

EXPERIMENTAL STUDY OF THE NON STOICHIOMETRY OF CESIUM ANTIMONIDE

$\approx \text{Cs}_3\text{Sb}$

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Received May 29, 1989; accepted July 12, 1989

ABSTRACT

Non stoichiometric $\approx \text{Cs}_3\text{Sb}$ was synthesized at 200°C by a reaction of solid antimony with cesium vapor under controlled pressure. The compositions obtained correspond to atomic ratios $3.04 > \text{Cs/Sb} > 2.95$. Measurements of the Seebeck coefficient, diffuse reflectance spectra and X-ray studies indicate that the predominant defects are singly charged interstitial cesium when $\text{Cs/Sb} > 3$ and singly charged interstitial cesium when $\text{Cs/Sb} < 3$; the band gap is close to 1.35 eV in the whole composition range.

INTRODUCTION

Several intermetallic compounds exist in the cesium-antimony system [1-2-3]. The first of them to appear on the cesium rich side, with the ideal formula Cs_3Sb , is known to have interesting photoemissive properties, and more particularly a high quantum yield in the UV and visible range [4, 5]. These features make it a material of practical interest for the manufacturing of photocathodes. Industrially, thin layers of Cs_3Sb are produced through a reaction of cesium vapors on predeposited antimony, at a temperature of about 200°C [6].

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The phase α - Cs_3Sb can be obtained as a powder from direct reaction between the two components mixed in approximately stoichiometric amounts. X-ray diffraction studies on such powders reveal a cubic structure in the F mode, but no further information can be gathered from this method since the atomic diffusion factors of antimony ($Z = 51$) and Cs ($Z = 55$) are very close to each other [7-8]. However, more information on the structure was obtained from electron diffraction on thin layers [9], showing that Cs_3Sb , like Cs_3Bi or Rb_3Bi has the anti- BiF_3 structure (Fig. 1). Furthermore the study showed that the lattice parameter depends on the processing conditions, which is attributed, according to Jack and Wachtel [8] to an antimony-cesium substitution leading to the formula $(\text{Cs}_{\text{Cs}})_3(\text{Cs}_{\text{Sb}})_x(\text{Sb}_{\text{Sb}})_{1-x}$ with $0 \leq x \leq 0.05$.

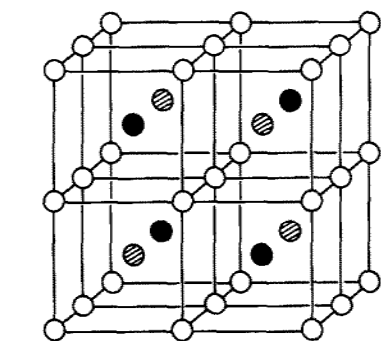


Fig. 1. Crystallographic structure of Cs_3Sb , after Gnutmann [7].

The electrical and optical properties of thin layers of Cs_3Sb are quite well known [6-11]: their electrical conductivity shifts from p to n type when the partial pressure of cesium used for the synthesis is increased; the quantum yield of the p-type material is higher than that of the n-type, which is due to the bending of the conduction band in the vicinity of the interface [12].

The aim of the present study is to determine quantitatively how the composition of $\approx\text{Cs}_3\text{Sb}$ depends on the partial pressure of cesium used for its synthesis and at the temperature of 200°C which is of industrial interest.

EXPERIMENTAL

The phase $\approx\text{Cs}_3\text{Sb}$ is synthesized by the action of cesium vapor, generated from a pure liquid at a temperature T' , on pure solid antimony held in a reactor at a temperature $T'' > T'$ in order to avoid distillation. Applying the phase rule to the reactor at T'' , where the chemical potential of cesium is imposed by the temperature T' of the generator, shows that no more than one condensed phase, and with definite composition, can be synthesized in such conditions.

The apparatus that we used is shown on Fig. 2. The pyrex tube is first outgassed at 400°C , then filled with the components and sealed under vacuum (10^{-3} Pa). Several syntheses were made for various generator temperatures T' , the reactor temperature always remaining equal to 200°C . As already mentioned, T' is set lower than T'' in order to avoid distillation of the alkali metal towards the reactor [13]. Furthermore, T' shall remain above 100°C in order for P_{Cs} to exceed its equilibrium value at 200°C in the equilibrium :

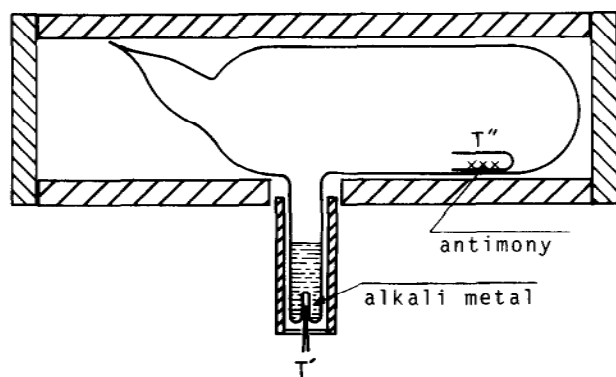
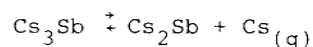


Fig. 2. Reactor set up.

Indeed the difference $T''-T'$ was such that no significant transport of antimony could occur from the reactor towards the generator. After several trials, we established that a time of 200 h was needed to combine all the antimony. At the end of this period, the pyrex vessel was quenched in air in such a way that the generator was always at a temperature lower than that of the reactor. Due to the reactivity of both cesium and antimonide with respect to oxygen and nitrogen, opening of the tube and further manipulations were performed under an atmosphere of purified argon ($O_2 + N_2 + H_2$ less than 10 ppm).

The phases obtained were characterized by X-ray powder diffraction using the K_α line of copper. The increase in mass, measured after the treatment of antimony by the alkali vapor, led to the ratio Cs/Sb in the phase synthesized. Seebeck measurements, taken on sintered samples (6 mm diameter, 1 mm thickness) and using a difference of temperature of 6°C , gave the sign of the predominant electric carriers.

RESULTS AND DISCUSSION

Our results, summarized in Table I, indicate that Cs_3Sb exists, at 200°C , in a range of composition which corresponds to $3.04 \geq \text{Cs/Sb} \geq 2.95$. Since the atomic masses of cesium and antimony are close to each other, it was not possible to correlate these results with density measurements.

Table I. Experimental results.

T'	P_{Cs} atm.	Cs/Sb ± 0.01	$a \pm 0,01$ (\AA)	Type of conductivity	$d_{\text{exp.}}$
100°C	7.10^{-7}	2.95	9.14	p	4.42 ± 0.05
145°C	8.10^{-6}	3.00	9.16		4.44 ± 0.05
190°C	8.10^{-5}	3,04	9.19	n	4.46 ± 0.05
$T'' = 280^\circ\text{C}$					
200°C	9.10^{-5}	3.00	9.16		4.44 ± 0.05

The variations in stoichiometry of $\approx \text{Cs}_3\text{Sb}$ can result from either predominant substitutional, interstitial or vacancy defects. The possible mechanisms are listed in Table II, using Kröger and Vink notations [15].

Indeed, for a given type of defect, the volumetric concentration (d) depends on the partial pressure of cesium, P_{Cs} , in equilibrium with the $\approx \text{Cs}_3\text{Sb}$ phase. The same remark holds for the electrical conductivity.

If we admit that, except for the compositions close to the ideal formula, the defects due to departure from stoichiometry predominate largely over those due to thermal disorder, and that departure from Henry's law is not significant, then a definite slope of the straight lines :

$$\log(d) \propto \log P_{\text{Cs}}$$

$$\log \sigma \propto \log P_{\text{Cs}}$$

can be attributed to each of the mechanisms listed in Table II.

Hagino and Takahashi [11] have measured, at the temperature of 200°C, the electrical conductivity of $\approx \text{Cs}_3\text{Sb}$ films as a function of P_{Cs} . Their results indicate that $\log \sigma$ is actually proportional to $\log P_{\text{Cs}}$, with a coefficient close to 1/2 when $\text{Cs/Sb} > 3$ and close to -1/2 when $\text{Cs/Sb} < 3$. These values are consistent with the existence of singly charged interstitial cesium in the first case (mechanism 2 on Table II) and that of singly charged cesium vacancies in the second case (mechanism 6 on Table II). Our own determinations of the Seebeck coefficient, which indicate a n-type conductivity when $\text{Cs/Sb} > 3$ and a p-type conductivity when $\text{Cs/Sb} < 3$ are in agreement with these results. According to our X-ray studies (Table I) the lattice parameter of $\approx \text{Cs}_3\text{Sb}$ decreases when the ratio Cs/Sb is lowered. Since the Sb^{3+} ion is smaller than the Cs^+ ion, this indicates then that the predominant defects shall not be interstitial or substitutional Sb^{3+} , but rather cesium vacancies. In a likewise manner, one can assert that, when $\text{Cs/Sb} > 3$, only interstitial cesium is likely to increase the lattice parameter which, on the contrary, would be decreased if antimony vacancies or substitutional cesium were responsible for the departure from stoichiometry. The latter possibility, although suggested by Jack and Wachtel [8] is very improbable because of the difference in electrone-

Table II. Defect reactions in $\approx \text{Cs}_3\text{Sb}$.

Cs/Sb > 3	
1) Substitution of antimony by cesium	
$4\text{Cs}_{(\text{vap})} + 3\text{Cs}_{\text{Cs}}^{\times} + \text{Cs}_{\text{Sb}}^{4\cdot} + 4e'$	(i)
$4\text{Cs}_{(\text{vap})} + 3\text{Cs}_{\text{Cs}}^{\times} + \text{Cs}_{\text{Sb}}^{3\cdot} + 3e'$	(ii)
2) Interstitial cesium	
$\text{Cs}_{(\text{vap})} + \text{Cs}_i^{\cdot} + e'$	
3) Antimony vacancies	
$3\text{Cs}_{(\text{vap})} + 3\text{Cs}_{\text{Cs}}^{\times} + \text{V}_{\text{Sb}}^{3\cdot} + 3e'$	(i)
$3\text{Cs}_{(\text{vap})} + 3\text{Cs}_{\text{Cs}}^{\times} + \text{V}_{\text{Sb}}^{2\cdot} + 2e'$	(ii)
$3\text{Cs}_{(\text{vap})} + 3\text{Cs}_{\text{Cs}}^{\times} + \text{V}_{\text{Sb}}^{\cdot} + e'$	(iii)
Cs/Sb < 3	
4) Substitution of cesium by antimony	
$4\text{Cs}_{\text{Cs}}^{\times} + \text{Sb}_{\text{Sb}}^{\times} + 4\text{Cs}_{(\text{vap})} + \text{Sb}_{\text{Cs}}^{4\cdot} + 4h^{\cdot}$	(i)
$4\text{Cs}_{\text{Cs}}^{\times} + \text{Sb}_{\text{Sb}}^{\times} + 4\text{Cs}_{(\text{vap})} + \text{Sb}_{\text{Cs}}^{3\cdot} + 3h^{\cdot}$	(ii)
$4\text{Cs}_{\text{Cs}}^{\times} + \text{Sb}_{\text{Sb}}^{\times} + 4\text{Cs}_{(\text{vap})} + \text{Sb}_{\text{Cs}}^{2\cdot} + 2h^{\cdot}$	(iii)
$4\text{Cs}_{\text{Cs}}^{\times} + \text{Sb}_{\text{Sb}}^{\times} + 4\text{Cs}_{(\text{vap})} + \text{Sb}_{\text{Cs}}^{\cdot} + h^{\cdot}$	(iiii)
5) Interstitial antimony	
$3\text{Cs}_{\text{Cs}}^{\times} + \text{Sb}_{\text{Sb}}^{\times} + 3\text{Cs}_{(\text{vap})} + \text{Sb}_i^{3\cdot} + 3h^{\cdot}$	(i)
$3\text{Cs}_{\text{Cs}}^{\times} + \text{Sb}_{\text{Sb}}^{\times} + 3\text{Cs}_{(\text{vap})} + \text{Sb}_i^{2\cdot} + 2h^{\cdot}$	(ii)
$3\text{Cs}_{\text{Cs}}^{\times} + \text{Sb}_{\text{Sb}}^{\times} + 3\text{Cs}_{(\text{vap})} + \text{Sb}_i^{\cdot} + h^{\cdot}$	(iii)
6) Cesium vacancies	
$\text{Cs}_{\text{Cs}}^{\times} + \text{Cs}_{(\text{vap})} + \text{V}_{\text{Cs}}^{\cdot} + h^{\cdot}$	

gativity between cesium and antimony. Furthermore, it would lead to a slope equal to $4/5$ for the $\log \sigma \propto \log P_{\text{Cs}}$ curve, in disagreement with the results of Hagino and Takahashi [11].

The defect structure of $\approx \text{Cs}_3\text{Sb}$, i.e. Cs interstitials and Cs vacancies for $\text{Cs/Sb} > 3$ and $\text{Cs/Sb} < 3$ respectively, suggests a predominant Frenkel disorder of cesium ions at a stoichiometric composition. If we assume that, in the p domain, the number of acceptor levels equals that of cesium vacancies, then our limit composition ($\text{Cs/Sb} = 2.95$) would correspond to 3×10^{20} carriers per cm^3 . in good agreement with the values obtained by Sakata et al. [16, 17] after Hall effect measurements on thin films (10^{20} up to 1.8×10^{23} carriers per cm^3). It is worthwhile noting that the value 10^{18} carriers per cm^3 calculated by Hagino and Takahashi from their conductivity measurements depends on an hypothesis on the mobility value.

Another interesting feature is that the vapor pressure for which we obtained the stoichiometric composition Cs_3Sb corresponds closely to that for which Hagino and Takahashi observed the shift from n to p conductivity.

Diffuse reflectance spectra for the compositions $\text{Cs}_{2.95}\text{Sb}$, Cs_3Sb and $\text{Cs}_{3.04}\text{Sb}$ are given in Fig.3. Below about 1.35 eV, the reflectance increases linearly and the deviations from stoichiometry bring about only minor variations. Several authors found good agreement between the band gap energy of semiconductors and the beginning of the linear increase in reflectance (or photoacoustic) spectra [18, 19]. In these conditions, the band gap can be estimated as close to 1.35 eV for the whole composition range.

It is usually considered that the alkali-antimonides with a cubic symmetry (anti BiF_3 -type) would be p-type conductors while those with an hexagonal symmetry (Na_3As type) would be n-type conductors. Such considerations originate in the fact that it is relatively easy to introduce interstitial alkali metals in the hexagonal structure, which is the less compact; rather than in the other way, the cubic structure, which would be easily alkali deficient [21]. The present study, and also the variations of the electrical conductivity of cubic $\approx \text{Cs}_3\text{Sb}$ with the partial pressure of cesium, indicate that, as expected, this compound can be a p-type conductor when it contains cesium vacancies ($\text{Cs/Sb} < 3$). But $\approx \text{Cs}_3\text{Sb}$ can be as well an n-type conductor

when its departure from stoichiometry originates in the presence of cesium interstitials ($\text{Cs/Sb} > 3$). It can then be concluded that its actual crystalline structure is likely to be far more complex than it appears on the model illustrated in Fig. 1. In reality, the environment of the antimony ions is probably distorted enough to allow the insertion of alkali atoms, without creating apparent changes in the cubic structure.

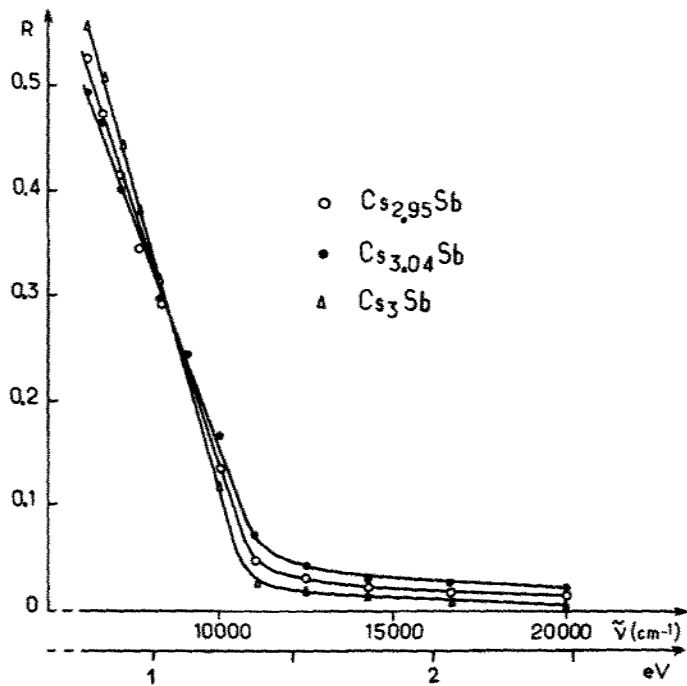


Fig. 3. Diffuse reflectance spectra for the antimonides studied.

ACKNOWLEDGEMENTS

This research was supported by the Ministère de l'Industrie et de la Recherche

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