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X-Ray Studies on the Thermal Expansion of Tellurium Dioxide

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Using a Unicam 19 cm high temperature powder camera, the precision lattice parameters of tellurium dioxide have been determined at different temperatures in the range 30 to 461 °C. Using this data, the coefficients of thermal expansion, $\alpha_{\parallel}$ and $\alpha_{\perp}$, parallel and perpendicular to the principal axis respectively, have been evaluated. The temperature dependence of the coefficients of thermal expansion is represented by the following equations:

$$\alpha_{\parallel} = 29.673 \times 10^{-6} + 1.552 \times 10^{-8}\,T + 1.069 \times 10^{-10}\,T^2$$

$$\alpha_{\perp} = 9.875 \times 10^{-6} - 5.440 \times 10^{-9}\,T + 4.572 \times 10^{-12}\,T^2$$

Here T is the temperature in °C. The thermal expansion of tellurium dioxide has been explained in terms of the interionic distances.

1. Introduction

Tellurium dioxide, TeO_2, was reported by Goldschmidt [1] to have a typical ionic structure of the rutile type, space group $P4_2/mnm$. Later Stehlik and Balak [2, 3] redetermined this structure by the trial-and-error method, using single crystal X-ray data, and found that the c parameter of the original rutile type unit cell was doubled. As a consequence the space group was changed to $P4_12_12$ or $P4_32_12$. Since the accuracy of the oxygen parameter determination is reduced on account of the large X-ray scattering power of Te as compared to 0, Leciejewicz [4] made a neutron-diffraction study of the structure of TeO_2. Room-temperature lattice parameters have been reported by these workers in the course of their studies but no data on the thermal expansion of TeO_2 seem to be available. Also since TeO_2 is related to the rutile family in having a distorted rutile type structure, it was thought that it would be of interest to study its thermal behaviour.

2. Experimental Procedure and Results

The TeO_2 sample used in this study was kindly supplied by the K and K Laboratories, Inc, New York. To obtain good pictures the sample was preheated to about 500 °C. Though the colour of the sample changed from white to yellow on heating, the X-ray diffraction pattern of the heated sample did not reveal any change in the structure. The specimen for the thermal expansion study was prepared by pasting this powder on to a thin glass fibre with Araldite. Powder photographs were taken at different temperatures, up to 461 °C, with a Unicam 19 cm high-temperature powder camera and CuKα-radiation. The experimental setup and the procedure have been described earlier [5].

The precision lattice parameters at different temperatures were evaluated from the six unambiguously indexed reflections, (5 1 3) α_1, (4 3 4) α_1, (4 4 2) α_1, (4 3 5) α_1, (4 4 3) α_1 and (4 4 3) α_2, recorded in the Bragg angle region 60° to 74°, using Cohen's [6] analytical method. Independent measurements and calculations were made on several films, and the deviation of the individual values from the mean was taken as the error. The coefficients of thermal expansion at different temperatures were evaluated by the graphical method described earlier [5].

The lattice parameters of TeO_2 obtained at different temperatures are given in table I. In table II the lattice parameters evaluated at room temperature (30 °C) are compared with the values obtained by the earlier workers. In this table the c value reported by Goldschmidt [1] has been doubled for comparison with the rest of the values. The lattice parameters obtained in this investigation are in fair agreement with the values reported by the National Bureau of Standards [7].

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attice parameters of TeO_2 at different mperatures

(°C)	a (Å)	c (Å)
[illegible]	4.8120	7.6092
165	4.8190	7.6405
267	4.8210	7.6746
361	4.8267	7.7050
461	4.8304	7.7435

TABLE II Lattice parameters of TeO_2 at room temperature

Source	a (Å)	c (Å)
Goldschmidt [1]	4.79	7.54
Stehlik and Balak [2]	4.805	7.609
Stehlik and Balak [3]	4.796	7.594
National Bureau of Standards [7]	4.810	7.613
Leciejewicz [4]	4.796 ± 0.002	7.626 ± 0.002
Present study	4.8120 ± 0.0002	7.6092 ± 0.0002

The temperature-dependence of the coefficients of thermal expansion, $\alpha_{\parallel}$ and $\alpha_{\perp}$, parallel and perpendicular to the principal axis respectively, is represented by the following equations:

$$\alpha_{\parallel} = 29.673 \times 10^{-6} + 1.552 \times 10^{-8} T + 1.069 \times 10^{-10} T^2$$

$$\alpha_{\perp} = 9.875 \times 10^{-6} - 5.440 \times 10^{-9} T + 4.572 \times 10^{-12} T^2$$

The coefficients of thermal expansion obtained at different temperatures are shown graphically in fig. 1. It can be seen that while the value of $\alpha_{\parallel}$ increases rapidly with increasing temperature, $\alpha_{\perp}$ decreases slowly with increase of temperature.

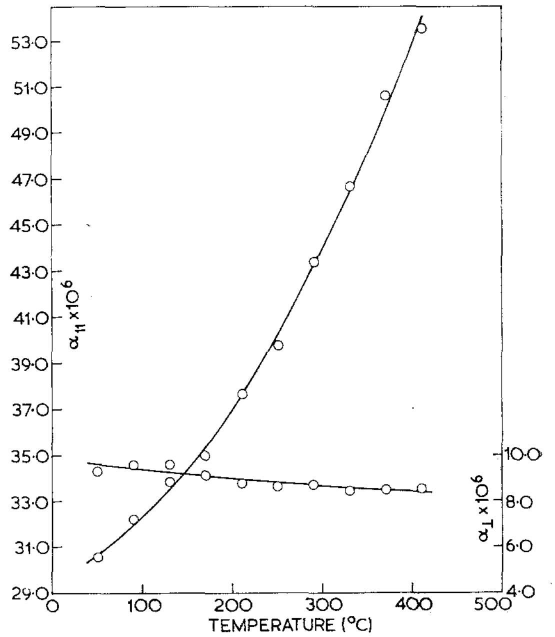

Figure 1 Variation of coefficients of thermal expansion of TeO_2 with temperature.

3. Discussion

The structure of tellurium dioxide is similar to that of α-cristobalite [8]. In TeO_2, each Te atom is linked to four oxygen atoms, two at a distance of 1.91 Å (S_2 bonds) and the other two at a distance of 2.09 Å (S_1 bonds). The co-ordination polyhedron of the tellurium atom thus formed is a distorted square pyramid with the Te atom at the apex. The closest oxygen-oxygen approach distances in the pyramids are: two at a distance of 2.65 Å (A_1 bonds) and two at a distance of 2.75 Å (A_2) bonds. The various interatomic distances in the TeO_4 pyramids are shown in fig. 2. Two more oxygen atoms are linked to the Te atom at a larger distance, 2.89 Å (S_1'), resulting in weak bonding. These distances are shown in the figure by dashed lines. If the S_1' distances are also considered, then the Te atom will have six oxygen neighbours which form a distorted octahedron. Thus, the structure of TeO_2 can be considered as a kind of superstructure of the rutile type having a distorted TeO_6 octahedral arrangement. This distortion occurs because the Te atom chooses four of the

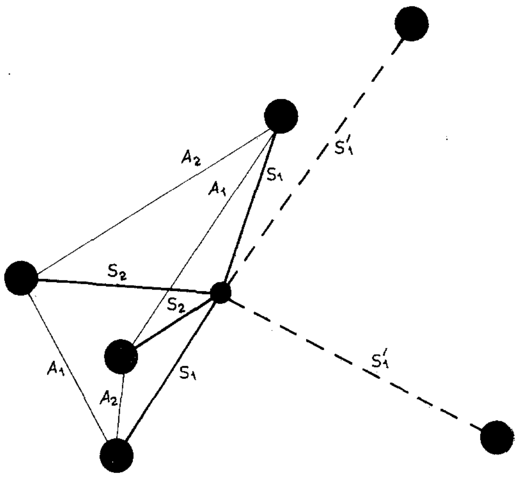

Figure 2 Interatomic distances in the TeO_4 pyramids in TeO_2. Small sphere: Te. Large spheres: O.

six surrounding oxygens for the formation of TeO_4 pyramids.

The thermal expansion behaviour of TeO_2 is very much different from that of the rutile type compounds. It has a large expansion coefficient along the *c*-direction which increases rapidly with increasing temperature while the expansion coefficient along the *a*-direction has a comparatively small value which shows a slight decrease with increasing temperature. At 25° C the coefficients of thermal expansion from this study are

$$\alpha_{\parallel} = 30.13 \times 10^{-6}\,\text{deg}^{-1}$$
$$\alpha_{\perp} = 9.74 \times 10^{-6}\,\text{deg}^{-1}$$

The thermal expansion of TeO_2 can be explained in terms of the interatomic distances, as was done earlier in the case of rutile and anatase [9]. The interatomic distances in the TeO_4 pyramids are given in table III along with the sum of the ionic radii and the covalent radii (corrected for electronegativity) and the inclination of the bonds to the *c*-axis.

From the table it can be seen that the bond lengths S_2, S_1 and A_1, being much less than the sum of the ionic radii, are fairly strong while the A_2 bonds are weak. The two strong bonds S_2 and A_1 affect equally the thermal expansion along the *a* and *c* directions. The other strong bond, S_1, contributes more towards the *a*-direction. Hence, the coefficient of thermal expansion along the *a*-direction ($\alpha_{\perp}$) is less than that along the *c*-direction ($\alpha_{\parallel}$).

TABLE III Interatomic distances in the TeO_4 pyramids

Bonds	Bond length	Inclination to the *c*-axis	Sum of the ionic radii	Sum of the covalent radii
S_2	1.91 Å	44°	2.21 Å	1.90 Å
S_1	2.09 Å	76°	2.21 Å	1.90 Å
A_1	2.65 Å	44°	2.80 Å	—
A_2	2.75 Å	72°	2.80 Å	—

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