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STABILITY OF SOME SOFT-X-RAY MONOCHROMATOR CRYSTALS IN SYNCHROTRON RADIATION

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Abstract

The stability in synchrotron radiation of β -alumina and beryl has been investigated by exposing the crystals in a white beam at CHESS operating at 5.2 GeV electron energy over a period of ~100 hours at an average radiant power of 28 W/cm². Rocking curves at the CuK α energy were used to monitor the diffraction properties before and after exposure to synchrotron radiation. A Si(220) crystal was used as the first crystal. It was found that both materials exhibit no catastrophic material failure. β -alumina is clearly proven stable with no degradation of its rocking characteristics. There was in fact indication of reflectivity improvement after exposure. Results on beryl are not conclusive because the starting material (a mineral specimen) had a lot of inherent microstructural and crystallographic defects. Rocking curves in the soft x-ray region at 10.5 Å were also determined using a (10 $\bar{1}$ 0) RAP crystal as first crystal. A 19-layer 50 Å d-spacing Nb-C sputtered film was also characterized for comparison.

Introduction

There is revived interest and need for crystals for long wavelength spectroscopy in the soft x-ray region of 6-30 Å⁽¹⁾ using high intensity γ and band synchrotron radiation. Property requirements for use as soft x-ray dispersing elements in synchrotron sources may be classified according to (1) x-ray dif-

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is 1980eV, which is just below the K-edge of phosphorus. With increasing interest in lower Z element EXAFS, say down to Na at ~1KeV at the Brookhaven NSLS, larger 2d crystals are desirable for the softer x-ray region (see Table 2). Mica has been used at LURE in Orsay with moderate success⁽⁵⁾. Beryl and β -alumina are also attractive alternatives, especially because of their materials properties. Preliminary calculations and recent x-ray tube measurements by Burek⁽⁶⁾ indicated these two materials possess good diffraction properties in the soft x-ray region. In fact a 3-crystal system using Ge(111), InSb(111) and beryl (1010) has been developed at Stanford to extend the soft x-ray range down to 800eV.⁽⁷⁾

Multilayer metal films are synthetic thin-film structures obtained by sequential vapor deposition (usually by sputtering) of alternate layers of 2 dissimilar metals (like Nb, Cu) or a metal and a nonmetal (e.g., W, C). The effective 2d value of the structure is obtained by controlling deposition rates of each composite film⁽⁸⁾. Two synchrotron radiation exposure tests, one done at SSRL for a 2 1/2 months and another at ACO for 300 hours for some W/C films, showed no physical damage and no detectable reflectivity change at CuK_α energy⁽⁹⁾.

These multilayer metal films are promising as soft x-ray dispersing elements as they satisfy essentially all the materials requirements of vacuum compatibility, thermal stability, fabricability in large-area pieces by sputtering (e.g., 2" diameter or larger), radiation resistivity because of good electrical and thermal conductivity. Furthermore, an additional advantage is that when deposited on a bendable substrate, like Si wafers, they can also be used to focus the x-ray beam. Disadvantages, however, are the small glancing angle and the large width of their rocking curves⁽¹⁰⁾.

However, little is known about the stability of β -alumina and beryl in a synchrotron beam. This is of particular concern in the case of β -alumina, in which the mobile Na^+ ions are situated in planes binding the spinel block layers in the structure. The present paper reports results of stability studies of β -alumina and beryl exposed in a white beam at CHESS. The rocking curves at $\text{CuK}\alpha$ were used to monitor the diffracting properties before and after 100 hours of exposure in the beam. In addition, the rocking curves and structure uniformity of a 19-layer $21\text{\AA}$ Nb + $29\text{\AA}$ C sputtered film have also been measured to evaluate the potential usefulness of multi-layer metal films as soft x-ray monochromator in a synchrotron radiation source.

Experimental

Single crystal specimens of (002)-oriented β -alumina about $20\text{mm} \times 20\text{mm} \times 2\text{mm}$ thick were cut from a parent boule $\sim 25\text{mm}$ diameter and 15cm long grown by Carbon and Carbide Inc., San Diego. Specimens of $(10\bar{1}0)$ -oriented beryl about $30\text{mm} \times 50\text{mm} \times 3\text{mm}$ thick were cut from a mineral specimen obtained from the National Stockpile (at Curtis Bay, Md.). The polished crystals were prepared by first rough-cutting with a 15 mil wire coated with 100 mesh (125 μ) diamond. The cut face was x-ray oriented to within 0.25° of the desired orientation in a two circle x-ray diffractometer. A flat was ground by feeding the oriented crystal directly from the diffractometer to a diamond grinder. Polishing were done successively with 500 mesh diamond, 600 mesh SiC 800 and 1200 mesh alumina, and finally with $0.03\mu\text{m}$ Al_2O_3 .

Rocking curves in the hard x-ray region were measured with $\text{CuK}\alpha$ radiation from a tube source operating at 20kV, 15 mA. A $\text{Si}(220)$ was used as a first crystal. To check for uniformity each crystal was rocked at 4 positions obtained by rotating 90° about an axis normal to its diffracting surface. Rocking curves in the soft x-ray region were measured in a double crystal

vacuum spectrometer. Radiation from an OFHC copper anode operating at 8kV, 30mA was monochromatized at $10.5\text{\AA}$ using a freshly cleaved (10 $\bar{1}$ 0) RAP (tributyl acid phthalate $2d = 26.12\text{\AA}$) as a first crystal. Using a match pair of crystals, the width of RAP at $10.5\text{\AA}$ was determined to be ~ 70 arc seconds which is much narrower than any of the test samples (see discussion). Synchrotron radiation exposure experiments were performed in air at the White Beam Station, Cave B, in CHESS with CESR operating at 5.2GeV and 10mA initial current. Accumulative exposure times of ~ 100 hours were used. The average radiant power in each specimen was calculated to the 28W/cm^2 .

Results and Discussion

(1) Synchrotron Radiation Stability and Hard X-ray Measurements

β -Alumina

Fig. 1 shows the CuK α rocking curves for a polished crystal of β -alumina rotated at right angles about an axis normal to the (002)-surface. At 0° and 180° orientations the α_1 and α_2 lines were resolved (i.e. no overlap at half width heights). The widths of the α_1 line are 108 and 120 sec of arc and agree to within 10%. Compared with the Darwin width of 11 sec of arc calculated⁽¹¹⁾ from the known structure factor for the (002) reflection⁽¹²⁾ the measured width is about 10-fold broader. In Table II, $\Delta\theta$ for both β -alumina and beryl are calculated for various soft x-ray energies assuming an energy resolution ΔE of 1eV. Also, the curves for the 90° and 270° orientations are much broader still indicative of mosaic spread giving rise to multiple peaks and loss of resolution of the α_1 and α_2 peaks. These results were obtained after the polished crystal was annealed at 400°C at 10^{-6} Torr for 2 hours and serve to illustrate the degree of uniformity of the specimen used.

The same polished crystal was used sequentially to test the effect of thermal anneal and synchrotron radiation exposure. In Fig. 2 the CuK α rocking curves for the as polished, 400°C anneal at 10^{-6} Torr for 2 hours, 1650°C

anneal in N_2 in a reservoir of β -alumina powder, and after 100 hours of synchrotron radiation exposure at CHESS are shown. The $400^\circ C$ anneal essentially eliminates the effects of adsorbed or diffused water in the polished crystal while the $1650^\circ C$ anneal relieved any mechanical strain or damage due to grinding and polishing. After irradiation in the synchrotron beam, a faint yellow band is visibly detectable in the area where the beam hits the specimen, indicative of color centers. There was no catastrophic material failure. The width of the rocking curve remained essentially unchanged as that prior to exposure. This is encouraging and shows that β -alumina is synchrotron radiation stable, at least over 100 hours exposure at an average radiant power of $28 W/cm^2$ at 5.2 GeV electron energy at CHESS.

Cleaved specimens of β -alumina were also tested. The (002) planes which contain the mobile Na^+ ions in the β -alumina structure cleaves easily, and hence are prone to moisture attack. The $CuK\alpha$ rocking curves for an as-cleaved crystal which was then sequentially exposed in laboratory air for 4 days and synchrotron radiation for 100 hours are shown in Fig. 3. There is definitely loss of reflectivity after air exposure due to moisture attack. The peak intensity at the α_1 energy dropped to 62% of the as-cleaved value. Interestingly enough exposure to synchrotron radiation brought the peak reflectivity to 75% of the original as-cleaved value, and appears to indicate some radiation annealing effects on the air exposed crystal, probably due to water desorption.

Beryl

Results on the beryl specimens are less conclusive. Polished surfaces of the materials, even well away (a few mm) from the original mineral surface, revealed micro- and macroscopic fissures as well texturing. X-ray fluorescence analysis indicated that K, Cs and Fe are present beside the basic Be, Al, Si, and O elemental constituents. The Fe impurity is inhomogeneously distributed as can be seen from the variation of the brown coloration of the

specimen. Laue reflection photographs indicated that the mineral specimen is not a truly single crystal. These structural features are reflected in large width of the rocking curve. At $\text{CuK}\alpha$, the width varies from 760 to 1600 sec of arc depending on specimen area. No resolution of α_1 and α_2 was observed except for two areas out of the sixteen measured. Even then, in these two areas the width at the α_1 energy varies from 1522-1196 sec of arc. The 2nd order curves are narrower and were measured to be 350 and 640 sec of arc in two areas. These widths were reduced further to 210 and 300 sec of arc respectively after 100 hours exposure in the synchrotron beam. It appears that beryl suffer little if any radiation damage in these experiments.

Multi-layer Metal Film

The $\text{CuK}\alpha$ rocking curve (Fig. 4(a)) of a 19 layers of Nb-C composite film is characterized by a broad, asymmetric line at 0.88° , the width of which is 456 sec of arc and varies somewhat with area of the specimen. The film was prepared by sequential sputter-deposition in a rotating Si substrate under a multi-target magnetron machine. A SIMS (secondary ion mass spectrometry) in-depth profile (Fig. 4b) analysis shows that indeed the film consists of 19 layers with rather good overall in depth uniformity. The spatial resolution of this technique is not high enough to determine quantitatively the regularity and sharpness of the Nb-C interface. Auger electron spectroscopy is more appropriate for this purpose. We can estimate the expected width of the Bragg peak using the Scherrer equation⁽¹³⁾ $\Delta\theta = 2(\lambda^2 / a^2 \sin^2 \theta)^{1/2}$ for line broadening where $\Delta\theta$ = width of a Bragg line at θ , λ = x-ray wavelength, N = average number of Nb-C layers participating in the diffraction event and a = average thickness of the Nb-C layers. We calculated from the estimated width of the α_1 component shown in Fig. 4(a) $N = 887$. This corresponds to $a = 46.7\text{\AA}$ which is in excellent agreement with $50\text{\AA}$ obtained in thickness calibration of the sputtered film.

(2) Soft X-ray Measurements

A pair of RAP crystals were first set up in the parallel mode to reflect x-ray near $10.5\text{\AA}$ (1180eV) from the copper anode operating at 8kV and 30mA. Care was taken to place a fresh RAP crystal face in the first crystal position so as to insure that the rocking curves were characteristic of non radiation damaged RAP. One crystal was rocked, and the rocking curve so obtained had a full width at half maximum of between 130 and 140 seconds. In order to check on the possible influence of higher order reflections, the x-ray tube voltage was reduced to 3000 volts. The second order reflection is nearly forbidden in RAP, for these wavelengths, and on the third order reflection is beyond the short wavelength limit at 3000 volts excitation. The rocking curve was remeasured, and found to be unaffected in width by the lowered excitation voltage. Therefore, in measurements carried out as $10.5\text{\AA}$ with this same RAP crystal in the first position, the excitation voltage could be increased to the original value without concern for the effect of higher order reflections.

The angular width due to the first RAP crystal alone was, from the above measurements, determined to be in the neighborhood of 70 arc seconds. This width is much narrower than the widths of any of the test samples; therefore, in test measurements nearly the entire width was due to the beryl, β -alumina, and Nb-C multilayer respectively.

With RAP as the first crystal, the rocking curves of as-cleaved β -alumina and as-polished beryl and the 4th order rocking curve for the Nb-C multilayer film were measured. Some checking for tilt effects was carried out. The beryl rocking curve did not change much for 90° and 180° rotations of the crystal mount. Similarly, the β -alumina rocking curve was not much changed by a 180° crystal rotation. It seems inconceivable that a rocking curve as broad as that exhibited in the Nb-C data could be significantly effected by tilt error; thus,

only one measurement was taken of this sample. The results are summarized in Table III.

Concluding Remarks

The exploratory tests performed in the present study are quite encouraging especially in the case of β -alumina for which the material stability in a high energy synchrotron radiation beam is now established. In the future, we plan to characterize systematically the soft x-ray properties of β -alumina in-situ with a synchrotron beam. With better quality beryl specimens, we hope to re-examine the synchrotron stability of this material. The results on the Nb-C film is interesting. We plan to study such multilayer films with larger N value to achieve narrow $\Delta\theta$ value or higher energy resolution. Also, $\text{Ca}_{0.6}\text{Al}_2\text{O}_3$ of the magnetoplumbite structure⁽¹⁴⁾ is a possible substitute for β -alumina to obviate the water problem. Another possibility is provided by cubic pyrochlores $\text{A}_2\text{B}_2\text{O}_7$ which have lattice parameter $\sim 10\text{\AA}$ ⁽¹⁵⁾. The 2d values for the (111) planes = $12\text{\AA}$ and will disperse x-ray above 1.1keV. However, these will require substantial development in crystal growth to obtain large single crystal specimens.

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TABLE 1

Range of Monochromated Energies as a Function of Bragg Angle
for Various Large d-Spacing Crystals

Crystal	Ge(111)	InSb(111)	Beryl(10 $\bar{1}$ 0)	Mica(002)	β -Al ₂ O ₃ (002)	MLS*
2d(Å)	6.532	7.48	15.95	19.84	22.53	30
$\theta = 10^\circ$	10,930	9551	4475	3596	3169	2380
15	7333	6404	3002	2414	2126	1596
20	5549	4846	2272	1827	1609	1208
30	3796	3314	1554	1249	1100	826
40	2952	2578	1208	872	856	643
50	2477	2163	1014	813	718	539
60	2191	1913	897	721	635	477
70	2019	1763	826	665	585	439
80	1982	1683	789	634	558	419

*MLS stands for multilayer structure

Table

Calculated θ Values for Beryl and β -Alumina
at Various Energies Assuming an Energy Resolution ΔE of 1eV

Energy(eV)	$\Delta \theta$ (Sec)	
	Beryl(10 $\bar{1}$ 0) 2d=15.95Å	β -Alumina(002) 2d=22.53Å
3000	18	13
2500	27	19
2000	43	30
1500	83	54
1000	253	136

Note: $\theta = \frac{\Delta E}{E} \tan \theta$, θ corresponding Bragg angle

TABLE III

Width of Rocking Curve $\Delta\theta$ and Energy Resolution ΔE of β -alumina
Beryl and Nb-C Film at $10.5\text{\AA}$ (1180eV)

System	$\Delta\theta$ (sec)	ΔE (eV)
β -alumina (cleaved)	580	6.6 ± 0.5
Beryl (polished)	1560	10.5 ± 1.0
Nb-C film (as deposit)	5600*	80 ± 20 (very roughly)

*This rocking curve is so broad that the tails fade into the x-ray scattered radiation.

Fig. 1 XPS spectra of a polished crystal of p-nitrobenzene as a function of rotation to the (001) surface. The crystal was first "degaussed" by annealing at 400°C.

Fig. 2 XPS spectra of p-nitrobenzene: (a) as polished; (b) after annealing at 400°C for 2 hr at 10^{-6} Torr; (c) after annealing at 1650°C in O_2 ; and (d) after 120 hr exposure to CH₃F at 5.2 eV electron energy.

Fig. 3 XPS spectra of a cleaved p-nitrobenzene (7621): (a) as cleaved; (b) after 4 days exposure to air; and (c) after 100 hr exposure to cyclohexane.

Fig. 4 (a) XPS spectra of a 10-layer film of p-nitrobenzene on Si at a grazing angle of 0.00°; (b) SPS depth profile of the same film showing the 10-layer structure.