

STRUCTURAL CHARACTERIZATION OF DIBENZOTHIOPHENE 5,5-DIOXIDE BY X-RAY POWDER DIFFRACTION

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Sulfones have been synthesized in our laboratory for identification and modeling of several thiophenic compounds found in petroleum derivatives. Dibenzothiophene 5,5-dioxide was obtained by the reaction between the dibenzothiophene and hydrogen peroxide according to the methodology described by Drushel and Miller [1]. The product was recrystallized in ethanol and obtained as colorless crystals. The purpose of this work is to report the structure of this compound by X-ray powder diffractometry. The powder diffraction data were collected at 293(1) K on a Rigaku D/MAX diffractometer. From the corrected peak positions, DICVOL91 and TREOR97 suggested a monoclinic unit cell. This result was subsequently least-squares refined using NBSAIDS*83 with FOM's M20 = 37.0 and F30 = 36.4. The space group (C2/c, No.15) was derived from systematic absences and checked with the program Chekcell. The structure was refined with the Rietveld program FULLPROF99. The atomic parameters of dibenzothiophene sulfone known from multiple film Weissenberg photographs were used in the initial model [2]. Final refinement of the data yielded a = 10.106(3), b = 13.815(4), c = 7.129(2) Å and β = 91.639(7)°, RF = 12.62 and RB = 7.17. The molecular structural parameters obtained were correlated with those found by means of *ab initio* methods applying Functional Density Theory at B3LYP level using basic set 6-31G(d,p).

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References

- [1] H.V.Drushel and J.F.Miller Anal. Chem. 30,7,1271(1958).
 [2] L.R.Kronfeld and R.L.Sass Acta Cryst. B24,981(1968).

Keywords: DIBENZOTHIOPHENE 5,5-DIOXIDE, STRUCTURAL CHARACTERIZATION, POWDER DIFFRACTION.

X-RAY RIETVELD ANALYSIS OF THE DIFFRACTION PATTERN

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The determination of lattice constants, atomic positions, amplitudes of the thermal vibrations and stoichiometry indices is very important in the study of crystal structure. At present paper these characteristics were defined for the β-pentoxide tantalum and pyrolytic dioxide manganese powders. X-Ray Rietveld analysis was used for investigation structure of these oxides. This method has been more popular with crystallographers than the integrated-intensity method since it applies the superposition problem directly and allows more complex structures to be refined. Intensity measurements were carried out on X-Ray diffractometer using Cu Kα, Fe Kα, Co Kα, Mo Kα radiations monochromatised by pyrolytic graphite crystal. The new models of the structure of the studying oxides were suggested. It was determined that the structure of the β-pentoxide tantalum powder is orthorhombic with a=6.217 Å, b=3.677 Å, c=7.794 Å. It was defined that structure of manganese dioxide obtained repeated pyrolysis is the structure nonstoichiometry β-dioxide manganese. Value index nonstoichiometry is lower. The manganese dioxide obtained single pyrolysis has partially non-ordering structure. In last case along with X-Ray Rietveld analysis was used Finbak-Warren method.

Keywords: RIETVELD ANALYSIS, POWDER OXIDES, X-RAY DIFFRACTION

POWDER DIFFRACTION STUDIES OF NEW FIBRILLAR MOLIBDATES WITH ORGANIC CATIONS

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Molybdenum compounds have been widely investigated due to their potent catalytic properties in various, important for industry and environment, reactions. Recently a novel method of fibrillar trimolybdates synthesis has been elaborated. In this method fibrillar silver trimolybdate reacts with relevant chloride resulting in a compound with structure based on a polymeric anionic chain with a desired cation. This method seems to be very promising for synthesis of trimolybdates with organic cations since the time consuming heating and considerably long period of crystallization is avoided. For test purposes two already known compounds, that is potassium and aniline trimolybdates [1,2] were synthesised according to the new procedure. Then, after successful tests, unknown so far, trimolybdates of methylamine, tetrabutylamine and pyridine were obtained. These compounds were investigated by powder diffraction methods. The lattice parameters and space groups were determined using PROSZKI package. Subsequently, initial structure models were built using EXPO or SHELXS programs. Final refinements were performed using XRS-82 Rietveld system [3]. Obtained so far results confirmed the existence of polymeric anions (responsible for fibrillar morphology of the crystals) in all the investigated compounds.

References

1. Lasocha, W., Jansen, J., Schenk, H., J. Solid State Chem., 115, 225(1995)
 2. Lasocha, W., Jansen, J., Schenk, H., J. Solid State Chem., 117, 103 (1995)
 3. Baerlocher, Ch., The X-Ray Rietveld System., Zurich 1982.

Keywords: FIBRILLAR CRYSTALS, POWDER DIFFRACTION, RIETVELD METHOD

ASYMMETRY FROM AXIALLY FOCUSING MONOCHROMATORS D.M. Toebbens

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The use of an axially focusing monochromator in combination with a wide detector opening increases the observed intensity but has a large impact on the peak shape. Common descriptions used for the axial asymmetry function (AAF) of this type of instrument consider the effects of sample and detector heights only but neglect the high axial convergence angles. Inclination of an individual ray illuminating a sample region effects the AAF similar to a displacement out of the macroscopic diffraction plane. In this geometry those two effects are correlated; a focus length higher than the monochromator-sample distance leads to partial cancellation. The shape of primary source and monochromator influences this correlation. Since the diffraction angle dependency of the effects is different, a distinct non-linear behaviour of the AAF results. For typical instrument configurations those effects include a strong asymmetry and a broadening of Lorentzian character. The numerical model presented here for the calculation of the AAF uses an analytical expression for the projection of the Laue cone of each individual ray on the cylindrical detector. The distribution of rays in the beam illuminating the sample is calculated by ray tracing. Considered instrumental parameters are height and distances of primary source, monochromator, sample, detector and slits as well as monochromator focusing length and angle and the typical construction of focusing monochromators from a number of individual flat single crystals. The resulting peak shape gave superior fits when tested on data measured at E9 (HMI, Berlin).

Keywords: PEAK SHAPE, POWDER DIFFRACTION, ASYMMETRY