Local structure of Europium complex oxides

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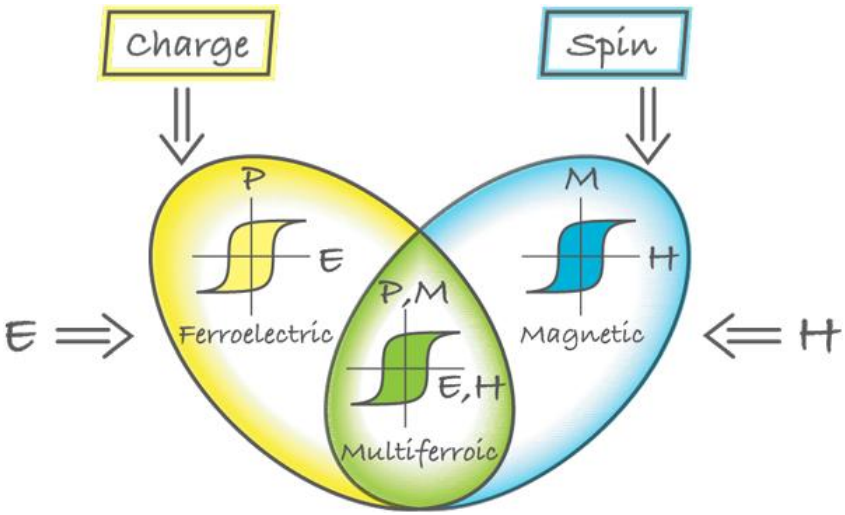
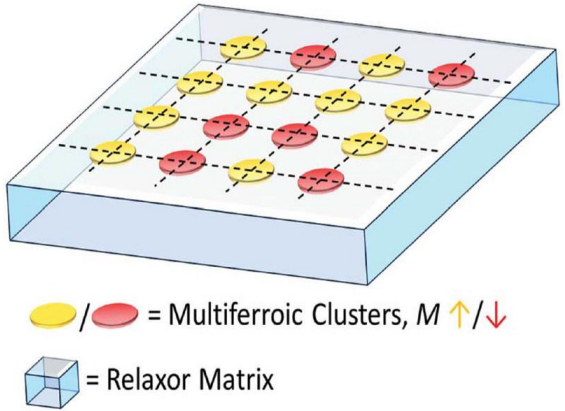
Application and properties

Multiferroic ordering



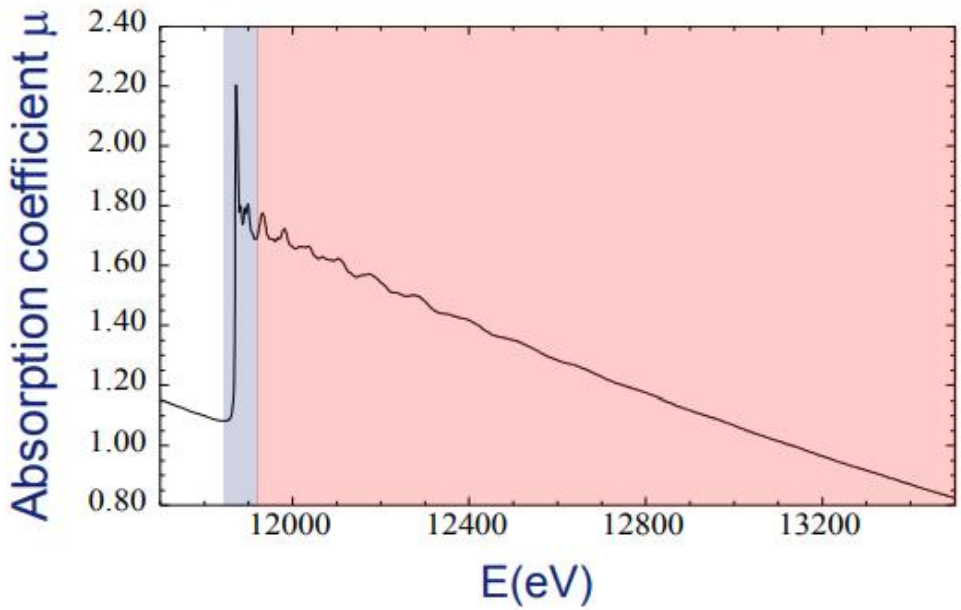
J.F. Scot // Journ. of Mat. Chem., 2012, 22(11), pp. 4567-4574



It is possible to control magnetic properties by electric field and to control electric polarization by magnetic field

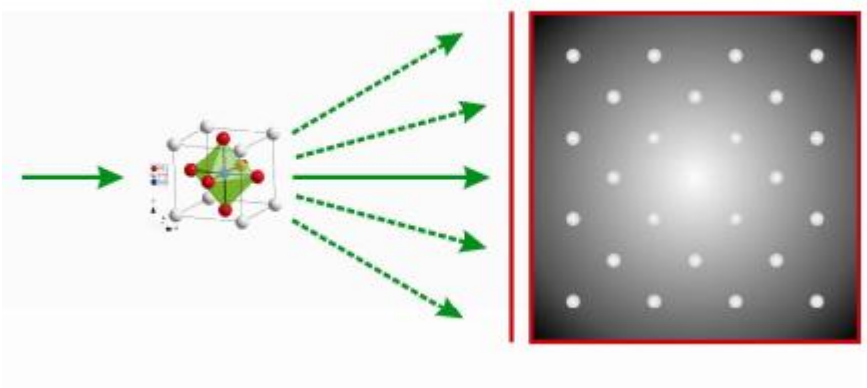
Multiferroic materials can be applied in multiferroic memory devices where the information can be written electrically and read magnetically thus non destructively

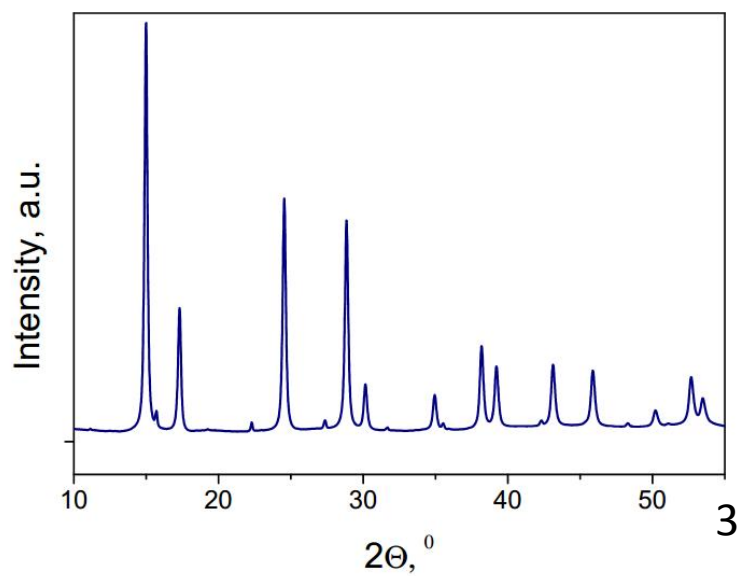
Our instruments



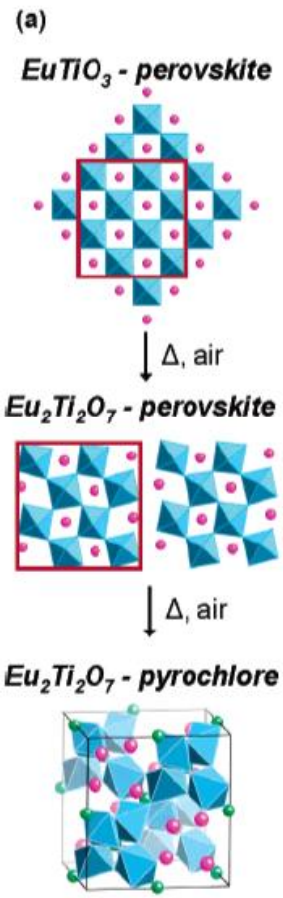
X-ray Absorption spectroscopy (XANES and EXAFS)

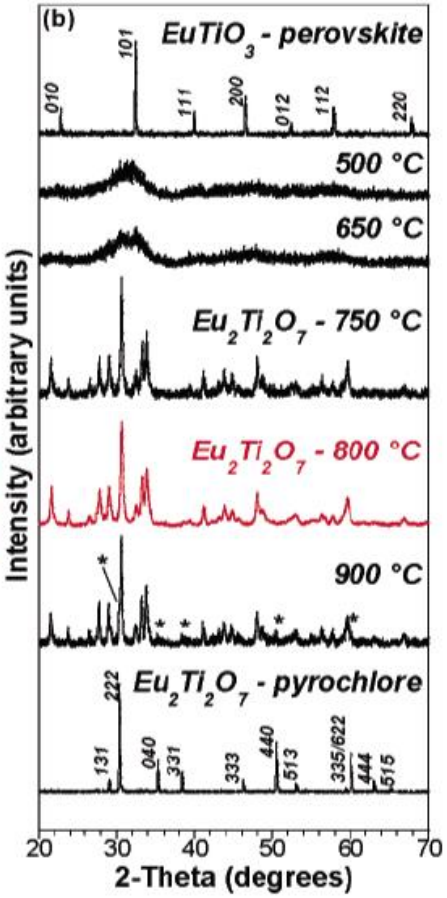
X-ray Powder Diffraction

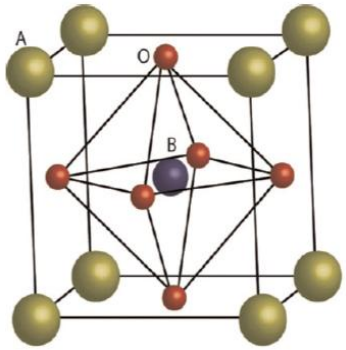




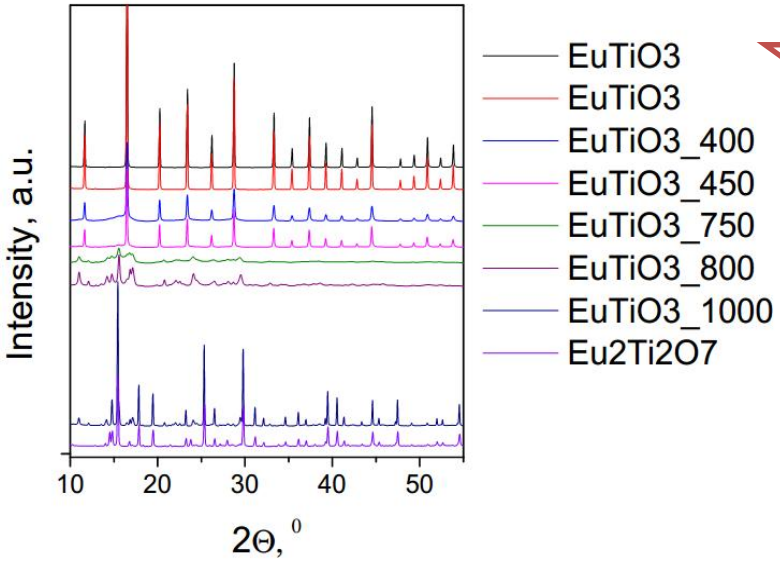
Crystal structure







$ABO_3 = EuTiO_3$



$Eu^{3+}{}_2Ti_2O_7$

1000⁰C
4 hours
H2

$Eu^{2+}TiO_3$

440-450-
750-800⁰C
O2

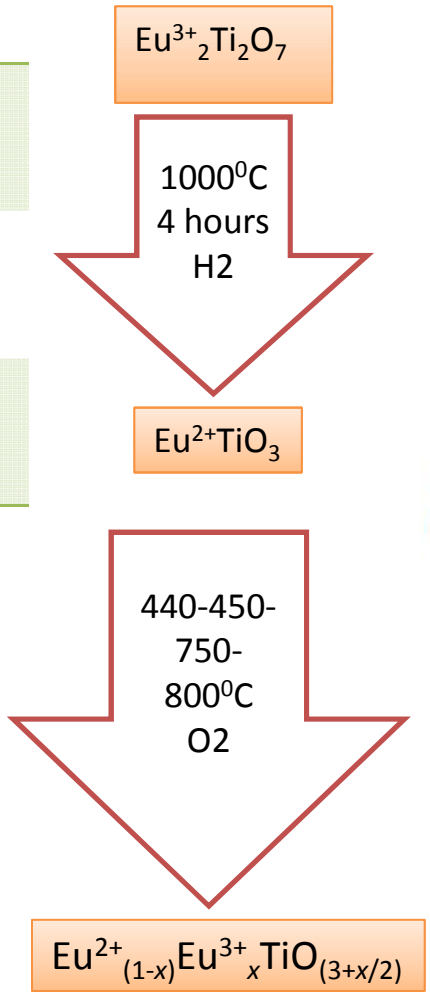
$Eu^{2+}{}_{(1-x)}Eu^{3+}{}_xTiO_{(3+x/2)}$

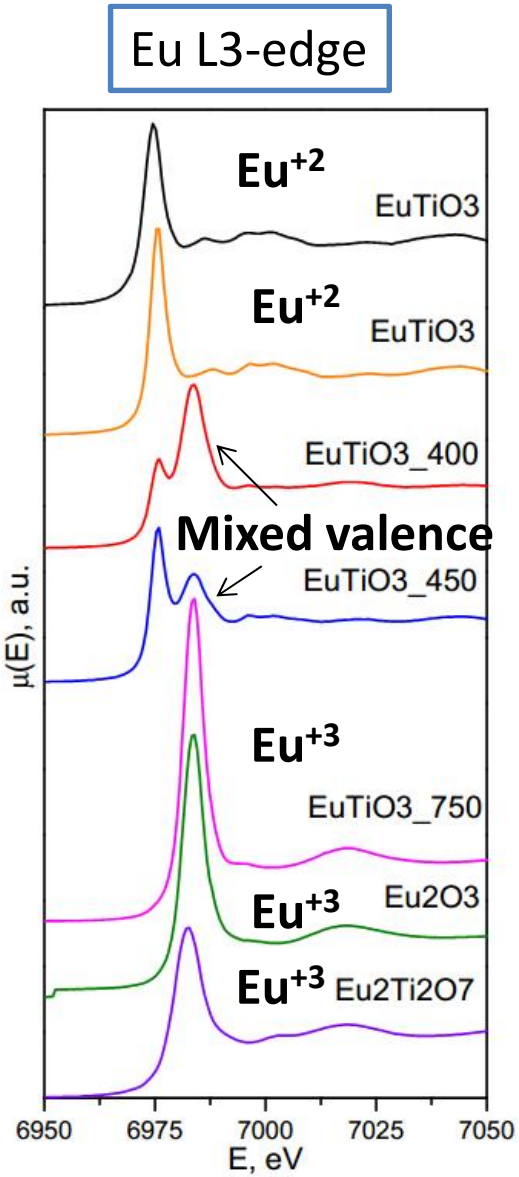
N.L. Henderson,J.Baek, P.S.Halasyamani // Chemistry of Materials, 2007, V. 19, N. 7, pp. 1883-1885

XANES: valence state

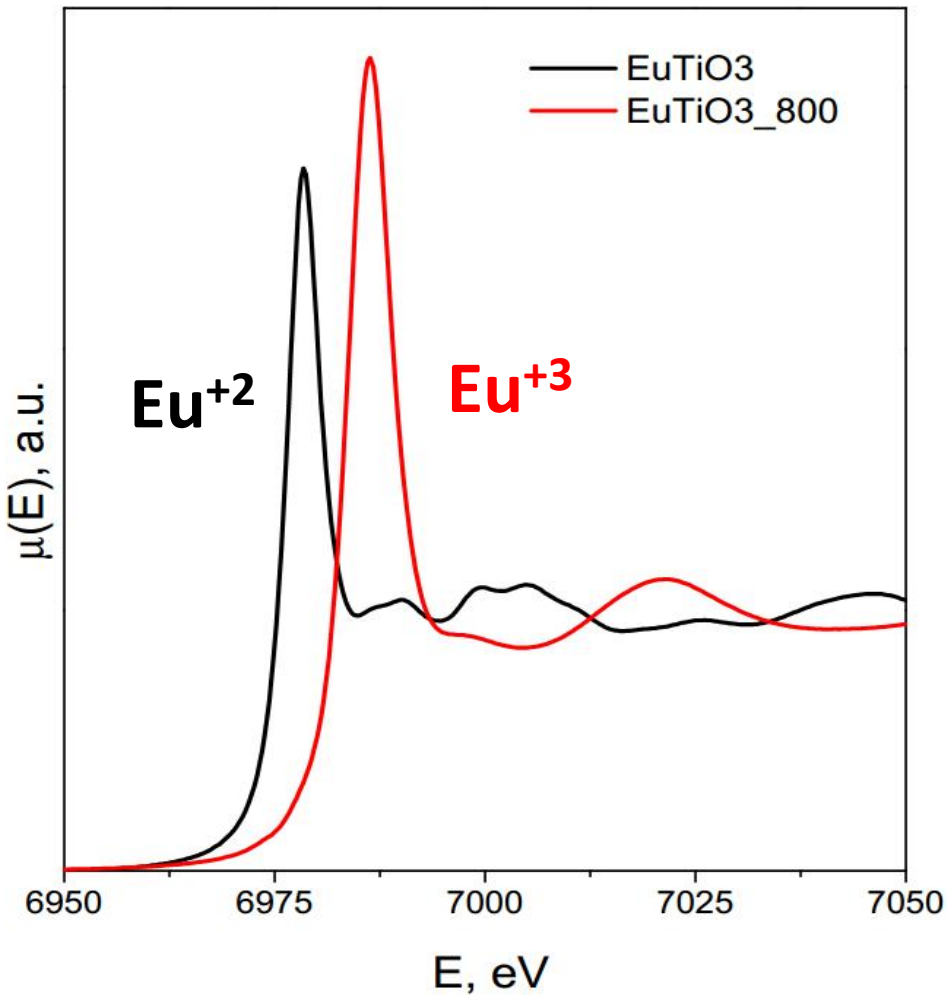
Compound	Eu^{2+}(%)	Eu^{3+}(%)
EuTiO3_400	43,1	56,9
EuTiO3_450	73,5	26,5
EuTiO3_750	**0**	**100**

Calculation results of the percentage of divalent and trivalent europium in the transitional compounds $Eu^{2+}_{(1-x)}Eu^{3+}_{x}TiO_{(3+x/2)}$.





XANES: Eu^{2+} and Eu^{3+}



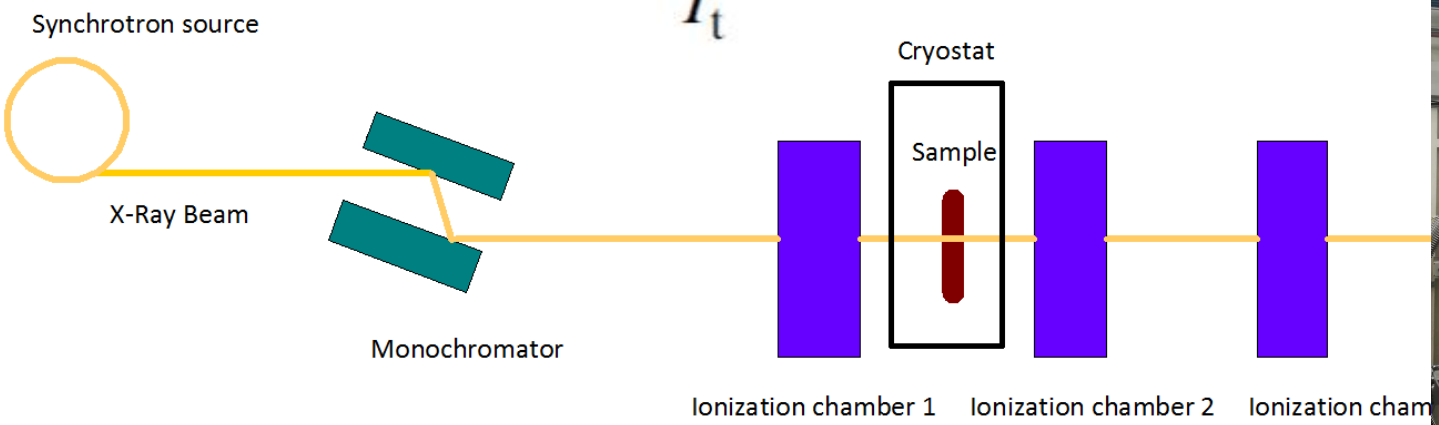
Eu L3-edge XANES spectra of $EuTiO_3$ before and after annealing in oxygen at 800 ^{0}C.

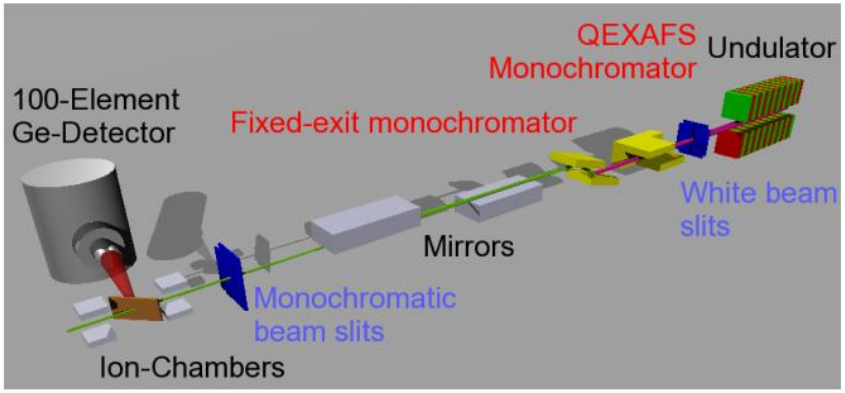
$EuTiO_3$ – Eu^{2+}, perovskite structure

$EuTiO_3$ + 800 ^{0}C = $Eu_2Ti_2O_7$ – Eu^{3+}, monoclinic structure

Low temperature measurements

$$\mu = \ln \frac{I_0}{I_t}$$

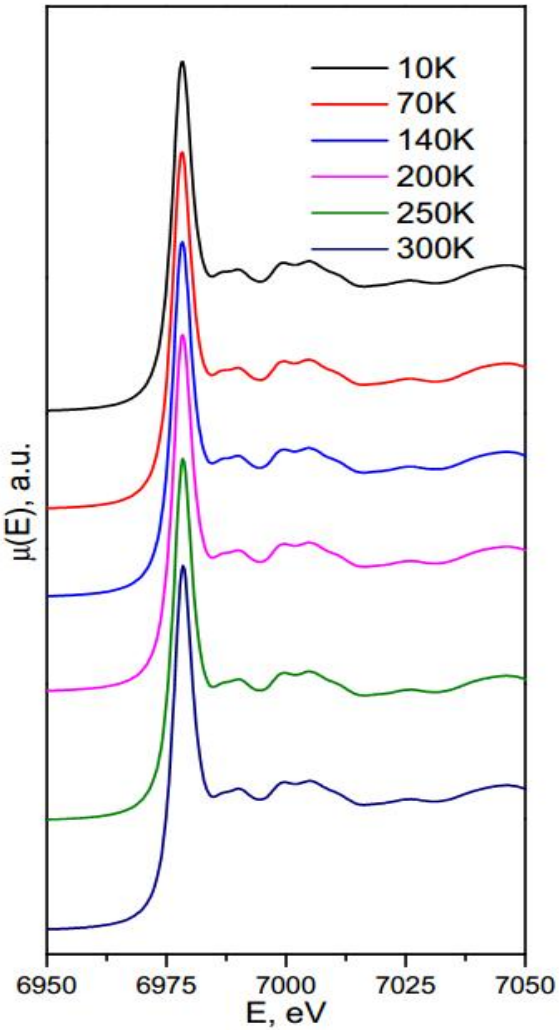




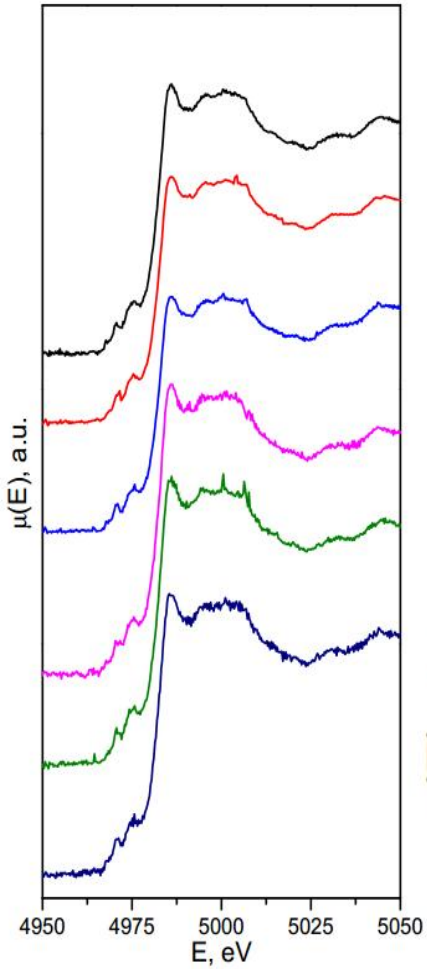
W.A. Caliebe, V. Murzin, A. Kalinko, M. Gorlitz // AIP Conf. Proc. 2054, 060031-1–060031-6

Low temperature measurements: XANES

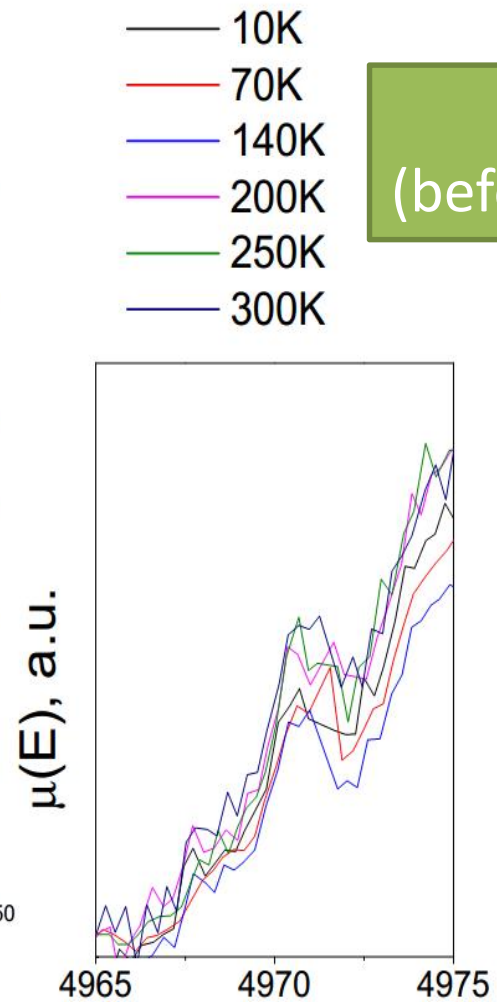
Eu L3-edge



Ti K-edge



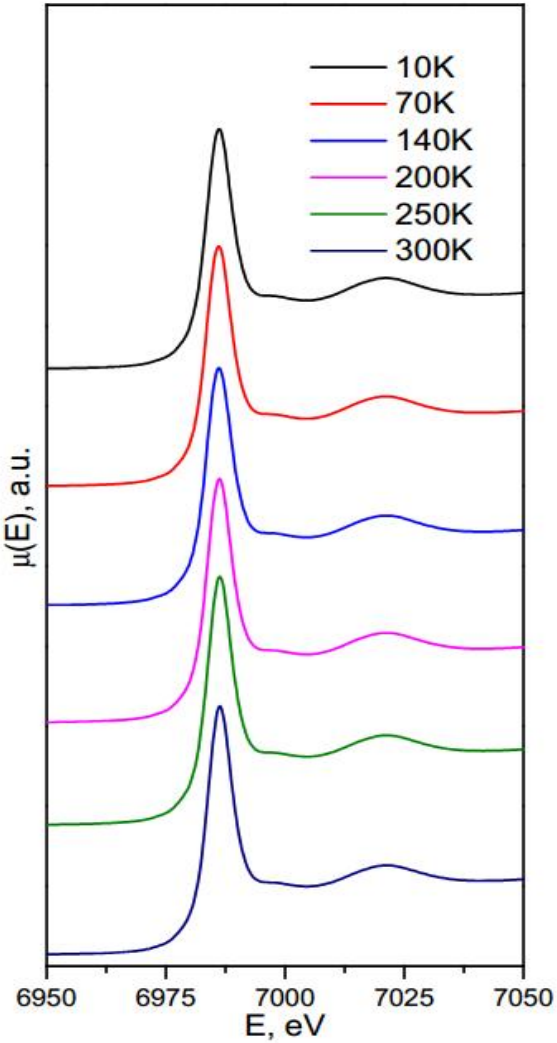
$EuTiO_3$
(before annealing)



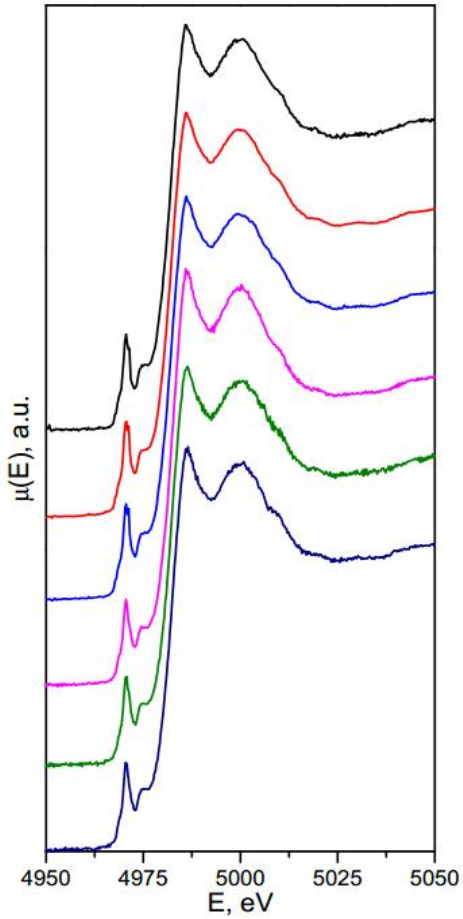
Pre-edge region of Ti K-edge XANES spectra $EuTiO_3$

Low temperature measurements: XANES

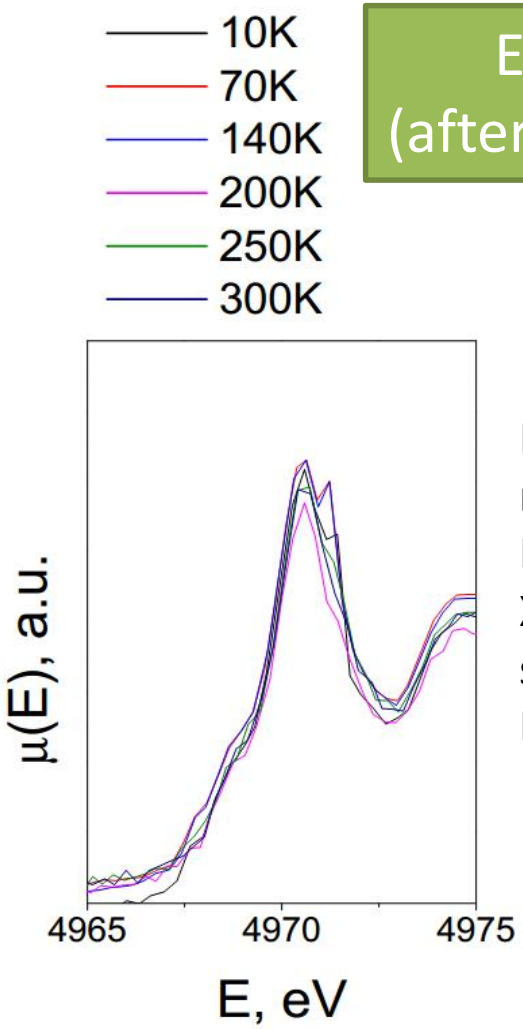
Eu L3-edge



Ti K-edge

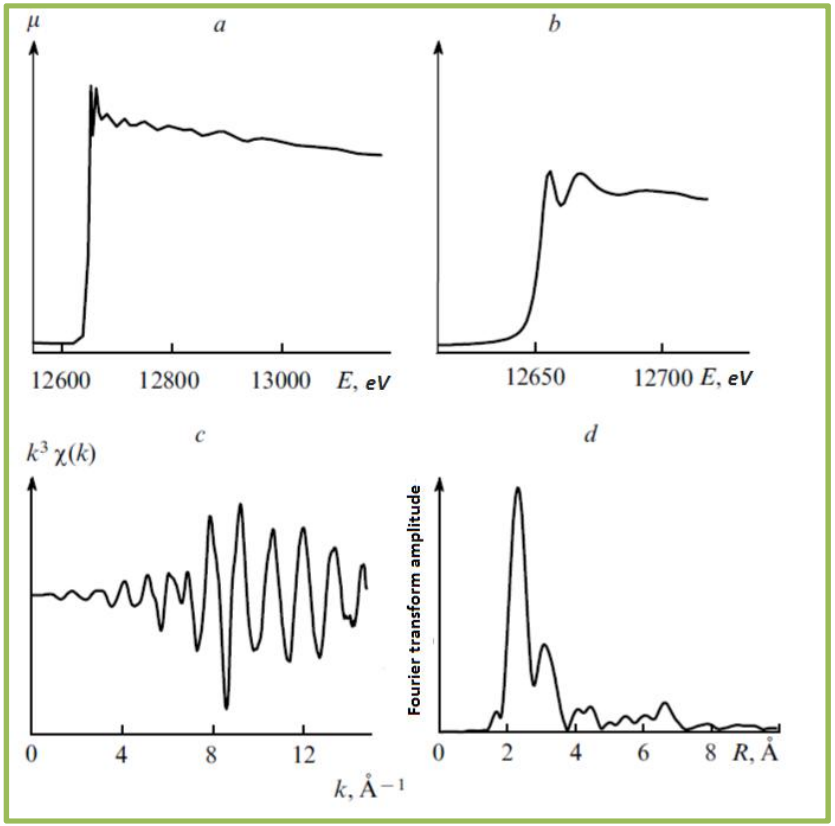


$Eu_2Ti_2O_7$ (after annealing)



Pre-edge region of Ti K-edge XANES spectra $EuTiO_3$

Extended X-Ray Absorption Fine structure (EXAFS)



a) Experimental spectrum of X-ray absorption
b) XANES region
c) Normalized EXAFS – oscillated part of an absorption coefficient
d) Fourier-transform of the normalized EXAFS

R distance to neighboring atom.
N coordination number of neighboring atom.
σ^2 mean-square disorder of neighbor distance.

From crystallography data

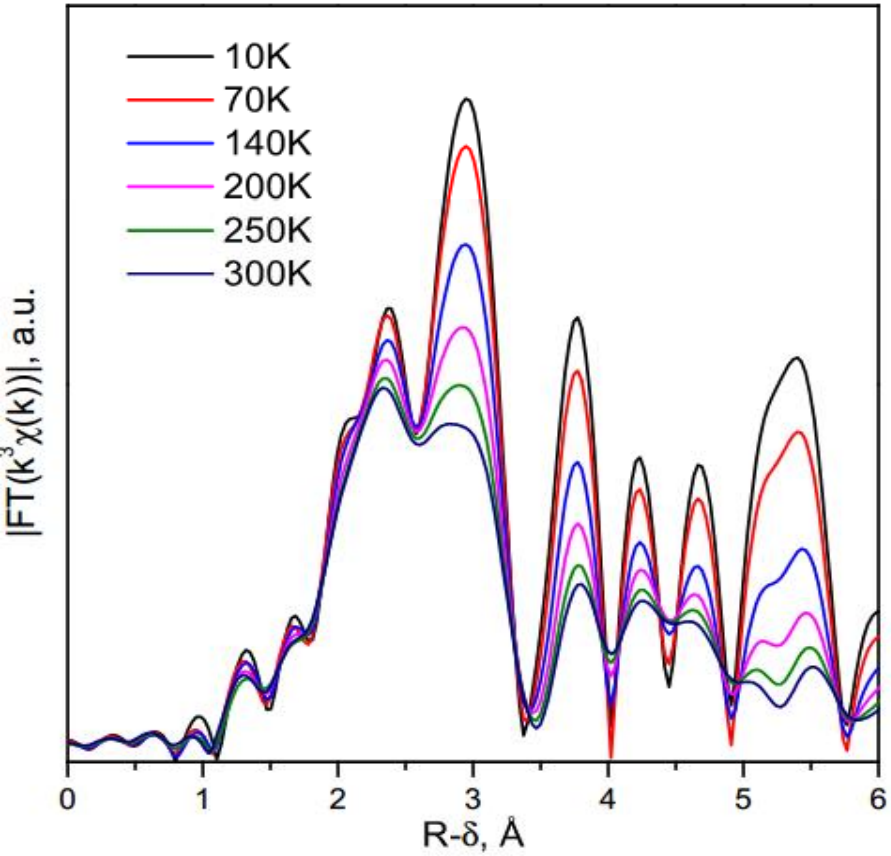
$$\chi(k) \sim S_0^2 \, \Sigma_j \, N_j \frac{f_j(k)}{kR_j^2} \, e^{-2R/\lambda(k)} \, e^{-2k^2\sigma_j^2} \sin\left[2kR_j + \delta_j(k)\right]$$

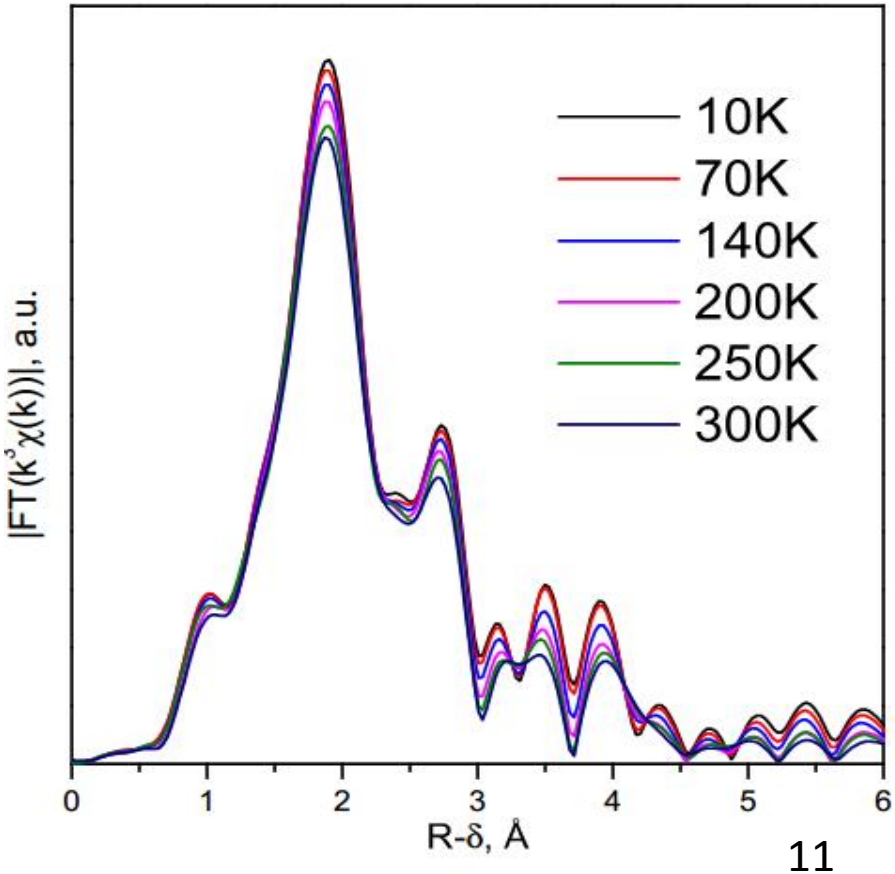
Low temperature measurements: EXAFS

$EuTiO_3$ (before annealing)

Eu L3-edge

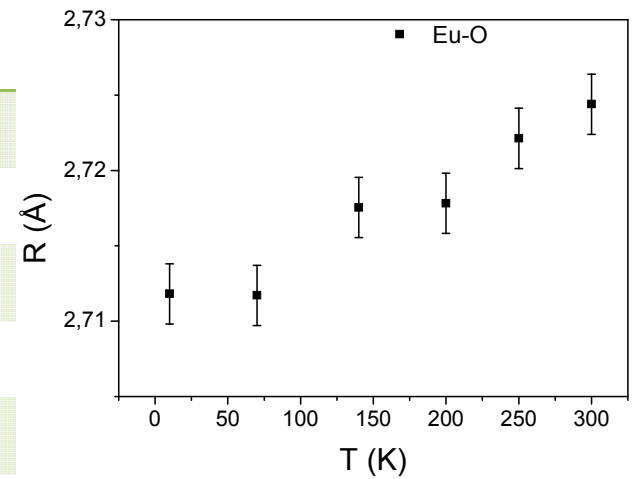
$Eu_2Ti_2O_7$ (after annealing)

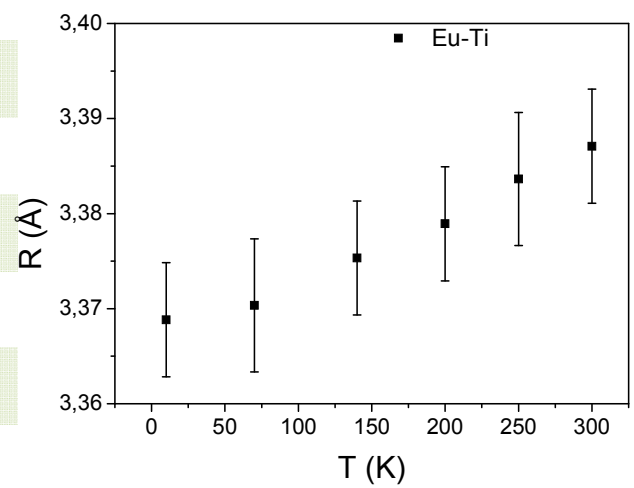




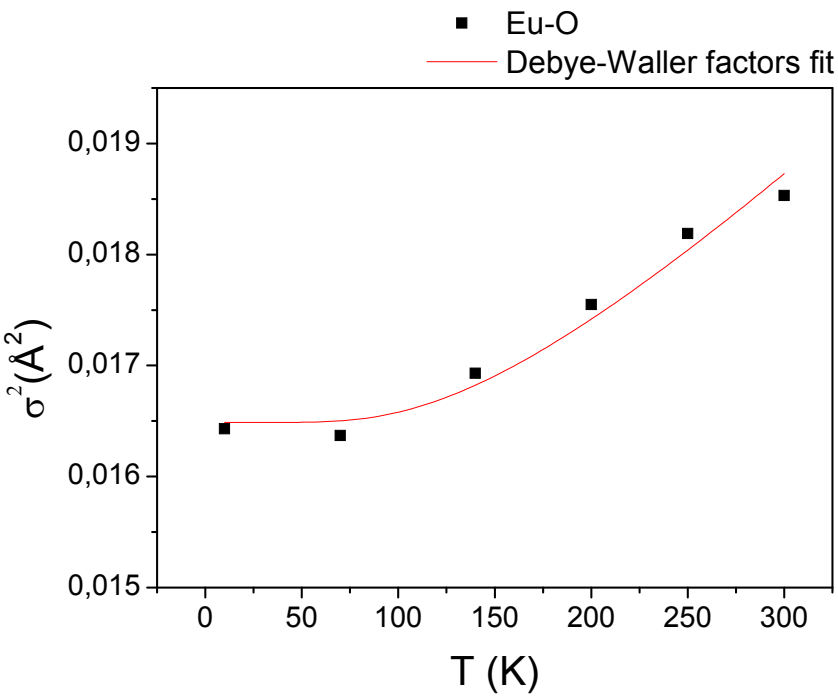
Low temperature measurements: EXAFS

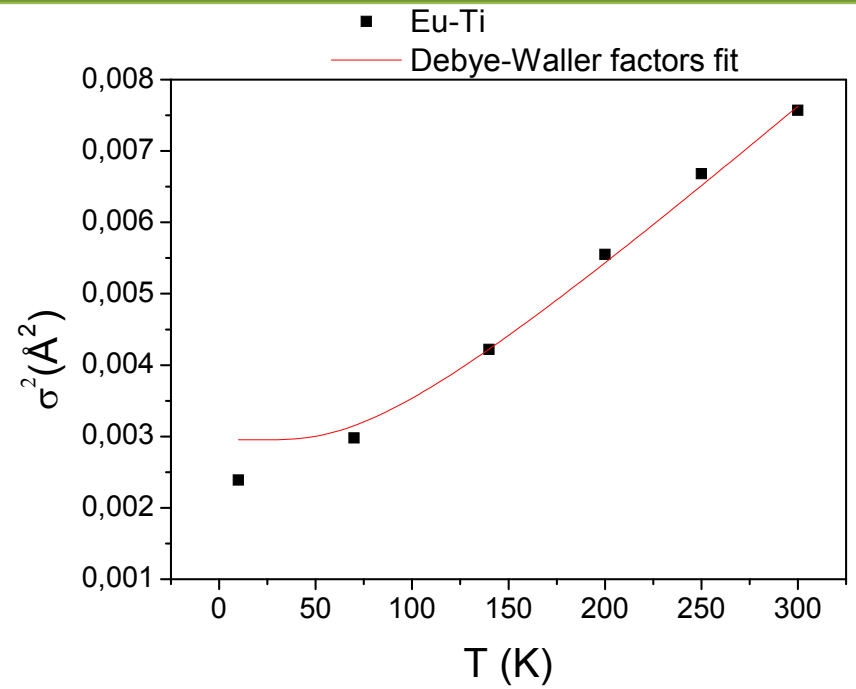
Temperature	Path	N (fixed)	R	Debye-Waller factors
300	Eu-O	12	2.72(0.02)	0.0185 (0.002)
	Eu-Ti	8	3.387(0.01)	0.0076 (0.0006)
250	Eu-O	12	2.722(0.02)	0.01819 (0.002)
	Eu-Ti	8	3.384(0.009)	0.00668(0.0005)
200	Eu-O	12	2.718 (0.02)	0.01755(0.002)
	Eu-Ti	8	3.379(0.009)	0.00555(0.0005)
140	Eu-O	12	2.718 (0.02)	0.01693(0.002)
	Eu-Ti	8	3.375(0.007)	0.00422(0.0004)
70	Eu-O	12	2.712(0.02)	0.01637 (0.002)
	Eu-Ti	8	3.370(0.007)	0.00298(0.0004)
10	Eu-O	12	2.712(0.02)	0.01643(0.002)
	Eu-Ti	8	3.369(0.004)	0.00239 (0.0004)





Temperature dependence of Debye-Waller factors





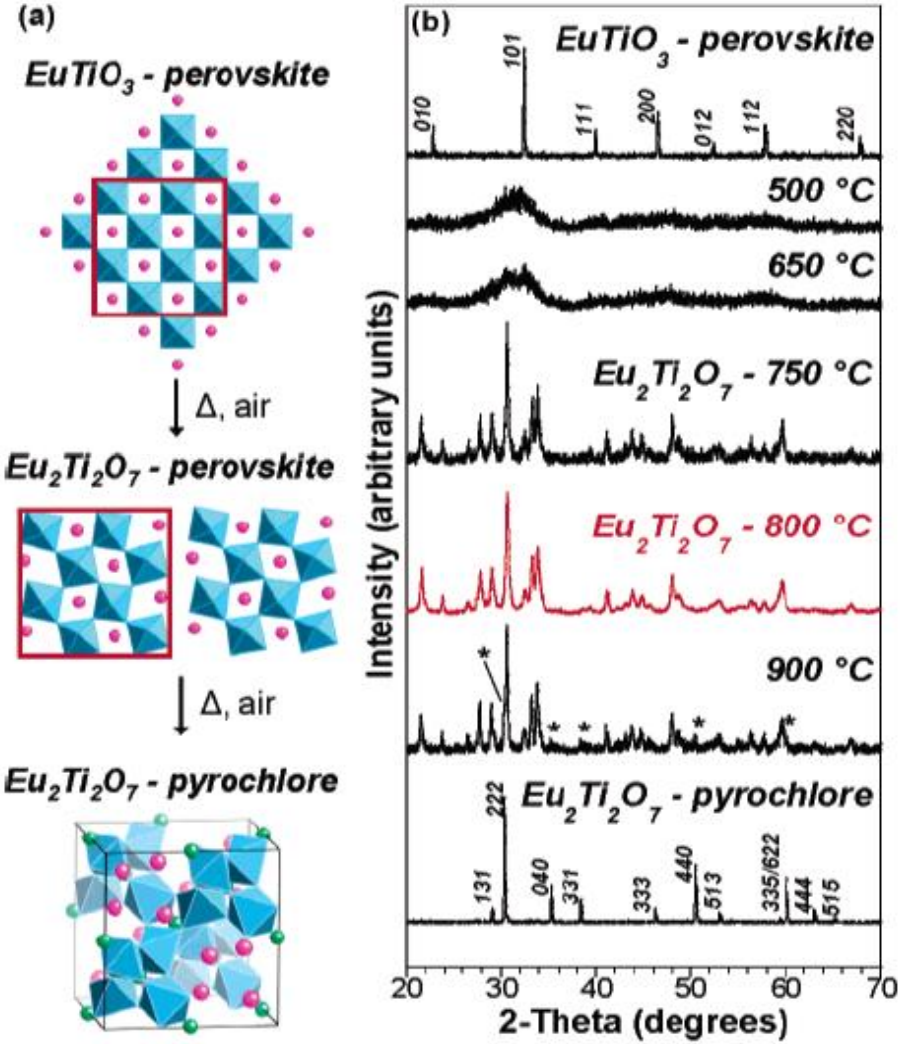
$EuTiO_3$
(before annealing)

$$\sigma^2 = \sigma^2_{stat} + \frac{\hbar^2}{2k\mu}\frac{1}{T_E}coth\left[\frac{T_E}{2T}\right]$$

Interatomic bond	T_E, K	σ^2_{stat}, Å²
Eu-O	442	0.013
Eu-Ti	236	0.00016

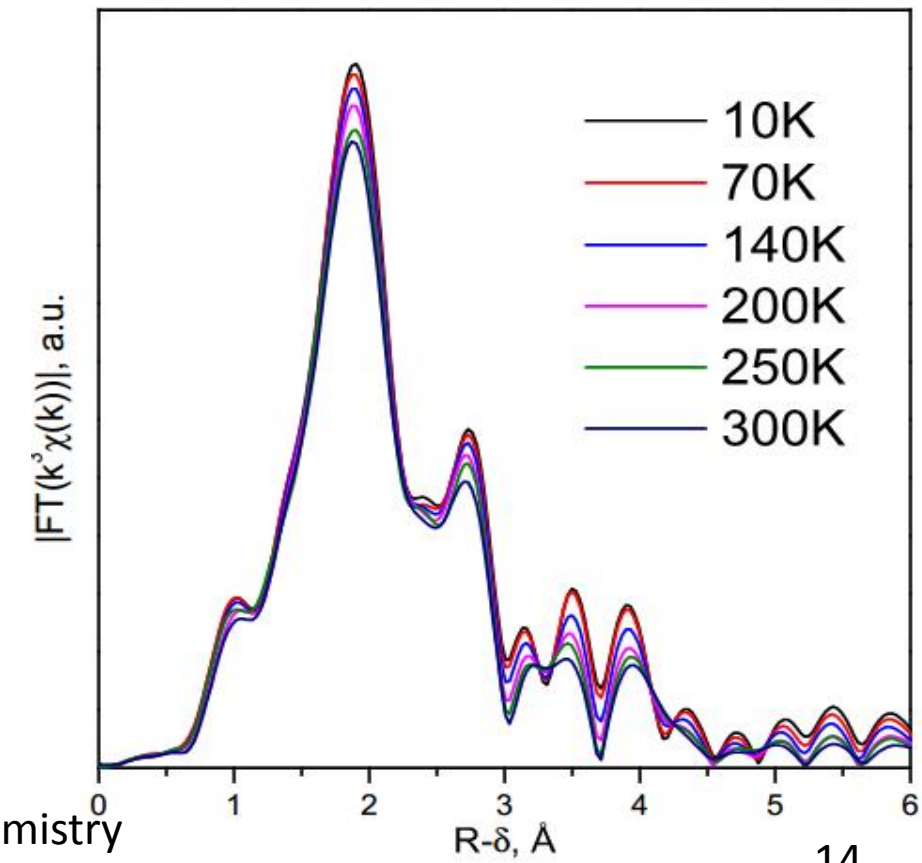
Temperature dependence of Debye-Waller factors for Eu-O bond and for Eu-Ti bond.

Annealed sample: crystal and local structure



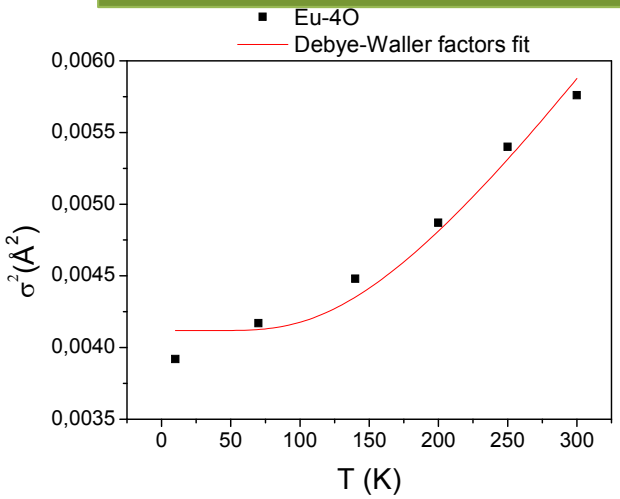
$Eu_2Ti_2O_7$
(after annealing)

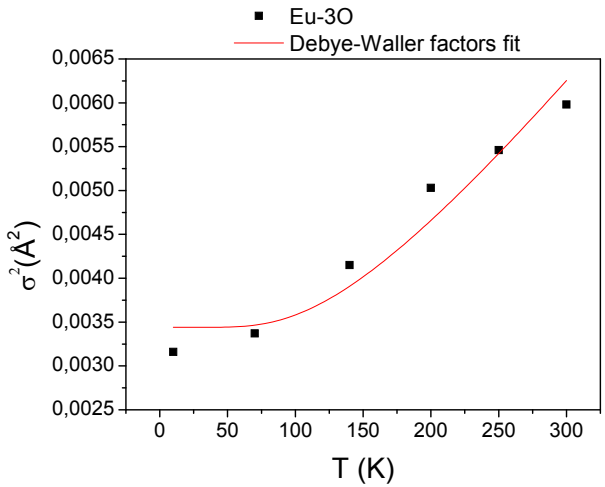
Eu L3-edge

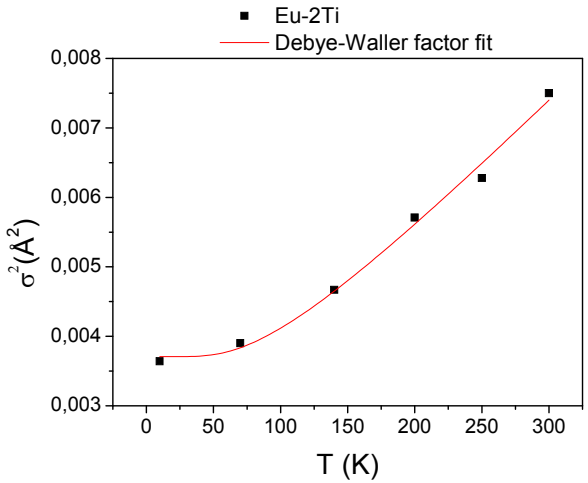


N.L. Henderson, J.Baek, P.S. Halasyamani // Chemistry of Materials, 2007, V. 19, N. 7, pp. 1883-1885

Temperature dependence of Debye-Waller factors







Interatomic bond	T_E, K
Eu-4O	479
Eu-3O	407
Eu-Ti	260

$$\sigma^2 = \sigma_{st}^2 + \sigma_d^2 + \sigma_{model}^2$$

$Eu_2Ti_2O_7$
(after annealing)

Temperature dependence of Debye-Waller factors for Eu-4O
bonds, for Eu-3O bonds and for Eu-2Ti bonds.

Conclusions

We investigated:

- Crystal structure of Eu complex oxides;
- Local structure and valence state of Eu complex oxides;
- Local disorder, connected to magnetic properties (application ☺)