CHEMICAL EFFECTS OF NEUTRON IRRADIATION ON ARSENIC SULFIDES

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Abstract. The distribution of valence states III and V of radioactive ^{76}As after neutron irradiations of thioarsenic compounds has been investigated in arsenic sulphides, optical glasses materials. Compounds were irradiated with neutrons at a flux of $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. The radioisotope formed by (n, γ) reaction is ^{76}As with $T_{1/2} = 26.4\text{h}$. Separations of valence states were performed by electrophoresis. Radiochemical yields of As V were higher than those obtained by other workers in the irradiation of arsenic oxygenated compounds; a similar high yield of Sb V was also found previously on the irradiation of thioantimony compounds and seems to be related to the covalent character of the As-S bond; likewise, internal conversion accounts for the primary oxidation of recoil atoms.

Key words: Radiative neutron capture, chemical consequences, arsenic thiocompounds, short range order, valence states distribution

1. INTRODUCTION

Arsenic and antimony thio-compounds as well as other chalcogenides are important components/materials of optical glasses according to their optical electronic properties [1-5]. They are part of materials that due to their particular electronic/bonding characteristics, the values of certain physical properties make them different from solids with covalent or metallic bonding; further from the former, closer to the latter [6]. Under neutron bombardment they should present changes in such properties as it happens, at very much lesser extent, when they are submitted *inter alia* to light or thermal induced processes [7]; and generate, therefore, chemical effects on the compounds.

Several studies have been performed on the distribution of the activities formed after neutron irradiation of arsenic and antimony oxocompounds [8-13], but on chalcogenide compounds, very few of such studies were made [14, 15].

Under irradiation, in arsenic oxycompounds internal conversion of the neutron capture gamma rays should result in oxidation of ^{76}As [8], but this was not observed, and electron transfer could have occurred in the solid state or in dissolution. In irradiated antimony oxides, the distribution of valence states indicated a much lower yield of ^{76}SbV [9] in comparison with the values of ^{76}AsV obtained on irradiating arsenic oxides [8,9]; nevertheless the yield of ^{76}AsV on the irradiation of As_2O_3 was low [10]. In regard to antimony thiocompounds bombarded with neutrons, the distribution of the valence states of radioactive atoms of antimony, was studied and compared with that found upon neutron irradiation of its oxygenated compounds. A higher yield of the Sb pentavalent state

was found for the sulphides as well as for the hydrated compounds. This effect was considered to be related to the covalent character of the Sb-S bond, to the degree of hydration of the compound and to the defects introduced in the lattice upon irradiation [13-15].

The present work consists of a comparative study of the distribution of activity of As-III and As V formed on irradiating tri and penta arsenic sulfides.

2. EXPERIMENTAL

2.1. Materials

Materials activated were amorphous [16] analytical grade As_2S_3 and As_2S_5 used without further purification.

2.2. Irradiations

Materials were irradiated in a nuclear reactor with flux of $2 \times 10^{12} \text{ n cm}^{-2} \text{ seg}^{-1}$ under nitrogen or in evacuated ampoules. When arsenic compounds are irradiated with neutrons, the radioisotope ^{76}As of known characteristics [17], is formed by (n γ) reaction; ^{76}As by β^- decay ($T_{1/2} = 26.4\text{h}$) originates stable ^{76}Se .

2.3. Analysis

The activated compounds were dissolved in 4.3% sodium sulfide solution in the presence of either, AsIII or As V carrier. The various valence states were separated by paper electrophoresis [18] using Whatman 3MM paper. The voltage gradient was 40V/cm and the electrolyte was a dissolution of 0.4% in Na_2S and 0.04% in NaOH .

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2.4. Measurements

The counting of the paper strips of 1 cm wide was carried out either with an end window GM counter or with a NaI (TI) crystal.

3. RESULTS AND DISCUSSION

The distribution of valence states III & V of radioactive arsenic according their activities is breakdown in Table 1.

Table 1. Distribution of *AsIII & *AsV

Compounds	As III %	As V %	Experiments (n)
As ₂ S ₃	28.2±3.4	71.0±3.8	(8)
As ₂ S ₅	1.0±0.9	99.0±0.9	(5)

Arsenic trisulfide As₂S₃, natural minerals orpiment & anorpiment, have layered structures [19] of As and S atoms bonded with covalent interatomic forces, and the interlayers, by Vander Waals bonding that originates a very stable high packing of layers [1]. The amorphous variety is constituted by clusters, i.e. microstructural units responsible of the short/middle range order [4,20].

In regard to the pentasulfide As₂S₅, its structure is unknown though from the study of amorphous As₂S₅ it is known that the short/middle range order is similar to that of amorphous As₂S₃, but the structure of As₂S₅ is more rigid [20]. According to ref [4] by quantum chem. calculations some cluster can be identified (are presented) as As₂S₅, As₄S₆, As₆S₉.

Under irradiation (see Table 1), the radiochemical yield here obtained of AsV was higher in the thiocompounds than in the oxides and as in the case of neutron activated antimony sulfides, this higher yield of pentavalent atoms can be attributed to the type of structure, to the covalent character of As–S, electronegativity difference $\Delta\chi = 0.5$; the energy difference of levels $3p-3d = 101.2\text{eV}$ and for the state s^1p^3 is 102.3eV , easily overlapping the electronic levels [21].

In the nuclear process $^{75}\text{As}(n,\gamma)^{76}\text{As}$ the prompt γ spectrum is very complex and broad; the number of gamma being $N_\gamma = 348$ with a wide de-excitation energy photon distribution: extended from 44.42 to 7284.07 KeV [22]; most intense of 559.10, 165.049, 86.788 KeV. Then, the recoil atoms energy spectrum must also be broad and most of them can not travel far in the solid before resting, only a few inter atomic, lattice distances. The more energetics, transfer their energy into the lattice and produce the ejection of atoms [23] in the chalcogenide structure originating cationic vacancies “incipient V centres” but most of them producing in the host atoms electronic excitation, vacancy cascades, ionizations as well as changes in the sulfides bandgap.

The lapse evolved from the very instant of the nuclear event (10^{-14}s) in the solid, the transit of the energetic atom through the crystal until its stopping during which the electrons and excitation of the host atom and its environment subside, is 10^{-7} to 10^{-6}s [23].

Also, it has been observed that when amorphous non irradiated As₂S₃ is annealed at the glass-transition temperature the medium-range order appears or increases, lessening the covalent bonding and increasing the chemical order [24]. Such an event was also seen on bombardment of amorphous ZrO₂ with Kr⁺ ions a small crystalline area is formed at the beginning [25].

In this regard, referring to changes in valence states in the irradiated arsenic thiocompounds internal conversion (IC) phenomena should occur in huge number [26] generating vacancies cascades and producing a large amount of free electrons that is, a reductive ambience for recoil/excited atoms and ions, formation of F centers, reduction of V centers etc. On irradiated As₂S₃, it is safe to postulate a similar mechanism to that of activated Sb₂S₃, AsIII hot atoms could result by IC in the formation of *AsV and *AsIV. The As IV valence state behaves [27] as a radical with a $d^{10} s^1$ configuration, which dissociates into AsIII and AsV. The activation could probably forms both, the IV or V valence states. However, in the irradiated compounds, the As IV disproportionates in the crystal into AsIII and AsV increasing the yield of *As III and decreasing that of *As V.

Thermal annealing experiments, carried out at 80 & 120 $\pm 1^\circ\text{C}$, confirm that of above exposed as it is shown in Fig 1. It is also shows that the *AsIII reach its final state in a short lapse after irradiation.

Figure 1. Annealing behavior of *AsIII & *As V distribution irradiated As₂S₃

These are assisted by large by the concentration/availability of electrons and F centers in those defects created in the irradiated material; in As₂S₅ the final state is reached immediately after the end of irradiation [28].

4. CONCLUSION

The higher yields of radioactive AsV in the sulfides, as compared to the oxides, can be attributed to the type of structure and to the higher covalent character of the As–S bond.

As per annealing behavior, in As₂S₃, *AsV atoms are reduced to *AsIII by the large availability of electrons and F centers decreasing the yield of the former and increasing that of the latter; the final yield is reached a few minutes after the end of irradiation. In As₂S₅ the retention is ~ 100% and the hot-atoms reach their final state during or immediately at the end of irradiations.

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