The CEM spectrum was observed for the same sample ground to a depth of $1\,\mu m$. Both singlet and sextet peaks were seen on the spectrum measured at 363 K, suggesting that two phases existed; the Curie point of one phase was below 363 K. Only the paramagnetic peak was observed when the CEM spectrum was measured at 507 K, indicating that the second iron nitride had a Curie temperature between 363 K and 507 K.

It was concluded that ϵ-$Fe_{2.3-2.4}N$ and ϵ-$Fe_{2.4-2.7}N$ deposited stably at a depth of $1\,\mu m$ below the top surface.

The CEM spectra of the sample ground to a depth of $5\,\mu m$ are shown in Fig. 1.

Only the paramagnetic peak appeared on the CEM spectrum taken at 507 K, whereas the sextet peaks were seen at 363 K as shown in Fig. 1b and c. The iron nitride was identified as ϵ-Fe_xN ($2.4 < x < 2.7$), since the Curie point was found to lie between 363 K and 507 K.

The nitrogen content decreased gradually with increasing distance from the top surface of the sample. If the surface layer is ground still further the phase corresponding to γ-Fe_4N is disclosed.

The distinct magnetically-split peaks were seen on the CEM spectrum after the heated sample was cooled to room temperature (see Fig. 1d). The spectrum indicated that the distorted and quadrupole-split phases were relaxed to the strainless crystal form by the thermal treatment up to 507 K. Comparison of Fig. 1a and d indicated that the iron nitride located at the exposed layer was well annealed. Nitrogen atoms combined with iron atoms were estimated to migrate slowly along the crystal to coalesce the distorted structure.

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Thermal expansion of spinel-type $AgIn_5S_8$ by the X-ray method

The Ag–In–S system is currently of much interest because of the particular semiconductive properties of the ternary compound $AgInS_2$, a potentially suitable material for opto-electronic devices [1]. The crystals prepared by normal freezing from the melt of stoichiometric mixtures, with $AgInS_2$ composition, crystallize in the chalcopyrite structure [2]. When an $AgInS_2$ sample was quenched from above its melting point, crystals with the $AgIn_5S_8$ composition, crystallizing in the spinel structure, were obtained by Roth *et al.* [3].

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Recently Gastaldi and Scaramuzza [4] examined the single crystals of $AgIn_5S_8$ thiospinel, grown by the iodine transport method, by X-ray diffractometry and assigned the space group *F*d3m for its spinel structure. It has been confirmed that $AgIn_5S_8$ crystallizes in a f c c lattice, spinel type, having four formula units per unit cell. A search of the literature shows that no studies on the thermal expansion of silver thiospinel $AgIn_5S_8$ seem so far to have been made. As a result the authors included this compound in a general programme of X-ray studies of chalcopyrite and spinel-type ternary semiconducting compounds.

Having in mind the interesting thermal behaviour observed in some of the chalcopyrite ternary semiconducting compounds in our earlier studies [5–7], it was thought desirable to determine precisely the lattice parameters of this ternary compound $AgIn_5S_8$ at different temperatures and to study its thermal expansion. The present note gives an account of these results.

The sample of $AgIn_5S_8$ used in the present investigation was kindly provided by Drs Paorici and Lucio Zanotti of the Laboratorio MASPEC, CNR, Parma, Italy, in the form of good single crystals. Details of the synthesis and purity of this sample are given in their recent publication [8].

For X-ray powder diffraction work, some good single crystals of $AgIn_5S_8$ were powdered and passed through a 325-mesh sieve. The specimen for the study was prepared by filling a 0.5 mm diameter thin-walled quartz capillary tube with this powder. Annealing of this powder, at approximately 400° C for about 10 h, was found to be essential in order to obtain good powder diffraction pattern results with resolution of all the high-angle reflections. Powder diffraction photographs were taken at different temperatures up to 685° C with a Unicam 19 cm high-temperature powder camera and CuKα radiation. Eight reflections, recorded in the Bragg diffraction angle region between 14 and 80° which remained sharp, well-resolved and of reasonable intensity up to a temperature of 685° C (the highest temperature studied), were used to evaluate the lattice parameters at different temperatures. The experimental details and the method of evaluating the lattice parameters and the coefficients of thermal expansion were described in an earlier paper [5].

TABLE I Lattice parameter values of $AgIn_5S_8$ at room temperature

Source	Lattice parameter (nm)
Roth *et al.* [3]	1.0827 ± 0.0001
Leonardo and Gastaldi [4]	1.08268(5)
Paorici and Zanotti [10]	1.0822
Present study	1.08288 ± 0.00001

TABLE II Lattice parameter values of $AgIn_5S_8$ at different temperatures

Temperature (° C)	Lattice parameter (nm)
28	1.08288
116	1.08376
234	1.08526
346	1.08638
442	1.08784
566	1.08945
685	1.09087

The X-ray powder diffraction pattern of $AgIn_5S_8$, obtained in the present study at room temperature, could be completely accounted for on the basis of a cubic spinel structure. All the reflections ranging from Bragg angle of 64 to 80° were indexed and all the *d*-spacing values (in nm) with *h k l* values and visually-estimated intensities were compared with the earlier data [3]. No extra lines were found in the powder pattern of this compound.

The least-square fit method of Cohen [9] was used to determine the lattice parameter of this compound at each temperature. The lattice parameter of $AgIn_5S_8$ at room temperature obtained in the present study is listed in Table I along with the other values available in the literature [3, 4, 10]. It can be seen that the present value is in good agreement with the reported values. The standard error in the value of the lattice parameter at room temperature is about $\pm 1 \times 10^{-5}$ nm and is found to be of the same order at higher temperatures. The lattice parameters of $AgIn_5S_8$ obtained at different temperatures are given in Table II and are shown graphically in Fig. 1. It can be seen that the value of the lattice parameter increases non-linearly with increasing temperature. The coefficients of thermal expansion evaluated at various temperatures are given in Table III. The

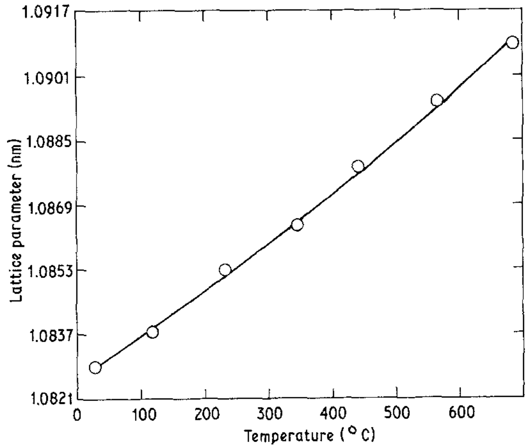

Figure 1 Variation of the lattice parameter of $AgIn_5S_8$ with temperature.

temperature dependence of the linear coefficient of thermal expansion, α_T, is represented by the following equation:

$$\alpha_T = [9.7430 \times 10^{-6} + 4.2950 \times 10^{-9} T + 6.0575 \times 10^{-13} T^2], \qquad (1)$$

where T is expressed in ° C and α is expressed in $° C^{-1}$. It can be seen that the coefficient of expansion increases non-linearly with increasing temperature. The values of the linear coefficient of expansion at room temperature and the mean coefficient of expansion over the temperature range from 28 to 685° C were found to be

$$\alpha_{28° C} = 9.86 \times 10^{-6}\ ° C^{-1}$$

and

$$\alpha_{28-685° C} = 11.23 \times 10^{-6}\ ° C^{-1},$$

respectively. No anomalous behaviour in the thermal expansion of this ternary semiconducting compound was observed, as has been observed in our earlier studies [5–7] on $AgInSe_2$, $AgGaSe_2$ and $AgGaS_2$. The continuous increase in the value of the coefficient of linear expansion of this compound with temperature is due to the increased anharmonicity of the lattice with temperature, which is a normal behaviour of most metals. Further studies, on some of the spinel-type ternary semiconducting compounds like $CdIn_2S_4$, $CdIn_2Se_4$, $CdCr_2S_4$ and $CdCr_2Se_4$, which are in progress, may permit a detailed discussion on the thermal behaviour of the spinel-type ternary semiconducting compounds with regard to their structure.

TABLE III Coefficients of thermal expansion of $AgIn_5S_8$ at various temperatures

Temperature (° C)	$\alpha (\times 10^6\ ° C^{-1})$	
	Observed	Calculated
50	9.93	9.96
90	10.16	10.14
130	10.39	10.31
170	10.39	10.49
210	10.62	10.67
250	10.85	10.85
290	11.08	11.04
330	11.31	11.23
370	11.54	11.42
410	11.54	11.61
450	11.77	11.80
490	12.00	11.99
530	12.01	12.19
570	12.47	12.39
610	12.47	12.59
650	12.93	12.80

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Chemical preparation of ultra-fine aluminium oxide by electric arc plasma

Aluminium oxide is extensively used in electronics, rocket production, atomic power energetics, the chemical industry, metallurgy and other branches of industry because it has a high boiling point, great mechanical stability and high dielectric parameters.

Al_2O_3 powder is usually prepared by alkali treatment of bauxite or by heating bauxite with soda. The Al_2O_3 thus prepared does not meet the requirements of modern technology since it contains different impurities and has particles of quite large size, $> 40\,\mu m$. Nowadays, the plasma-chemical method of preparation is in many cases the only one by which it is possible to obtain certain products with high dispersity and activity [1–3].

In the patent and general literature the preparation of Al_2O_3 under a plasma jet [4], high-frequency induction-coupled plasma [5–9] and glow discharge [10] is briefly mentioned. Usually the product has a specific surface 14 to 130 $m^2\,g^{-1}$ and a greater purity than that of reagents. The rate-determining step, as in the case of all heterogeneous plasma-chemical processes, is the evaporation of the refractory substances (Al_2O_3, Al) in the plasma jet. There are no data in the literature for direct preparation of Al_2O_3 from aluminium and oxygen under a plasma jet.

It is known [11, 12] that the reaction:

$$2\,Al + 1.5\,O_2 = Al_2O_3 + 1.67\,MJ\,mol^{-1} \quad (1)$$

is displaced to the right over a wide temperature range from 300 to 4000 K. The conversion of aluminium into aluminium oxide in this temperature range is practically complete. With the heterogenous oxidation process the reaction practically stops after protective filming of Al_2O_3 which hinders the diffusion of oxygen atoms to the aluminium. This restriction can be overcome if the process is realized at high temperature such that the reaction is carried out in the gas phase, i.e. using the high energy of the plasma.

The main purpose of the present short communication is to report the possibilities for the synthesis of a pure, highly-dispersed Al_2O_3, having a high specific surface and great chemical activity, from elementary aluminium and oxygen under a plasma jet.

The process flow diagram of the plasma reactor is shown in Fig. 1. Aluminium powder with an average particle size of 10 to 20 μm and specific surface, S, of 5 $m^2\,g^{-1}$, and oxygen (99% purity) are used as basic reagents. Argon is used for plasma-forming and as the powder-transporting gas. The specific surface is determined by the Kljatchko–Gurvitch method [13], based on low-temperature adsorbtion of air at 77.4 K. The quantity of non-reacted aluminium is defined complexonometrically [14] with complexon III by the method of residual titration. The degree of oxidation (in percentage) is determined by the difference in the general quantity of aluminium and the non-reacted aluminium related to the general quantity of aluminium. The preliminary tests are carried out using plasmatron with maximum effective power $W = 18$ kW at $0.708 \times 10^{-3}\,m^3\,s^{-1}$ flow rate of plasma-forming argon, $0.053 \times 10^{-3}\,m^3\,sec^{-1}$ flow rate of oxygen and $16.7 \times 10^{-3}\,g\,sec^{-1}$ consumption of aluminium powder. The temperature of the plasma jet and the reactor is determined on the basis of the energy balance.

The analysis of the prepared product shows

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