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FORMATION AND ELECTRICAL PROPERTIES OF SILVER ANTIMONY OXIDE

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Silver antimony oxide ($Ag_2Sb_2O_6$) having a defect pyrochlore structure has been synthesized by solid-state reaction between silver oxide and either Sb_2O_3 and Sb_2O_5. The reaction sequence has been shown by thermogravimetry, interdiffusion measurements on oxide pellets and electrical conductance measurements to involve the reduction of Ag_2O, followed by diffusion of silver and oxygen into the antimony oxide component. When the starting material is Sb_2O_3, initial diffusion of oxygen occurs, forming Sb_2O_4 into which silver and further oxygen subsequently diffuse. Comparison of the activation energies for diffusion and electrical conductance in the various oxide phases suggests that the rate of $Ag_2Sb_2O_6$ formation is controlled by the diffusion of oxygen rather than that of silver.

The compound $Ag_2Sb_2O_6$ has previously been prepared by Sleight [1] from mixtures of AgO with either Sb_2O_3 or Sb_2O_5. Regardless of the starting materials or the pressure of oxygen under which the preparation was carried out, the products all analyzed as $Ag_2Sb_2O_6$ and had X-ray powder patterns which were consistent with a pyrochlore structure of cell dimension 10.249 Å [1]. The chemistry of the solid-state reactions involved in the formation of this compound has not been investigated previously.

Present interest in inter-oxide compounds of this type arises from their possible use in energy conversion or storage applications, either for direct photoelectrolysis of water or as higher-temperature solid electrolytes. The usefulness of materials for this type of application is to some extent dictated by their electrical conductance, which for materials of pyrochlore structure can vary from typically semiconducting or insulating (as in $Ln_2Ti_2O_7$) [2] to typically metallic (as in $Cd_2Re_2O_7$) [2]. Silver antimony oxide is a defect pyrochlore whose electrical properties have not previously been reported; the few defect pyrochlores on which conductance studies have been made (e. g. $Pb_2B_2O_6$, where B = Ru, Re and Ir) exhibited metallic behaviour [3].

The objectives of this work were therefore to study the reaction sequence leading to $Ag_2Sb_2O_6$ formation from both Sb_2O_3 and Sb_2O_5, and to study the electrical conductance of the product as a function of temperature.

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Experimental

The starting materials were reagent grade Ag_2O, Sb_2O_3 and Sb_2O_5. The latter was stated by the manufacturer to be hydrated, and TG analyses showed the composition to approximate to $Sb_2O_5 \cdot 2\,H_2O$. Before use, this oxide was prefired to 1000° for 4 hr. Equimolar mixtures of both the trioxide and pentoxide with Ag_2O were fired in air at 900 – 1000° in covered alumina crucibles. Small samples ($\sim$ 0.9 mg) were also heated in a Stanton Redcroft TG 770 thermobalance at a heating rate of 20°/min in a static air atmosphere.

Interdiffusion experiments were made with pressed pellets of Ag_2O and prefired Sb_2O_5 held in close contact by binding with platinum wire and annealed at 850 – 1000°. The pellets were then separated, mounted with epoxy resin on glass slides and their reaction faces examined by X-ray diffraction. Thin layers of the pellets were then progressively ground off and the faces re-examined, semi-quantitative estimates of the reactant and product phases being made as af unction of the distance from the reaction interface on the basis of the relative X-ray peak intensities.

Electrical conductance measurements were made as a function of temperature on 10 mm dia. pellets of $Ag_2Sb_2O_6$ pressed at 3.0×10^3 kg cm^{-2} and sintered in closed crucibles for 2h. Electrical contacts to the faces of the pellets were made by vacuum evaporating a thin film of platinum and the measurements were carried out in air at 1592 Hz using a Wayne – Kerr model B642 bridge in conjunction with a conductance cell described elsewhere [4]. Similar measurements were also made on separate pellets of Sb_2O_5, Sb_2O_3 and Ag_2O.

Results and discussion

Chemistry of silver antimony oxide formation

Irrespective of the starting oxides, the product in every case showed the X-ray pattern reported by Schrewelius [5] for the pyrochlore-type compound $Ag_2Sb_2O_6$ [1, 5]. The colours of the compounds prepared from Sb_2O_3 and Sb_2O_5 in closed containers were respectively dark orange-yellow and pale yellow. This colour difference is probably due to slight deviations from ideal stoichiometry, which must, however, be too small to influence noticeably the lattice parameters of the crystal structure, since the X-ray patterns are identical in every respect. Since Sb_2O_3 is slightly volatile above about 450° (see next section), it is probable that the darker coloured compound formed from this oxide may be slightly silver rich (the alternative possibility, that the compound is oxygen-deficient because of its formation in a restricted oxygen supply is ruled out by the fact that this compound retains its orange colour even when re-heated at 1000° in air).

Since reduction and oxidation both play a role in the reaction mechanism, TG was used to provide further information.

(a) *Reaction between Sb_2O_5 and Ag_2O.* A typical TG curve of an equimolar mixture of Ag_2O with prefired Sb_2O_5 is shown in Fig. 1A. X-ray diffraction showed the prefired Sb_2O_5 to be of good crystallinity with no Sb_2O_4 detectable.

The initial 2.8% weight loss which starts at about 330° corresponds to the reduction of Ag_2O (theoretical weight loss for this reaction in the present mix = 3.0%). The onset temperature of this reaction also compares well with

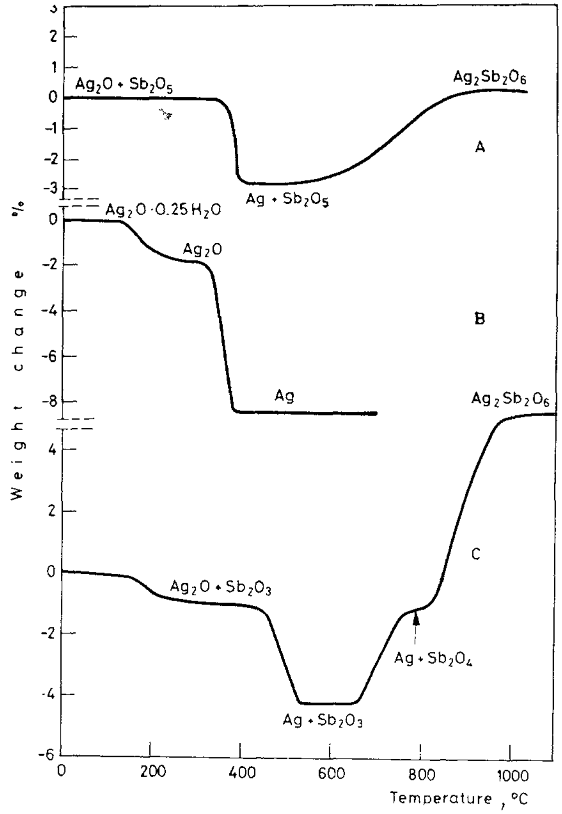

Fig. 1. TG curves for mixtures of silver oxides with antimony oxide. Heating rate 20°/min, atmosphere static air. A) $Ag_2O+Sb_2O_5$. B) Ag_2O alone; C) $Ag_2O + Sb_2O_3$

that of pure Ag_2O (Fig. 1B), and the theoretical weight loss for the disproportionation of pure Ag_2O (6.9%) is in agreement with the observed weight loss of 6.6% between 264 and 392°. A smaller, lower-temperature weight loss of 1.8% is apparently due to the removal of mechanically-held volatiles such as water, since the X-ray trace is unchanged by heating pure Ag_2O to 264°. This small weight loss corresponds approximately to 0.25 moles H_2O per mole Ag_2O.

Reaction between metallic silver, Sb_2O_5 and atmospheric oxygen proceeds smoothly in a single stage between about 520–890°, the theoretical and observed

Table 1

TG data for reaction sequences of silver oxide with antimony oxides

Reaction	Weight change, %		Temperature range, °C
	Theoretical	Observed	
A. $Ag_2O+Sb_2O_5$			
1. $Ag_2O+Sb_2O_5 \rightarrow 2\,Ag + Sb_2O_5 + \frac{1}{2}O_2\uparrow$	−3.0	−2.8	330−390
2. $2\,Ag + Sb_2O_5 + \frac{1}{2}O_2 \rightarrow Ag_2Sb_2O_6$	+3.0	+3.1	520−890
B. $Ag_2O + Sb_2O_3$			
1. $Ag_2O + Sb_2O_3 \rightarrow 2\,Ag + Sb_2O_3 + \frac{1}{2}O_2\uparrow$	−3.06	−3.2	310−370
2. $2\,Ag + \frac{1}{2}O_2 + Sb_2O_3 \rightarrow 2\,Ag + Sb_2O_4$	+3.2.	+3.0	610−760
3. $2\,Ag + Sb_2O_4 + O_2 \rightarrow Ag_2Sb_2O_6$	+6.1	+6.6	770−940

weight gain for this step being in good agreement. The reaction sequence is summarized in Table 1.

(b) *Reaction between* Sb_2O_3 *and* Ag_2O. A typical TG curve for this system is shown in Fig. 1C. The interpretation of this complex curve is assisted by comparison with the curves of the component oxides. The small initial weight loss below 320° is again due to the loss of volatiles from the Ag_2O which is then reduced in these samples at about 410°. In pure Sb_2O_3, a slight weight loss due to evaporation begins at about 520°, reaching a maximum of 12% just below the melting point, under the present experimental conditions. In mixtures containing Ag_2O, no weight loss attributable to evaporation was observed, neither were any signs of melting observed up to 1000°. This difference in behaviour in the presence of Ag_2O might be due to the overlap of the disproportionation reaction with the onset of Sb_2O_3 evaporation; both phases should at this stage be highly reactive, and the sorption of Sb_2O_3 vapour on the freshly-formed silver metal particles seems feasible.

Since the final product, $Ag_2Sb_2O_6$ contains Sb , oxidation of both the Ag and Sb^{III} must occur, either simultaneously or in consecutive steps. The TG curve (Fig. 1C) shows two weight gains, one of 3.0% up to 763°, the other of 6.6% up to 1000°. These results are in reasonable agreement with the weight gains involved in the uptake of half a mole and one mole of oxygen, respectively. The first step of oxygen uptake corresponds to the formation Sb_2O_4, since X-ray diffraction shows that samples heated to the inflexion temperature for a short period contain orthorhombic Sb_2O_4, metallic silver and a small amount of a defective form of $Ag_2Sb_2O_6$ in which the *d*-spacings are slightly larger than in the well-crystallized compound formed at higher temperatures. This $Ag_2Sb_2O_6$ may be the result of premature reaction between Sb_2O_3 vapour and freshly-formed silver metal grains, as mentioned previously.

In the second step of oxygen uptake, the diffusion of a further mole of oxygen into the mixed oxide lattice establishes the stoichiometry of the pyrochlore product phase in the bulk. The proposed reaction sequence is summarized in Table 1.

Interdiffusion studies in $Sb_2O_5-Ag_2O$ *pellets*

The results of a typical interdiffusion experiment are shown in Fig. 2, which shows that diffusion is predominantly of silver into Sb_2O_5 and not vice-versa.

At the annealing temperature, the Ag_2O pellet has been completely converted into metallic silver. Thus, the reaction in which $Ag_2Sb_2O_6$ is formed involves not only diffusion of Ag into Sb_2O_5, but also the diffusion of oxygen into the reaction zone between the pellets. Since $Ag_2Sb_2O_6$ is the only silver-containing phase observed within the pellet, either the gaseous diffusion is at least as rapid as the diffusion of silver, or alternatively the process by which silver diffuses into Sb_2O_5 may depend on the co-operative movement of oxygen. Evidence for an oxygen gradient within the Sb_2O_5 pellet is provided by differences in the colour of the $Ag_2Sb_2O_6$, which appears darker within the centre of the pellet (Fig. 2, inset). Evidence gained in the preceding experiments suggests that the darker coloured phase contains a slight excess of silver, although still occurring as the pyrochlore.

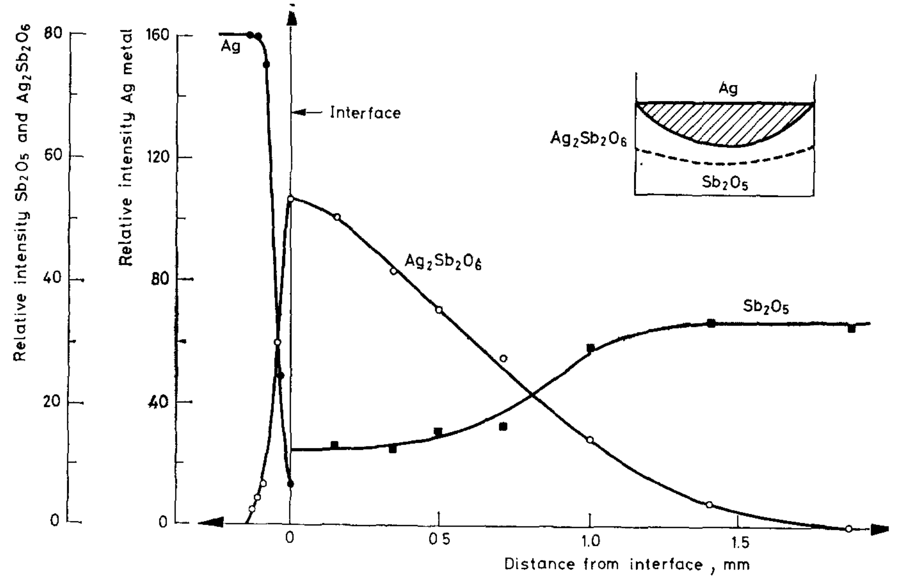

Fig. 2. Phase distribution in pellets of Ag_2O and Sb_2O_5 annealed in contact at 950° for 2h. Inset: Appearance of diffusion couple after annealing. Shaded area indicates region of darker colour, possibly silver-rich $Ag_2Sb_2O_6$

Since $Ag_2Sb_2O_6$ was the only silver-containing phase occurring in the Sb_2O_5 pellet, its concentration profile could provide information about the diffusion of silver-bearing species in Sb_2O_5. Fig. 2 shows that the profile of $Ag_2Sb_2O_6$ is typical of homogeneous diffusion into a semi-infinite solid in which the surface composition is not constant [6], under these boundary conditions the concentration C of diffusing species at a point X within the sample after time t is given by [6].

$$C = C_0/2(\pi Dt)^{1/2} \exp(-X^2/4Dt) \tag{1}$$

where C_0 is the concentration of diffusing species at the surface and D is their diffusion coefficient.

Thus, a plot of $\ln C$ *vs.* X^2 should be linear with a slope $-1/4Dt$, or at the point where the concentration has dropped to half that at the interface,

$$D = X_{1/2}^2/2.77t. \tag{2}$$

Although these relations are only strictly true for tracer diffusion, the present interdiffusion experiments at several different tempratures were analyzed in this

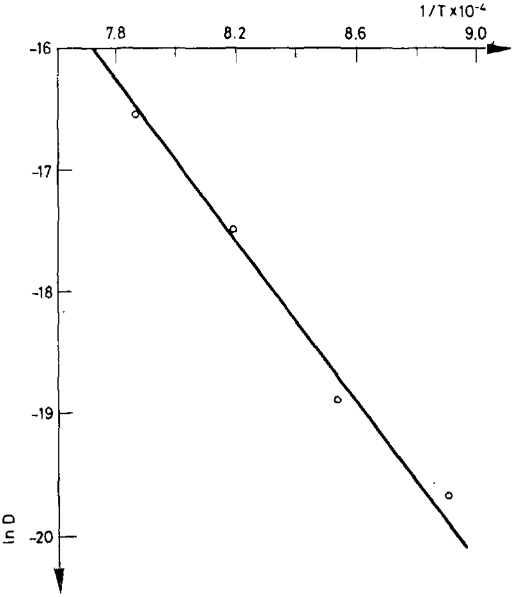

Fig. 3. Arrhenius plot of interdiffusion data for Ag/Sb_2O_5 couples

Table 2

Diffusion data for Ag/Sb_2O_5 couples

Temperature, °C	Diffusion time, S	$X_{1/2}$, cm	D, cm^2S^{-1}	ln D
850	9.00×10^4	2.7×10^{-2}	2.92×10^{-9}	-19.65
900	8.82×10^4	3.9×10^{-2}	6.23×10^{-9}	-18.89
950	7.20×10^4	7.1×10^{-2}	2.53×10^{-8}	-17.49
1000	2.52×10^4	6.8×10^{-2}	6.62×10^{-8}	-16.53

way, and the apparent diffusion coefficients of the silver-bearing species in Sb_2O_5 thus obtained are presented in Table 2.

The apparent activation energy for the diffusion process was found from an Arrhenius plot (Fig. 3) to be 258.5 kJ/mole. The complete expression for the diffusion coefficient (in cm^2S^{-1}) over this temperature range is given by:

$$D = 3.07 \times 10^3 \exp(-258.500/RT) \tag{3}$$

(where R is in joules. deg^{-1} $mole^{-1}$).

The mechanistic significance of this result is discussed in the next section.

Electrical conductance of $Ag_2Sb_2O_6$.

Plots of the conductance of this phase and its constituent oxides are shown as a function of temperature in Fig. 4.

The conductance of $Ag_2Sb_2O_6$ increases steeply above about 250°, reaching a value similar to that of the contact resistance of the measuring cell by about 700° (the apparent tailing-off of the conductance at higher temperature is due to this effect).

The conductances of the constituent oxides under the same experimental conditions are as expected; silver oxide becomes increasingly conductive up to the temperature of its disproportionation into silver metal and oxygen, whereupon it exhibits metallic conductance. The conductance plots of Sb_2O_5 pellets pre-sintered at 1100° indicate a lower-temperature region in which the conductance is virtually

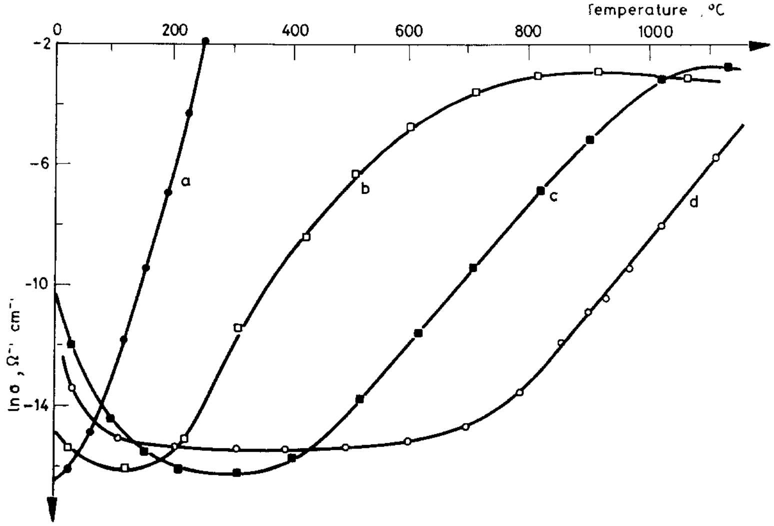

Fig. 4. Electrical conductance of oxide phases in the silver-antimony system. a) Ag_2O b) $Ag_2Sb_2O_6$ c) Sb_2O_4 (data derived from Sb_2O_3 pellet, re-heated), d) Sb_2O_5

temperature-independent. Above about 650°, the conductance increases regularly with temperature. The conductance of Sb_2O_3 pellets was extremely variable, especially at the onset of melting at 600–700°. At higher temperatures the pellets were progressively converted to Sb_2O_4, which, when cooled and re-cycled, exhibited reproducible conductance changes with temperature (Fig. 4C).

The activation energies for the conductance of the various oxides obtained from the appropriate Arrhenius plots are shown in Table 3.

The similarity in conductance energies of Ag_2O and $Ag_2Sb_2O_6$ suggests that the conducting species may be the same in both materials, and is probably Ag^+; the silver ions remain mobile in the pyrochlore over a greater range of temperature, however, since this compound is considerably more thermally stable than Ag_2O. The activation energy for conductance in Sb_2O_5 is much higher, suggesting a different conduction mechanism in that material.

Table 3

Activation energies for electric conduction in $Ag_2Sb_2O_6$ and its component oxides
Column A: derived from ln σ vs. $1/T$
Column B: derived from ln(σT) vs. $1/T$

Oxide	Activation energy, kJ/mole A.	B.	Temperature range, °C
$Ag_2Sb_2O_6$	99.6	96.7	230–700
Ag_2O	83.2	95.4	110–250
Sb_2O_5	262.5	266.4	840–1100

It is of interest to compare the activation energy for the diffusion of silver-bearing species into Sb_2O_5 with the conduction energies derived from plots ln (σT) *vs.* $1/T$ (Table 3, Column B), from which it appears that the diffusion process is dissimilar to the conduction process in the pyrochlore phase. If the assumption that the latter process involves the movement of silver ions is valid, then the rate-limiting step of the diffusion process must involve some other species, possibly oxygen, which is also required for the formation of the pyrochlore phase. Unfortunately, no data exist for the self-diffusion of oxygen in antimony oxides, so confirmation that the diffusion coefficients measured here are those of oxygen diffusion cannot be made in this way.

A further interesting point is the close similarity between the present diffusion activation energy and that for electrical conductance in Sb_2O_5. This may merely be fortuitous, but it is also possible that these two processes are related. Fig. 2 shows that the diffusion of antimony plays little or no part in the formation of the pyrochlore, and it is possible that the conductance process likewise is more dependent on the movement of oxygen than of antimony. Even though gross changes in oxygen stoichiometry due to changes in the valency of the antimony have not been observed in this work, the possibility of small changes in oxygen stoichiometry during heating cannot be ruled out, and indeed seem quite likely. Thus, differences in the oxygen partial pressure inside the powder compact during heating could well dominate the conductance behaviour in Sb_2O_5.

Conclusions

1. Silver antimony oxide of defect pyrochlore structure is formed by heating Ag_2O with either Sb_2O_3 or Sb_2O_5. The product from Sb_2O_3 is darker in colour, and may be slightly silver-rich.
2. Thermogravimetry shows that the reaction sequence involves reduction of the Ag_2O at $> 330°$. At $520-890°$, the resulting finely divided Ag metal then reacts smoothly with Sb_2O_5 in a single step. The reaction with Sb_2O_3 proceeds in two stages, the first corresponding to the formation of Sb_2O_4 (confirmed by X-ray diffraction) and the second stage being the diffusion of silver and oxygen necessary to establish the pyrochlore composition.
3. Interdiffusion studies of pellets of the two oxides indicate preferred diffusion of Ag into Sb_2O_5 and not vice-versa. The apparent diffusion coefficient estimated from the concentration profile of the product phase has an activation energy of 258.5 kJ/mole.
4. The activation energy for electrical conductance in $Ag_2Sb_2O_6$ is similar to that for pure Ag_2O, suggesting that the conduction process in the former involves silver ions. On this basis, the diffusion coefficients obtained in the interdiffusion studies probably do not represent a process in which the limiting step is the diffusion of silver, since the respective activation energies are quite different. These diffusion coefficients may therefore represent the movement of oxygen into the sample. A similar movement of oxygen may also control the electric conductance of Sb_2O_5, which has an activation energy similar to that for the diffusion process.

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RÉSUMÉ — L'oxyde d'argent antimonié ($Ag_2Sb_2O_6$) à structure pyrochlore imparfaite a été synthétisé par réaction en phase solide entre l'oxyde d'argent et Sb_2O_3 ou Sb_2O_5. La séquence de réaction étudiée par thermogravimétrie, par mesures d'interdiffusion sur pastilles d'oxyde et par mesures de conductibilité électrique consiste en la réduction de Ag_2O suivie par la diffusion de l'argent et de l'oxygène dans le composant d'oxyde antimonié. Quand le matériau de départ est Sb_2O_3, la diffusion initiale d'oxygène a lieu et donne Sb_2O_4 dans lequel l'argent et l'oxygène en excès diffusent ensuite. La comparaison des énergies d'activation pour la diffusion et la conductivité électrique dans les diverses phases d'oxydes suggère que la vitesse de formation de $Ag_2Sb_2O_6$ est contrôlée par la diffusion de l'oxygène plutôt que par celle de l'argent.

ZUSAMMENFASSUNG — Silber-Antimonoxid ($Ag_2Sb_2O_6$) von defekter Pyrochlorstruktur wurde durch eine Festphasenreaktion zwischen Silberoxid und entweder Sb_2O_3 oder Sb_2O_5 synthetisiert. Durch Thermogravimetrie, Interdiffusionsmessung an Oxidpillen, sowie elektrische Leitfähigkeitsmessungen wurde erwiesen, daß die Reaktionsfolge die Reduktion von Ag_2O mit darauffolgender Diffusion des Silbers und Sauerstoffs in die Antimonoxidkomponente enthält. Bei Sb_2O_3 als Ausgangsmaterial erfolgt eine Diffusion des Sauerstoffs wodurch Sb_2O_4 entsteht, in welches dann Silber und weiterer Sauerstoff diffundiert. Der Vergleich der Aktivierungsenergien der Diffusion und der elektrischen Leitfähigkeit in den verschiedenen Oxidphasen läßt vermuten, daß die Bildungsgeschwindigkeit des $Ag_2Sb_2O_6$ eher durch die Diffusion des Sauerstoffs als durch die des Silbers bedingt ist.

Резюме — Реакцией в твердом состоянии окиси серебра и трёх окиси или пятиокиси сурьмы был синтезирован антимонат серебра ($Ag_2Sb_2O_6$), обладающий нарушенной пирохлорной структурой. Последовательность реакций исследована с помощью термогравиметрии. Измерения интердиффузии и электропроводности на гранулах окисей свидетельствуют о восстановлении окиси серебра, с последующей диффузией серебра и кислорода на окись сурьмы. Когда исходным материалом является трёхокись сурьмы, первоначально происходит диффузия кислорода с образованием Sb_2O_4 и на которую в дальнейшем диффундируют серебро и кислород. Сравнение энергий активаций диффузии и электропроводности различных окисных фаз, наводят на мысль, что скорость образования $Ag_2Sb_2O_6$ определяет ся скорее диффузией кислорода, чем серебра.