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Final Report on LDRD Program

New XAFS Spectroscopic Investigations in the 1-2keV Region

Joe Wong, M. Fröba and E. Tamura
Lawrence Livermore National Laboratory

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New XAFS Spectroscopic Investigations in the 1-2 keV Region

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Joe Wong, M. Fröba and E. Tamura
Lawrence Livermore National Laboratory, University of California,
PO Box 808, Livermore, CA 94551
Chemistry and Materials Science

Overview - Until recently x-ray absorption fine structure (XAFS) measurements in the 1-2 keV region remained a challenging experimental task. This was primarily due to the lack of an adequate monochromator crystal that possessed both the required x-ray properties (large d-spacing, high resolution and reflectivity) and materials properties (ultra-high vacuum (UHV) compatibility, damage resistance in a synchrotron radiation beam, absence of constituent element absorption edges and stability, both thermal and mechanical). Traditionally, XAFS spectra in this photon energy range have been measured in a piece-wise fashion using a combination of monochromator crystals: beryl (1010) which covers from 780 to 1550 eV, quartz (1010) which covers 1480-1830 eV, InSb (111) which covers 1800-3700 eV and Ge(111) from 2000 eV upwards [1].

Very recently [2], we have an experimental breakthrough in XAFS spectroscopy in this soft x-ray region. This energy region is of great importance for materials and basic research since the K-edges of Na (1070 eV), Mg (1303 eV), Al (1559 eV) and Si (1839 eV), the L-edges of some 4p elements from Ga to Sr and the M-edges of the rare-earth elements fall within this energy window of the electromagnetic spectrum [3]. YB_{66}, a complex binary semiconducting yttrium boride having a cubic crystal structure with a lattice constant of 23.44 Å [4] has been singled out as a candidate monochromator material for synchrotron radiation in the 1-2 keV region [5,6]. There is no intrinsic absorption by the constituent elements in this region, which can adequately be dispersed by the (400) reflection having a 2d value of 11.76 Å (see Fig. 1). In terms of vacuum compatibility, resistance to radiation damage, thermal and mechanical stability, YB_{66} satifies all the material requirements for use as a monochromator in a synchrotron beam . In the past few years, LLNL in collaboration with a number of other research institutes [7], has pioneered the development of this unique man-made crystal for use as soft x-ray monochromator with synchrotron light sources for materials science studies. This effort led to an RD-100 Award in 1991[8], and a successful installation of YB_{66} in January 1993 [2] as a double-crystal monochromator on the JUMBO beamline at SSRL.

Technical Accomplishments - The technical accomplishments are summarized as follows:
Experimental

• Observed direct effects of ligand electronegativity & coordination number on edge energy shift and whiteline intensity respectively in tetrahedrally coordinated Si-containing solids: Si,

SiC, Si_3N_4, SiO_2; and Al-containing compounds: Al_4C_3, AlN, Al_2O_3, AlF_3. Similar systematics were also observed for Mg compounds with ligands and coordination (see Fig. 2)

- Obtained first experimental evidence and elucidated the dependence of multiple scattering in both the Al and Si XANES on the Al-O-Si bond angle in a series of well characterized crystalline aluminosilicate sodalites of known Al-O-Si bond angle [9].
- Correlated intensities of bound-state transitions in the Al XANES spectra with the Al coordination in the Al_2SiO_5 polymorphic model compounds.
- Obtained correlation of disorder (inversion) in $MgAl_2O_4$ spinel with Mg K-edge XANES.
- Obtained correlation of width of Si K-edge whiteline with crystallinity in silica compounds.
- Obtained correlations of strength and shape of multiple scattering features with the degree of interactions between the host framework and guest molecules in silica sodalites.
- Identified dehyration sites in muscovite (mica) at the 6-fold coordinated Al octahedra.
- Completed Si K-edge measurements in orthosilicates (SiO_4 units), pyrosilicates (Si_2O_7 units), chain silicates SiO_2)n, layered silicates $(SiO_3)_n$ and 3-dimensional network silicates.
- Completed experimental work on a series of transition metal (3d, 4d and 5d) disilicides.
- Obtained quality Br L-edge spectra to establish feasibility of L-edge investigations for the elements: Ga, Ge, As, Br,..... , Rb, Sr which are important in environmental science.

Theoretical

- Successfully tested our computational code using a Fully Relativistic KKR Green Function Method, and obtained good agreement between the calculated and experimental spectra for both Cu and Al metal [10].
- Successfully developed an imbedded cluster approach to account for the long-range coulombic potential in ionic sytems to compute XANES of MgO in good agreement with experiment.

Beamline Instrumentation

- Over the last 2 years of operation, established the long-term stability of YB_{66} as an UHV compatible and high resolution monochromator in the 1-2 keV region
- Implemented a diamond window to isolate sample chamber from SPEAR UHV, thus enabling a wide range of powder specimens and model compounds to be measured under high vacuum conditions.
- Implemented a quick-change sample holder to maximize usage of beam time.
- Transpose data collection package from the original pdp 11/34 to a microVax.
- Successfully implemented a new Sc-doped YB_{66} crystal pair with a higher (~25%) energy resolution. Thus we have now the world's ***(only)*** two pairs of working YB_{66} monochromators on the JUMBO beamline at SSRL.

Our results in the past two years confirm not only an early prediction [5] for the use of YB_{66} as synchrotron radiation-compatible soft x-ray monochromator, but also open up a new energy window for studying the bonding and structure of Mg-, Al- and Si-bearing materials ***not readily possible*** before [11,12]. Furthermore, with YB_{66}, Al EXAFS spectra can now be routinely recorded to 2060 eV, some 500 eV above its K-edge to give a much wider and usable EXAFS data range to $k = 11$ Å^{-1}. In the case of Mg-bearing materials, XAFS spectra may now be recorded from 1250 to 2000 eV, a range of 700 eV above the Mg edge to yield a k_{max} value to ~13.5 Å^{-1} (see Fig. 3). This is compared with a much shorter k-range of ~8 Å^{-1} available with beryl monochromator which limits data to just below the K-edge of its Al constituent [13].

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Soft X-ray Monchromators for Synchrotron Radiation

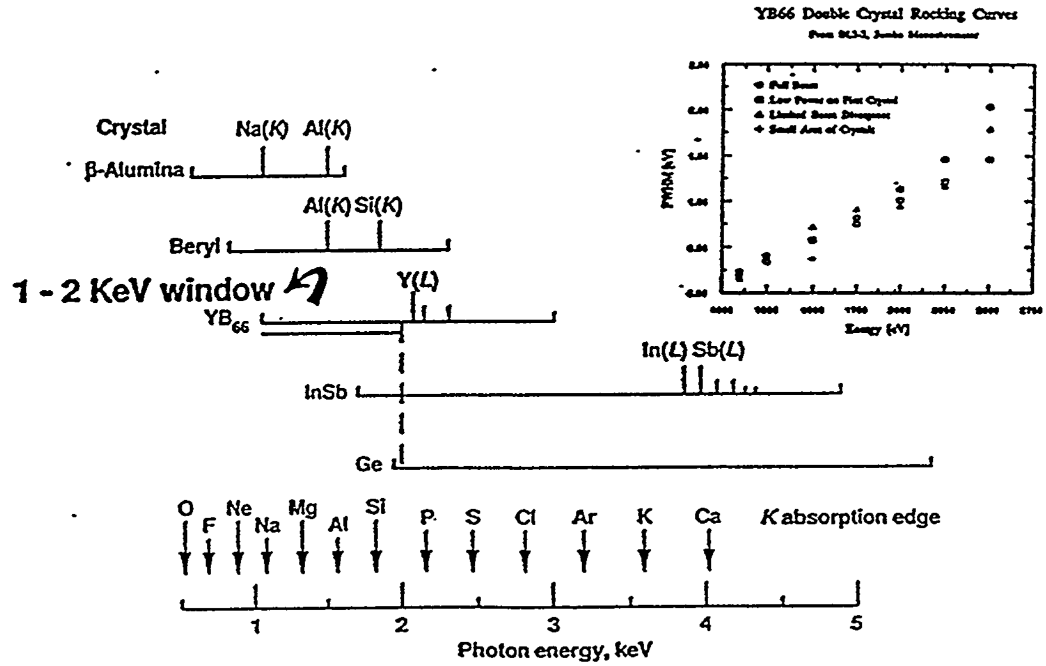

Figure 1. Soft X-ray monochromators for synchrotron radiation showing the unique features of YB_{66} in the 1-2 keV region. Positions of K absorption edges are marked by vertical arrows for the elements. Inset is a plot of FWHM of YB_{66} double crystal rocking curves as a function of photon energy under various beam conditions.

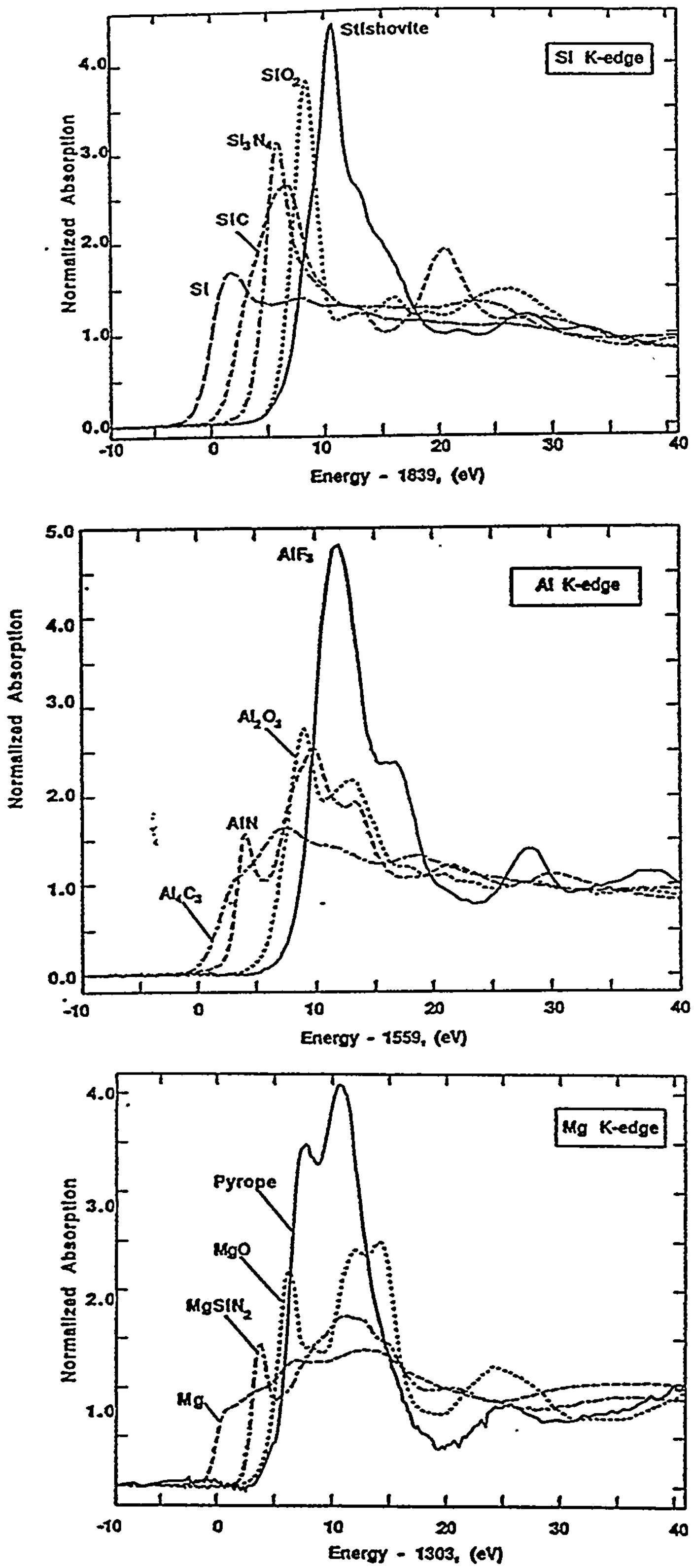

Figure 2. Normalized K-edge XANES spectra of selected Si, Al and Mg model compounds showing systematic edge shift and increase of whiteline intensity of the 1s →3p transition as a function of ligand type (electronegativity) and coordination number.

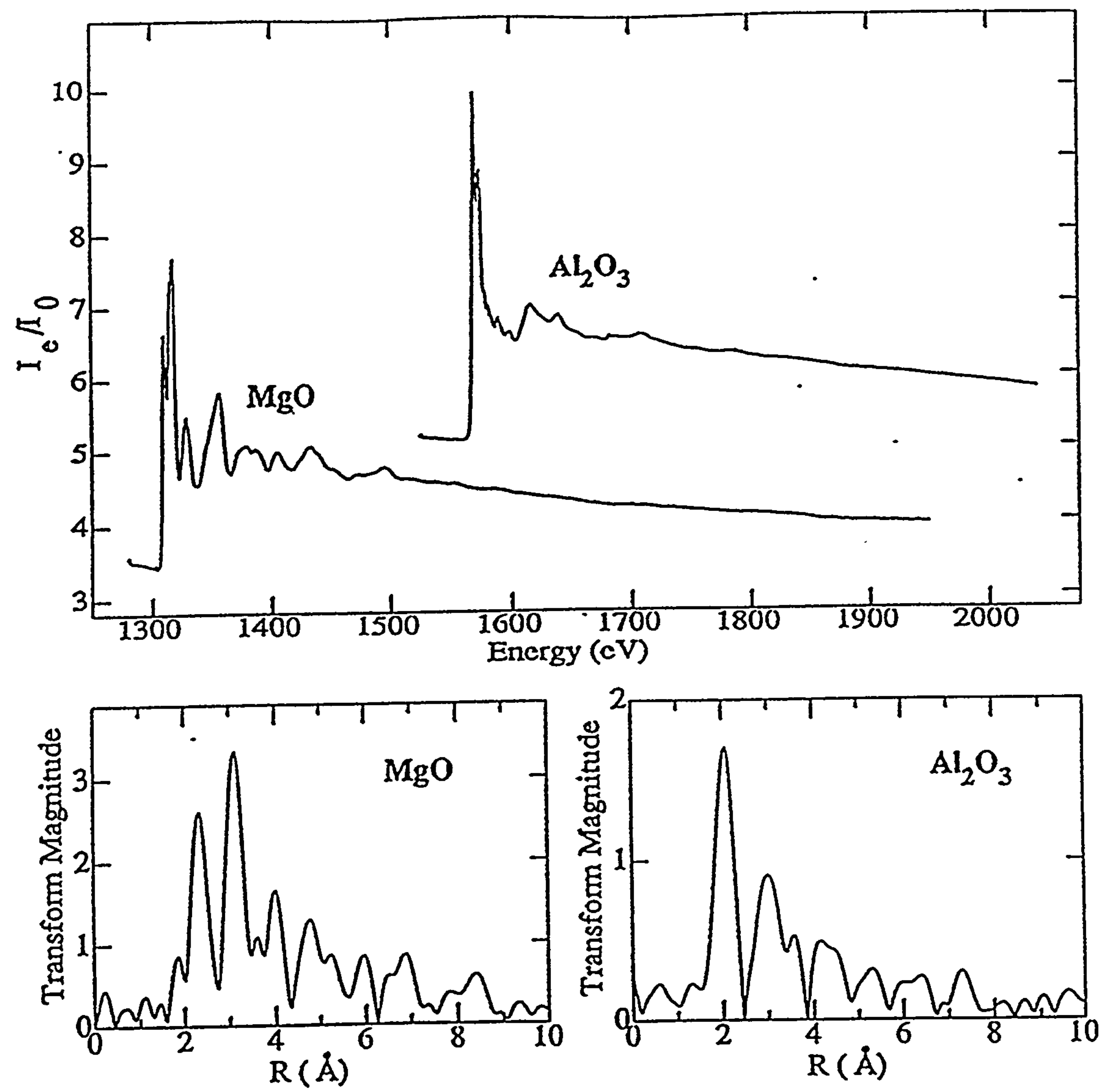

Figure 3. Experimental Mg K-edge XAFS spectrum of MgO and Al K-edge spectrum of Al_2O_3 illustrating the energy span of EXAFS data collectible with the YB_{66} monochromator. The small panels are the corresponding phase-corrected (for the 1st oxygen shell) and k^3-weighted Fourier transform of the extracted EXAFS signals.

L- & M-edge Spectroscopy in the 1-2 keV Region

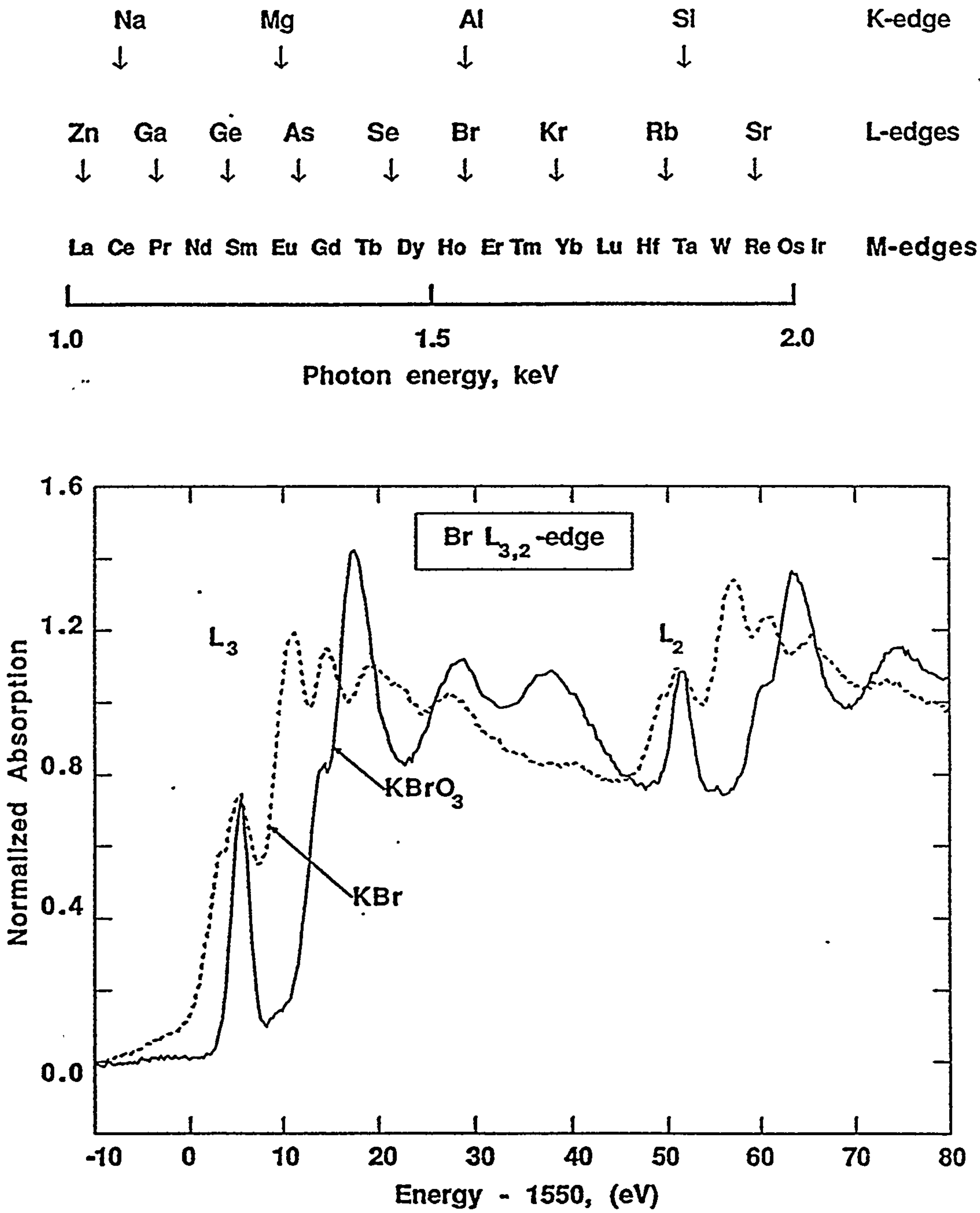

Figure 4. List of elements with L and M absorption edges in the 1-2 keV (top). Normalized $L_{3,2}$-edge XANES of Br in KBr and $KBrO_3$ showing richness of the spectral features with bonding and structure of Br in each of the material (bottom).