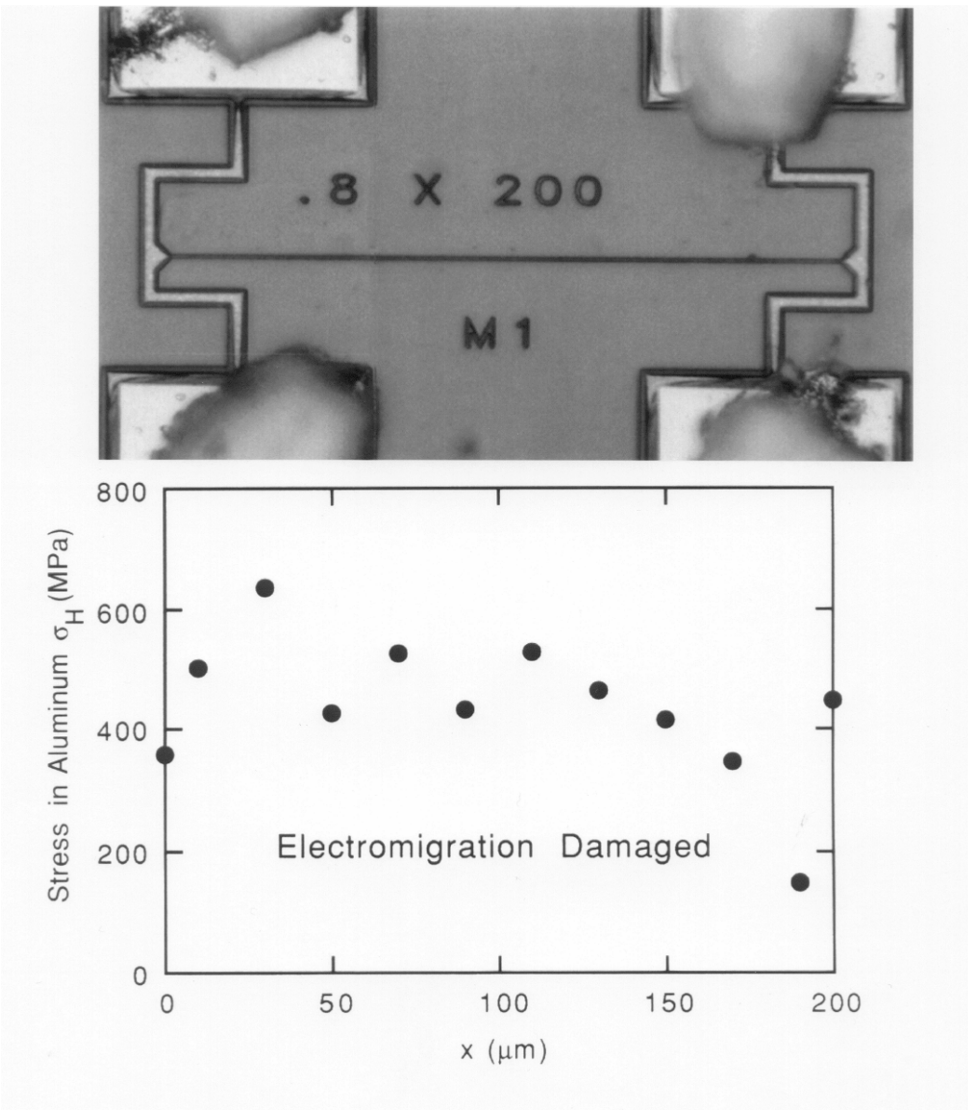
Frequency shift

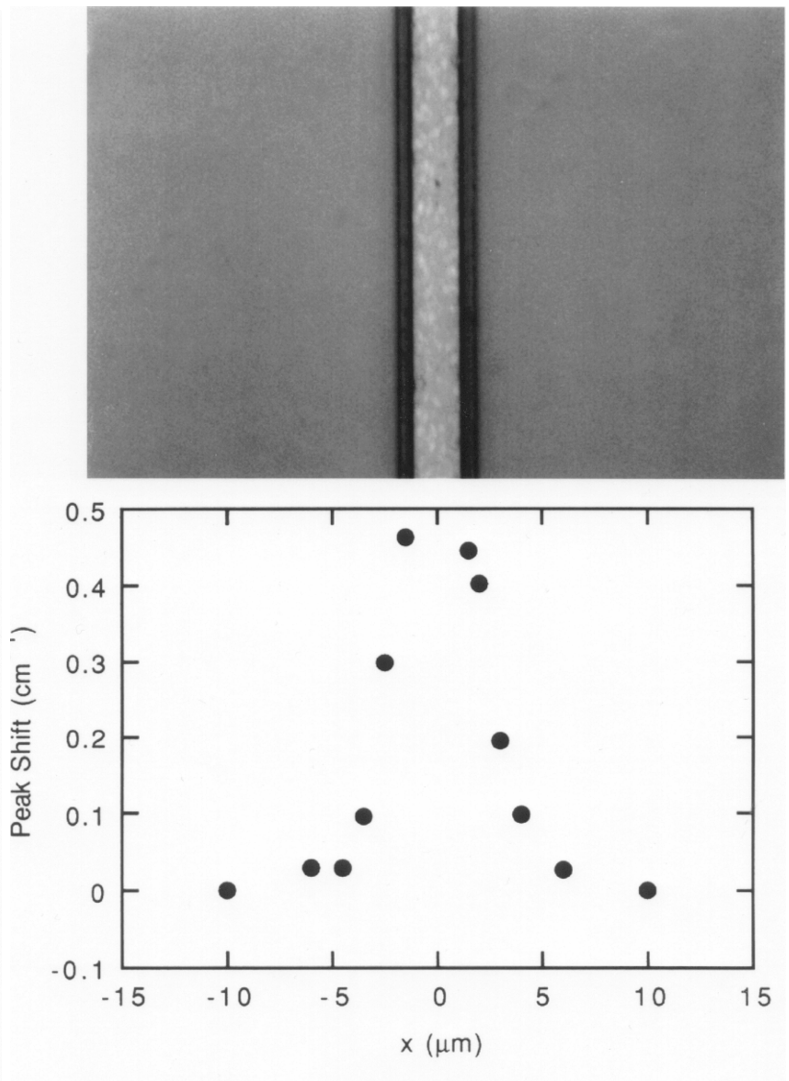
$$\Delta\nu_i = \nu_i - \nu_0 \cong \lambda_i/2\nu_0$$

Deformation Potentials (Anastassakis, 1985)

$$p = -1.43\nu_0^2, \quad q = -1.89\nu_0^2, \quad r = -0.59\nu_0^2$$

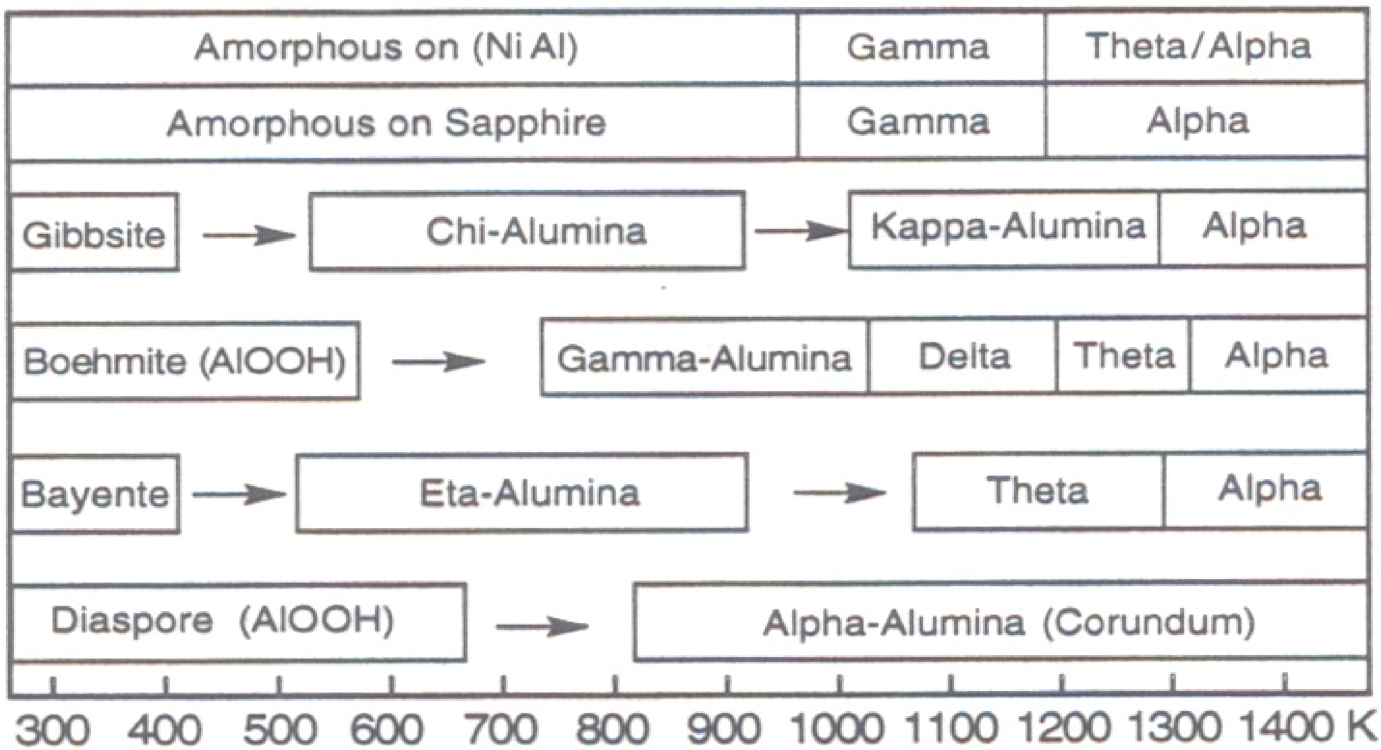
Raman Piezospectroscopy In Electromigration



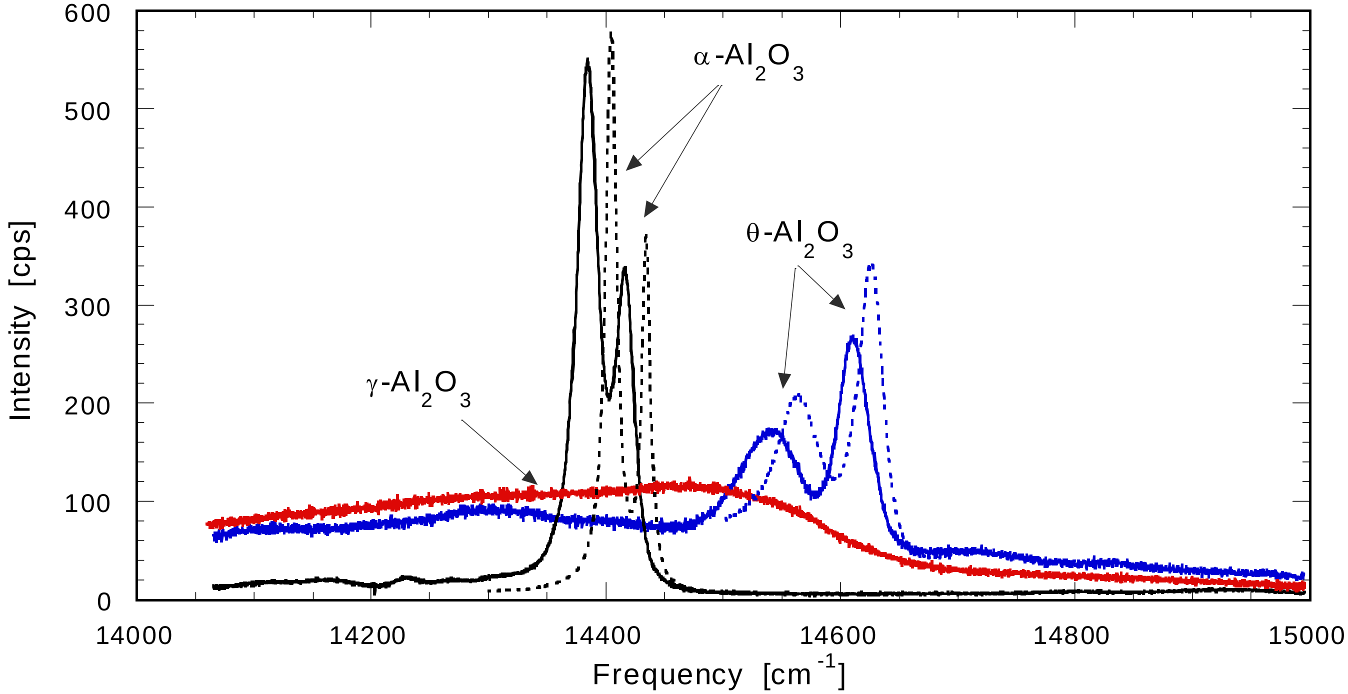


Phase Transformations in Alumina During High Temperature Oxidation

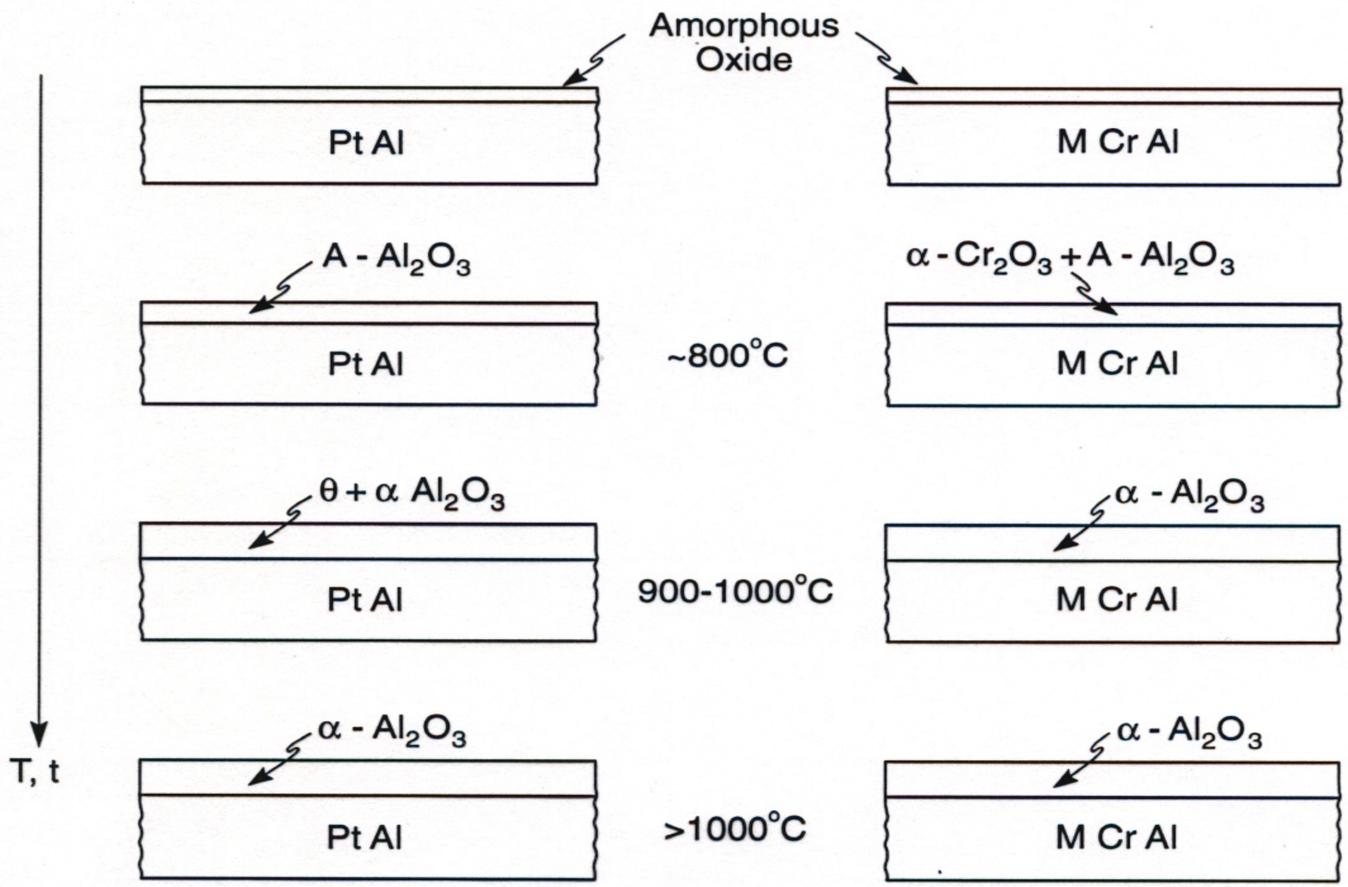
Reported Phase Transformations in Alumina Ceramics, Powders and Films



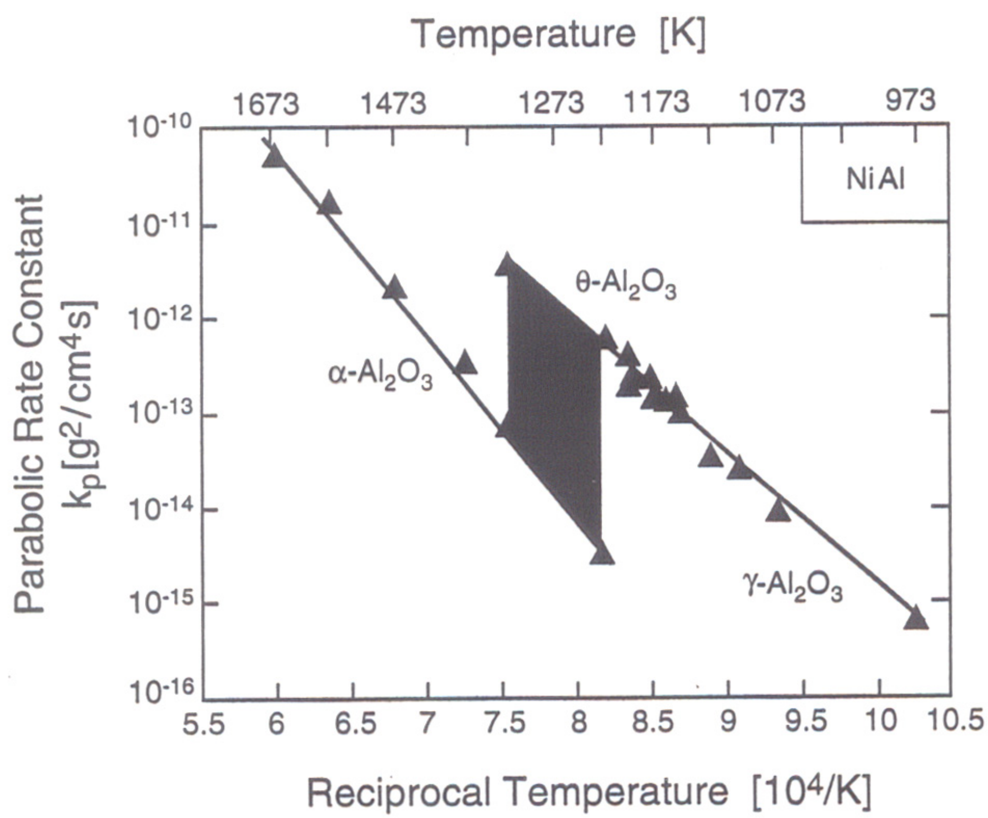
Luminescence Identification of Alumina Phases



Oxidation Induced Transformation Sequence on MCrAl vs NiPtAl



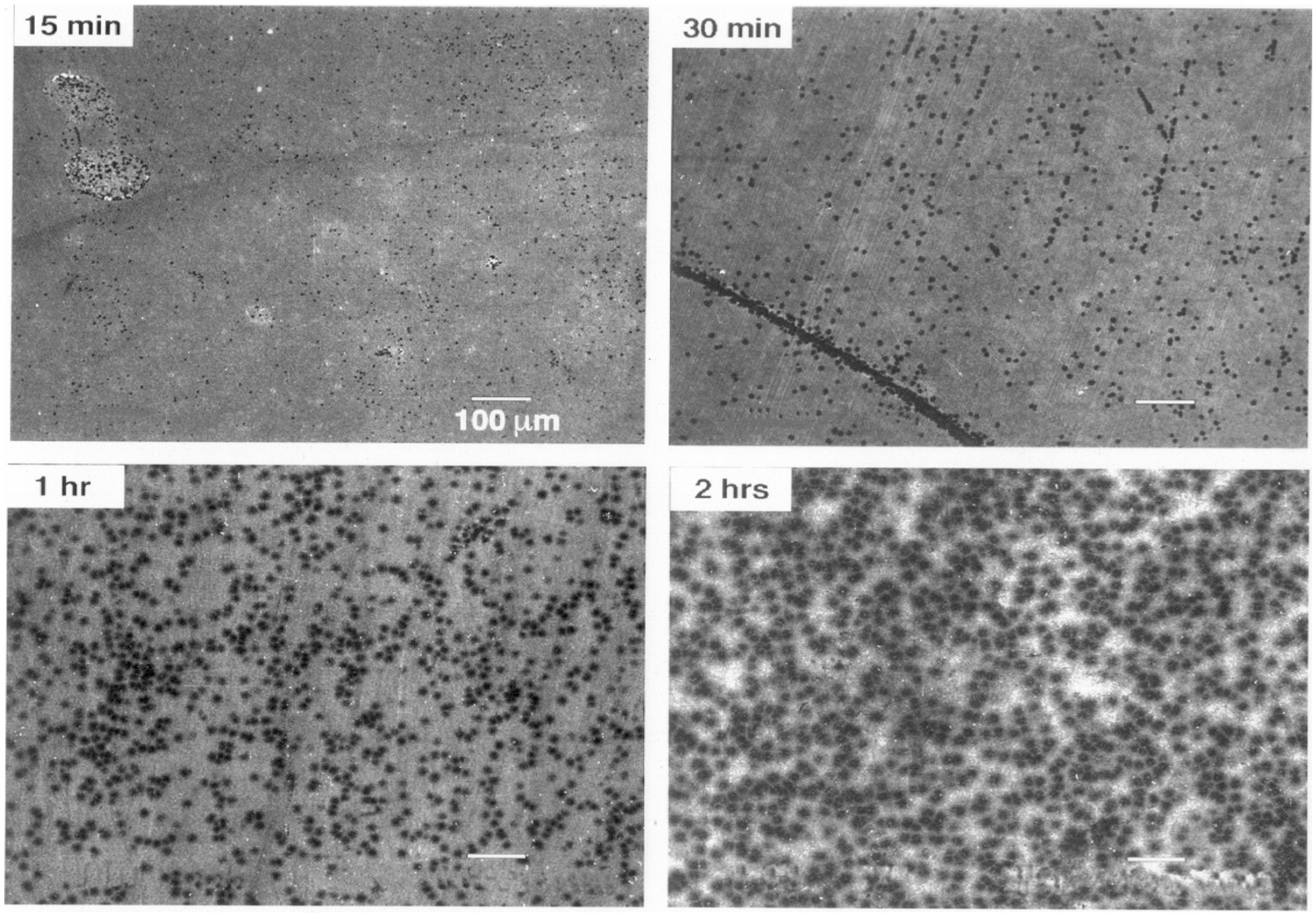
Alumina Transformation Kinetics on NiAl



Phase identification by X-ray diffraction

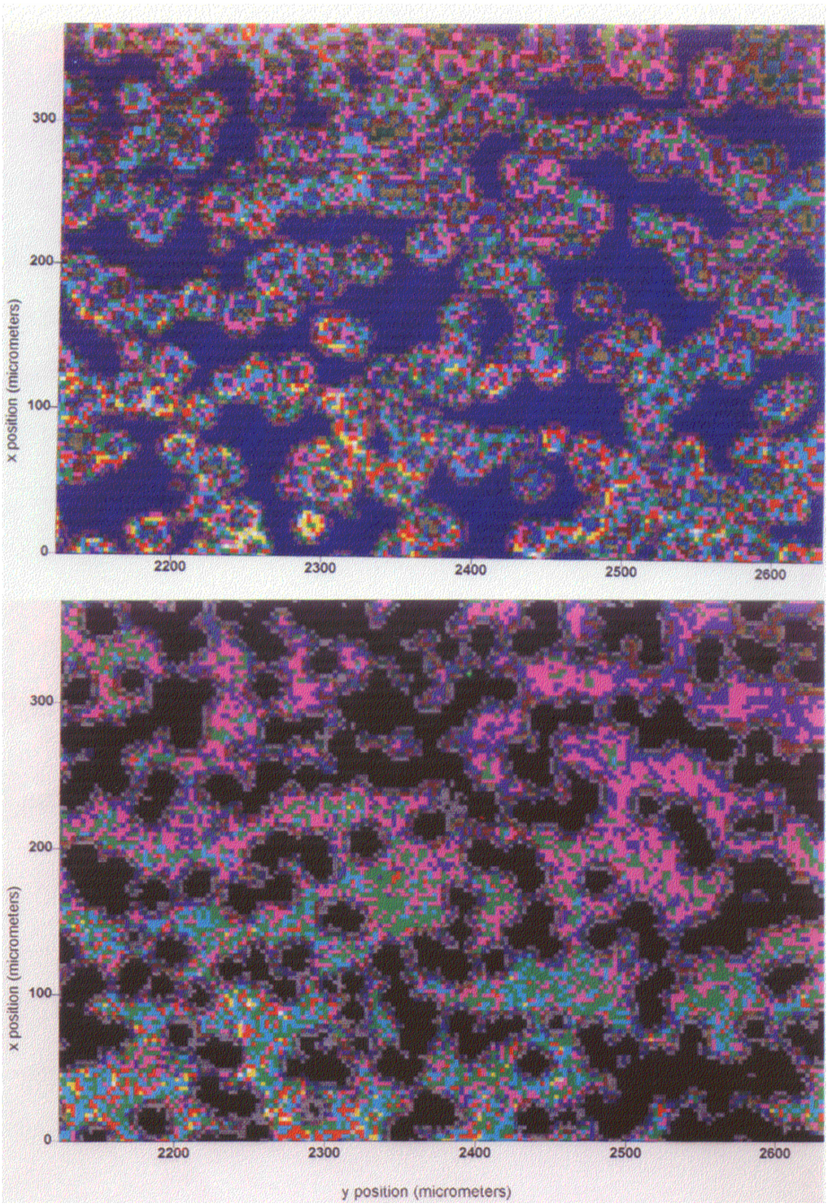
Grumm and Grabke

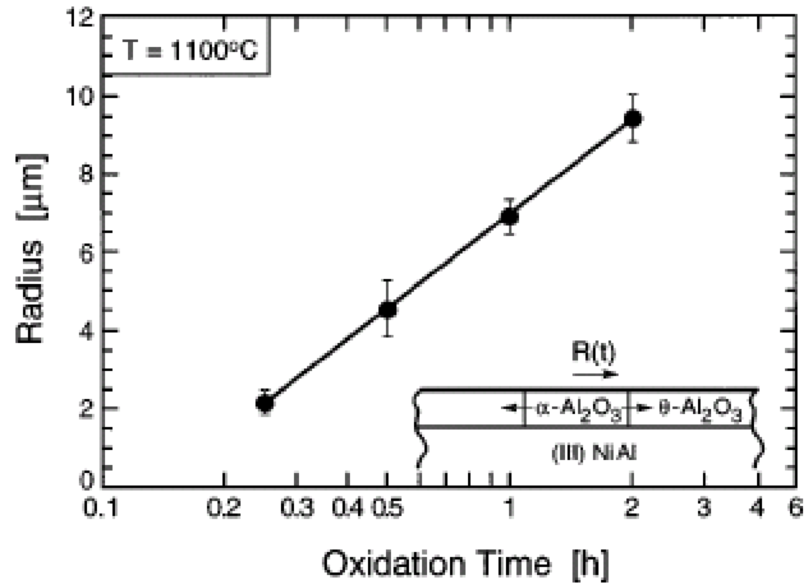
Nucleation and Growth of α-alumina on NiAl



Oxidation Temperature 1100^{o}C

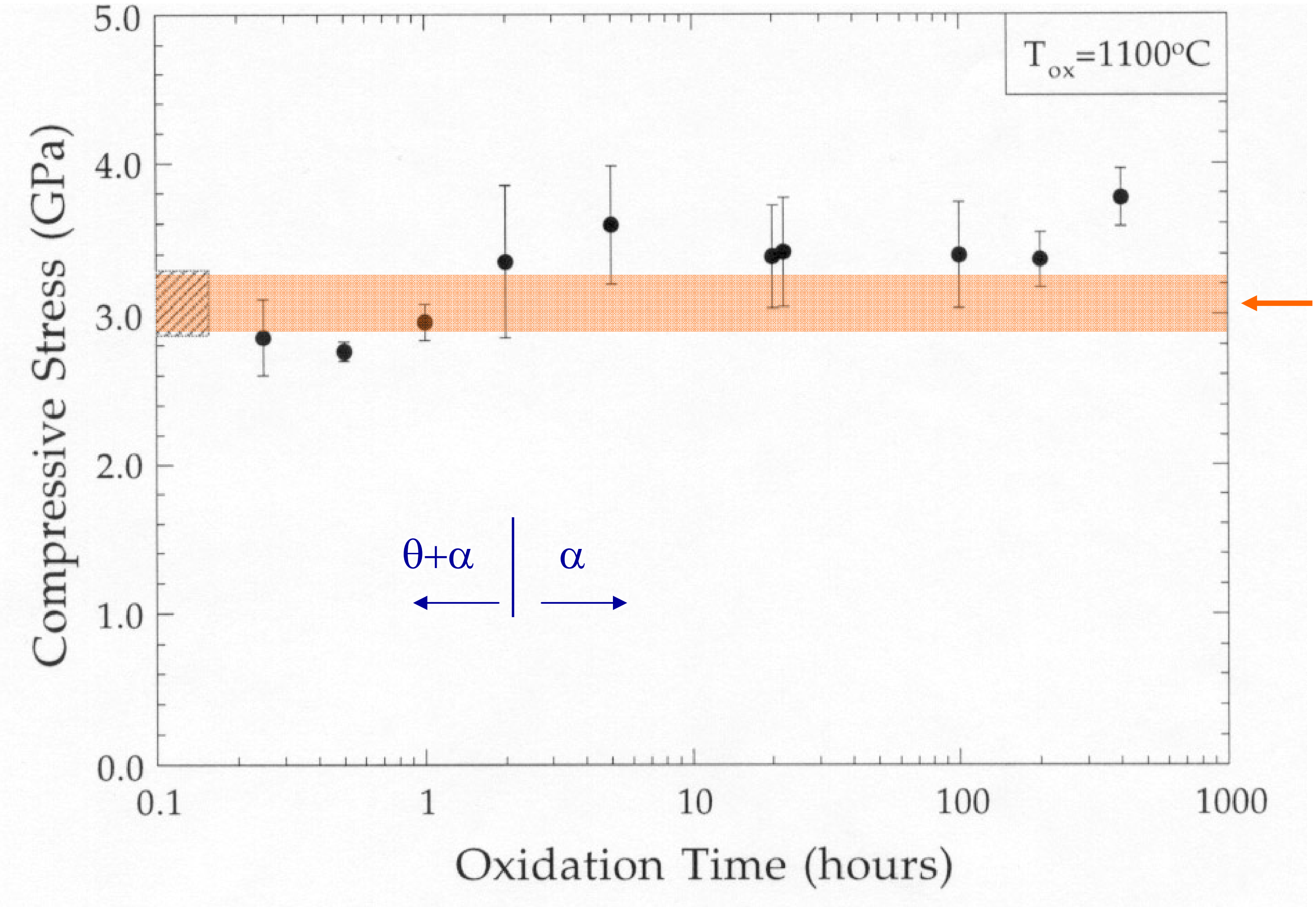
Luminescence Mapping For Transformation Kinetics





$$R = A + B \log t$$

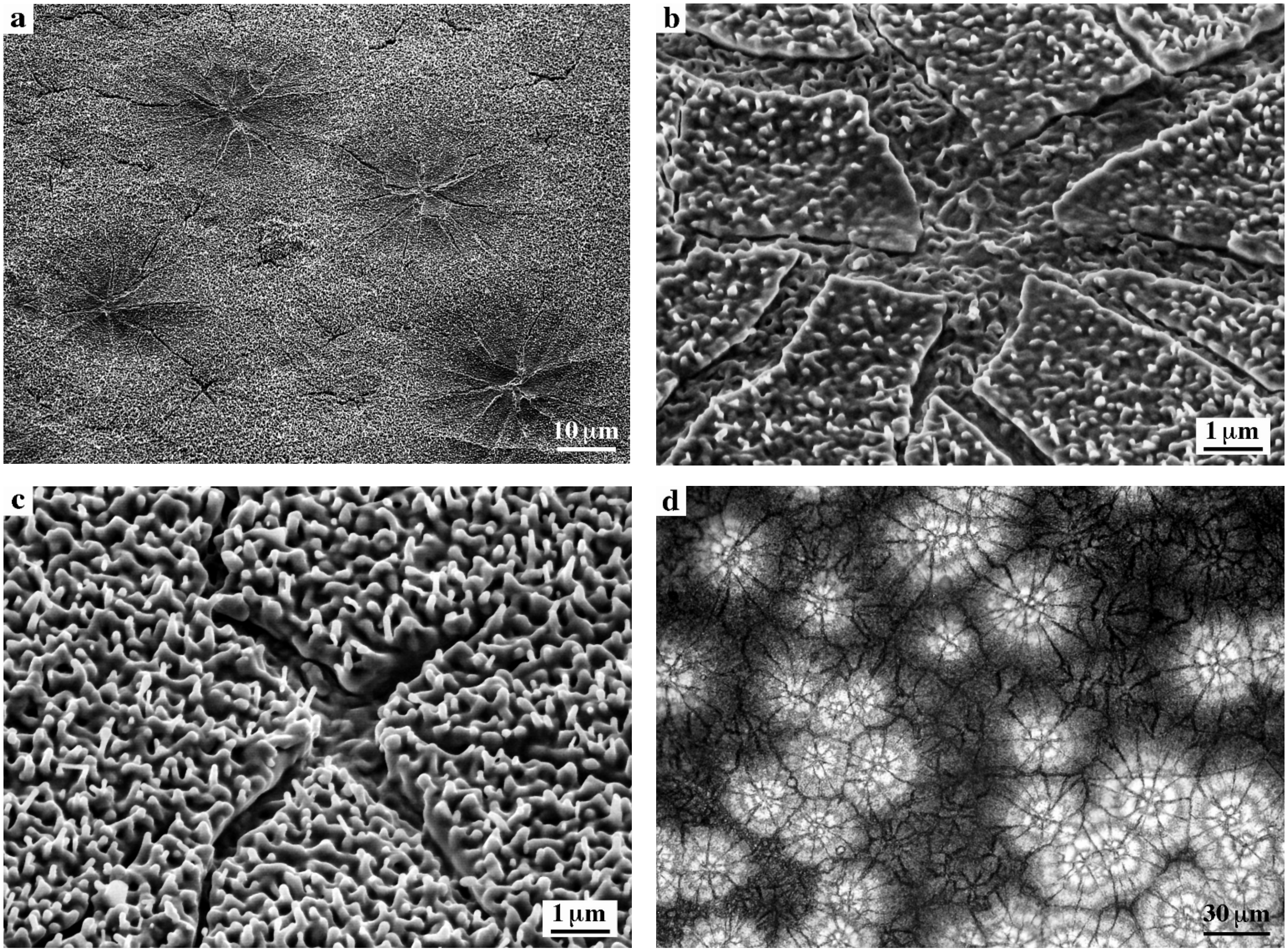
Evolution of Stress in NiAl Single Crystal



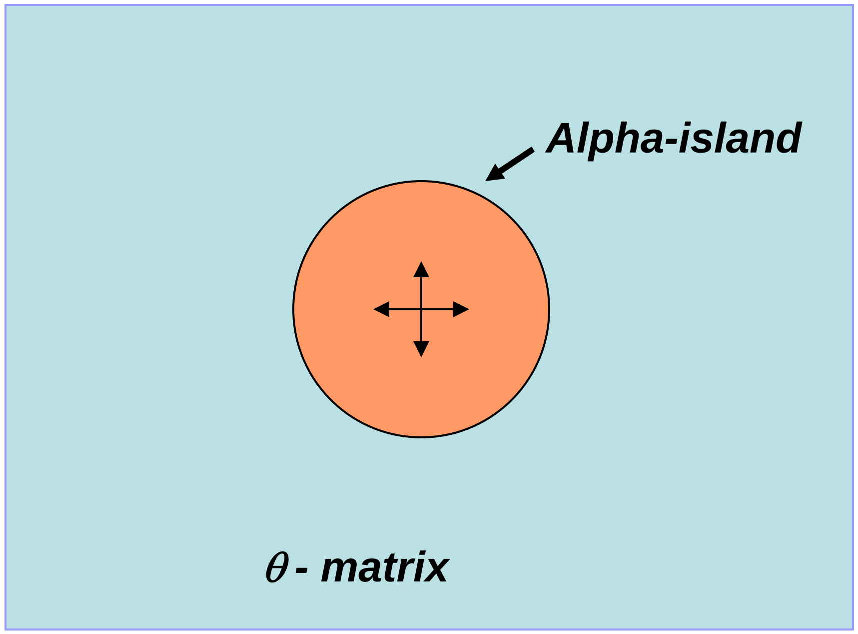
Thermal expansion stress

NB. Alpha phase is under net tension under transformation is complete. Then oxide is under compression.

Nucleation and Growth of a-Alumina During Oxidation



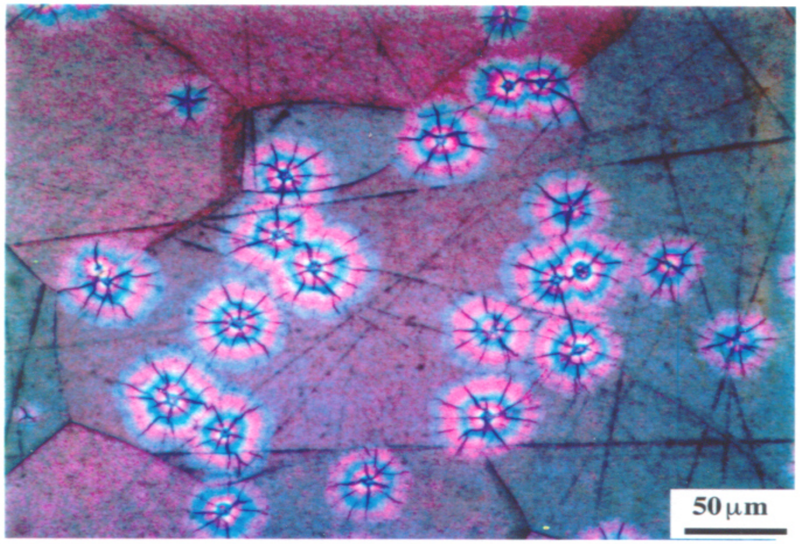
Origin of Transformation Stresses

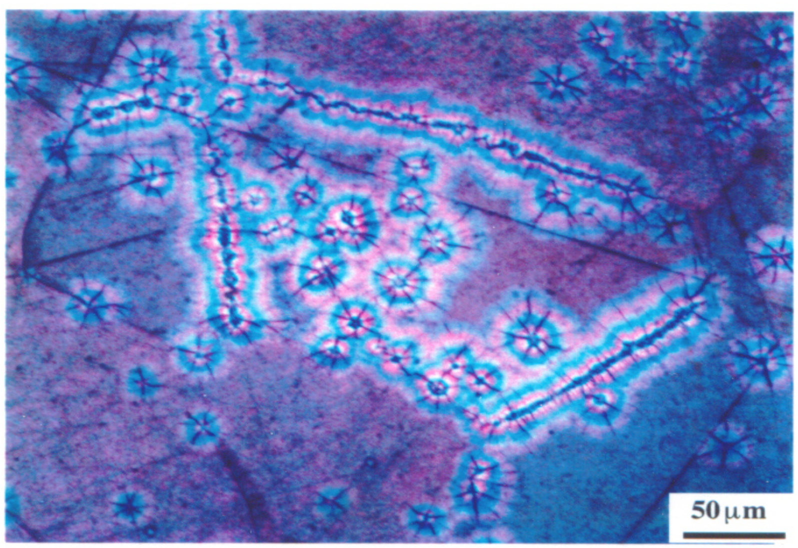


$\theta \rightarrow \alpha$ **transformation is accompanied by a 9.5 % volume decrease.**

The transformation is constrained by the surrounding θ oxide, placing the α - islands under tension. This causes "tearing" of islands.

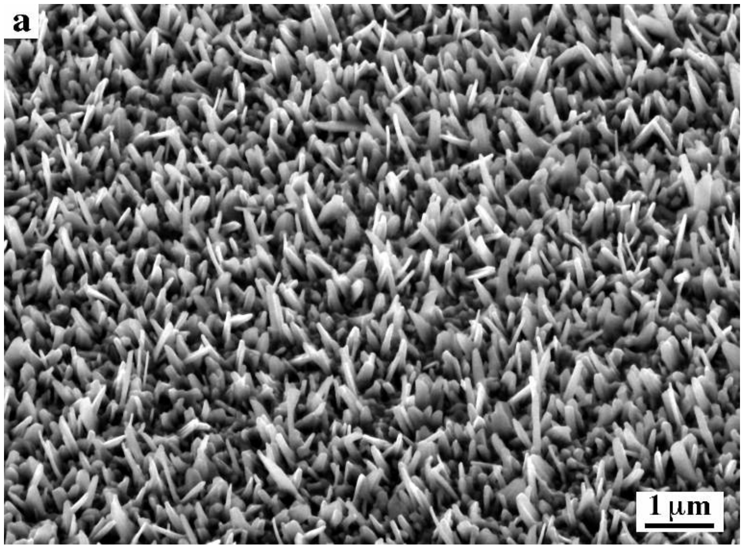
Heterogeneous Nucleation and Growth of α-alumina on NiAl



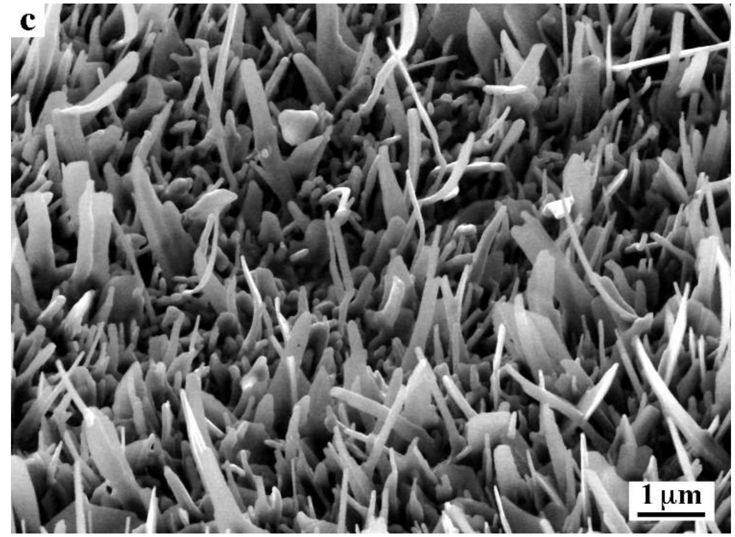


Note the radial cracks in the islands, giving the "star" contrast

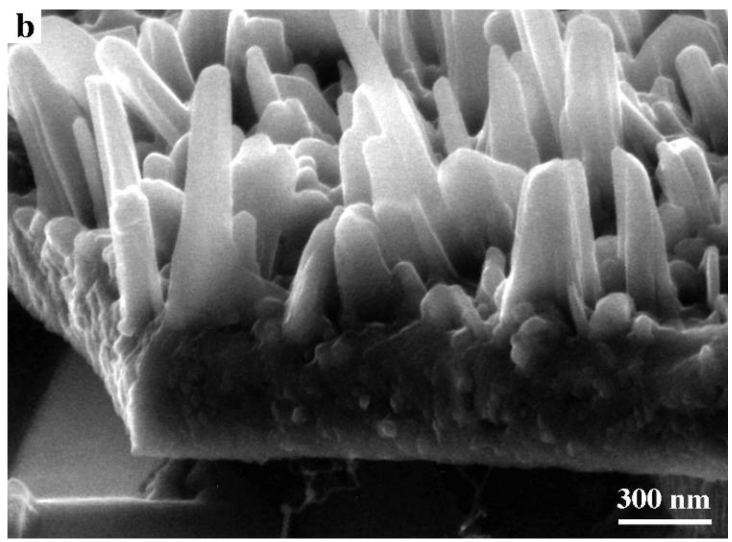
TGO Morphology at 1000°C



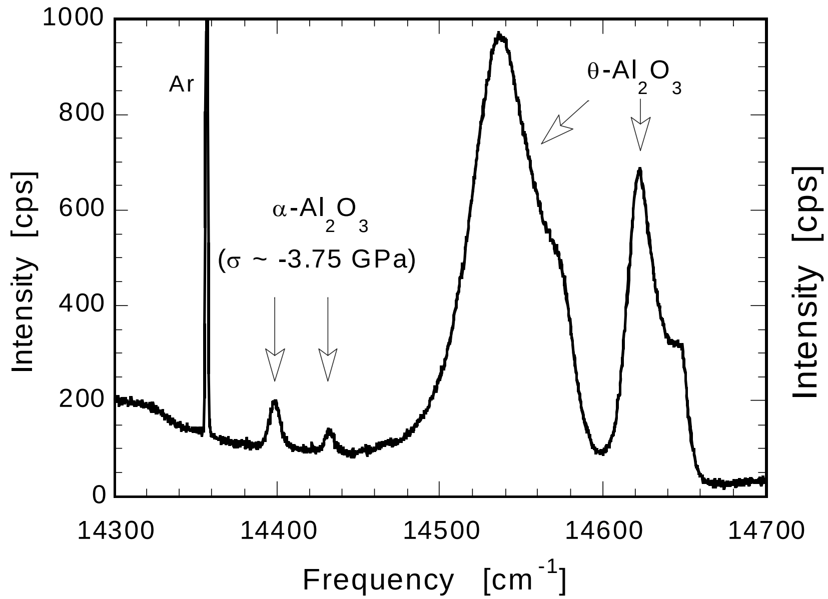
1 hour θ ~ 0.5 μm thick

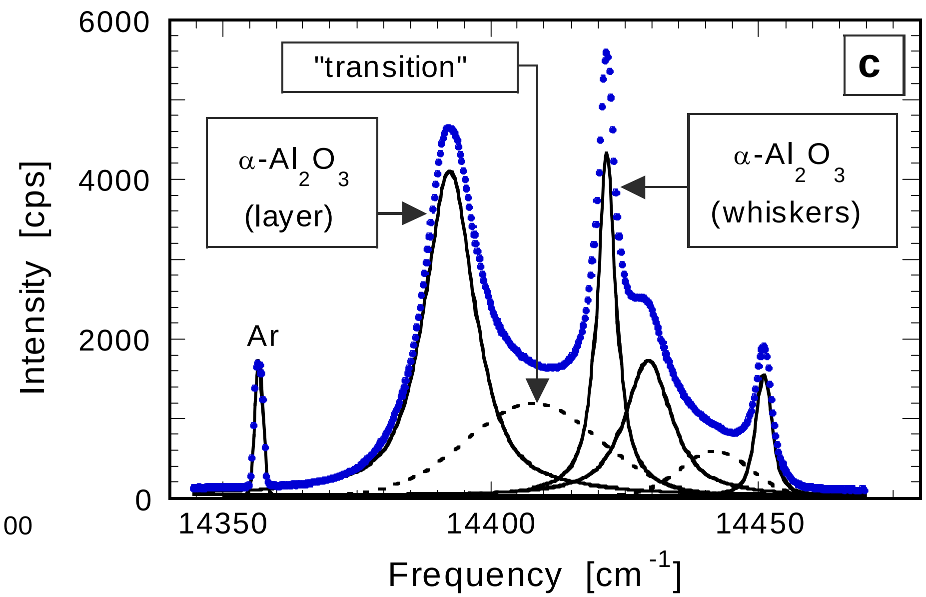


25 hour mixed α + θ



Fibrous θ-phase Transforms to α–alumina





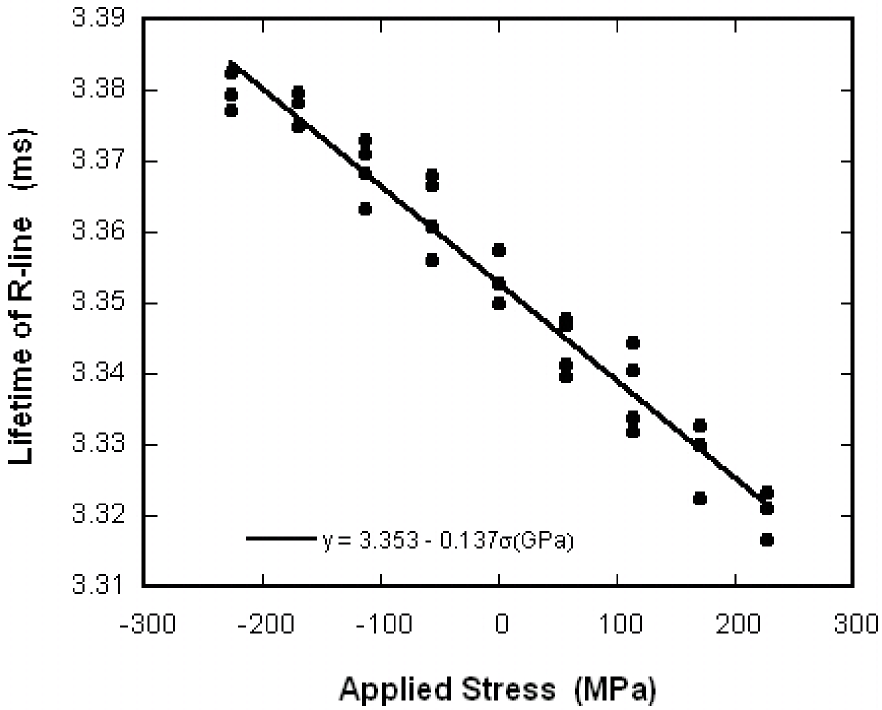
1 hour at 1100ºC

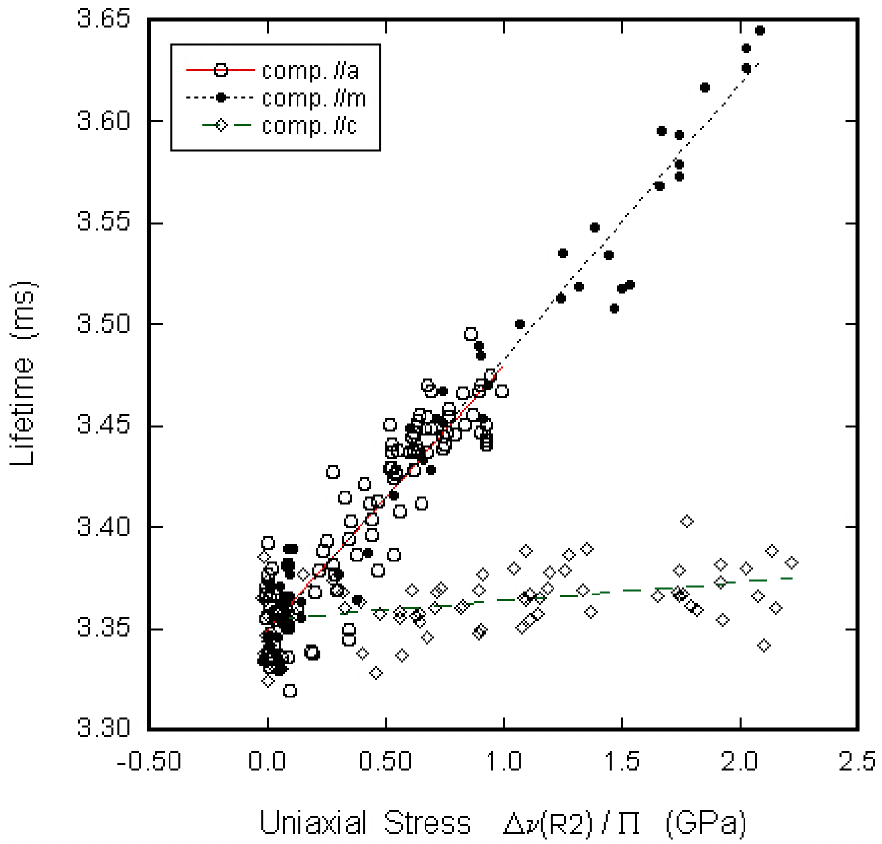
25 hour at 1100ºC

Recent Developments

Stress Effects on the Luminescence Lifetime

Polycrystalline alumina



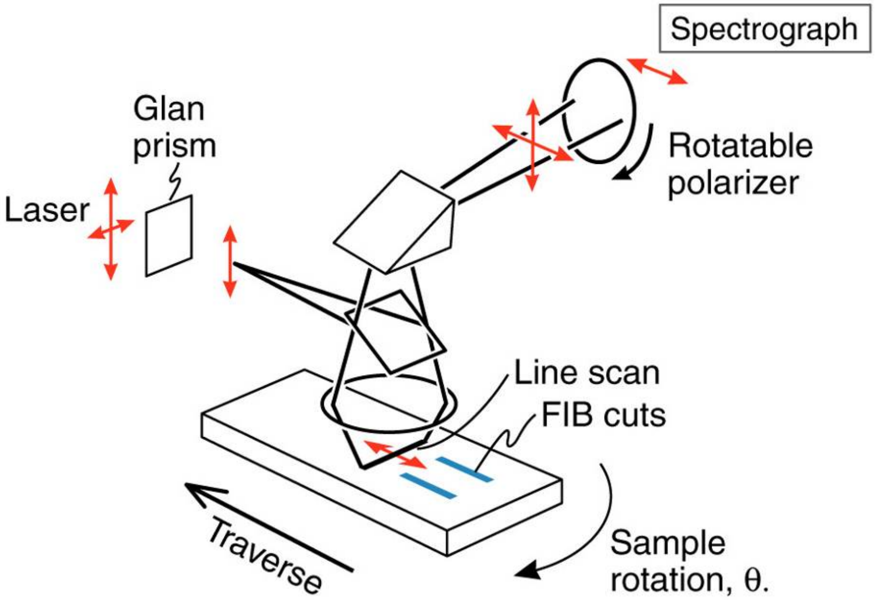


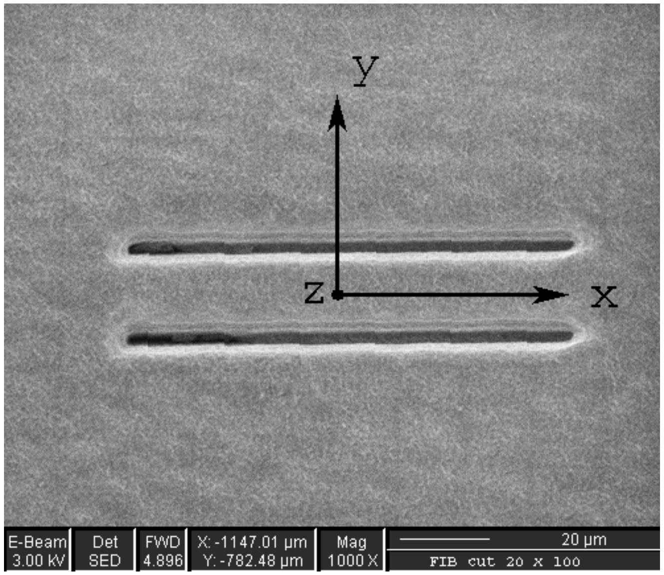
Lifetime varies with crystallographic direction and linearly with stress

Use of Polarization to Distinguish Stress Components

Frequency shift proportional to mean stress in polycrystalline alumina:

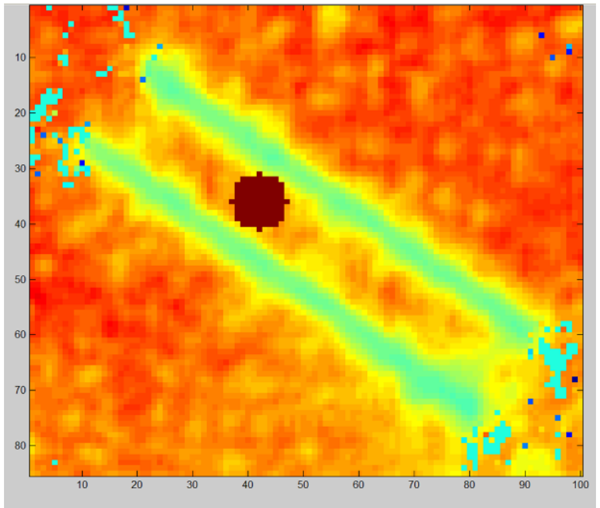
$$\Delta \nu_{R2} = 7.62\left(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}\right)/3$$





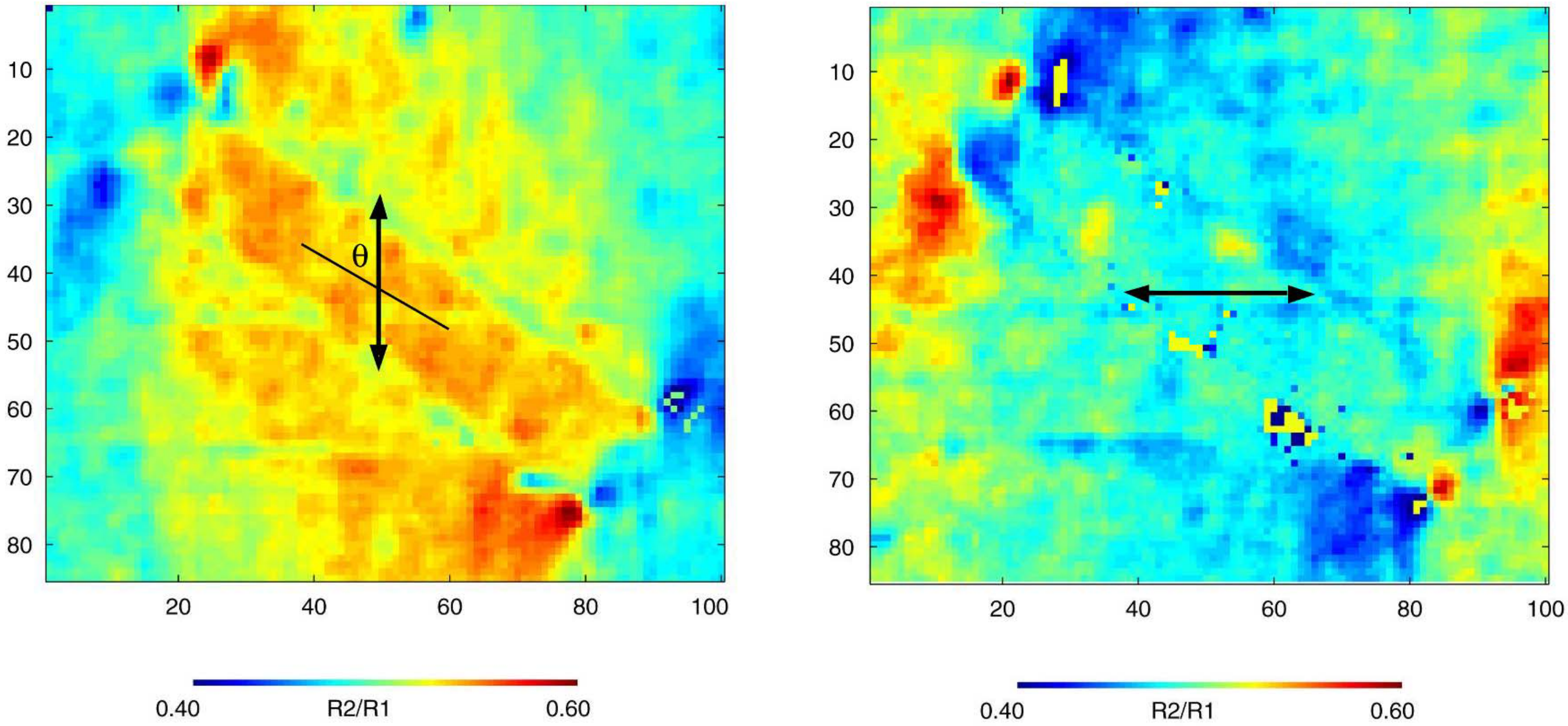
FIB cuts create a strip under uniaxial stress

Luminescence intensity map around strip



Use of Polarization to Distinguish Stress Components

Imaging under different polarization conditions reveals directions of principal stresses by affecting R2/R1 peak area ratio.



End of Part I