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X-ray crystallographic analysis of by-products produced in photochromism of dithienylcyclopentenes

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Diarylethenes undergo thermally stable photochromic reactions even in the crystalline phase as well as in solution. Among the diarylethenes, dithienylperfluorocyclopentenes have a characteristic of fatigue resistance. However, dithienylcyclopentenes are not really investigated. Here we focused on analysis of side reactions in the photochromic reactions of 1,2-bis(2-methyl-5-phenyl-3-thienyl) cyclopentene (**1**), 1,2-bis(2-methyl-5-(p-methoxyphenyl)-3-thienyl) cyclopentene (**2**), and 1,2-bis(2,4-dimethyl-5-(p-methoxyphenyl)-3-thienyl)cyclopentene (**3**). Upon alternate irradiation with ultraviolet and visible light, the dithienylcyclopentenes (**1-3**) exhibited photochromism in hexane. When the solution was irradiated with ultraviolet light for more than 10 min, the coloration/decoloration performance was declined. By-products were isolated by HPLC, and their molecular structures were determind by ^{1}H-NMR spectra, Mass spectra, and X-ray crystallographic analysis of the single crystals. To know the relationship between the molecular structure of the dithienylcyclopentene and the formation rate of the by-product, we determind quantum yields of not only the photocyclization and photocycloreversion reactions but also the by-product formation. The quantum yields of the by-product formation of **1** and **2** were about 10 times larger than that of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**4**). This indicates that the dithienylcyclopentenes were more fatigable than the dithienylperflu orocyclopentenes. In contrast, by the introduction of methyl groups at the 4-positions of the thiophene in the dithienylcyclopentene, the coloration/decoloration cycles of **3** can be repeated as well as that of **4**. In conclusion, the side reactions were suppressed by the introduction of methyl groups.

Keywords: photochromism, diarylethene, photoreaction

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X-ray diffraction of laser-heated silicon at high pressures

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The phase diagram of silicon is complex : it exhibits seven distinct polymorphs at pressures below 100 GPa, and the melting curve has a minimum at ~10 GPa and ~1000 K. In order to explore the high temperature phase diagram, we performed simultaneous angular-dispersive x-ray diffraction and laser heating at beamline ID27 at the ESRF. We present x-ray diffraction of Si in the laser heating diamond cell between 30 and 70 GPa at temperatures bettwen 1500 and 3000 K. Particular attention is paid to determination of the melting curve at high pressures.

Keywords: silicon, high pressure, laser heating

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Rochelle salt thermal expansion coefficients determined by synchrotron radiation renninger scan

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The thermal expansion coefficients of Rochelle salt single crystal have been determined by using the Synchrotron radiation Renninger scan (RS) that acts as a 3D fine probe in these experiments. The angular peak shift clearly observed for sensitive secondary reflections in the RS due to the temperature variation allows for simultaneously detecting subtle distortions along the three crystallographic directions of the sample. These secondary reflections present a small angle between the entrance and exit position of the secondary reciprocal lattice point of the Ewald sphere by sample rotation around the diffraction vector (normal to the primary planes). The UNWEG program (Rossmanith, J. Appl. Cryst. (2003) 36, 1467) has allowed to calculate the Rochelle salt RS pattern by using the X-ray diffraction kinematical theory. The chosen sensitive secondary reflections were: (-2 4 1)(12 4 -1),(-2 5 2)(12 5 2) and (-1 4 1)(11 4 1), and from the peak shift measurements in the orthorhombic phase (T> 24ºC) we were able to obtain the lattice parameters with very good resolution. The Rochelle salt thermal expansion coefficients determined from the lattice parameter variation ($\alpha_{[100]}$=62(2)x10^{-6} C^{-1}, $\alpha_{[010]}$=38(8)x10^{-6} C^{-1} and $\alpha_{[001]}$=45(5)x10^{-6} C^{-1}) are in very good agreement with the literature values ($\alpha_{[100]}$=(58-62)x10^{-6} C^{-1}, $\alpha_{[010]}$=(42-54)x10^{-6} C^{-1} and $\alpha_{[001]}$=(43-54)x10^{-6} C^{-1}).

Keywords: X-ray multiple diffraction, thermal expansion, inorganic crystals

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Monocrystal like structural, stochastic and microstructural information from polycrystalline samples

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In the last several years we have demonstrated methods whereby single crystal quality data can be extracted from polycrystalline materials. These data can be used not only for high-quality structure solution and refinement, but also to study sample heterogeneity. By determining structural of each crystallite in a polycrystalline sample, we can characterise not only the average properties of samples by the distribution of these properties. As the individual orientation matrices of the crystallites are determined, it is furthermore possible to correlate chemical properties with microstructural properties of the crystals such as their strain state and orientation. In situ studies allow the dynamic behaviour to be correlated with all these properties, and finally spatially resolved studies allow the probing of inter-crystalline effects. We will provide examples from the latest results of these studies.

Keywords: crystal structure determination, materials

structure and characterization, polycrystalline X-Ray diffraction

P11.16.125

Structural and thermal analytical study on *trans*-diammine-bis(nitrito) complex of Pd(II) and Pt(II)

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Aqueous ammonia solutions of $Pd(NH_3)_2(NO_2)_2$ and $Pt(NH_3)_2(NO_2)_2$ are used, after impregnations and heat treatments between 150 and 350 $^\circ$C, for a successful sensitization of SnO_2 layers for CO gas [1]. In order to identify the active sensing chemical species of residues from the Pd or Pt solutions, a detailed study on thermal decomposition of solid *trans*-$Pd(NH_3)_2(NO_2)_2$ (**1**) and *trans*-$Pt(NH_3)_2(NO_2)_2$ (**2**), crystallized from the used solutions, has been carried out. Compounds **1** and **2** have been characterized by their FTIR spectra and XRD profiles. Their composition and trans configuration have also been identified by reference IR spectra [2] and XRD reference patterns (PDF 00-45-598 and PDF 00-54-155) [3]. The crystal and molecular structure of *trans*-$Pd(NH_3)_2(NO_2)_2$ (**1**) has been determined by single crystal X-ray diffraction (R = 0.0515). The obtained crystallographic data of the triclinic crystals of (space group P-1, a = 5,003(1) Å, b = 5,419(1) Å, c = 6,317(1) Å, α = 91.34(2) $^\circ$, β = 111.890(10) $^\circ$, γ = 100.380(10) $^\circ$) has been found close to that was reported earlier [4]. A better understanding of mechanism and dynamics of the gas evolution from these solid complexes **1** and **2** probably sensitive to shock seems to be essential during a scaling up of sensor fabrication.

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Keywords: theophylline, co-crystals, salt

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Crystal structure of synthetic hydrotungstite, $WO_2(OH)_2(H_2O)$

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Hydrotungstite, $WO_2(OH)_2(H_2O)$ or $H_2WO_4(H_2O)$ (PDF 00-016-0166 and 00-018-1420) occurs as an alteration product in the oxidized zone of a hydrothermal tungsten ore deposit at the Calacalani mine in Bolivia, and thin films of hydrotungstite have been used as humidity sensors. It is reported to crystallize in $P2/m$ with a = 7.379(5), b =

6.901(5), c = 3.748(5) Å, and β = 90.36(16)$^\circ$. The powder pattern of a greenish yellow precipitate from an inductively-coupled plasma (ICP) specimen preparation of a W-containing sample matched that of hydrotungstite well, but the unit cell and powder pattern were more complicated than had been reported. Application of lattice matching techniques to the reported unit cell yielded the chemically-plausible analogue "yellow molybdic acid", $MoO_3(H_2O)_2$, which has the ICSD formula type AX5. A further search for Mo-containing compounds having this formula type yielded the mineral sidwellite, $MoO_3(H_2O)_2$, which crystallizes in $P2_1/n$ with a = 10.487(1), b = 13.850(1), c = 10.617(1) Å, and β = 91.62(9)$^\circ$, and has been studied using neutron powder diffraction. The sidwellite cell is an 8 × supercell of the reported hydrotungstite cell, and the sidwellite structure served as a good initial model for a Rietveld refinement of the hydrotungstite structure. The hydrogen positions were determined by a quantum chemical geometry optimization, which permitted analysis of the hydrogen bonding pattern. The structure consists of corner-sharing layers of tilted WO_6 octahedra in the *ac* plane. Pointing into the interlayer region *trans* to each tungsten atom are a coordinated water molecule and a W=O group. The interlayer region is occupied by water molecules, which are hydrogen bonded to the layers. Hydrotungstite is properly formulated $[WO_3(H_2O)]$ (H_2O). The structure of the mineral tungstite, $WO_3(H_2O)$, has been reported, but the topologies of the layers in sidwellite and tungstite differ. A combination of quantum calculations and Rietveld refinement was used to determine the best model for the topology of the hydrotungstite layer. The quantum calculations help establish the relative energies of hydrotungstite and tungstite.

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Periodic properties of atomic matter

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A relationship between the periodicity of atomic matter with natural-number patterns was unveiled recently[1]. Almost a century ago W.D. Harkins[2] noted that for stable nuclides the proton/neutron ratio converged to a value Z/N of 0.62 (the neutron had not been discovered at that time). This value has now been recognized as the number tau, well known in number theory and popularly referred to as the 'golden ratio' [3]. The periodic nature of the stable nuclides has also been demonstrated in other ways, such as by considering experimentally observed properties of nuclides including the nuclear binding energy (NBE), spin, abundance and thermal cross section. There is an undeniable link to number theory: Fibonacci numbers, the golden ratio and Farey sequences, established without any assumptions about the nuclear properties of the 264 known stable nuclides. Fig. 1. A/N or A/Z vs. mass number for nuclides with A=4n converge to limiting values close to tau+2 or tau+1.

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