

Redetermination of oxygen parameters in xenotime, YPO_4

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Auszug

Um die Bindungslängen der isotypen Minerale Zirkon und Xenotim zu vergleichen, wurden die Sauerstoff-Parameter des Xenotims verfeinert. Die Untersuchung ergab, daß das verschiedene Verhalten der beiden Minerale gegenüber der Metamiktisierung sich nicht allein aus dem Kation—Anion-Abstand ableiten läßt.

Abstract

Oxygen parameters in xenotime have been refined in order to compare bond lengths in two isostructural minerals, zircon and xenotime. The results have shown that the different behaviour toward metamictization of these minerals could not be explained on the basis of cation—anion distances alone.

The crystal structure of xenotime was determined by VEGARD¹ and by STRADA and SCHWENDIMAN², the results being in fairly good agreement. The structure is of the zircon type with the space group $I4_1/amd$ and with four formula units in the unit cell. Since the bond lengths in the structures of zircon and xenotime have been used in the discussion of the metamict state, and since the oxygen parameters in zircon have already been refined³ a redetermination of the oxygen positions in xenotime appeared to be of interest in order to compare bond lengths in these two compounds.

The specimen used was a xenotime from Hitterö, Norway. The cell dimensions determined from oscillation and Weissenberg photographs are

$$a = 6.878 \pm 0.003 \text{ \AA}, \quad c = 6.036 \pm 0.003 \text{ \AA}.$$

¹ L. VEGARD (1927), The structure of xenotime and the relation between chemical constitution and crystal structure. *Phil. Mag.* **4**, 511—525.

² M. STRADA and G. SCHWENDIMAN (1934), La struttura cristallina di alcuni fosfati dei metalli trivalenti, II. Arseniato e fosfato di ittrio. *Gazz. Chim. Ital.* **64**, 662—674 [cited after *Strukturbericht* **3**, 429].

³ I. KRSTANOVIĆ (1958), Redetermination of the oxygen parameters in zircon (ZrSiO_4). *Acta Crystallogr.* **11**, 896—897

With an integrating Weissenberg goniometer twenty five $h0l$ and thirteen $hk0$ reflections were recorded; a powder diagram was obtained with a Geiger-counter spectrometer (strip-chart recorder). In all cases filtered copper radiation was used. The intensities of the spots of the Weissenberg diagrams were measured with the Kipp photometer and were corrected for polarization-Lorentz factor and for the absorption. In the subsequent stages of the work the relative-intensity values were scaled to calculated ones using appropriate constants. For the calculation of structure amplitudes VEGARD's parameters and the atomic scattering factors from "Internationale Tabellen" (1935) were used.

Table 1. Observed and calculated structure factors

h k l	F_o	F_c												
2 0 0	98	95	5 0 1	19	11	1 0 3	29	- 35	4 0 4	48	- 47	2 2 0	55	- 43
4 0 0	75	81	7 0 1	19	21	3 0 3	17	- 10	6 0 4	35	- 35	4 2 0	65	- 61
6 0 0	65	72	2 0 2	35	- 35	5 0 3	25	- 28	1 0 5	24	- 21	6 2 0	50	- 56
8 0 0	38	46	4 0 2	16	- 16	7 0 3	20	- 15	3 0 5	15	- 8	8 2 0	21	- 22
1 0 1	29	25	6 0 2	0	- 1	0 0 4	39	- 37	5 0 5	22	- 22	4 4 0	36	41
3 0 1	47	46	8 0 2	13	- 14	2 0 4	51	- 58	1 0 7	18	13	6 4 0	28	27
									5 0 7	16	15	6 6 0	15	- 17

For the refinement for the oxygen parameters F_o , $F_o - F_c(Y + P)$ and $F_o - F_c$ syntheses were used. The minimum value for the reliability index R , 10%, was obtained for the following oxygen parameters: $x = 0.064$ and $z = 0.234$. Further attempts to reduce R by small changes in parameters failed. With VEGARD's oxygen parameters R becomes 20%.

On the basis of this redetermination the atomic distances are

$$\begin{array}{ll}
 P - O = 1.50 \text{ \AA} & O - O = 2.41 \text{ \AA} \text{ (two)} \\
 Y - O = 2.27 \text{ \AA} \text{ (four)} & O - O = 2.56 \text{ \AA} \text{ (four)}. \\
 Y - O = 2.56 \text{ \AA} \text{ (four)} &
 \end{array}$$

The error in bond lengths is estimated to be 0.05 Å.

The interatomic distances in the PO_4 tetrahedron are, within the limits of experimental error, in agreement with the more recent values found by other investigators. The opinion was expressed⁴ that the difference between xenotime and zircon with respect to metamictization could be explained by considering xenotime as more stable due to its more regular Y—O-distances. This was based upon the structural evidence given by VEGARD who reported the following cation—anion distances: 2.04 Å and 2.41 Å for Zr—O and 2.23 Å and 2.24 Å for Y—O. However, the present results and those obtained earlier on zircon contradict such explanation. In this connection the results⁵ of the refinement of the oxygen positions in monacite, $CePO_4$, may be mentioned. This strongly radioactive mineral, never found in a metamict state, shows very irregular oxygen polyhedra around cerium, the distances ranging from 2.45 Å to 2.95 Å.

⁴ O. HUTTON (1950), Studies of heavy detrital minerals. Geol. Soc. Amer. Bull. **61**, 635—710.

⁵ To be published.