Improved EPMA Analysis of Rare Earth and Trace Elements Using a New Precision Germanium WDS Crystal

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POWERING NEW PERSPECTIVES

M&M 2024
MICROSCOPY & MICROANALYSIS
July 28-August 1 • Cleveland, OH

C08.3 - Vendor Symposium

Wednesday, July 31, 2024
2:30 PM – 2:45 PM

Basic details

- Rigaku Innovative Technologies (RIT), has developed technology for creating high precision single crystal Johansson monochromators using Si and Ge materials. https://www.rigakuoptics.com/crystals.php
- A special manufacturing process (a) uses elastic bending to virtually eliminate lattice distortions which result from traditional bent crystal techniques and (b) produces very high-quality crystal surfaces and high focusing circle precision.
- These are manufactured using crystal materials of semiconductor origin for the quality of their atomic structure.
- These characteristics yield improved X-ray spectral resolution and intensity which are especially useful for demanding applications involving REE, trace-elements, and/or spectral interferences.

Basic details

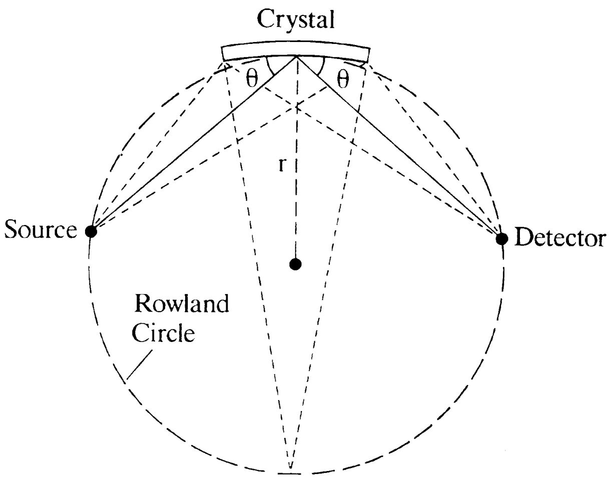
- Prototype Ge<111> crystals for EPMA have been produced for the ARL SEMQ spectrometer geometry and field tested at Concord University and Advanced Microbeam.
- These crystals provide a spectral range similar to PET but offset toward shorter X-ray wavelengths / higher energies.
- They perform well in comparison to LiF and PET crystals with respect to intensity, predicted detection limits, and spectral resolution.
- Ge<111> also suppresses higher-order diffractions, further reducing spectral interferences.

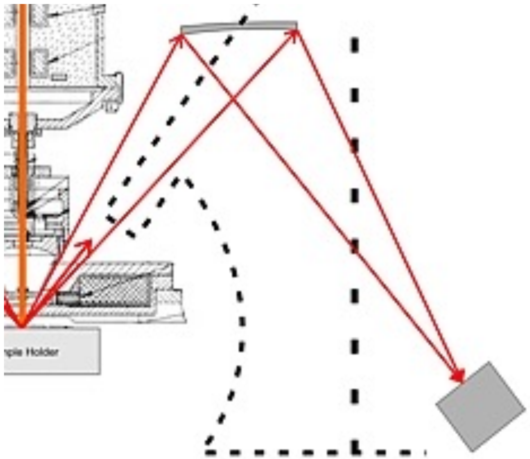
Basic details

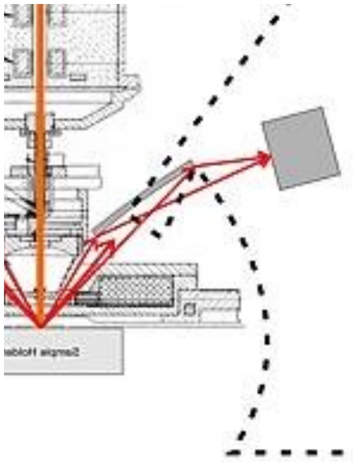
- Field test instrument configuration:
  - ARL SEMQ electron probe microanalyzer with 6 WDS spectrometers
  - 52.5 take-off
  - Roland circle diameter 127 mm (5.0 in) – Slightly smaller than standard JEOL (140 mm, 5.5 in), Smaller than Cameca (160 mm, 6.3 in), Larger than JEOL H-type (100 mm, 3.9 in)
  - Xenon and P-10 gas proportional counters
  - Multiple detector entrance slit sizes tested

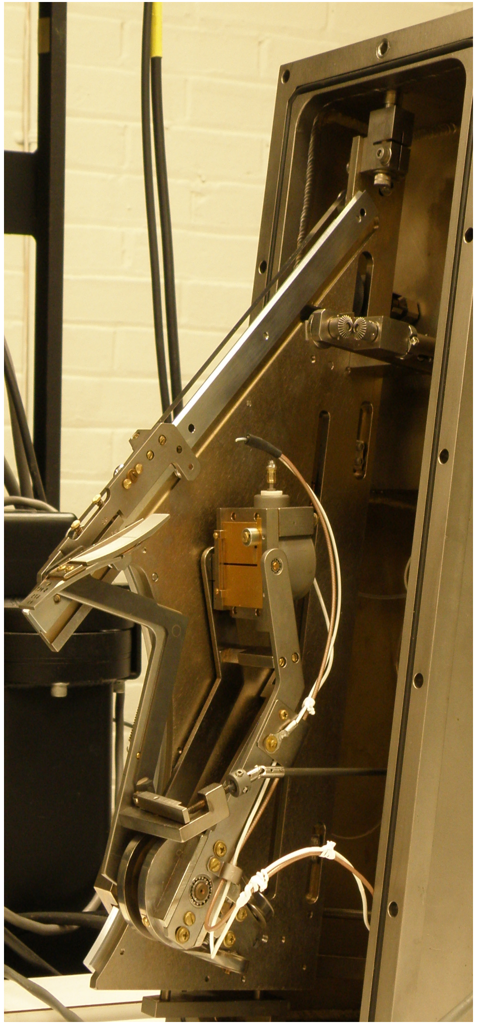
- ARL crystal dimensions:
  - 44 x 12.8 mm length x width
  - 563 mm^2 surface area
  - Same dimensions as OV60, RAP, TAP, PET, and LIF crystals

EPMA WDS Spectrometers utilizing Bragg-Brentano diffraction



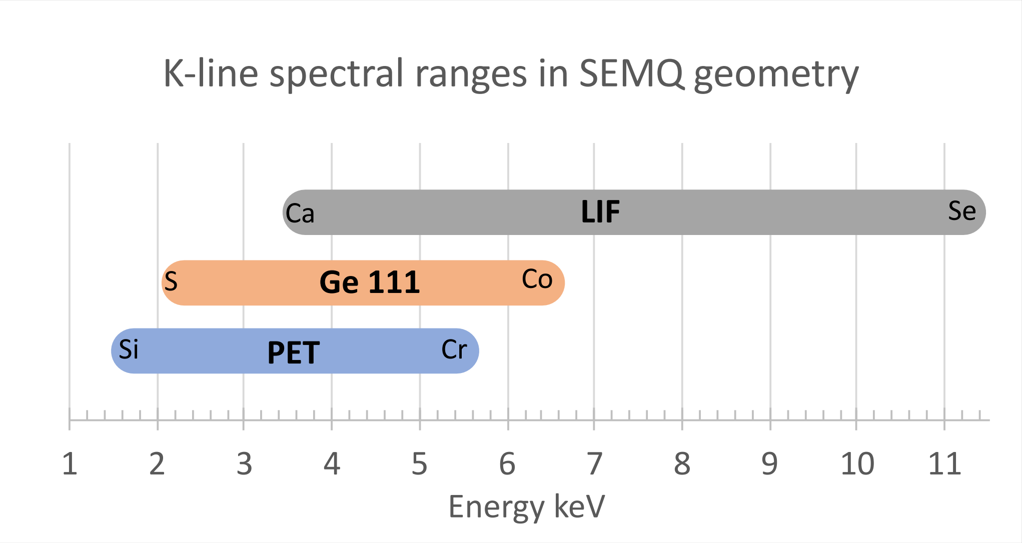


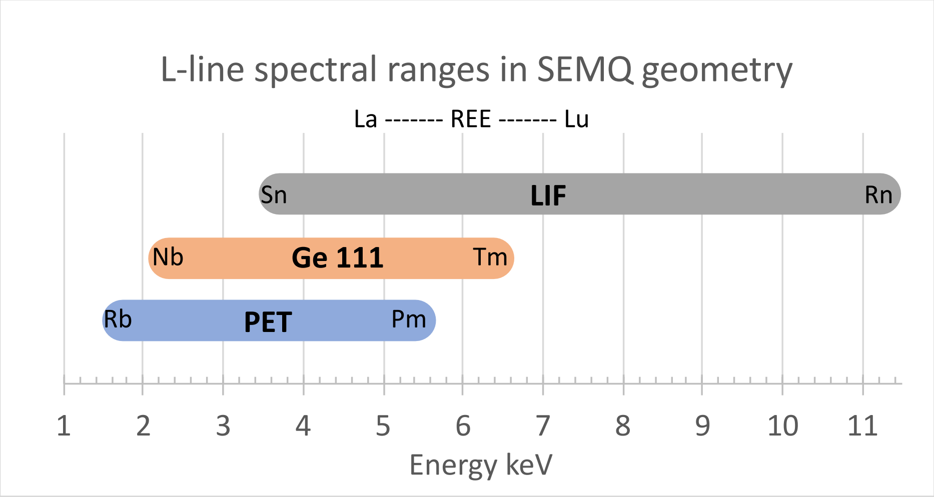


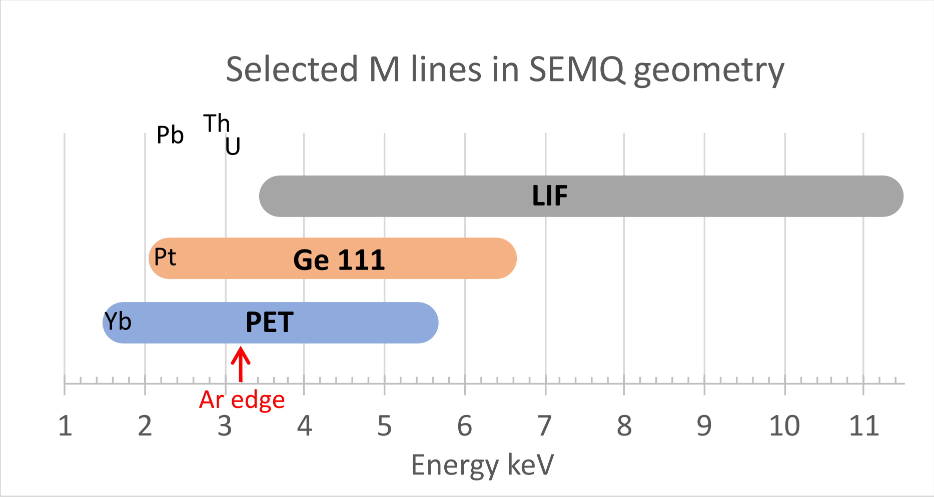


Ge 111 Spectral Range

- Covers S to Co K-lines
- Covers most REE element L-lines
- Also covers Pb, Th, and U which are often present in REE-minerals like bastnasite, monazite, allanite, and xenotime

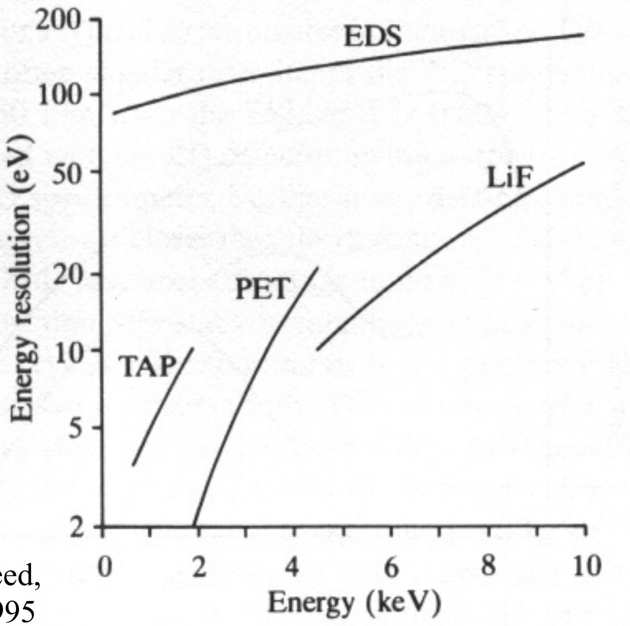




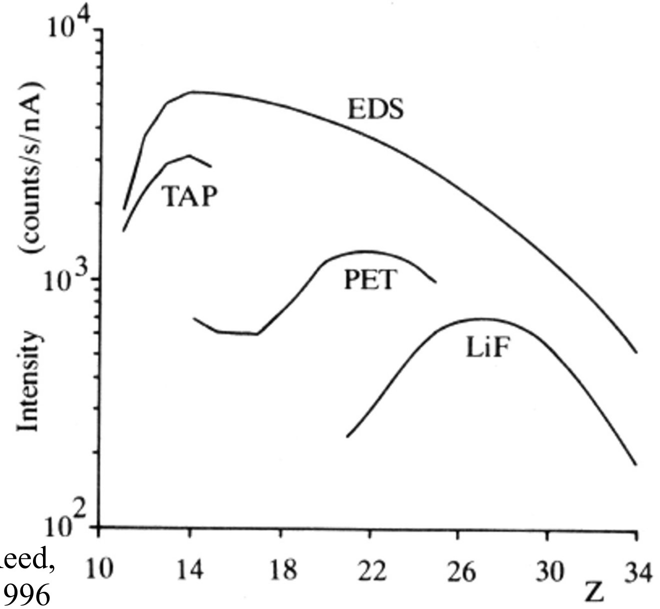


Traditional intensity vs. resolution trade-off

- PET to LIF:
  - Improves resolution, but lowers intensity
- LIF to PET:
  - Increases intensity, but degrades resolution
- LIF to Ge:
  - Improves both resolution **and** intensity



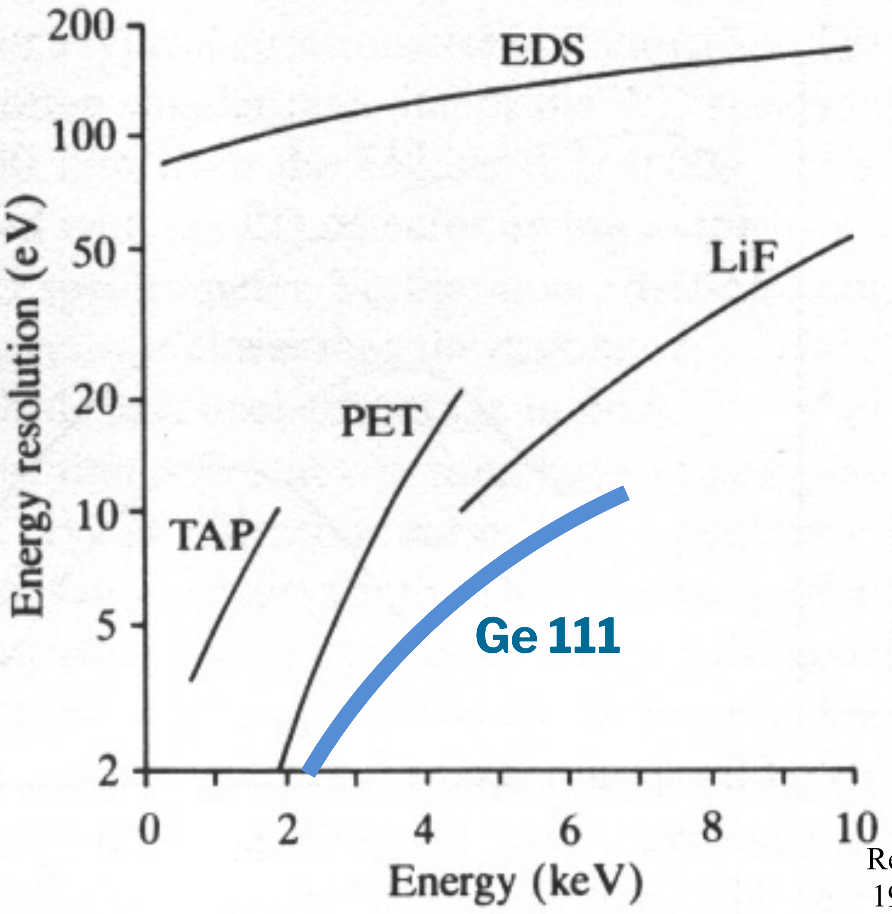
Reed, 1995



Reed, 1996

Spectral Resolution

- Ge 111 provides superior resolution to both PET and LIF. *Both peak widths and peak to background ratios are improved.*
- Switching from LIF to Ge increases intensity too!
- In contrast, switching from LIF to PET to gain intensity has a cost in loss of resolution.
- Ge intensity is intermediate between PET and LIF.



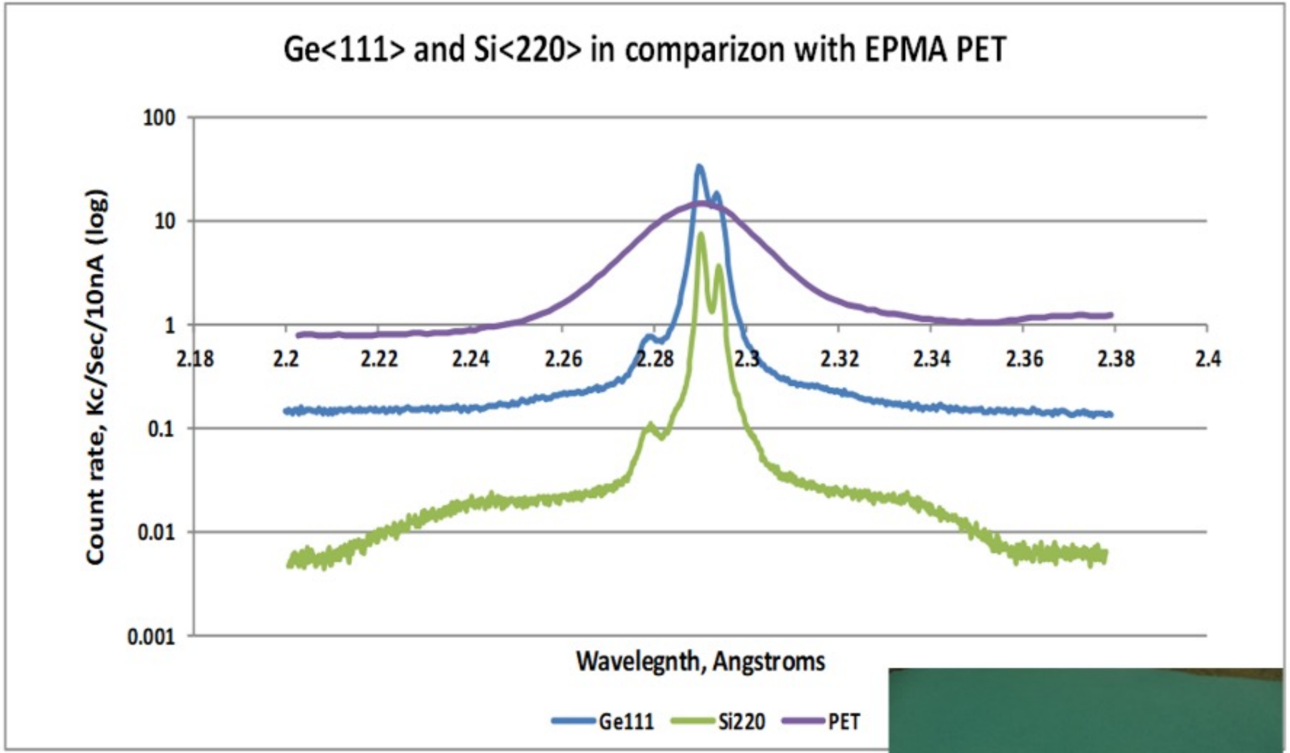
Reed, 1995

Rigaku internal lab test

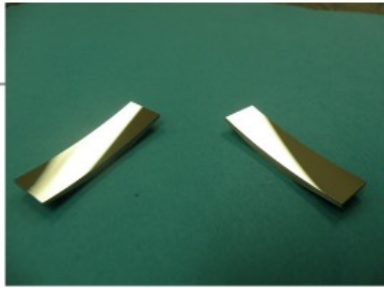
Ge and Si versus PET for EPMA

- Ge 111 and Si 222 both provide superior resolution and superior peak to background ratio versus PET

RIT Ge and Si and a typical EPMA PET crystals. Cr K α1-2 scan.



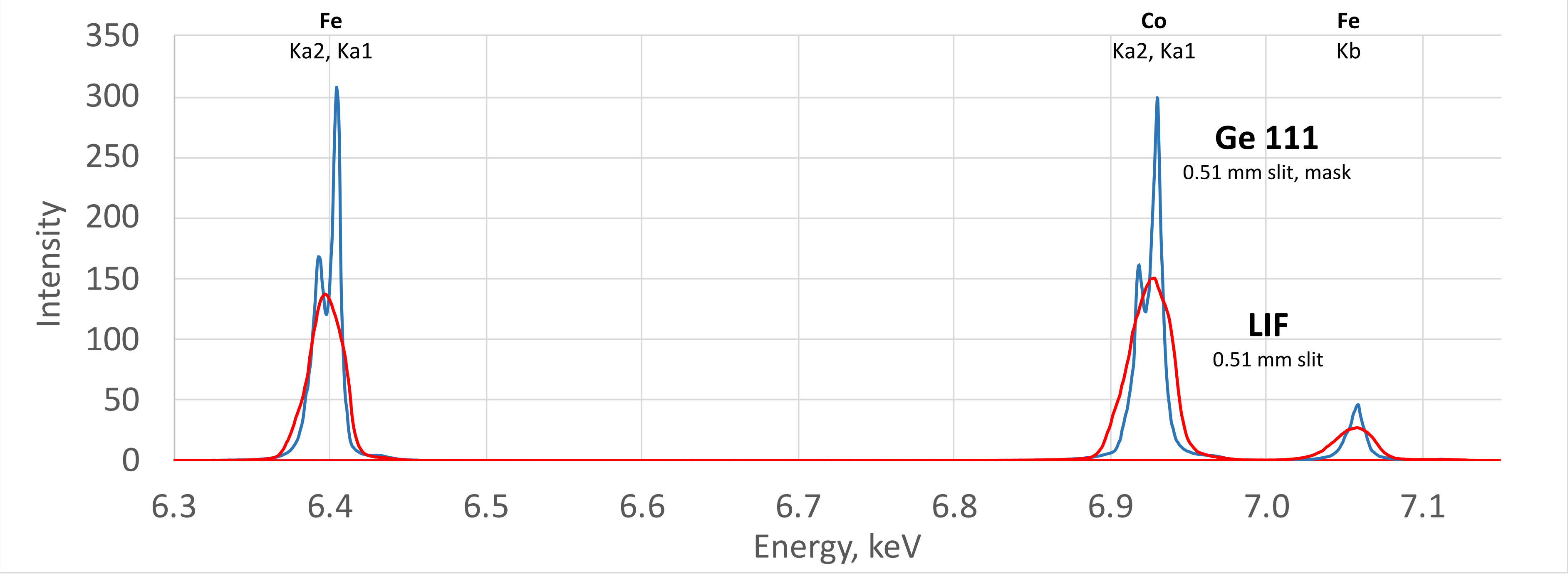
RIT crystals provides a significantly better resolution and one-two orders of magnitude higher peak-to-background ratio, improving the limit of detection.



Client field test, LIF comparison

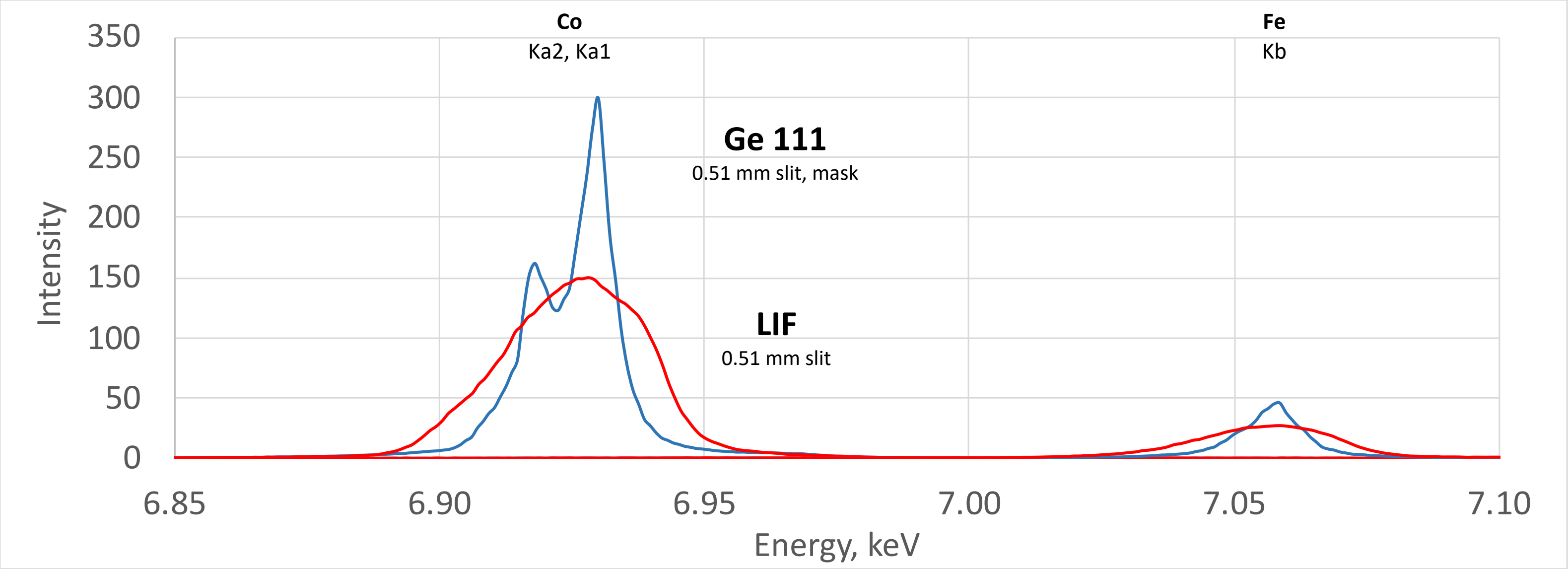
- Ge 111 provides superior resolution and superior intensities versus LIF

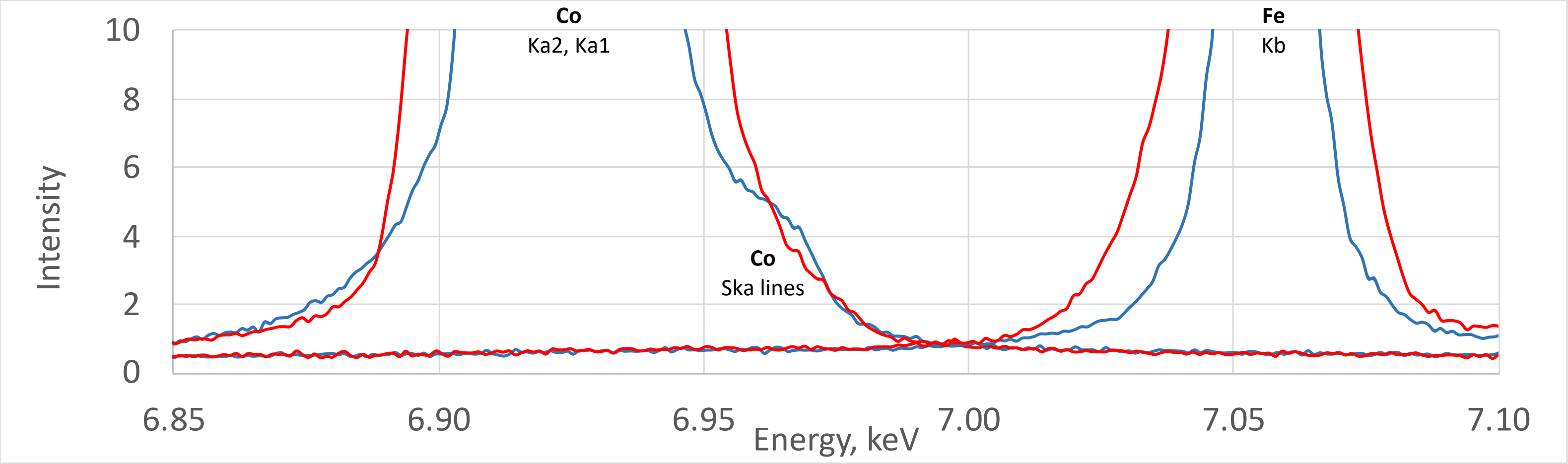
- This test was run with an additional mask on each side of the detector slit which further enhances resolution at the cost of intensity.
- In a separate test on V metal, removing the mask increased intensity by another +70% with only a small cost in resolution.
- Co is the last element in range for Ge in the ARL geometry. The physical spectrometer position here at the limit closest to the sample is *least* favorable for resolution but most favorable for intensity.



LIF comparison

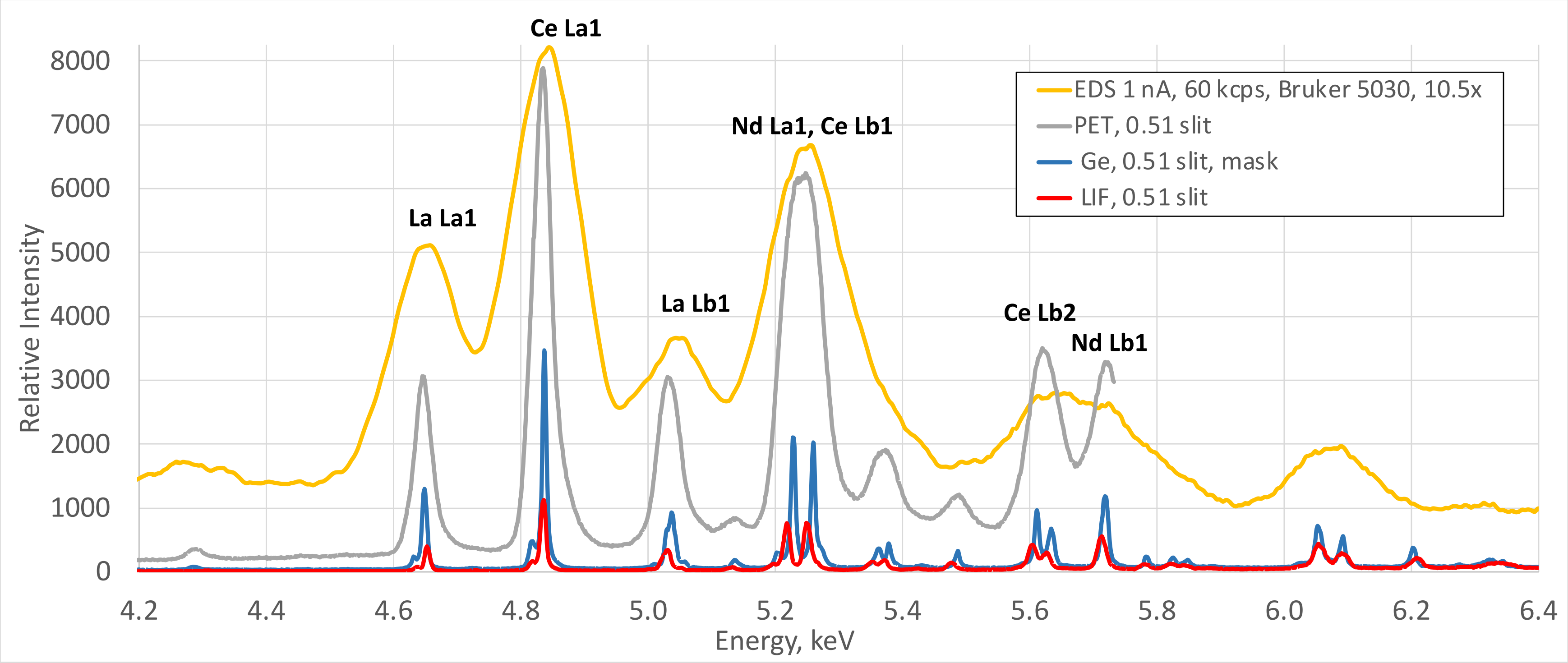
Co and Fe metals





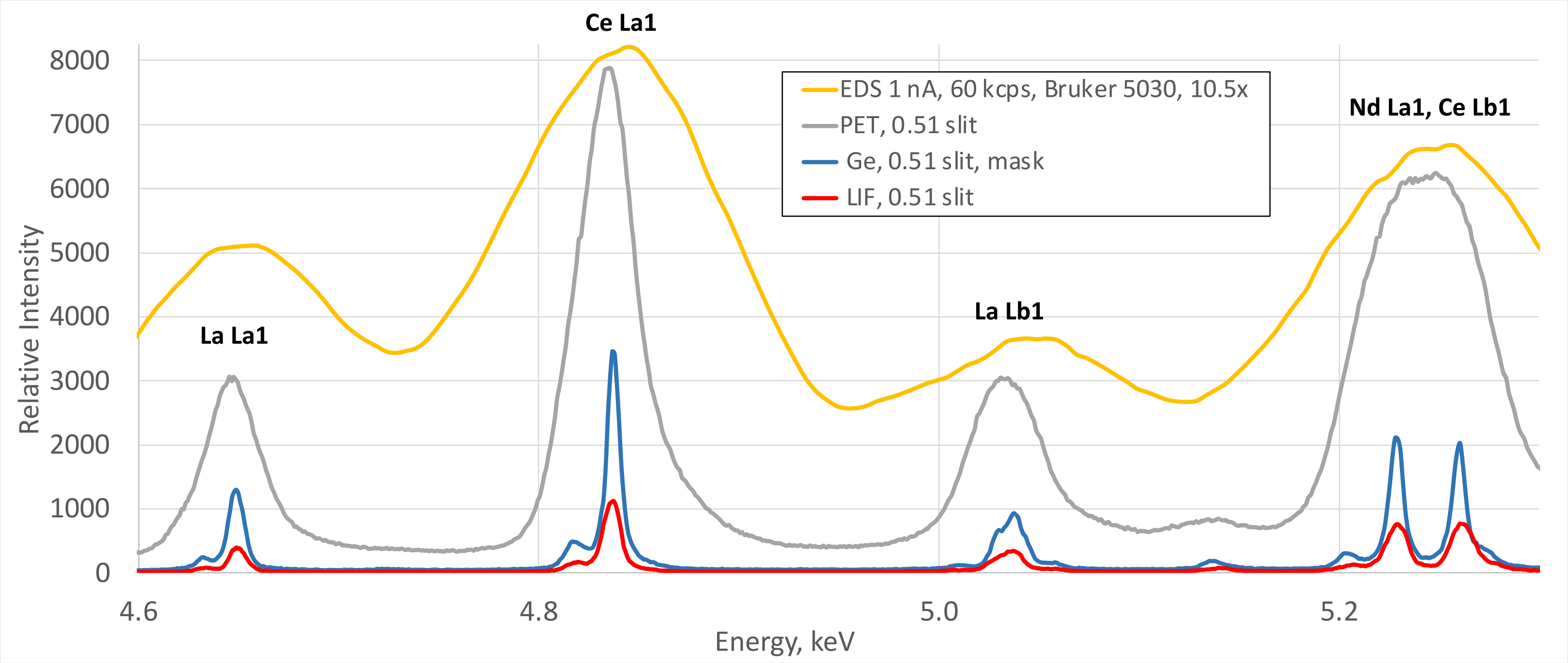
REE Example - Monazite (Ce,LREE,Th,U,Ca)PO4

- REE L-lines are many and closely-spaced, requiring excellent resolution to separate
- Ge 111 provides superior resolution and covers more REE elements versus PET



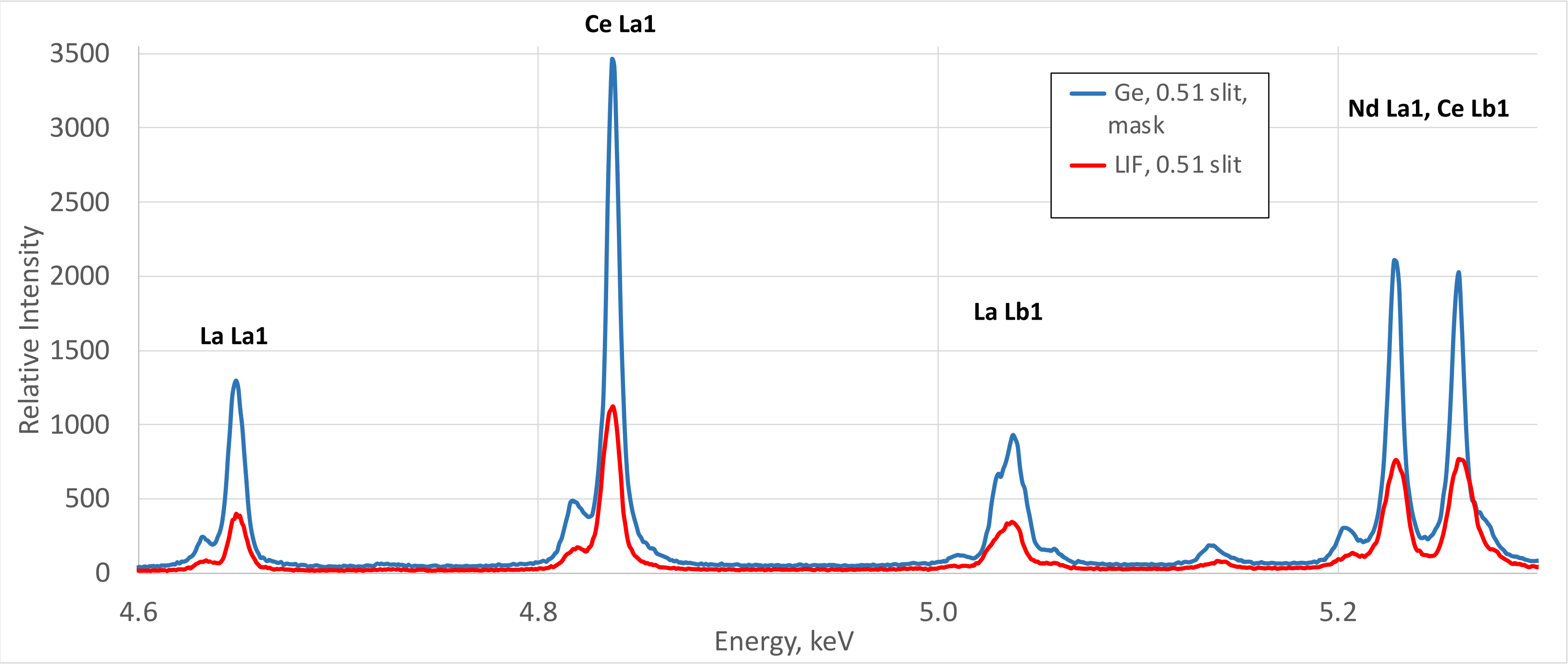
REEE Example - Monazite (Ce,LREE,Th,U,Ca)PO4

- Here Ge 111 provides much better resolution than PET and better peak to background ratio, but lower overall intensities



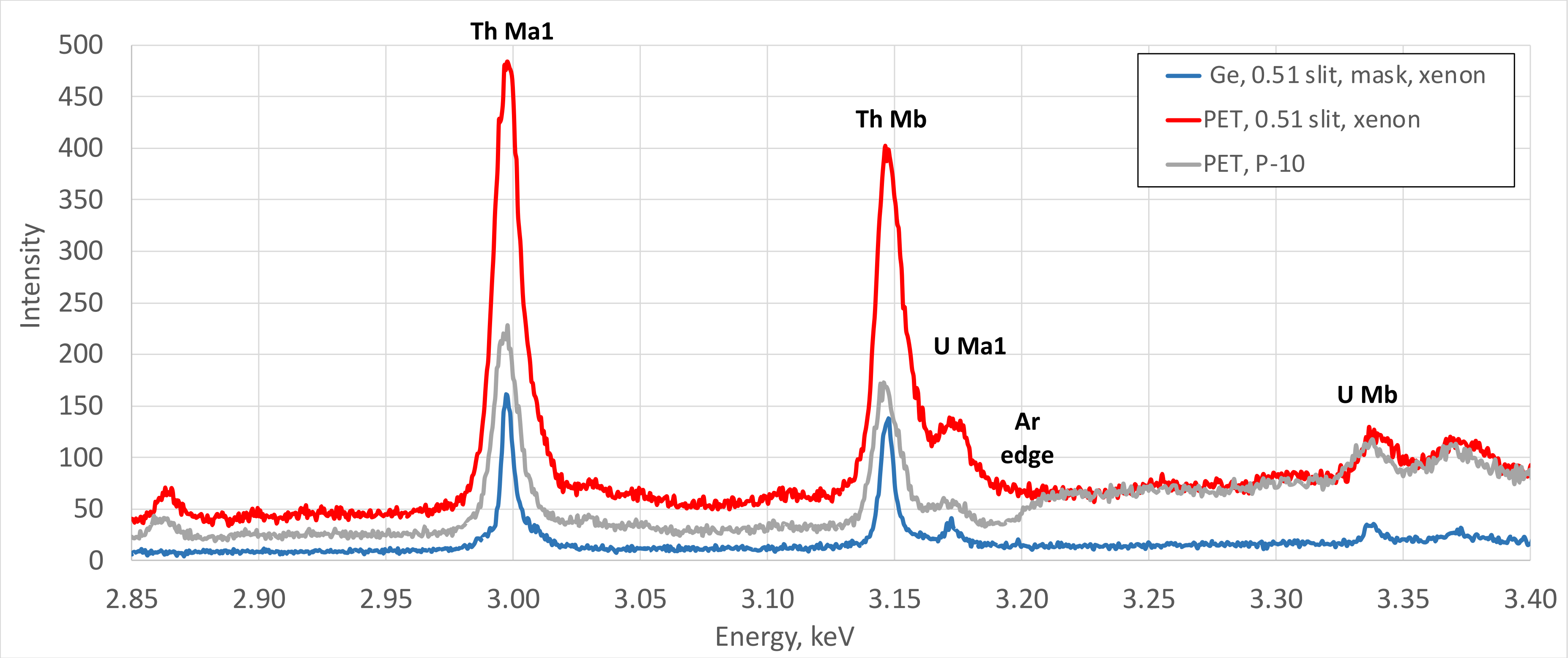
REEE Example - Monazite (Ce,LREE,Th,U,Ca)PO4

- Traditionally, LIF would be used for its better resolution versus PET
- But, Ge 111 provides some additional improvement in resolution plus substantially better intensities



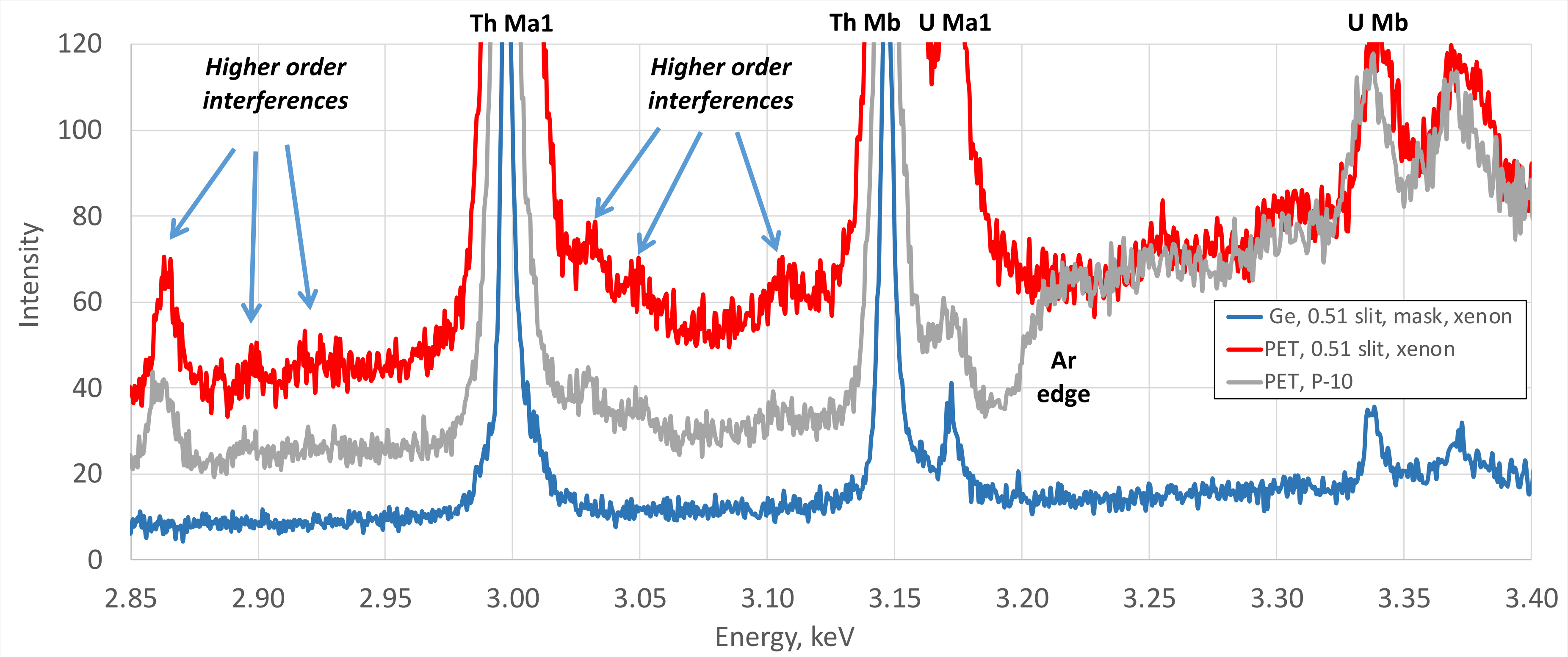
Th-U Example - Monazite (Ce,LREE,Th,U,Ca)PO4

- Ge 111 has greater resolution but lower intensity versus PET
- P-10 gas detectors lose intensity in this region due to the Ar absorption edge



Th-U Example - Monazite (Ce,LREE,Th,U,Ca)PO4

- Ge 111 also suppresses higher order diffractions resulting in far less spectral interference from REE L-lines.



Detection Limit Improvement Ge vs. LIF

Ba CDL99	
Ge - 2024	0.018
LIF - 2023	0.049
Ratio	2.7

- Method: Routine silicate glass Software: Probe for EPMA
- Focused on major elements with some minor and trace elements included
- Targets volcanic glasses from basalt to rhyolite with some elements ranging over 2-3 orders of magnitude
- Accommodates beam-sensitive materials and small (~4-5 micron) targets
- 6 WDS spectrometers, 14 kV, moderate 10 nA current, defocused beam, 3-minute acquisition
- MAN modeled backgrounds, so all acquisition time is peak time
- Ge used without mask in this test
- StDev scales with the square of peak intensity. 2x improvement in StDev requires 4x improvement in peak intensity if no other change.
- For trace elements, the peak/background ratio also has a strong effect on detection limits and StDev.

Target	Crystal	Mean or StDev	BaO wt%	Replicates
BHVO-2G	LIF - 2023	Mean	0.015	49
		StDev	0.021	
	Ge - 2024	Mean	0.014	55
		StDev	0.007	
		Relative improvement in StDev	3.1	
Lipari obsidian 3506	LIF - 2023	Mean	-0.001	49
		StDev	0.017	
	Ge - 2024	Mean	0.001	47
		StDev	0.006	
		Relative improvement in StDev	3.0	
NKT-1G	LIF - 2023	Mean	0.076	49
		StDev	0.018	
	Ge - 2024	Mean	0.080	55
		StDev	0.009	
		Relative improvement in StDev	2.0	
Orthoclase Glass GFOR	LIF - 2023	Mean	-0.003	49
		StDev	0.019	
	Ge - 2024	Mean	0.001	44
		StDev	0.006	
		Relative improvement in StDev	2.9	
		Mean improvement	**2.8**	

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