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Thermal decomposition of alkali metal, copper(I) and silver(I) thiocyanates

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Abstract

Thermal decomposition of alkali metal thiocyanates of the general formula MSCN (M=Na, K, Rb, Cs), CuSCN and AgSCN has been studied. Thermal analysis curves and diffraction patterns of the solid intermediate, and final, products of their pyrolysis are presented. Gaseous products of the decomposition, SO_2 and CO_2, were quantified. Thermal, X-ray and chemical analyses have been used to establish the nature of the reactions occurring at each stage of decomposition. © 1998 Elsevier Science B.V.

Keywords: AgSCN; Alkali metal thiocyanates; CuSCN; DTA; DTG; Pyrolysis; TG; X-ray analysis

1. Introduction

Intermediate products of thermal decomposition of analytically important complex salts of bismuth(III) with the general formulae $M_3[Bi(SCN)_6]$ (M=Li, Na, K, Rb), $M[Bi(SCN)_4]$ (M=Rb, Cs) and $M_2M'[Bi(SCN)_6]$ (M=K, Rb, Cs; M′=Li, Na), including alkali metals thiocyanates, have been studied previously [1]. Some of these compounds have found application in the so-called thermo-alkalimetric methods for quantitative determination of cesium [2] and sodium [1], which involve heating of the compounds to an appropriate temperature, determined from the thermal analysis curves, absorption of the sulphur dioxide liberated as a result of decomposition in tetrachloromercurate solution and titration of the acid with standard sodium hydroxide solution. Thermal decomposition of copper thiocyanate has been used to analyse thiocyanates [3], in the presence of Cl^-, Br^-, I^-, S^{2-} and $S_2O_3^{2-}$, i.e. the anions which hinder precipitation in redoximetric methods of determination of SCN^-. Thiocyanates which are present in the solution along with chlorides, bromides or iodides can also be determined by precipitation of these anions using silver nitrate and thermal decomposition at 600°C. The sulphur dioxide released as a result of AgSCN decomposition is determined by alkalimetry [4].

Copper(I) and silver can be simultaneously determined with satisfactory accuracy and precision by precipitating CuSCN and AgSCN from a solution containing both the metals, and decomposing these compounds at an appropriate temperature [5].

Until now, thermal decomposition of thiocyanates of alkali metals, copper and silver has not been a subject of a closer investigation, and we intend to study the reactions involved in their thermal decomposition in this paper.

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2. Experimental

2.1. Preparation

NaSCN and KSCN (Merck) were used in the analyses. Rubidium and cesium thiocyanates were obtained by dissolving their carbonates in fresh thiocyanic acid and crystallizing RbSCN and CsSCN.

In order to prepare AgSCN, 1 cm^3 of nitric acid (1+2) was added to 15 cm^3 of 0.1 mol dm^{-3} ammonium thiocyanate solution, and the solution was then heated to boiling. An aliquot of 0.1 mol dm^{-3} of silver nitrate was added dropwise with continuous stirring. A slight excess of $AgNO_3$ was necessary. The solution was cooled and left to crystallize in the dark. The precipitate was filtered off, washed with methanol and dried in air.

In order to prepare CuSCN, water was added to 40 cm^3 of 0.1 mol dm^{-3} $CuSO_4$ solution and 120 cm^3 of a reducing solution (NH_4Cl+hydroxylamine) to obtain 400 cm^3. The mixture was boiled until it lost its colour. Thereafter, 40 cm^3 of NH_4SCN solution were added. CuSCN precipitated and was filtered off, washed with methanol and dried in air at ca. 90°C.

2.2. Apparatus

Thermal analyses of the compounds were carried out using an OD-102/1500°C derivatograph. The samples were heated in air over temperatures in the 20–1000°C range at the rate of 5°C min^{-1}, using the mass of 100 mg. TG sensitivity – 100 mg, DTA sensitivity – 1/15, DTG sensitivity – 1/20. α-Al_2O_3 was used as reference material.

X-ray analysis of the compounds and their sinters were carried out by means of a Siemens D5000 diffractometer, using CuK_α radiation monochromatised by means of a secondary graphite monochromator. The curves were recorded over the $2<2\theta<90^\circ$ range with a scan step of 0.04° and time of scan step 1 s.

Sulphur dioxide evolved in the thermal decomposition of the thiocyanates was determined by the following procedure. A weighed amount of the compound was heated in a furnace which is a part of a C.I. Electronics balance with programmed temperature and computer recording of results. The released SO_2 was absorbed in washers filled with sodium tetrachloromercurate solution. The acid produced was titrated with standard sodium hydroxide solution. Carbon dioxide liberated on heating the thiocyanates was adsorbed on ascarite and determined gravimetrically.

2.3. Thermal analysis

The thermal analysis curves of the examined compounds are shown in Fig. 1. The small loss of mass at lower temperatures in the TG curves resulted from the drying of the hygroscopic samples. Alkali metal thiocyanates melt before they decompose and the melting points established on the basis of the TG curves are: NaSCN – 320°C, KSCN – 190°C, RbSCN – 195°C and CsSCN – 210°C. Silver and copper thiocyanates decomposed without melting. Broad exothermic peaks in the DTA curves over the ranges of 480–590°C (NaSCN), 540–630°C (KSCN), 500–600°C (RbSCN) and 500–620°C (CsSCN) and mass losses in the TG curve (14, 10, 7 and 5%, respectively) are due to the thermal decomposition and oxidation of the decomposition products. The endothermic peak at 890°C in the DTA curve of sodium thiocyanate corresponds with the polymorphous transformation of sodium sulphate, a final product of NaSCN decomposition.

Thermal analysis curves of AgSCN and CuSCN indicate that these compounds decompose in several steps. The endothermic peak at 970°C in the TG curve of silver thiocyanate corresponds with the melting point of silver.

2.4. Analysis of products of thermal decomposition

In order to examine the course of thermal decomposition of the compounds under study, they were heated in a furnace at a rate of 5°C min^{-1} up to characteristic temperatures, determined from the thermal analysis curves. Alkali-metal thiocyanates were heated to 600°C, silver thiocyanate to 280°, 600° and 970°C and copper thiocyanate to 450°, 600° and 850°C. Figs. 2–7 show the diffraction patterns of the examined thiocyanates and their sinters at different temperatures.

The gases liberated during the thermal decomposition of thiocyanates, sulphur dioxide and carbon dioxide, were determined by the above-described methods. The results are presented in Tables 1 and 2.

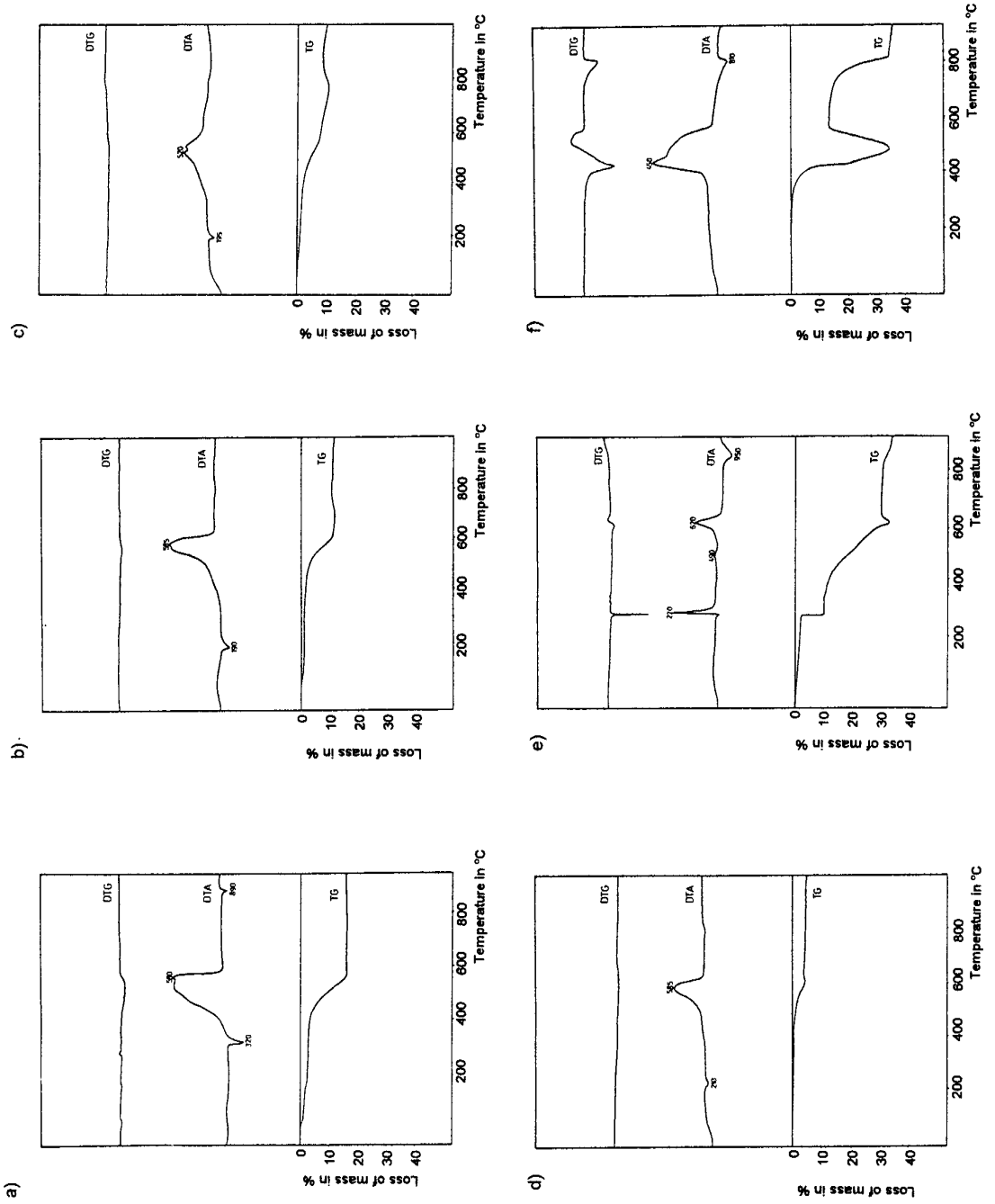

Fig. 1. Thermal decomposition curves of: (a) NaSCN; (b) KSCN; (c) RbSCN; (d) CsSCN; (e) AgSCN; and (f) CuSCN.

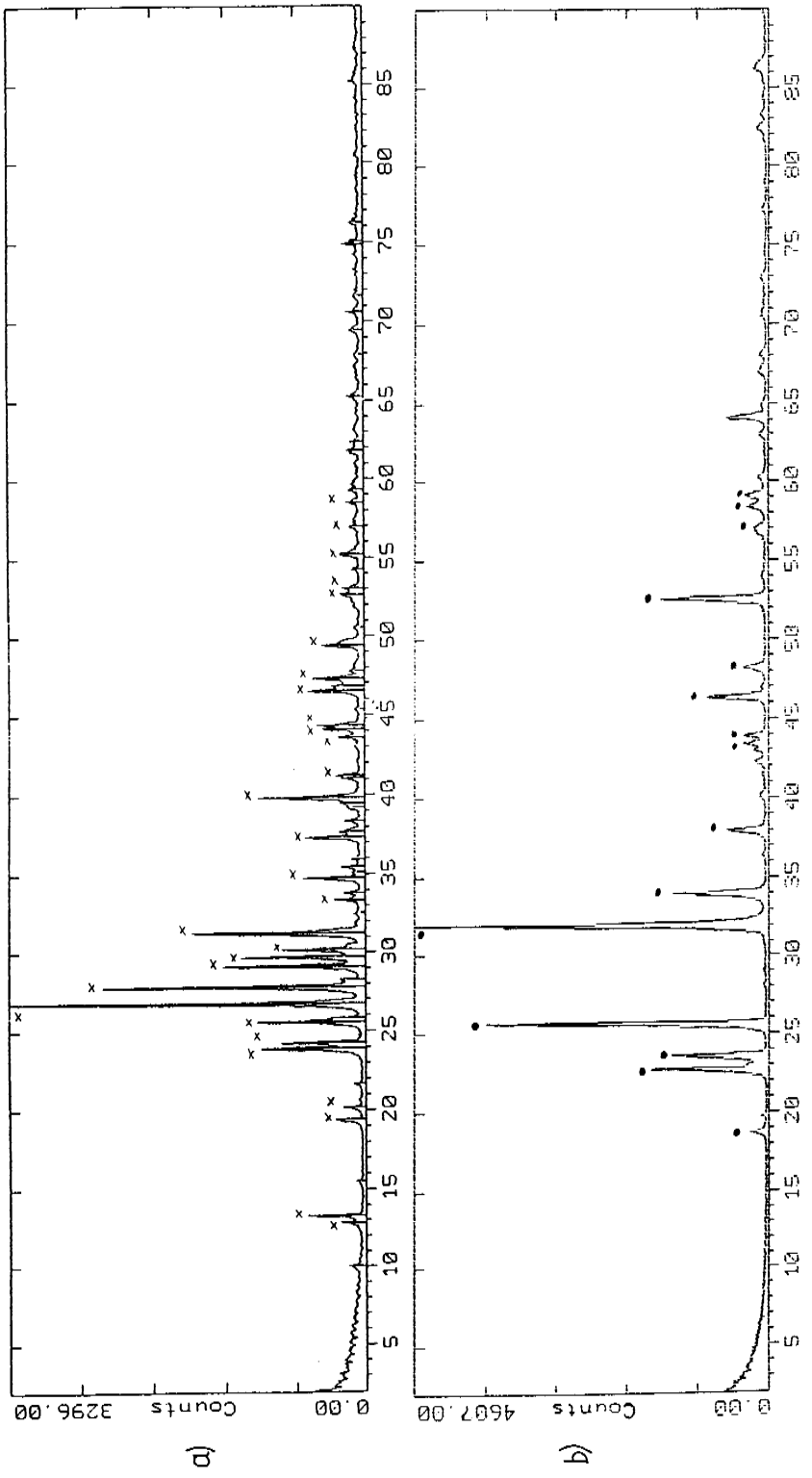

Fig. 2. Diffractions patterns of (a) NaSCN, and (b) its sinter at 600°C. (×) NaSCN; and (●) Na_2SO_4.

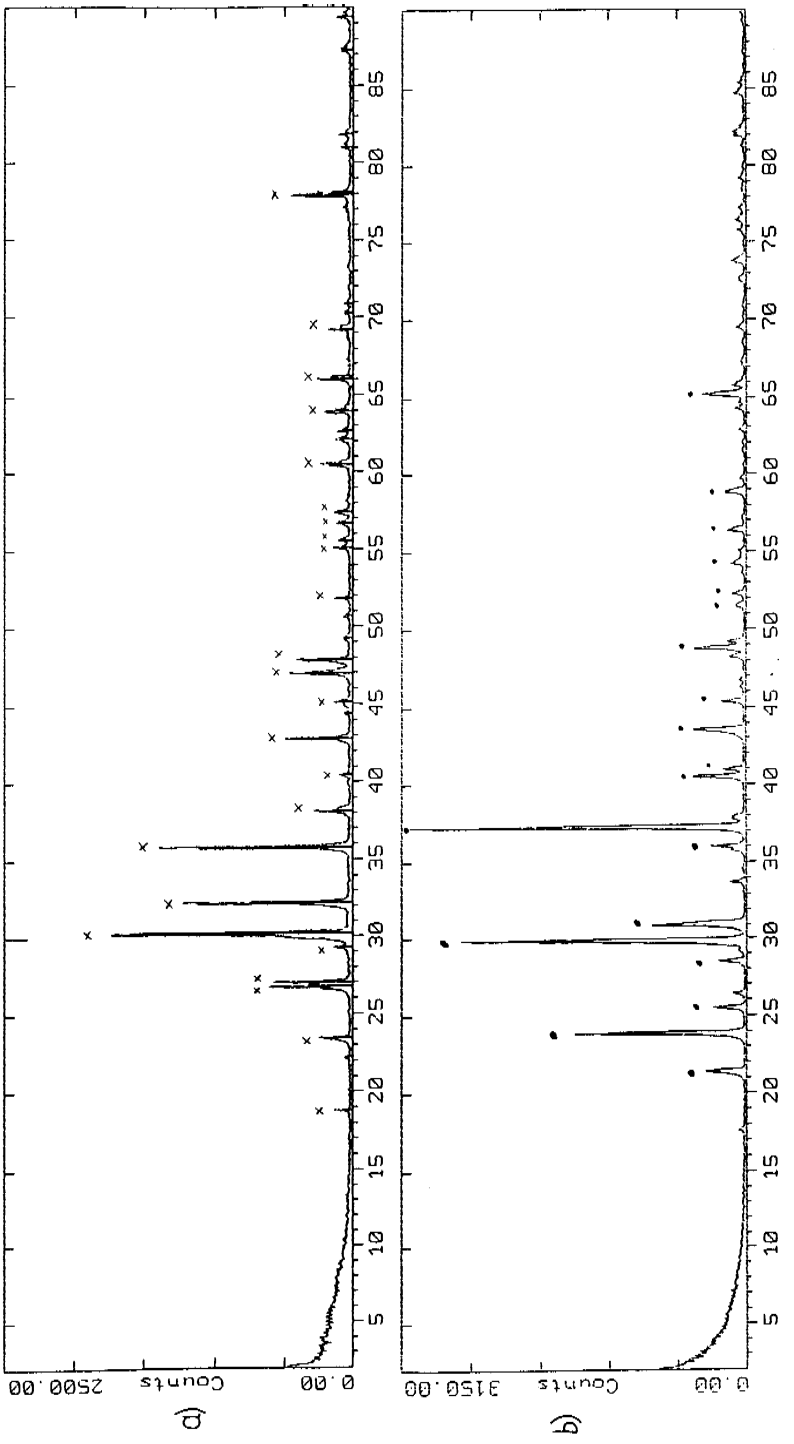

Fig. 3. Diffractions patterns of (a) KSCN, and (b) its sinter at 600°C. (×) KSCN; and (●) K_2SO_4.

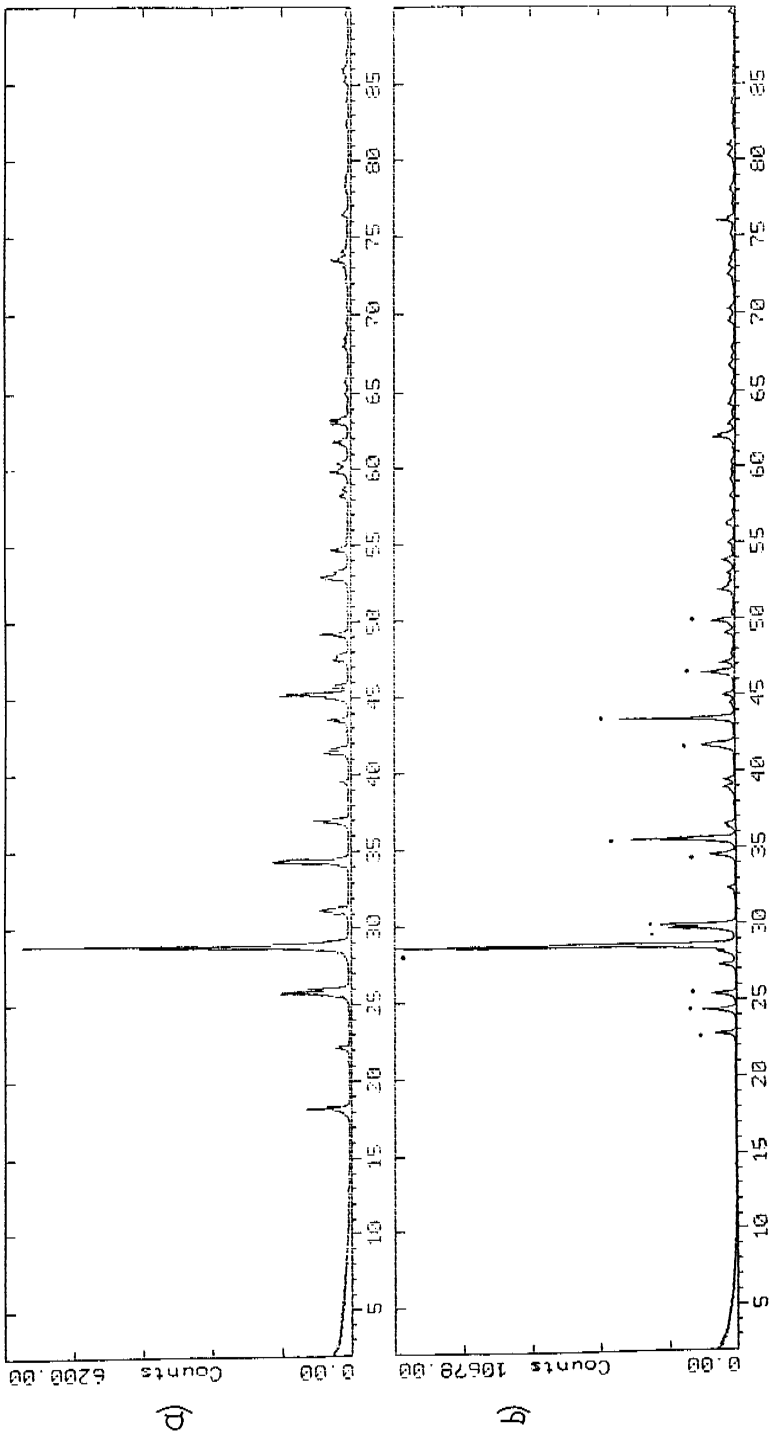

Fig. 4. Diffractions patterns of (a) RbSCN, and (b) its sinter at 600°C. (●) Rb_2SO_4.

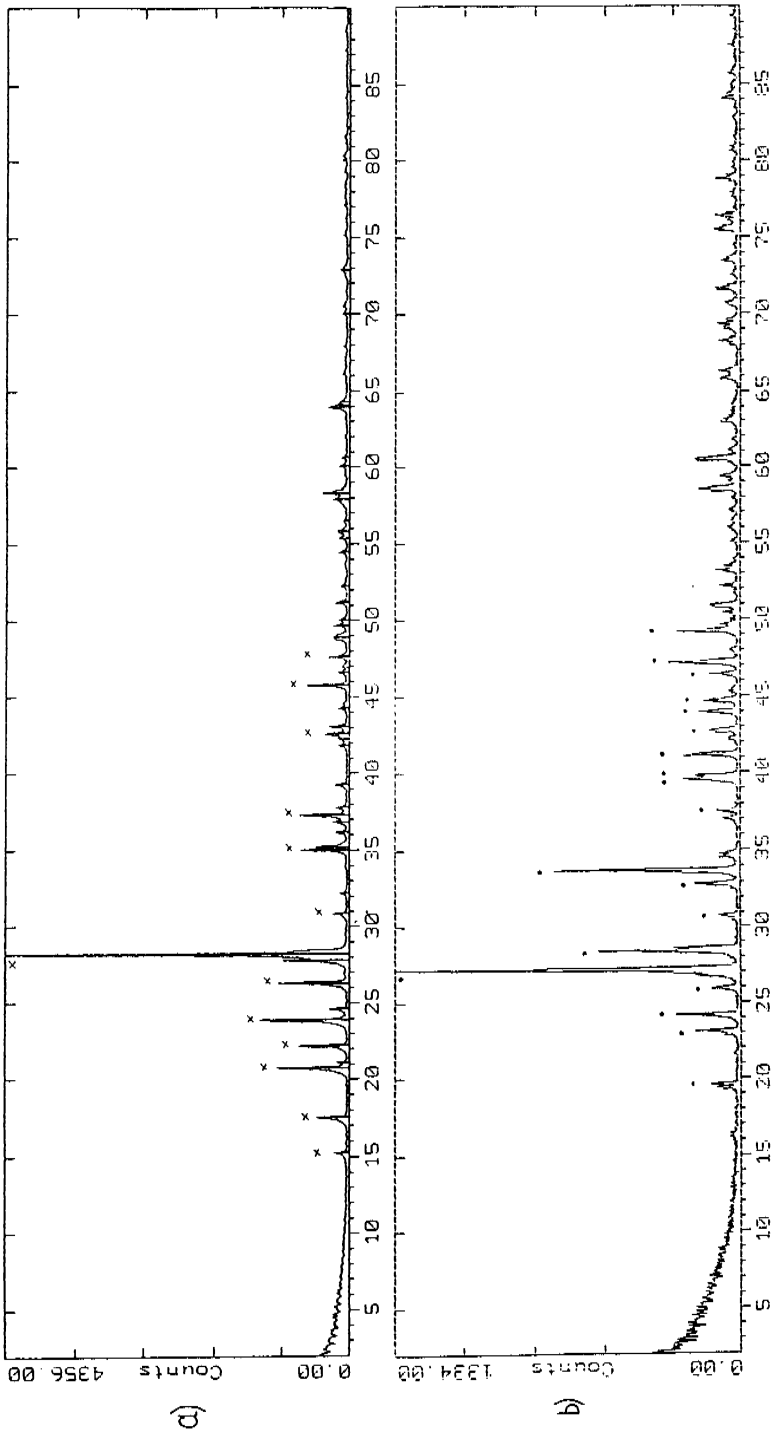

Fig. 5. Diffractions patterns of (a) CsSCN, and (b) its sinter at 600°C. (×) CsSCN; and (●) Cs_2SO_4.

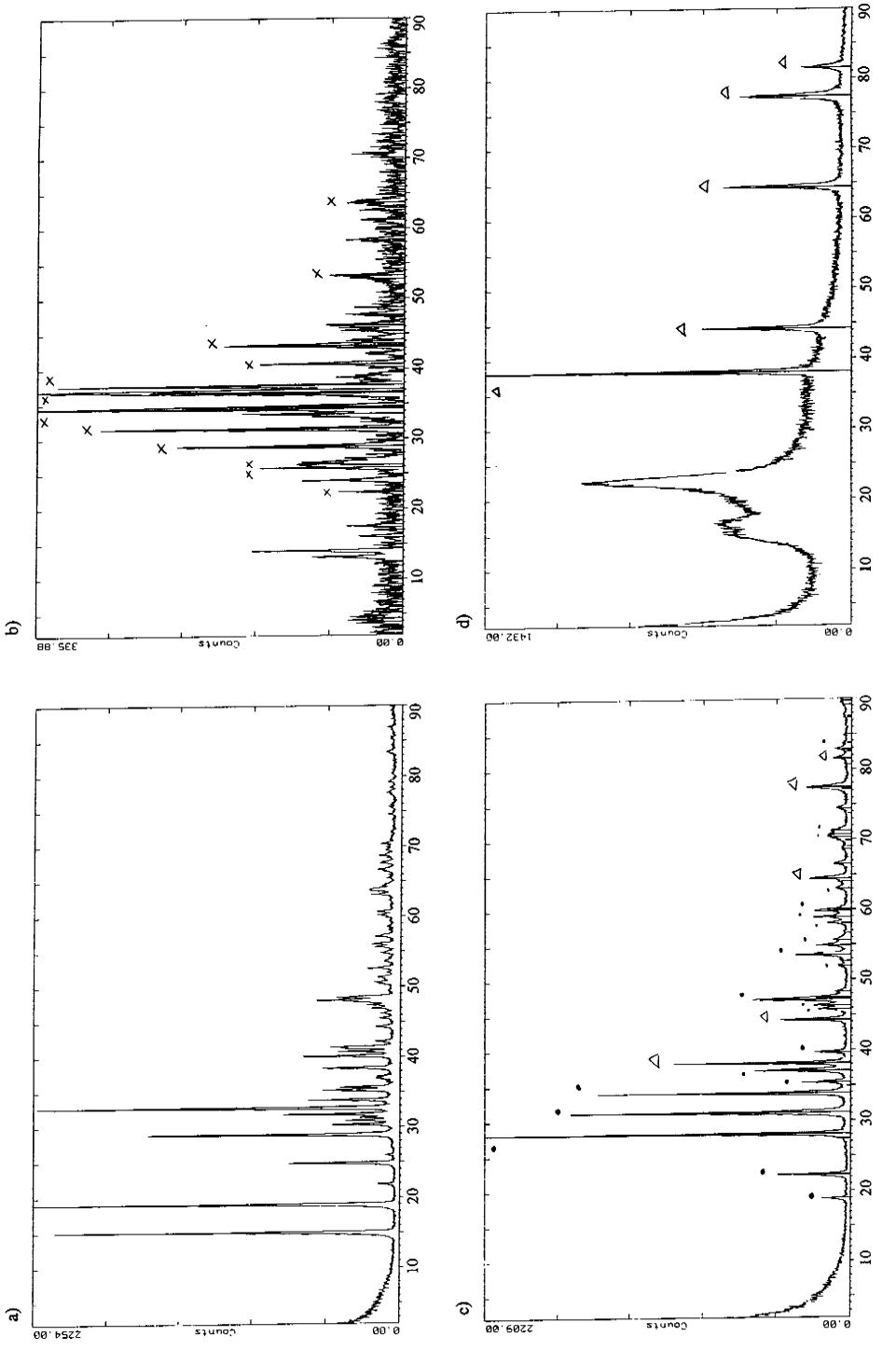

Fig. 6. Diffractions patterns of (a) AgSCN, its sinters at 280°C, (c) 600°C, (d) 970°C. (×) Ag_2S; (●) Ag_2SO_4; and (△) Ag.

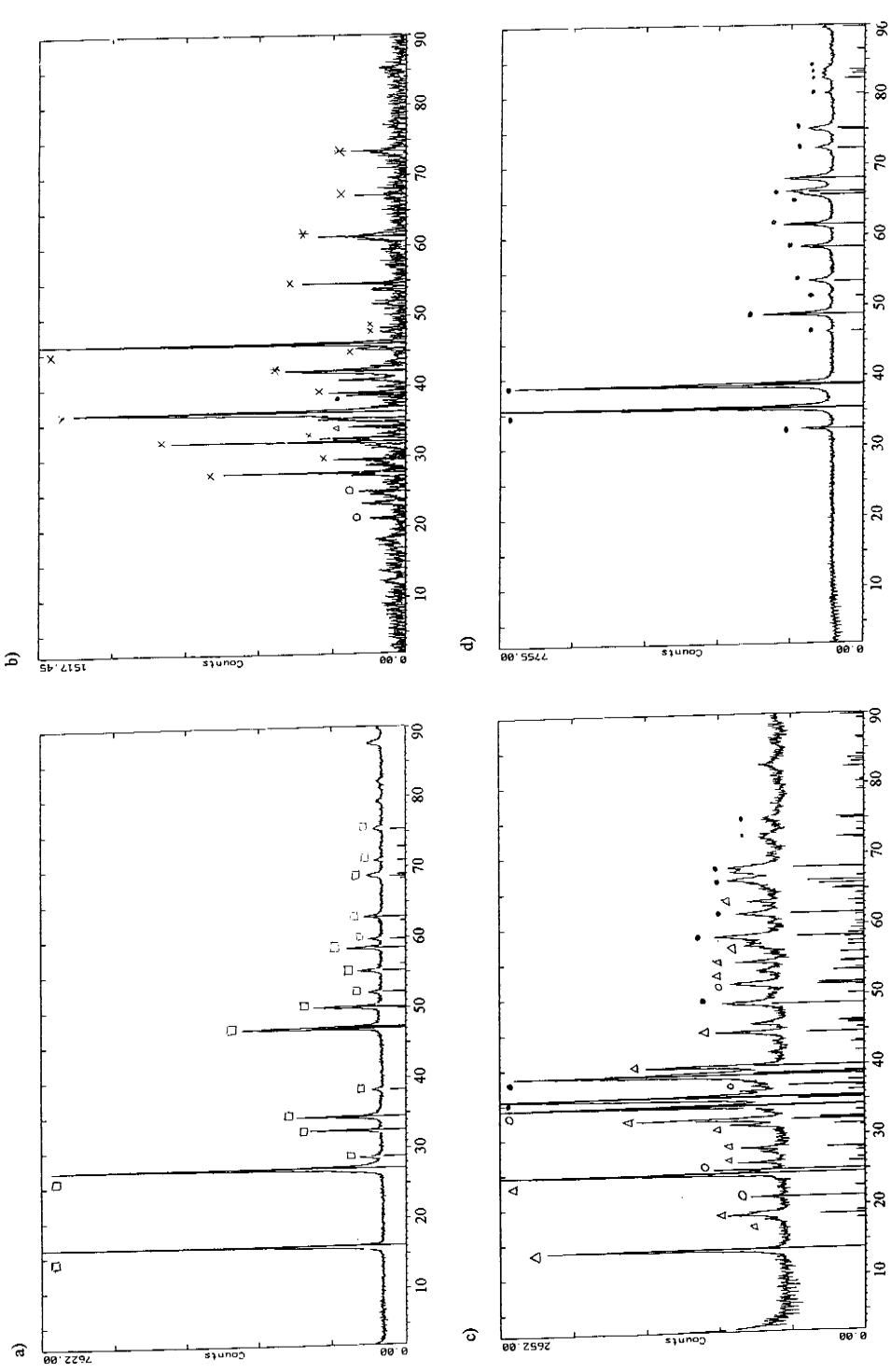

Fig. 7. Diffractions patterns of (a) CuSCN and (b) its sinters at 450°C, (c) 600°C, (d) 850°C. (□) CuSCN; (×) Cu_2S; (●) CuO; (○) $CuSO_4$; (△) Cu_2OSO_4; and (*) Cu_2O.

Table 1
Average results of determination of SO_2 released while thermal decomposition of thiocyanates

Compound	SO_2 determined/%	SO_2 calculated/%
NaSCN	37.87	39.51
KSCN	36.48	32.96
RbSCN	22.43	22.31
CsSCN	17.65	16.77
AgSCN	19.68	19.30
CuSCN	38.01	35.11

Table 2
Average results of determination of CO_2 released while thermal decomposition of thiocyanates

Compound	CO_2 determined/%	CO_2 calculated/%
NaSCN	58.06	54.27
KSCN	44.61	45.28
RbSCN	31.91	30.65
CsSCN	26.13	23.04
AgSCN	25.60	26.51
CuSCN	38.52	36.18

3. Discussion

X-ray analysis shows that the only solid product of pyrolysis of the alkali-metal thiocyanates is the sulphate of the alkali metal. Moreover, analysis of SO_2 and CO_2 in the gaseous products of decomposition indicates that alkali-metal thiocyanates heated to ca. 600°C decompose according to the following scheme of reaction:

$$2MSCN + 5O_2 \rightarrow M_2SO_4 + SO_2 + 2CO_2 + N_2 \ (M = Na,\ K,\ Rb,\ Cs)$$

The thermal analysis curves of AgSCN (10% mass loss and a peak in the DTA curve at 270°C) show that the sharp DTA peak at T=270°C and the loss of mass Δm=9.7% correspond with the conversion of the initial compound AgSCN into a compound whose proposed composition is AgSCN·AgCN, which is in agreement with literature date [6,7], but was not confirmed by X-ray analysis. Starting at 280°C, a relatively slow mass loss follows to T=600°C. The shape of the TG curve indicates a complicated course of reactions, whose stages we are unable to establish.

Diffractometric analysis shows explicitly that, beyond 280°C, Ag_2S begins to form and is gradually oxidized to Ag_2SO_4 which, in turn, decomposes at high temperatures (>850°C), giving pure metallic silver as the final product of decomposition. This is confirmed by the DTA peak at T=950°C, which corresponds with the melting point of silver.

The postulated schemes of chemical reactions occurring during thermal decomposition of AgSCN are as follows:

$$2AgSCN \rightarrow AgSCN \cdot AgCN$$

The TG curve indicates that, within the 260–600°C range, the following reactions occur simultaneously:

$$AgSCN \cdot AgCN + 3O_2 \rightarrow Ag_2S + 2CO_2 + SO_2 + N_2$$

$$Ag_2S + 2O_2 \rightarrow Ag_2SO_4$$

and above 600°C silver is formed, which was found by diffractometric analysis [7].

In the case of CuSCN, the 34.1% mass loss observed in the TG curve at 450°C corresponds with the following reaction:

$$6CuSCN + 11O_2 \rightarrow 2Cu_2S + 2CuO + 4SO_2 + 6CO_2 + 3N_2$$

The theoretical loss in mass corresponding with this reaction is 34.6%.

Similarly, the decomposition of copper(I) thiocyanate may involve formation of copper(I) oxide, which is confirmed by diffraction analysis of sinters obtained by heating the initial compound within the 350–400°C range. For this reason, the determined loss in mass does not correspond with that calculated from the proposed reaction.

Above 480°C, the intermediate products of decomposition are oxidized, which is reflected in the TG curve by the increase of mass and by the exothermic effect recorded in the DTA curve. The analysis of difftaction patterns indicates the presence of the following products of oxidation: $CuSO_4$, $Cu_2O(SO_4)$ and CuO, which is confirmed by the calculated loss in mass (12.6%), consistent with that established on the basis of the TG curve (13%) (Fig. 7c).

The TG curve shows that within the 550 – 800°C range, further decomposition of the above-mentioned compounds takes place, and the final product of CuSCN decomposition (>800°C) is CuO. According to literature data this, in turn, is converted slowly into Cu_2O, which corresponds with the slow loss in mass in the TG curve.

The endothermic DTA peak at 810°C corresponds with the reaction of thermal decomposition of $CuSO_4$ to CuO.

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