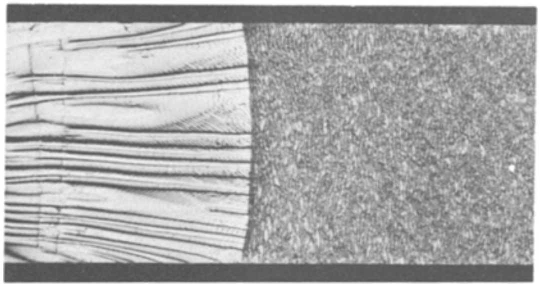

Figure 4 Fracture surface of PMMA $M_w = 115\,000$ showing transition from slow to fast crack propagation. Specimen thickness shown corresponds to 4.75 mm (crack propagation direction from left to right)

By way of comparison, the fracture surface of a specimen with $M_w = 115\,000$ is shown in Fig. 4. Despite the clear difference between low and high molecular weight PMMA (see Fig. 2) in appearance of the fracture surface in the fast propagation region, the fracture surfaces in the slow propagation region appear very similar, thereby suggesting a similar fracture mechanism up to the transition.

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References

1. J. G. WILLIAMS, *Appl. Mater. Res.* 4 (1965) 104.
2. *Idem, Int. J. Fract. Mech.* 8 (1972) 393.
3. F. A. JOHNSON and J. C. RADON, *Eng. Frac. Mech.* 4 (1972) 555.
4. *Idem J. Polymer Sci. A2* 11 (1973) 1995.
5. W. DÖLL, *Colloid Polymer Sci.* 252 (1974) 880.
6. R. WEICHERT and K. SCHÖNERT, *J. Mech. Phys. Solids* 22 (1974) 127.
7. L. J. BROUTMAN and T. KOBAYASHI, in "Dynamic Crack Propagation", edited by G. C. Sih (Noordhoff, Leyden, 1973) pp. 215–25.
8. G. W. WEIDMANN and W. DÖLL, *Colloid Polymer Sci.* 254 (1976) 205.
9. W. DÖLL, *Eng. Frac. Mech.* 5 (1973) 259.
10. H. RICHTER, Bericht 9/74, Institut für Festkörpermechanik (1974).

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Precision lattice parameters and thermal expansion of paraelectric phase potassium nitrate

Potassium nitrate (KNO_3) exhibits polymorphic transitions. The stable phase at room temperature (II) is of the aragonite type. On heating, phase II transforms into phase I at about 120° C. The structure of phase I, the paraelectric phase, is closely related to the calcite structure and belongs to the space group $R\bar{3}m$. A number of physical properties of various phases of KNO_3 are reported in the literature. Although many investigators have reported the lattice parameters of potassium nitrate, there is a variation of 0.11 Å among the values of the *c* parameter reported by Fischmeister [1] and Chen and Chernow [2] (Table III). Similar remarks hold good in the case of thermal expansion. As the thermal expansion of paraelectric phase is very interesting, in showing large expansion along the trigonal axis and negative expansion in the perpendicular direction, it is thought worth while to determine its precision lattice parameters at various temperatures and to evaluate the coefficients of thermal expansion.

The potassium nitrate powder used in this investigation was prepared from crystals obtained from solution in water of an Analar grade sample. Using a Unicam 19 cm high-temperature camera, powder photographs were taken with Fe*K* radiation from a Raymax-60 X-ray unit in the temperature range 145 to 315° C. With Cu radiation, a considerable overlap of the reflections is observed in the high Bragg angle region. Hence, Fe*K* radiation is preferred. Details of the experimental technique and the method of evaluating the precision lattice parameters and the coefficients of thermal expansion have been described in an earlier paper [3]. Seven reflections $(3\,2\,4)_{\alpha 1}$, $(3\,2\,4)_{\alpha 2}$, $(4\,1\,0)_{\alpha 1}$, $(4\,1\,0)_{\alpha 2}$, $(3\,2\,8)_{\alpha 1}$, $(3\,2\,8)_{\alpha 2}$, and $(4\,1\,6)_{\alpha 1}$ (in terms of hexagonal unit cell)

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TABLE I Lattice parameters of KNO_3 at different temperatures

Temperature (° C)	a (Å)	c (Å)
145	5.4202	19.4460
165	5.4193	19.5495
184	5.4172	19.6629
217	5.4159	19.8404
267	5.4146	20.0548
315	5.4086	20.2716

recorded in the Bragg angle region 67 to 82° were used in evaluating the lattice parameters at different temperatures.

The lattice parameters obtained are given in Table I. It can be observed from the table that c increases rapidly and that a decreases slowly with increases in temperature. The temperature dependence of the coefficients of thermal expansion $\alpha_{||}$ along the c-axis and $\alpha_{\perp}$ at right angles to the c-axis are represented by Equations 1 and 2

$$\alpha_{||} = 223.801 \times 10^{-6} + 14.106 \times 10^{-8}\,T - 7.771 \times 10^{-11}\,T^2 \quad (1)$$

$$\alpha_{\perp} = -8.277 \times 10^{-6} + 2.658 \times 10^{-8}\,T - 1.881 \times 10^{-12}\,T^2, \quad (2)$$

where T is in °C.

The coefficients of expansion at different temperatures are given in Table II along with values calculated from Equations 1 and 2.

The lattice parameters at 152°C obtained in the present investigation are compared in Table III. There is agreement between the values of the present investigation and those reported by Kawabe *et al.* [5] and Chen and Chernow [2]. Although the value of a obtained by Tahvonen [4] and Fischmeister [1] is in agreement with the data reported by other investigators, the value of c reported by them shows a large deviation probably due to the low Bragg angles in the range 20 to 25° used in their work to evaluate the lattice parameters.

TABLE II Coefficients of expansion of KNO_3 at different temperatures

	$\alpha_{\perp} \times 10^6$		$\alpha_{||} \times 10^6$	
	obs.	calc.	obs.	calc.
150	−8.30	−8.52	242.36	243.21
170	−9.40	−9.19	246.47	245.54
190	−10.23	−10.02	246.99	247.80
210	−10.97	−10.99	250.07	250.00
230	−11.99	−12.12	252.65	252.13
250	−13.38	−13.39	255.73	254.21
270	−14.57	−14.82	255.73	256.22
290	−16.60	−16.39	257.28	258.17

The coefficients of thermal expansion reported by various investigators are given in Table IV. The value of $\alpha_{||}$ obtained by Sawada *et al.* [6] is found to be very much lower than the other values. The mean coefficients of thermal expansion of potassium nitrate between 145 and 315°C obtained from the present data are $\alpha_{||} = 249.74 \times 10^{-6}$ °C^{-1} and $\alpha_{\perp} = -12.58 \times 10^{-6}$ °C^{-1} and obtained by Fischmeister [1] between 128 and 335°C are $\alpha_{||} = 308 \times 10^{-6}$ °C^{-1} and $\alpha_{\perp} = -8 \times 10^{6}$ °C^{-1}. Table II shows that the numerical value of $\alpha_{\perp}$ tends to increase with increasing temperature as in the case of calcite [3].

TABLE III Lattice parameters of KNO_3 at 152° C

Reference	a (Å)	c (Å)
Tahvonen [4]	5.396	19.410
Fischmeister [1]	5.420	19.410
Kawabe *et al.* [5]	–	19.500
Chen and Chernow [2]	5.420	19.522
Present study	5.4199 ± 0.0003	19.4908 ± 0.0020

TABLE IV Comparison of coefficients of thermal expansion of KNO_3

Reference	Method	Temp. (° C)	$\alpha_{\perp}$	$\alpha_{||}$
Fischmeister [1]	X-ray	128–335	−8	308
Sawada *et al.* [6]	Dilatometer		–	120
Yanagi [7]	X-ray		–	230
Present study	X-ray	150	−8.52	243.21

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References

1. H. F. FISCHMEISTER, *J. Inorg. Nucl. Chem.* 3 (1956) 182.
2. A. CHEN and F. CHERNOW, *Phys. Rev.* **154** (1967) 493.
3. K. V. KRISHNA RAO, S. V. NAGENDER NAIDU and K. SATYANARAYANA MURTHY, *J. Phys. Chem. Solids* 29 (1968) 245.
4. P. E. TAHVONEN, *Ann. Acad. Sci. Fennicae, Ser. A* **I** 44 (1947) 1.

5. U. KAWABE, T. YANAGI and S. SAWADA, *J. Phys. Soc. Japan* 20 (1965) 2059.
6. S. SAWADA, H. MARUYAMA, T. YANAGI and Y. ASAO, Preprint, Divisional meeting of the *Phys. Soc. Japan*, Nagoya, October (1962).
7. T. YANAGI, *Phys. Soc. Japan* 20 (1965) 1351.

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Ultrafine TaC powders prepared in a high frequency plasma

In recent years, various attempts have been made at preparing ultrafine, i.e. submicron, refractory particles. Stokes *et al.* [1] obtained tantalum and tungsten carbides as a result of reactions in a flame, between the corresponding metal or oxide and methane. The conversion ratios were of the order of 70% and 25%, respectively. Sizable amounts of Ta_2C, or even tantalum metal, could also be detected in the reaction products. Similarly, Neuenschwandter [2] used an arc plasma torch as a heat source to synthesize various transition metal carbides, including TaC. The resulting particle sizes typically ranged between 10 and 100 nm. The vapour-phase reactions involved hydrogen, hydrocarbons and the appropriate metal chloride. A quench then followed and the fine particles were deposited onto a cooled metal substrate, which they impinged with a fairly high velocity. This, together with the presence of chlorinated species such as HCl, is probably responsible for the presence of impurities such as Fe, Ni or Cr, which are usually detected [3] in the condensation products. In an attempt to avoid at least some of these difficulties and obtain as pure an ultrafine TaC powder as possible, a technique has been developed which starts from typical carbide powders, commercially available in the micron range, and uses a radio frequency argon plasma.

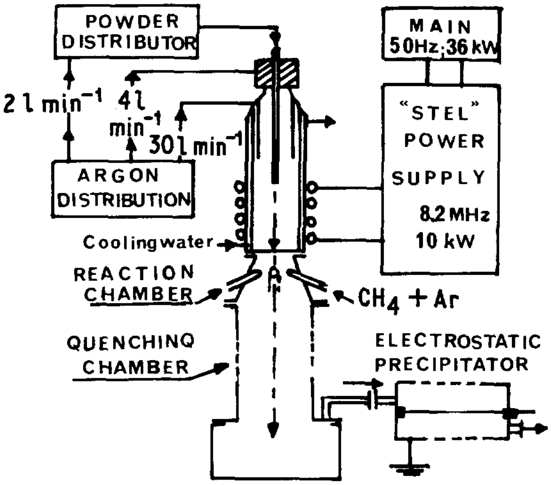

Figure 1 Schematic illustration of the ultrafine powder preparation apparatus.

Basically, the process, which was previously described in the case of ultrafine nitrides preparation [4], consists in the dissociation–vaporization of the primary powders, followed by a vigorous quench of the resulting vapours in a water-cooled stainless steel chamber, and collection of the condensed products from the walls of this chamber and a cylindrical electrostatic precipitator. Fig. 1 shows a schematic illustration of the various parts of the experimental apparatus, as well as its principal operating conditions. It will be noticed that gaseous injections can be made radially into the tail of the plasma flame, when the primary powders have been fully vaporized. Methane and argon–CH_4 mixtures have been used in the present case, in order to separately adjust the average carbon potential in the reaction chamber and study its influence on the composition and structure of the reaction products. It was qualitatively observed that both the amount of CH_4 molecules introduced in the reaction chamber (Fig. 1) in the unit of time, and the initial velocity of the reacting gas, bear a strong influence on the course of reactions and the composition of the final products. High methane ratios and/or high initial velocities, the latter allowing improved blending of the reacting species, were found necessary for eliminating Ta_2C from the condensed powders.

The physical and chemical properties of a typi-

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