Interlayer confinement mediated oxidation of Americium by sodium bismuthate and stability of its higher redox states in acidic solution

Parveen K. Verma, Arunasis Bhattacharyya*, Prasanta K. Mohapatra *

Radiochemistry Division, Bhabha Atomic Research Centre,
Mumbai, Maharashtra, INDIA

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Table S1: Common methods for oxidizing Am^{3+} to AmO_2^{2+} in acidic medium.

Initial	Conditions	Final	Ref.
Am^{3+}	$NaBiO_3$ at room temperature in nitric acid	AmO_2^{2+}	1, 2
	$NaBiO_3$ at room temperature in H_3PO_4		3
	Cu^{3+}-iodate in nitric acid		4
	Excess $(NH_4)S_2O_8$ in 0.1 M nitric acid at 85°C		5
	Na_4XeO_6/Ag^+ in 1 M nitric acid		6
	0.013 M $CsSO_4F$/0.001 M Ag^+ in 0.9 M nitric acid		7
	0.5% $AgNO_3$ / 2.5% $(NH_4)S_2O_8$ in 0.3 M nitric acid		8
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$NaBiO_3$ characterization

X-ray diffraction analysis

The XRD data of the $NaBiO_3$ used in the present study matched well with the JCPDF file number PDF # 30-1161, suggesting the presence of hydrated form of $NaBiO_3$ as $NaBiO_3.xH_2O$ (x= 2-3)(NBO).[12] The previous literature studies on the Am^{3+} oxidation by $NaBiO_3$ is mainly done in HNO_3 medium, except that by Rice et al.,[3] where other acidic mediums were chosen Therefore, it essential to understand the structural changes in $NaBiO_3$ upon contact with HNO_3. The previous study[13] in this direction showed color change of pristine $NaBiO_3$ to dark brown upon contact with HNO_3. The study used different HNO_3: $NaBiO_3$ molar ratios and the mixture were equilibrated for 2 hours and the structural changes were followed by XRD. Since the overall composition, purity, nature of impurity in sodium bismuthate, can vary from source to source and can have profound effect on its properties; we have revisited the effect of HNO_3 on

$NaBiO_3$ at a lower acidity (pH 1) suitable for the present studies. The $NaBiO_3.xH_2O$ (x= 2-3)was equilibrated with pH 1 HNO_3 for 24 hours and the solid was collected after centrifugation, air dried followed by which the XRD was recorded. The color of $NaBiO_3.xH_2O$ (x= 2-3) changed from light yellow to brown (Fig. 1(a)) in <30 minutes of equilibration with pH1 HNO_3 which was also observed by others.[13] The XRD of the acid equilibrated $NaBiO_3.xH_2O$ (x= 2-3)(H^+-form) suggested loss of crystallinity and formation of a different amorphous phase than $NaBiO_3.xH_2O$ (x= 2-3)(Fig. 1(a)) as also observed by Kozma et al.[13]

ATR-FTIR of $NaBiO_3.xH_2O$ (x= 2-3)and its derivatives

The FTIR spectra showed change in the 1000-2000 cm^{-1} region for the acid treated $NaBiO_3.xH_2O$ (x= 2-3)as compared with the pristine compound (Fig. S1). The ATR-FTIR of the $NaBiO_3.xH_2O$ (x= 2-3)and acid treated $NaBiO_3.xH_2O$ (x= 2-3)shows substantial difference. The peak in the 500-1000 Cm-1 region due to the Bi-O-Bi stretching[14] is shifted from 846 cm-1 to 820 cm^{-1} suggesting structural changes in the BiO_6 octahedra of $NaBiO_3.xH_2O$ (x= 2-3). The Bi-O stretching peak at 1390 cm-1 also shifted to 1378 cm-1, with a new peak at 1328 cm-1. These changes can be attributed due to the in situ conversion of Bi^{5+}→Bi^{3+} in the BiO_6 octahedra of $NaBiO_3.xH_2O$ (x= 2-3).[13, 15] Strong absorption peaks in the range of 1600–1700 cm−1 and 3000–3800 cm−1 are characteristic absorptions of water[16], along with some BiO_3^- absorption peaks. Although, the exact assignment of the BiO3- and water in 1600–1700 cm−1 region is difficult but the change in the water structure after acid treatment can be pointed out by change in the >3000 cm^{-1} region.

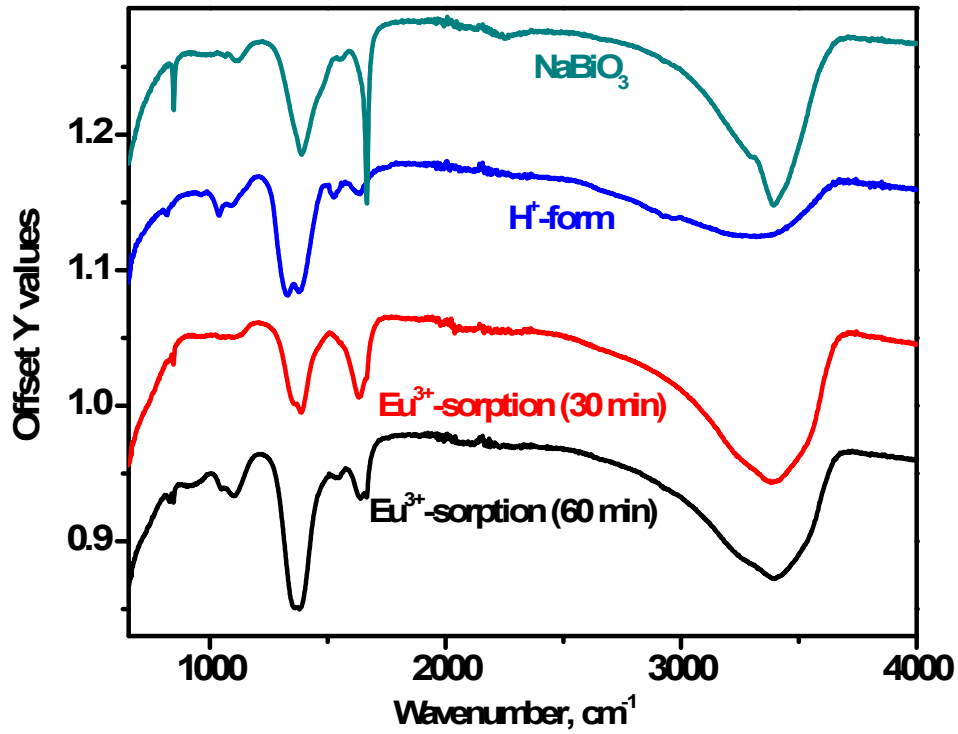

Figure S 1. The ATR-FTIR of pristine, acid treated (H^+-form), and Eu^{3+} sorbed $NaBiO_3.xH_2O$ (x= 2-3) at different time of equilibration.

The FTIR of Eu^{3+} sorbed $NaBiO_3.xH_2O$ (x= 2-3) at two different equilibration time (30 minutes and 60 minutes) was also recorded. The two FTIR spectra are mainly dominated by the features corresponding to the H^+-form of the $NaBiO_3.xH_2O$ (x= 2-3), especially when equilibrated for longer time interval. The ATR-FTIR after 30 minutes of equilibration shows features due to both $NaBiO_3.xH_2O$ (x= 2-3)and H^+-form due to its incomplete conversion to H^+-form.

Hexavalent Americium reduction rate

The reduction of AmO_2^{2+} after equilibration with $NaBiO_3.xH_2O$ (x= 2-3)at pH 1 HNO_3 was followed with time at different temperature. All the equilibration for oxidation was carried out at 25 °C and the sample was transferred in 1 ml screw cap quartz cuvette with 10 mm path length for temperature and time dependent spectral measurements. The temperate dependent reduction of AmO_2^{2+} was followed using coupled Peltier attachment of Jasco V-530 double beam spectrophotometer. We didn't observed any definite trends for the AmO_2^{2+} decay with temperature and the rates of the decay also varies just by changing the centrifugation speed for

separation of solid $NaBiO_3.xH_2O$ (x= 2-3)from suspension. The reasoning for this variation along with other observation is discussed in main manuscript.

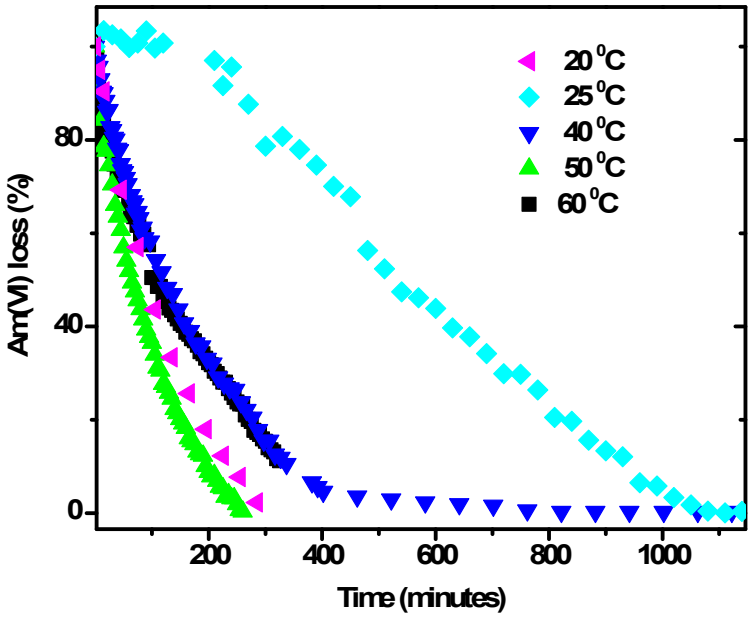

Figure S 2. Variation in the rate of AmO_2^{2+} conversion to the lower valent Am oxidation state.

DLS studies

The DLS studies were performed to understand the effect of colloidal particle density on the Am^{3+} oxidation and its stability of its higher oxidation states. The $NaBiO_3$ was equilibrated with pH 1 for 15-20 minutes and centrifuged at 500RCF and 3000 RCF for different time. The particle size distribution in the supernatant was followed using Particle size analyzer (Corduan, France). The 30 nm standard (Nanosphere™ size standard (Thermo fisher)) was used prior to the supernatant measurements to check the machine performance. The standard shows a value of 31.0 (±0.2) nm using inbuilt cumulant algorithm for the auto correlation function (ACF) fitting. The decay of ACF for sample centrifuged at 500 RCF for 5 minute and 10 minutes confirms the presence of $NaBiO_3$ particle sin the supernatant. However, supernatant obtained after 3000 RCF centrifugation for 10 minutes shows poor ACF decay and the cumulant analysis fails to give any suitable size (**Fig. S3**). This poor ACF decay suggests absence of any particle in the supernatant.

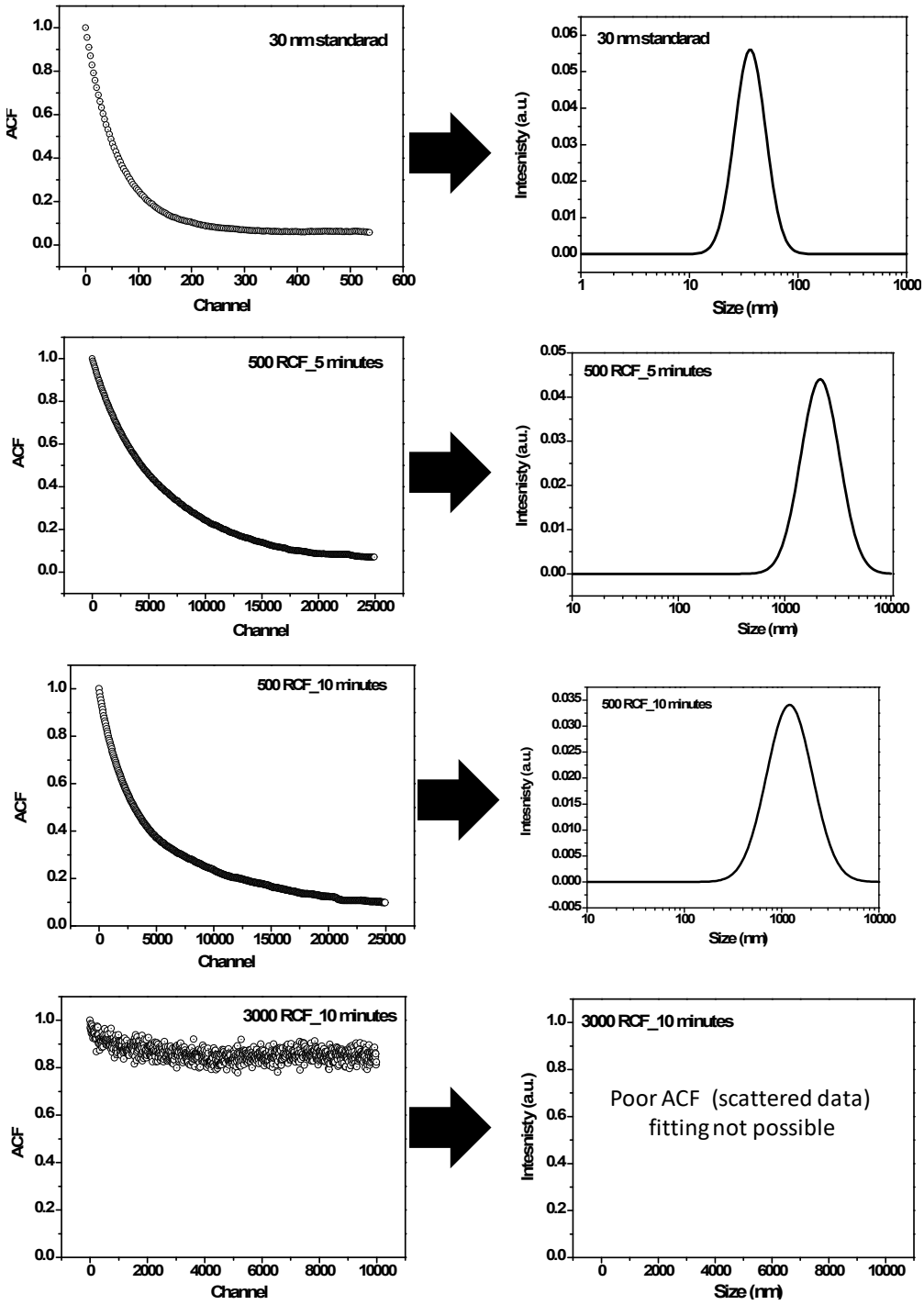

Figure S3. The variation in the autocorrelation function (ACF) after centrifugation at 500 RCF for 5 and 10 minutes and 3000 RCF for 10 minutes for $NaBiO_3$ suspension equilibrated with pH 1 HNO_3 (left).The resultant size distribution using cumulant algorithm under different centrifugation conditions (right).

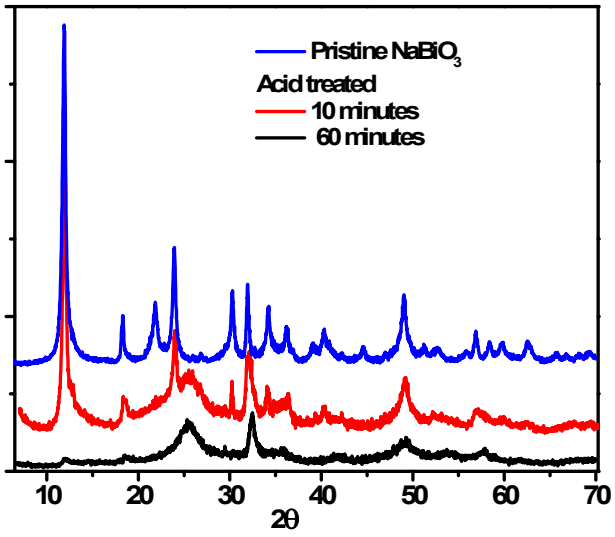

Figure S4.Comparison of XRD spectra of pristine $NaBiO_3$, with acid equilibrated $NaBiO_3$ at different time intervals in pH 1 HNO_3.

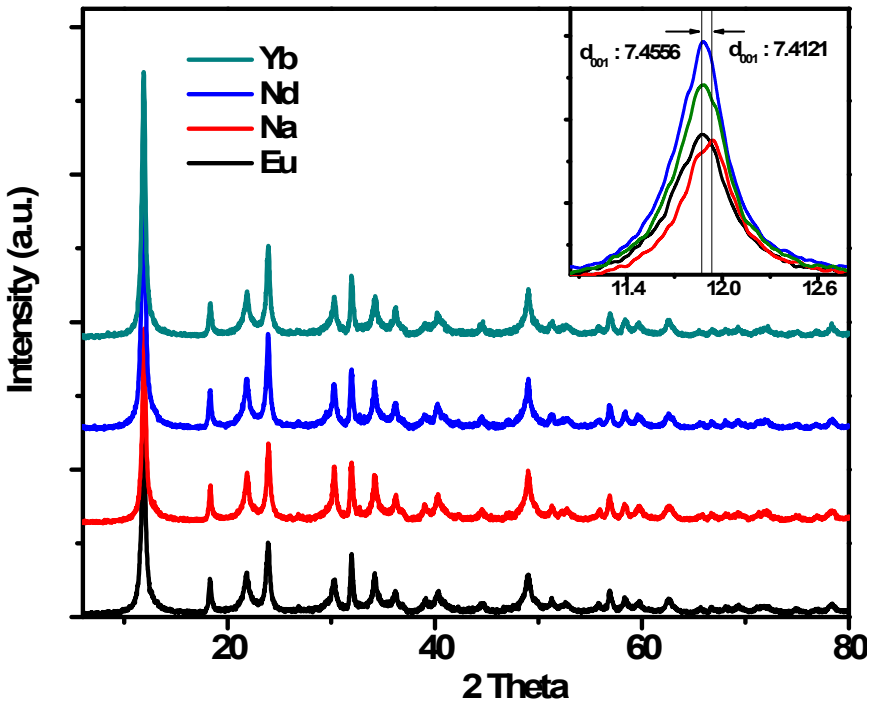

Figure S5. The XRD of the pristine $NaBiO_3$ and lanthanides loaded NaBiO3, pH ~4, Time of equilibration: 24 hrs, [Ln]: 0.1 M, $NaBiO_3$: 30 mg/ml.

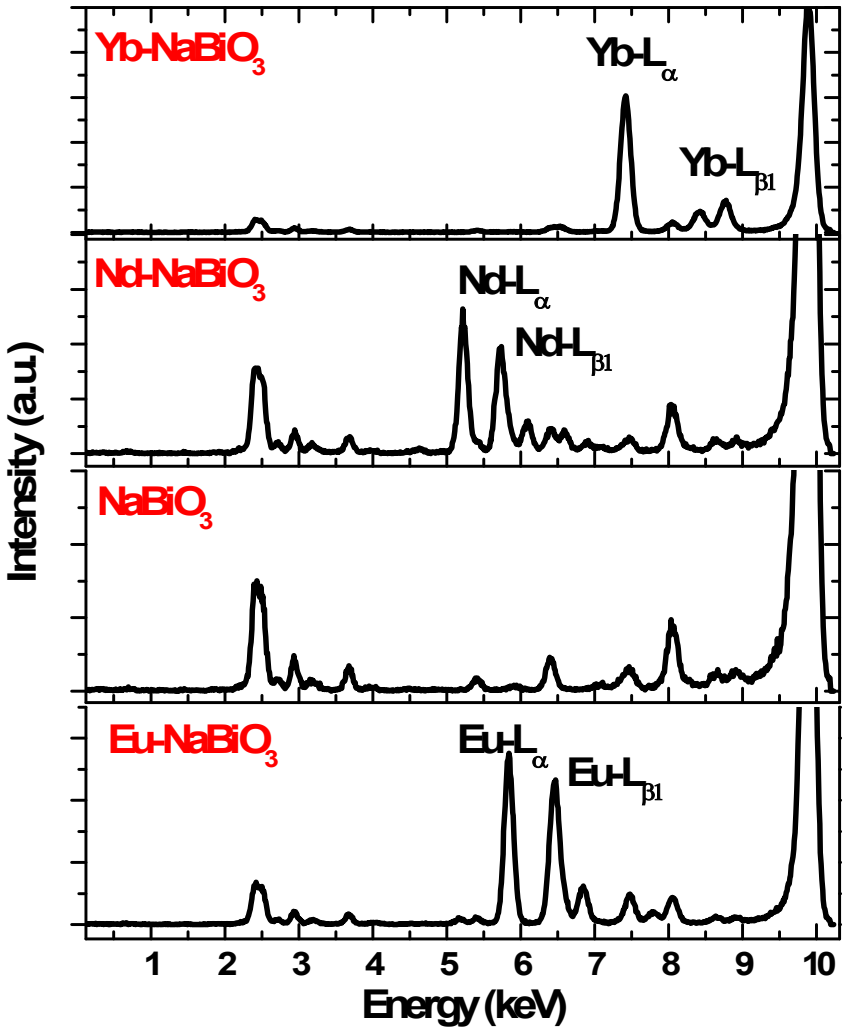

Figure S6. The XRF of the pristine $NaBiO_3$ and lanthanides loaded NaBiO3, pH ~4, Time of equilibration: 24 hrs, [Ln]: 0.1 M, $NaBiO_3$: 30 mg/ml.

Am^{3+} oxidation at higher ionic strength

The oxidation of Am^{3+} at higher ionic strength (1M $NaClO_4$) was carried out at pH 1 HNO_3 and the results were compared to the Am^{3+} oxidation without any $NaClO_4$. The quantitative oxidation of Am^{3+} (>95 %) was observed in the absence of $NaClO_4$ within 20 minutes whereas only 80-83% oxidation of Am^{3+} was observed at higher ionic strength even after 120 minutes of equilibration with $NaBiO_3.xH_2O$ (x= 2-3)in pH 1 HNO_3.

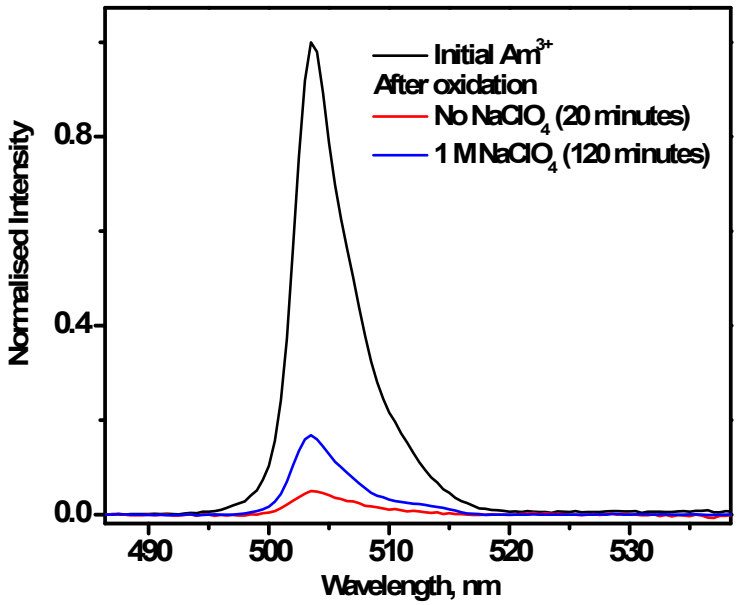

Figure S 7. The vis-NIR spectra of initial Am^{3+} and after its oxidation in presence and absence of 1 M $NaClO_4$ in pH 1 HNO_3

Americium oxidation assisted dissolution of $NaBiO_3.xH_2O$ (x= 2-3)

The dissolution of $NaBiO_3.xH_2O$ (x= 2-3) was investigated in the presence of redox inactive Eu^{3+} and redox active Am^{3+} in pH 1 HNO_3. The photoluminescence of the Eu^{3+} aqueous solution before and after equilibration with $NaBiO_3.xH_2O$ (x= 2-3) studies suggested >99% uptake of Eu^{3+} onto the $NaBiO_3.xH_2O$ (x= 2-3)(Fig. S4). The Uv-vis spectra of the supernatant of Eu^{3+}-$NaBiO_3.xH_2O$ (x= 2-3) system lacks any peak of BiO3- even after 72 hrs of equilibration. However, distinct peak for BiO_3^- (Fig. S4, yellow region,) along with peak at 503 due to residual Am^{3+} (grey region, Fig. S5) was seen for Am^{3+}-$NaBiO_3.xH_2O$ (x= 2-3) system. The lack of peak in the Eu^{3+}-$NaBiO_3.xH_2O$ (x= 2-3) system and its presence in Am^{3+}-$NaBiO_3.xH_2O$ (x= 2-3)system, suggest role of Am^{3+} redox transformation in the dissolution of $NaBiO_3.xH_2O$ (x= 2-3)even at pH 1 HNO_3.This observation along with Ce3+ oxidation and discussed in the main manuscript.

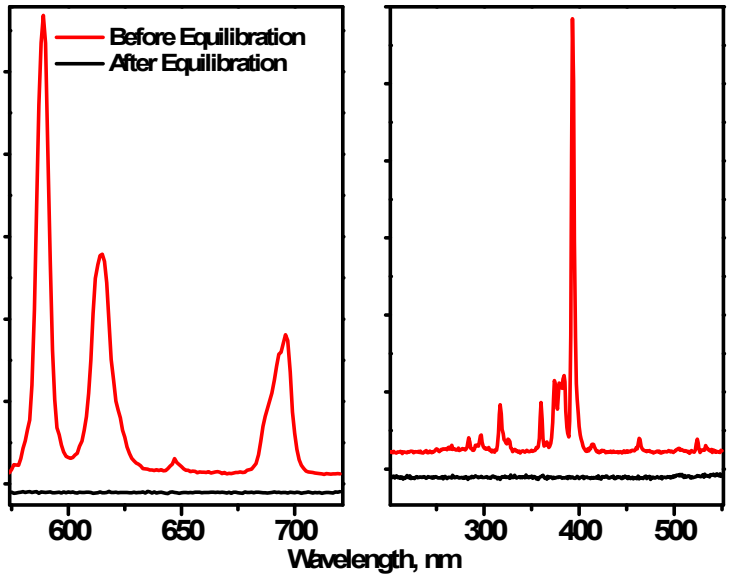

Figure S8. The emission and excitation spectra Eu^{3+} of aqueous phase before and after equilibration with $NaBiO_3.xH_2O$ (x= 2-3).

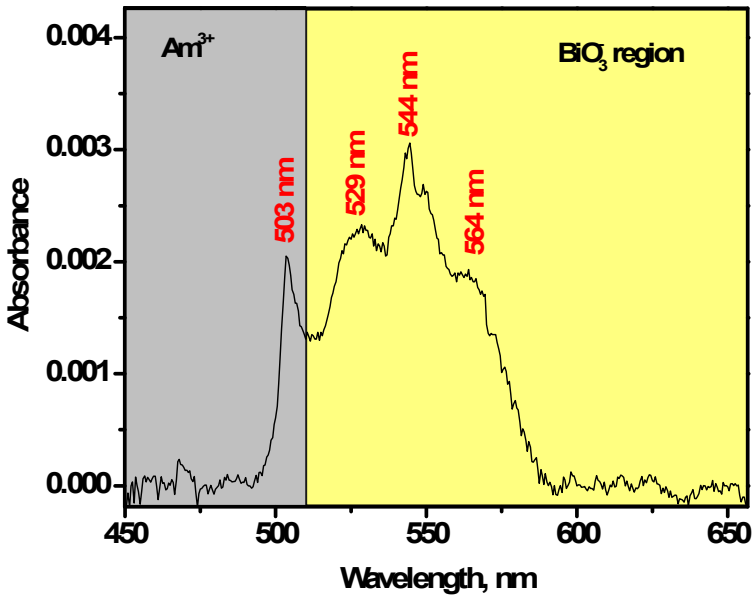

Figure S 9. The vis-NIR spectra of Am-$NaBiO_3.xH_2O$ (x= 2-3) supernatant after 20 minutes of equilibration at pH 1 HNO_3

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