Characterization of Sb-doped Bi_2UO_6 Solid Solutions by X-ray Diffraction and X-ray Absorption Spectroscopy

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The preparation and characterization of Sb-doped Bi_2UO_6 solid solutions, in a limited composition range, is reported for the first time. The solid solutions were prepared by solid-state reactions of Bi_2O_3 , Sb_2O_3 and U_3O_8 in the required stoichiometry. The reaction products were characterized by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) measurements at the Bi and U L_3 edges. The XRD patterns indicate the precipitation of additional phases in the samples when Sb doping exceeds 4 at%. The chemical shifts of the Bi absorption edges in the samples, determined from the XANES spectra, show a systematic variation only up to 4 at% of Sb doping and support the results of XRD measurements. These observations are further supported by the local structure parameters obtained by analysis of the EXAFS spectra. The local structure of U is found to remain unchanged upon Sb doping indicating that Sb^{+3} ions replace Bi^{+3} during the doping of Bi_2UO_6 by Sb.

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Introduction

Uranates of different elements are reported in the literature since they may form by interactions of uranium nuclear fuel with fission products, cladding as well as coolants in the operating and transient conditions of a reactor.¹ Due to large difference in the densities of the uranates and uranium/uranium oxide/mixed oxide fuel, the formation of these compounds play an important role in safety issues arising from any rupture of the cladding materials due to swelling of the fuel.² In addition, the uranates have applications as magnetic materials, catalysts *etc.*³⁻⁵ Bismuth uranates are a special class of compounds having relevance in several areas *e.g.* nuclear technology and the demethylation of toluene,^{6,7} as well as having good oxide ion-transport properties. India is proposing to produce nuclear power using compact high-temperature reactors with Pb-Bi alloys as the coolant and uranium as nuclear fuel. In the case of the fuel-coolant interaction under transient conditions, Bi and Pb uranates are likely to form in such nuclear reactors.⁸ Antimony uranates are also being applied in the field of catalysis for variety of industrial processes. Though, various studies on Bi_2UO_6 ^{9,10} have been reported in the literature, the similar antimony uranate has not been reported so far, despite both Sb and Bi being from the same group of the periodic table. A few studies have been reported in the literature on the preparation of uranium-doped $\text{Bi}_4\text{V}_2\text{O}_{11}$ and Bi_2WO_6 , it was observed¹¹ that U^{+6}

takes the position of V^{+5} in $\text{Bi}_4\text{V}_2\text{O}_{11}$, whereas U replaces W in solid solutions of Bi_2WO_6 and Bi_2UO_6 .¹² In similar work on Zr doping of Bi_2UO_6 , it has been observed that Zr atoms go to U sites.¹³ Since Bi^{+3} and Sb^{+3} have similar ionic radii, it should be possible to dope Bi_2UO_6 with Sb^{+3} . Such solid solutions may show properties different from undoped Bi_2UO_6 . Keeping the above points in mind, a study to prepare and characterize Sb^{+3} doped Bi_2UO_6 by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS): extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge spectroscopy (XANES) measurements was initiated. The results obtained in this study are reported in the present manuscript.

Experimental

Preparation of the compounds

The starting materials, Bi_2O_3 and Sb_2O_3 , used were of AR grade, whereas U_3O_8 used was of nuclear grade. The compound Bi_2UO_6 was prepared by mixing Bi_2O_3 and U_3O_8 in stoichiometric ratios, and heating at 800°C for about 100 h continuously in a platinum boat inside a furnace. Sb-doped Bi_2UO_6 solid solutions were prepared by heating stoichiometric amounts of Bi_2O_3 , Sb_2O_3 and U_3O_8 appropriate for the formation of $\text{Bi}_{2-x}\text{Sb}_x\text{UO}_6$ solid solutions having $x = 0.04, 0.08, 0.12, 0.16$ and 0.40 .

XRD measurements

Powder X-ray diffraction studies on the samples were carried out using a Cu anode-based powder diffractometer operating in the Bragg-Brentano focusing geometry, and a curved crystal monochromator in the diffraction beam. Structural refinements

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were performed using the Rietveld refinement program, FULLPROF.¹⁴ In all the refinements, the background was defined by a sixth-order polynomial in 2θ . A Thompson-Cox-Hastings pseudo-Voigt with an axial divergence asymmetry function was chosen to define the profile shape for the X-ray diffraction peaks. Except for the occupancies of the atoms, all other parameters *i.e.*, scale factor, zero correction, background and half-width parameters along with mixing parameters, lattice parameters, positional coordinates, and thermal parameters, were refined.

For a better purity check, the XRD patterns of some of the reaction products were also measured using the angle dispersive X-ray diffraction beam line (BL-12)¹⁵ at Indus-2 synchrotron source at RRCAT, Indore, India. The beam line consists of a Si(311) based double-crystal monochromator with bendable focusing optics. These measurements were done at 11000 eV using an image-plate area detector (MAR 345). Photon energy calibration for this set of samples was done using powder diffraction of the LaB₆ standard (NIST). For the above measurements, a few mg of a powdered sample was pressed in between two sticky layers of cellophane tapes.

XAS measurements

For XAS measurements, samples of appropriate weight, estimated to obtain a reasonable edge jump, were taken in powder form and mixed thoroughly with cellulose powder to obtain a total weight of about 100 mg; homogenous pellets of 15 mm diameter were prepared using an electrically operated hydraulic press. XAS measurements were carried out at the dispersive EXAFS beam line (BL-8) in the transmission mode at the INDUS-2 Synchrotron Source.¹⁶⁻²⁰

The above mentioned beam line uses a Si(111)-based bent crystal as polychromator and a position-sensitive CCD detector; the full XAS spectrum of a sample at any specified absorption edge can be obtained as a single shot within a time frame of 300 ms. For the present measurement on Bi₂UO₆ samples, the Si(111) crystal was set at a proper Bragg angle to obtain a band of energy around 13419 eV for XAS measurements at Bi L₃ edge, and around 17166 eV for XAS measurements at the U L₃ edge. Pellets of standard powders of Bi₂O₃ and PbO (L₃-edge of Pb being 13037 eV) were used for calibration of the CCD channels for measurements at the Bi L₃ edge, while standard samples of U₃O₈ and Y₂O₃ (Y K-edge being at 17050 eV) were used for measurements at the U L₃ edge.

Results and Discussion

XRD measurements

The X-ray powder diffraction measurements for Bi₂UO₆ at ambient temperature confirmed that the sample was single-phase. All reflections could be indexed with the cell parameter of the low-temperature phase of Bi₂UO₆ with space group C2 reported in the literature.¹³ The XRD pattern of Bi₂UO₆ along with the Rietveld profile is shown in Fig. 1(a). The XRD patterns of reaction products obtained while preparing Bi_{2-x}Sb_xUO₆ solid solutions for $x = 0.04, 0.08, 0.12$ and 0.16 are shown in Fig. 1(b). The appearance of some extra peaks, in addition to that reported for Bi₂UO₆, could be seen in the range of $28 - 30^\circ$ in the XRD patterns of the products with x values of more than 0.4 , possibly due to the formation of an additional phase. The additional new lines start appearing in the XRD patterns of the samples with Sb doping of 4 at%, and become clearly visible for samples with Sb doping of more than 6 at% ($x \geq 0.12$). However, the intensities of these additional peaks were very

Fig. 1 (a) Rietveld fitting of XRD pattern of Bi₂UO₆ (closed circle, Experimental; continuous line, best-fit theoretical curves obtained after the Rietveld refinement of Bi₂UO₆ using monoclinic C2 space group; bottom line: difference profiles.) (b) Evolution of powder XRD patterns of reaction products obtained while preparing Bi_{2-x}Sb_xUO₆ samples for different values of x in the 2θ region of ($26 - 34^\circ$).

weak and could be observed only in the expanded scale of the XRD patterns. Several intense XRD lines of this phase could be seen at $x = 0.40$. However, this additional phase could not be identified. Rietveld profile fits were also carried out on the XRD patterns of the above mentioned reaction product, and the variations of the best-fit cell parameters as a function of the value of x are shown in Figs. 2(a) and 2(b). It was observed that the cell parameters (a, b, c values, monoclinic angle β and cell volume) generally decrease upon Sb doping up to 4 at% (*i.e.* $x = 0.08$ in Bi_{2-x}Sb_xUO₆) in Bi₂UO₆, after which the cell parameters are invariant with the composition. These observations were further supported when the XRD patterns of Bi_{2-x}Sb_xUO₆ ($x = 0.4$) samples were measured using a synchrotron-radiation source.

Bi-edge EXAFS

XAS studies on different uranates are reported in the literature for obtaining information about the local uranium environment and its valence state.^{4,5} The XAS studies were performed on Sb-doped Bi₂UO₆ for this information. The near-edge or XANES regions of the normalized absorption spectra ($\mu(E)$ vs. E) measured at the Bi L₃-edge are shown in Fig. 3(a) for solid

Fig. 2 Variation of the structural parameters (lattice constants and cell volume) for products obtained while preparing $\text{Bi}_{2-x}\text{Sb}_x\text{UO}_6$ samples for different Sb doping concentrations.

Fig. 3 Normalized X-ray absorption spectra (XANES region) of $\text{Bi}_{2-x}\text{Sb}_x\text{UO}_6$ samples measured at (a) the Bi L_3 edge and (b) the U L_3 edge.

solutions having different Sb doping concentrations. It can be seen that there is a considerable shift in the Bi absorption edge position from sample to sample. The actual edge positions of the samples were obtained by the “half-edge step” method in each case from their respective $\mu(E)$ vs. E spectrum. The edge shift (ΔE) value *i.e.*, the difference in the edge energy with respect to the edge energy of an undoped Bi_2UO_6 sample, are tabulated in Table 1. Since Bi is in Bi^{+3} state in all of the samples, the edge shift must be because of a change in the chemical environment surrounding the Bi sites due to Sb doping. Similar shifts in the X-ray absorption edges due to change in the chemical environment of the absorbing species have been observed by several other authors in different systems.²¹⁻²³ Figure 3(a) shows that the edge energy values are shifted towards the higher energy side as the Sb doping concentration increases up to 4% ($x = 0.08$) and beyond that edge shift start decreasing as the doping concentration further increases. This

Table 1 Measured chemical shift and calculated effective charge

Sample	Chemical shift, $\Delta E/\text{eV}$	Effective charge q (electrons/atom)
Bi_2UO_6	0	0.54
$\text{Bi}_{1.96}\text{Sb}_{0.04}\text{UO}_6$	3.13	0.55
$\text{Bi}_{1.92}\text{Sb}_{0.08}\text{UO}_6$	3.27	0.57
$\text{Bi}_{1.88}\text{Sb}_{0.12}\text{UO}_6$	3.18	0.58
$\text{Bi}_{1.84}\text{Sb}_{0.16}\text{UO}_6$	2.15	0.6

shows that the Bi site is replaced by doped Sb properly up to 4% Sb doping only. At higher Sb doping concentrations, another phase starts precipitating, as also indicated by XRD studies. In the case of 20% Sb doping, the edge is almost at the same energy position as observed for undoped Bi_2UO_6 .

It is reported in the literature²¹⁻²⁵ that these effects of change in the chemical environment can be quantitatively presented by the “effective charge” (q). The formation of a chemical bond in a compound involves a redistribution of the valence electrons of the constituent atoms and the effective charge is a hypothetical parameter that gives a measure of the charge residing over the cation when it forms a bond with a ligand. Apart from the valency, it accounts for the electronegativity of the pair of atoms forming the bond, the covalent nature of the bond, the coordination number *etc.* and thus quantitatively represents the chemical environment around the absorbing metal ions.

Several empirical relations²¹⁻²⁵ have been proposed in the literature to estimate the effective charge on a metal cation in a compound. According to Suchet’s method,²⁶ the effective charge on a cationic species involved in the formation of a chemical bond is given by

$$q = n \left[1 - 0.01185 \left(\frac{Z}{r'} + \frac{Z'}{r} \right) \right] \quad (1)$$

where Z , r and n are, respectively, the total number of electrons, the ionic radius and the oxidation number of the cation. The primed symbols refer to the anion in the compounds.

In case of Bi_2UO_6 , where two cations are involved, the effective charge on Bi was estimated following the method described in Ref. 25 for LaMnO_3 . In such calculations, Bi_2UO_6 was considered to consist of two separate compounds *viz.*, Bi_2O_3 and UO_3 with Bi in the +3 oxidation state and U in the +6

oxidation state. The combination of these two compounds will yield the molecular formula Bi_2UO_6 . For Bi_2O_3 , we obtained $q_{\text{Bi}} = +0.54$ and $q_{\text{O}} = -0.36$ electrons/atom by using Eq. (1) given above. Similarly, for UO_3 we obtained $q_{\text{U}} = +0.66$ and $q_{\text{O}} = -0.22$ electrons/atom. When two individual molecules combine to produce Bi_2UO_6 , each oxygen atom would have an average charge of -0.29 electrons/atom. The charge on Bi atoms and U atoms would still be the same, *i.e.* $+0.54$ and $+0.66$ electrons/atom, thereby ascertaining a total charge neutrality of the Bi_2UO_6 molecule.

For calculating the effective charge on Bi in Sb-doped Bi_2UO_6 , we first calculated the q values of the Sb_2O_3 molecule using Eq. (1), which gave $q_{\text{Sb}} = +1.29$ and $q_{\text{O}} = -0.86$ electrons/atom. To calculate the contribution of oxygen in 2% Sb doped Bi_2UO_6 , we took the weighted average of the q value of oxygen as of 98% of Bi_2O_3 and 2% Sb_2O_3 , which is -0.37 electrons/atom. Considering the contribution of UO_3 , each oxygen atom has an average charge of -0.295 electrons/atom in the 2% Sb doped Bi_2UO_6 molecule. Since, as discussed later, Bi_2UO_6 is a layered compound that consists of a stacking of slabs of edge-sharing UO_8 polyhedra sandwiched between double BiO sheets and the U-polyhedra remains almost unperturbed by Sb doping, the charge on the U atoms in Sb-doped Bi_2UO_6 should be the same as in the case of undoped Bi_2UO_6 , which is 0.66 electrons/atom. Hence, to satisfy the total charge neutrality condition, the effective charge, q , on the Bi atom in 2% Sb doped Bi_2UO_6 should be $+0.55$ electrons/atom, which is higher than that in case of undoped Bi_2UO_6 ($+0.54$ electrons/atom). The above result is consistent with the fact that Sb, being more electronegative than Bi, Sb doping, should increase the effective positive charge at Bi sites. Using the above procedure, we calculated the effective charge, q , on the Bi atom in all Sb doped products, as tabulated in Table 1, along with the shift in the edge energy values (ΔE).

In order to take care of the oscillations in the EXAFS region of the absorption spectra, $\mu(E)$ has been converted to an absorption function, $\chi(E)$, defined as follows²⁷

$$\chi(E) = \frac{\mu(E) - \mu_0(E_0)}{\Delta\mu_0(E_0)} \quad (2)$$

where, E_0 is the absorption edge energy, $\mu_0(E_0)$ the bare atom background and $\Delta\mu_0(E_0)$ the step in the $\mu(E)$ value at the absorption edge. The energy-dependent absorption coefficient, $\chi(E)$, has been converted to the wave-number dependent absorption coefficient, $\chi(k)$ using the relation

$$K = \sqrt{\frac{2m(E - E_0)}{\hbar^2}} \quad (3)$$

where m is the electron mass, $\chi(k)$ is weighted by k^2 to amplify the oscillation at high k and the $\chi(k)k^2$ functions are Fourier transformed in R space to generate the $\chi(R)$ vs. R spectra in terms of the real distances from the center of the absorbing atom. The set of EXAFS data analysis available within the IFEFFIT software package have been used for EXAFS data analysis.²⁸ This includes background reduction and Fourier transform to derive the $\chi(R)$ vs. R spectra from the absorption spectra (using ATHENA software), the generation of theoretical EXAFS spectra starting from an assumed crystallographic structure, and finally fitting of the experimental data with the theoretical spectra using ARTEMIS software.

The structural parameters (atomic coordination and lattice parameters) of Bi_2UO_6 used for simulating theoretical EXAFS spectra of the samples were obtained from reported values in the

literature.^{6,9,10,13} Bi_2UO_6 is reported to display two polymorphs: a monoclinic form at 20°C that crystallizes in the $C2$ space group with $a = 6.8782\text{\AA}$, $b = 4.0057\text{\AA}$, $c = 9.6939\text{\AA}$, $\beta = 90.11^\circ$, and a trifocal fluorite-like structure stable above 800°C , with space group $P3$ and $a = 4.045\text{\AA}$, $c = 9.90\text{\AA}$.⁶ In the present analysis, theoretical EXAFS spectra of the samples were generated assuming the monoclinic form of the crystal in the $C2$ space group.

$\chi(R)$ vs. R spectra have been generated for all samples from the $\mu(E)$ versus E spectra following the methodology described above; also the best-fit $\chi(R)$ vs. R spectra of the samples are shown in Fig. 4(a), along with the experimental data for all samples. The bond distances, co-ordination numbers (including scattering amplitudes) and disorder (Debye-Waller) factors (σ^2), which give the mean-square fluctuations in the distances, were used as fitting parameters.

U-edge EXAFS

The near-edge or XANES regions of the normalized absorption spectra ($\mu(E)$ vs. E) measured at U L_3 -edge are shown in Fig. 3(b) for all Bi_2UO_6 samples having different Sb doped concentrations. This indicates that the U absorption edge is not affected by Sb doping. Figure 4(b) shows the radial distribution functions *i.e.*, $\chi(R)$ vs. R spectra of the samples with different Sb concentrations as obtained from the EXAFS portion of the absorption spectra, with theoretical fit curves up to $3.5\text{\AA}$. The theoretical EXAFS spectra were generated assuming the structure described above. The bond distances, co-ordination numbers (including scattering amplitudes) and disorder (Debye-Waller) factors (σ^2), which give the mean-square fluctuations in the distances, were used as fitting parameters.

Bi_2UO_6 is a layered compound that consists of a stacking of slabs of edge-sharing UO_8 polyhedra sandwiched between double BiO sheets. The BiO sheet resembles a fluorite structure, where Bi atoms are coordinated by 4 in-plane oxygen (O_2 type) and three out of plane oxygen (O_3 type) which connects it to the UO_8 polyhedra. In the UO_8 polyhedra, each uranium atom is coordinated with 8 oxygen atoms, of which two oxygens (O_3 type) form collinear uranyl bonds, and the rest of the 6 oxygen atoms (O_1 type) form a hexagon whose atoms lie a little above and below the plane perpendicular to the uranyl bond.¹³ Since the BiO sheets are relatively empty compared to the U-O planes, these layers are responsible for ionic conduction in Bi_2UO_6 systems. The Bi-O₂ and Bi-O₃ bond lengths and the U-O₁ and U-O₃ bond lengths, as obtained from the present EXAFS analysis, are found to agree well with that reported by Vannier *et al.*¹³

It should be noted that, Vannier *et al.*,¹³ while refining the neutron diffraction data of Bi_2UO_6 , have introduced an extra oxygen site in the double BiO sheet (named as O_{2b} site), and also another oxygen site (O_{1b}) in the equatorial plane of the U-O network. The present EXAFS study shows the presence of bond lengths corresponding to the Bi-O_{2b} and U-O_{1b} bonds in the case of the undoped and Sb-doped Bi_2UO_6 samples, which agree well with the values reported by Vannier *et al.*¹³

The average bond lengths ($R_{\text{AVG.}}$), total coordination number ($N_{\text{TOT.}}$) and average Debye-Waller factor ($\sigma_{\text{AVG.}}^2$) for the first two nearest oxygen shells surrounding the Bi atoms (as obtained from Bi edge EXAFS analysis) and average bond lengths, the total coordination number and the average Debye-Waller factor surrounding the U atoms (as obtained from U edge EXAFS analysis) are plotted in Fig. 5 as a function of x . It can be found from this figure that there are significant changes in the bond length, coordination number and σ^2 values up to $x = 0.08$ (4% Sb doped samples) with respect to the undoped sample. For

Fig. 4 Experimental $\chi(R)$ vs. R spectra at (a) the Bi L_3 edge and (b) the U L_3 edge with best-fit theoretical plots for products obtained while preparing $\text{Bi}_{2-x}\text{Sb}_x\text{UO}_6$ samples: (i) $x = 0.04$, (ii) $x = 0.08$, (iii) $x = 0.12$, (iv) $x = 0.16$, (v) $x = 0.4$. The solid line represents fitting data, and scatter points are measured data.

samples with a higher concentration of Sb doping, the above values, however, approach towards that of the undoped samples. Based on this observation it can be concluded that up to 4% concentration, Sb can efficiently substitute Bi, above which Sb precipitation takes place. This supports the XRD and XANES results discussed above. From Fig. 5 it can also be seen that the bond length, coordination number and Debye-Waller factors in the U surrounding do not change much, indicating that Sb atoms do not go to the U sites. This may be due to the fact that uranium in Bi_2UO_6 is in the U^{+6} oxidation state, but Sb is more stable in the Sb^{+3} oxidation state.

Conclusions

The XRD and EXAFS studies confirm that $\text{Bi}_{2-x}\text{Sb}_x\text{UO}_6$ solid solutions are formed properly with $x \leq 0.08$ i.e. up to 4 at% of Sb. The cell parameters (a , b , c values and cell volume) of the samples generally decrease with an increase in Sb atom, % in solid solutions up to 4 at% of Sb. However, when Sb doping is increased beyond 6%, a separate phase precipitates. The chemical shift of the Bi L_3 edge in XANES measurements of the samples also supports this observation. Though the oxidation state of Bi is +3 in all of these solid solutions, there is a chemical shift in the Bi L_3 edge, as observed in XANES measurements on the samples. This is due to the variation in the effective atomic charge at the Bi sites, due to Sb doping in the lattice, arising as a result of differences in the electronegativity of the Sb^{+3} and Bi^{+3} ions. The chemical shift increases with the Sb doping concentration up to 4% at%, beyond which it decreases; at higher Sb doping the edge position shifts towards the value

Fig. 5 Variation of the average bond length ($R_{\text{AVG.}}$), The total coordination number ($N_{\text{TOT.}}$) and average DW factor (σ^2) for the two nearest oxygen shells surrounding Bi and U sites as a function of x for the products obtained while preparing $\text{Bi}_{2-x}\text{Sb}_x\text{UO}_6$ samples.

observed for the undoped sample. The results of EXAFS measurements on the samples also support this observation, since the bond length, coordination number and σ^2 values are found to vary significantly for the Sb doping concentration up to 4% ($x = 0.08$). No chemical shift was observed for the U edge positions of the samples with the incorporation of Bi, indicating that Sb doping only affects the Bi sites and not the U sites.

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