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NOVEL INVESTIGATIONS ON THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSES OF ELEMENTAL, COMPOUND AND MIXED SEMICONDUCTORS

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A systematic study was made of the relative stability and various phase changes which take place when elemental compound and mechanically mixed semiconductors are heated. These were chalcogens, calcogenides and mixtures of the two. The interest in the present investigation is due to the useful application of the prepared materials in the transistor, radar, rectifier and other electronic industries. Thermogravimetry and differential thermal analysis were carried out in air in the temperature range 20–830°. The results led to the conclusion that the degree of stability of the mechanically mixed semiconducting components is much higher than that of either elemental or compound semiconductors. The results were discussed on the basis of the electronegativity differences and oxygen affinities of the non-metallic components. The thermal stability ranges were evaluated in each case for the materials investigated, for their subsequent physical measurements and their suitability for the production of semiconducting devices.

TG and DTA have opened up new possibilities for investigations of the synthesis of semiconducting materials. They are used to study for example the following features:

1) Direct synthesis of semiconductor materials from their constituents.
2) Kinetics of phase equilibration.

Antimony

It was earlier found [1, 2] that molten antimony is oxidized on heating in air ($\simeq 800°$). This method was used for the preparation of antinomy trioxide.

Sulphur

It was previously noticed [3] that, when sulphur is heated in air, it does not lose weight till 135°. Above this temperature, the combustion of sulphur follows smoothly, with weight loss. At 256°, the container is completely empty of sulphur.

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Selenium

Duval and Doan [4] studied the TG analysis of selenium of five different origins. They reported a temperature range of 330–370° for the occurrence of detectable loss, depending on the method of preparation.

Tellurium

Doan and Duval [5] examined the TG curves for tellurium prepared from eight different origins. They noted a temperature zone with loss or gain in weight ranging from 37° up to 945°, depending on the method of preparation.

Antimony trioxide

The only reference was that of Taimini and Tandon [6], who obtained antimony trioxide after heating antimony trisulphide to 310°. They found that the oxide formed remained stable up to 530° or 580°. From 580° up to 616°, a gain in weight was observed, due to the formation of antimony tetroxide (Sb_2O_4).

Antimony trisulphide

Antimony trisulphide of the grey-black type was found by Bacho [7] to manifest a loss in weight in the temperature range 190–230°. As concerns the TG curve, Morandat and Duval [8] found that, after the elimination of water and sulphur, the curve was perfectly horizontal, without any change in weight from 175° to 275°. Beyond this temperature, antimony trisulphide was oxidized to antimony trioxide and then to antimony tetroxide. The TG curve obtained by Taimni et al. [9] for well-dried antimony trisulphide showed no change in weight up to 310°. On further heating, the trisulphide was oxidized to antimony oxides. Hanafi and Ismail [10] found that grey-black antimony trisulphide did not suffer any detectable weight change from room temperature up to 280°.

Antimony triselenide and antimony tritelluride

As far as the author is aware, no mention has been made in the literature concerning the TG or DTA behaviour of antimony triselenide or antimony tritelluride. In view of the lack of information, the TG of the component element Sb, Se and Te and stoichiometric mechanical mixed of 2Sb + 3Se and 2Sb + 3Se (corresponding to the compounds, Sb_2Se_3 and Sb_2Te_3, respectively) has been systematically investigated. This was followed by an investigation of the TG and DTA of purely prepared and stoichiometrically adjusted specimens of Sb_2S_3, Sb_2Se_3 and Sb_2Te_3 semiconductors in order to establish their thermal stabilities and the various changes which may take place in each case.

Experimental

Antimony trioxide and antimony trisulphide were prepared by the wet process and heat treatment technique. Antimony triselenide was prepared by direct combination of the two components through melting under vacuum (10^{-6} mm Hg) in silica capsules. Antimony tritelluride was prepared by a similar method as that used for antimony triselenide; the stoichiometry of the compound was carefully completely adjusted using the multiple "master alloying technique".

Apparatus and mode of measurements

Thermogravimetric analysis (TG)

The various semiconducting materials were subjected to TG with an automatic recording thermobalance (Netzsch, Selb, W. Germany). The method consists in following the change in weight of the specimen as a function of temperature variation. The changes in weight and temperature were automatically recorded by a special device. The temperature of the furnace was regulated by two thermocouples to obtain a heating rate of 4 deg/min throughout the temperature range investigated (25–830°). The weighed powdered material on the specimen holder was subjected to heating after sliding the oven downwards easily through channels.

Differential thermal analysis (DTA)

In order to find if any detectable loss or gain in weight is accompanied by phase transformation, the material was subjected to DTA using a VEB Elektro Bad-Franken Hausen thermal analyser, in which the temperature was recorded as a function of time. This system possessed a sensitivity of ±0.5% in the investigated temperature range.

X-ray diffraction measurements

The X-ray diffraction patterns were obtained with a Philips diffractometer (Philips Corporation Type PW 1051/30) and a Berthold diffractometer (Solus Shall Limited, Great Britain [11]. Cu–K_α radiation and an adjustable slit at the focal point of the monochromator were employed. The Geiger–Müller tube was rotated at 2 deg/min and 1 deg/min for the two diffractometers, respectively. The amplifier counter output was recorded simultaneously on a chart set at its maximum speed (600 mm per hour), to give each reflection a reasonable breadth. The diffraction peak was taken to be the average of the positions of the "positive and negative"

Table 1 X-ray data

Authors	*hkl*	dÅ	I/I_0
Cambi and Elli [13]	120	5.24	80
	230	3.24	100
	240	2.62	81
Present author	120	5.24	45
	231	3.24	100
	240	2.62	80
A.S.T.M. [14]	231	3.25	70
	211	3.16	75
	221	2.87	100
Kuznetcov and Palkin [15]	201	3.26	80
	221	2.87	70
	132	1.76	100

halves of the Debye–Scherrer ring. This procedure eliminated any displacement from the true line position caused by the finite scanning rate and time constant of the recording circuit, as well as any small error in the alignment of the beam with the diffractometer scale zero position.

The above measurements were carefully checked and repeated several times on pure and well-dried material. In each case, reproducible and reliable results were obtained.

Results and discussion

Antimony

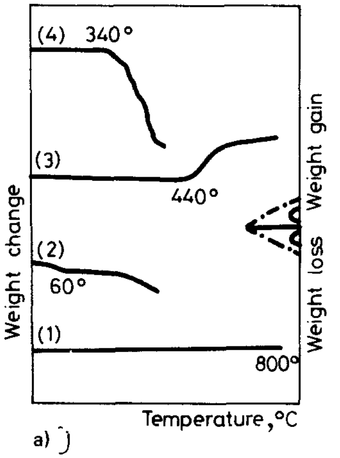
Figure 1a, curve 1 is the TG curve of pure antimony in the temperature range 20–600°. Weight gain started at 457°, which is attributed to the formation of antimony trioxide and higher antimony oxides [6].

Selenium

Figure 1a, curve 2 is the TG curve of pure selenium in the temperature range 20–600°. Weight loss is detected in the temperature range 60–300°. A sudden weight loss is correlated with the sublimation of elemental selenium, which overcompensates the weight gain due to the formation of selenium oxide. The second weight loss may be due to the sublimation of both elemental selenium and the selenium oxide formed.

Tellurium

Figure 1a, curve 3 is the TG curve of tellurium in the temperature range 25–700°. Weight loss is observed at 240°, which is due to tellurium sublimation. Gains in weight are detected at 440°, 520° and 579°. The results are very similar to those previously found by Doan and Duval [5] (curve 3). the weight gain is correlated with the formation of unsublimable tellurium oxides.



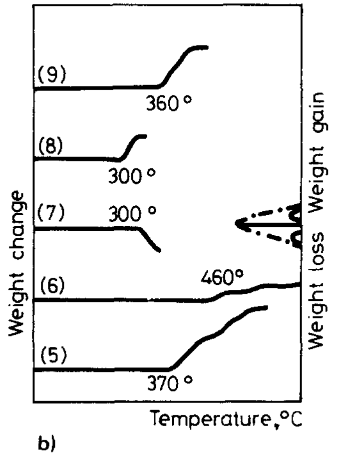


Fig. 1a An illustration showing thermogravimetric analysis of: (1) Antimony, (2) Selenium, (3) Tellurium, (4) 2Sb + 3Se mix

Fig. 1b Diagram showing thermogravimetric analysis of: (5) 2Sb + 3Te mix, (6) Sb_2O_3, (7) Sb_2S_3, (8) Sb_2Se_3 and (9) Sb_2Te_3 specimens

Antimony–selenium mix (2Sb + 3Se)

Figure 1a, curve 4 is the TG curve of the 2Sb + 3Se mix. In contrast to the situation for selenium (curve 2), there is a stable zone up to 340°. At this temperature, a gradual weight loss occurs up to 500°. The first loss corresponds to the sublimation of the selenium present, which outweighs the weight gain due to the formation of antimony oxide. The second sudden weight loss is probably due to the sublimation of the selenium oxide formed, together with an increased rate of selenium sublimation.

Antimony–tellurium mix (2Sb + 3Te)

Figure 1b, curve 5 is the TG curve of the 2Sb + 3Te mix. It can readily be seen that this mix remains stable up to 370°. A weight gain is detected at this temperature, followed other weight gains at 540° and 580°. The gain at 370° corresponds to the formation of antimony oxide only, since tellurium oxidation starts at 440° (curve 3). The other gains may be attributed to the formation of higher antimony oxides beside tellurium oxide, which remains in the crucible.

Antimony trioxide (Sb_2O_3)

Figure 1b, curve 6 is the TG curve of antimony trioxide in the temperature range 20–830°. Gains in weight are detected at 520° and 580°. This result agrees with that obtained by Taimni and Tandon [6] in the same temperature range. They attributed this gain in weight to the formation of antimony tetroxide (Sb_2O_4) and antimony pentoxide (Sb_2O_5).

The DTA of this oxide in the same temperature range (Fig. 2, curve 1) indicates a very weak exothermic peak at $\simeq 225°$. This peak may be due to the transformation of the cubic to the orthorhombic modification. This result indicates that the sample contains traces of the other modification. When the sample was heated at 580° for 12 hours [12] and the DTA run was repeated, the peak disappeared (curve 1). The increase in weight observed in the TG curve due to the formation of Sb_2O_4 and Sb_2O_5 is not manifested by endo- or exothermic peaks in the DTA curve. This may be due to the fact that the change in structure is not accompanied by any calorific variation, or the change is beyond the sensitivity of the DTA apparatus.

$$\underset{\text{(orthorhombic)}}{Sb_2O_3} \xrightarrow{(O)} \underset{\text{(orthorhombic)}}{Sb_2O_4} \xrightarrow{(O)} \underset{\text{(cubic)}}{Sb_2O_5}$$

Since it may be expected that the changes in the crystal system may not be accompanied by calorific changes.

Antimony trisulphide (Sb_2S_3)

Figure 1b, curve 7 shows the behaviour of grey-black antimony trisulphide. The weight of this specimen remains constant between 25° and 300°, where a decrease in weight takes place due to the formation of antimony oxides.

DTA measurements on this sample in the temperature range investigated Fig. 2, curve 2 indicate that no phase transformation takes place.

Antimony triselenide (Sb_2Se_3)

Figure 1b, curve 8 indicates that, antimony triselenide does not suffer any loss or gain in weight in the temperature range 25–310°, after which a gradual rise in weight is observed up to 350°. At about 370°, a sudden loss in weight is detected. It may be concluded that the first gain in weight may be due to the oxidation of antimony triselenide to antimony oxides and/or selenium oxides. If it is assumed that the antimony and selenium oxides remain in the crucible, we find that the value of the observed weight gain is about 50% of the calculated one, which suggests that at this temperature selenium begins to sublime, but at a very low rate. This rate increases at 370°, as recorded in the curve. From the TG curves of selenium metal prepared from different origins Duval and Doan [4] came to the conclusion that this metal sublimes appreciably between 350° and 370°, depending on the method of preparation and the origin. This is not the case for the 2Sb + 3Se mix.

Thus, for the 2Sb + 3Se mix, the rate of selenium sublimation exceeds that of antimony oxidation and hence a weight loss first occurs in the TG curve (curve 4) at 340°. In contrast, the results for antimony triselenide (Sb_2Se_3) indicate a higher rate of antimony oxidation than that of selenium sublimation, leading first to a weight gain in the TG curve (Fig. 1b, curve 8). This may lead us to conclude that the mixed component semiconductor possesses a higher degree of thermal stability (340°) than that for the elemental and compound semiconductors.

In order to detect whether antimony triselenide undergoes any phase transformation when heated in the same temperature range, DTA measurements were made.

Thus Fig. 2, curve 3 shows the DTA behaviour of this compound. It is clear that no phase transformation is observed in the temperature range 25–300°, whereas exotherms are found at 320° and 420°. This may be due to the oxidation of the antimony trioxide formed to higher antimony oxides.

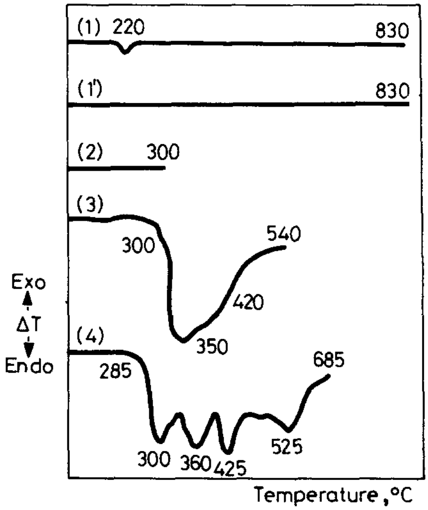


Fig. 2 A diagrammatical representation showing the differential thermal analysis of the different antimony chalcogenides: (1) Sb_2O_3, before heat treatment (Orth. + Cub.), (1') Sb_2O_3, after heat treatment at 580 °C, 12 hr (Orth.), (2) Sb_2S_3, (3) Sb_2Se_3, (4) Sb_2Te_3

Antimony tritelluride (Sb_2Te_3)

Figure 1b, curve 9 shows the temperature-dependence of the weight for antimony tritelluride. This compound remains stable up to 360°. An increase in weight is observed in the temperature range 350–420° due to the oxidation of antimony tritelluride. There is another peak at 460°, and a third one at 525°. These may be due to the formation of higher antimony oxides. Doan and Duval [5] stated that tellurium dioxide remains nearly constant in weight and does not vaporize up to 1000°, which is not the case for selenium oxide. This observation is slightly different from that for the 2Sb + 3Te mix.

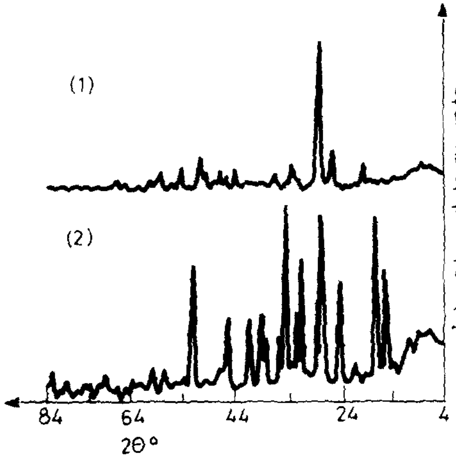


Fig. 3 The room temperature X-ray diffraction patterns of: (1) Antimony trioxide and (2) Antimony triselenide

The DTA behaviour of antimony tritelluride Fig. 2, curve 4 shows the beginning of an exothermic peak at 285°, followed by others situated 360°, 450° and 525°. The first one may be due to the rhombohedral →cubic transformation. The others coincide with the temperatures at which antimony tritelluride is oxidized to antimony oxides.

Figure 3, pattern 1 shows the room-temperature X-ray diffraction pattern of pure antimony trioxide. Comparison of the interplanar *d* spacings and the visually estimated relative intensities (I/I_0) with the corresponding values from the A.S.T.M. card proves that the compound exhibits an orthorhombic crystal form.

Figure 4, pattern 1 shows the room-temperature X-ray diffraction pattern of antimony trioxide (cut taken from the TG holder after heating to 580°). It can readily be seen that this pattern is very similar to the original pattern (1). This could be explained in that either antimony trioxide (Sb_2O_3) of antimony tetroxide

(Sb_2O_4) has the same orthorhombic crystal from or system [12]. This is turn may lead to no marked change in the X-ray diffraction pattern. Interpretation of the diffracted lines indicated an additional phase at $2\theta = 30°$. This is probably due to the propagation of antimony tetroxide at the expense of the antimony trioxide present.

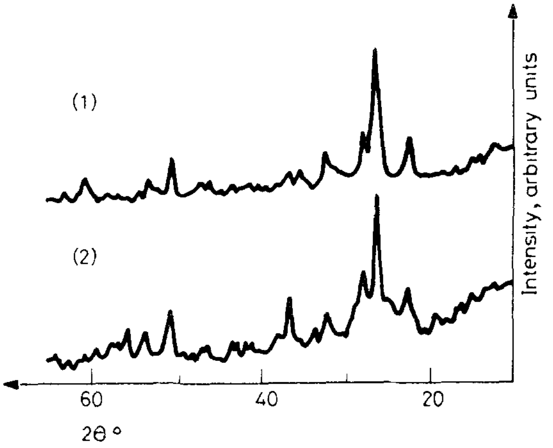


Fig. 4 The room temperature X-ray diffraction patterns of: (1) Antimony trioxide fired at 580 °C (cut from the TGA holder),
(2) Antimony triselenide fired at 580 °C (cut from the TGA holder)

Figure 3, pattern 2 represents the room-temperature X-ray diffraction pattern of antimony triselenide (cut taken from the TG holder after heating to 580°). It is clear that the pattern is very similar to pattern in Fig. 4. Some additional peaks are present in the patterns, which are probably correlated to the remaining unchanged antimony triselenide. This means that when antimony triselenide is heated at 580°, antimony trioxide and antimony tetroxide are formed at the expense of the antimony triselenice.

Accordingly, it was concluded that the results of the X-ray diffraction measurements are in good agreement with those obtained from the TG and DTA measurements.

Conclusion

TG and DTA led to the following findings: The thermal stability of mechanically mixed elemental semiconductors is higher than that of the pure individual elements or the corresponding compound semiconductors.

For the investigated compound semiconductors, the evaluated stabilities as follows:

$$Sb_2O_3 > Sb_2Te_3 > Sb_2Se_3 > Sb_2S_3$$

It is clear that the electronegativity differences and hence the bond-strength follow the sequence:

$$Sb_2O_3 > Sb_2S_3 > Sb_2Se_3 > Sb_2Te_3$$

Thus, the conclusion could be reached that the oxygen affinity of the non-metallic constituents (S, Se and Te) is the predominant factor affecting the thermal stability of the investigated materials. This factor outweighs that due to the subsequent decrease in electronegativity difference of the component elements, and hence the bond-strength, on going from antimony trioxide to antimony tritelluride. This may cause the above-mentioned stability sequence of the investigated materials for their industrial application in semiconducting and electronic devices.

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Zusammenfassung — Es wurde eine systematische Untersuchung der relativen Stabilität und verschiedener Phasenübergänge beim Erhitzen von Elemente-, Verbindungs- und mechanisch vermischten Halbleitern durchgeführt. Diese waren Chalkogene, Chalkogenide und Mischungen beider. Die Bedeutung vorliegender Arbeit knüpft an die nutzvolle Anwendung der hergestellten materialien auf dem Gebiet von Transistorempfängern, Radar, Gleichrichtern und anderen elektronischen Zweigen an. Die thermogravimetrischen und Differentielthermoanalysen wurden in Luft im Temperaturbereich 20–830 °C durchgeführt. Die Ergebnisse lassen darauf schliessen, dass der Stabilitätsgrad der mechanisch vermischten Halbleiter viel höher ist als der der einzelnen Halbleiterkomponenten. Die Ergebnisse wurden auf der Grundlage der Elektronegativitätsunterschiede und der Sauerstoffaffinitäten der nichtmetallischen Komponenten diskutiert. Für jedes der untersuchten Materialien werden zu späteren physikalischen Untersuchungen und zur Eignung für die Herstellung von Halbleiterprodukten die Bereiche thermischer Stabilität angegeben.

Резюме — Проведено систематическое изучение относительной устойчивости и фазовых изменений, имеющих место при нагреве исходных полупроводниковых компонентов, самого полупроводника и их механических смесей. В качестве таковых были исследованы халькогены, халькогениды и их смеси. Интерес проведенного исследования был вызван применением полученных материалов в электронной технике (транзисторы, радары, выпрямители и др.). ТГ и ДСК анализ полученных материалов был проведен в атмосфере воздуха в интервале температур 20–830°. Результаты показали, что степень устойчивости механически смешанных полупроводниковых компонент намного выше, чем чистых полупроводниковых компонент или самих полупроводниковых соединений. Результаты были обсуждены на основе различий в электроотрицательности и сродства к кислороду неметаллических компонент. Для каждого полученного материала были определены область их термоустойчивости, последующие физические измерения и пригодность их для получения полупроводниковых усройств.