Filter for X-ray Polarization Analysis

Design of a Solid Inclusion Compound with Optimal Properties as a Linear Dichroic Filter for X-ray Polarization Analysis**

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In the case of visible light, studies of polarization are dominated by the use of dichroic filters (e.g. the Polaroid sheet[1]), for which photons with polarization parallel to a certain axis in the material are preferentially attenuated over those with polarization perpendicular to this axis. In principle, materials analogous to the Polaroid sheet may be developed for applications as dichroic filters in other regions of the electromagnetic spectrum, and in the present paper we focus on the analysis of polarized X-ray radiation (produced, for example, from a synchrotron source). A suitable dichroic filter would be a crystal for which the absorption of polarized X-rays depends significantly on the orientation of the crystal. Such materials have considerable potential in a range of applications, for example in the field of magnetic X-ray scattering.[2]

While linear dichroism at X-ray absorption edges is well documented,[4] the exploitation of this effect in a filter material for X-ray polarization analysis was demonstrated for the first time only very recently.[5] This work explored the bromine K edge linear dichroism of the 1,10-dibromodecane/urea inclusion compound, in which 1,10-dibromodecane guest molecules are included within tunnels in the urea host structure.[6–9] This material exhibits a strongly dichroic resonance close to the absorption edge, with the ratio of absorption coefficients[10] attaining a value of $R_\gamma = 0.65$ (i.e. the attenuation is higher by a factor of about 3/2 for the crystal orientation with the tunnel axis parallel to the direction of incident X-ray polarization than the crystal orientation with the tunnel axis perpendicular). The 1,10-dibromodecane/urea material is thus effective for X-ray polarization analysis, and has indeed been tested successfully in the first dichroic polarization analysis of magnetic diffraction,[5] involving a study of antiferromagnetic holmium.

In spite of this success, however, the efficiency of 1,10-dibromodecane/urea as a dichroic filter is limited by the fact that the C–Br bonds undergo reorientation[11,12] around the tunnel axis at ambient temperature and are oriented at $\approx 35°$ to this axis.[5] Theoretical considerations, elaborated elsewhere,[5] suggest that a material in which all C–Br bonds are aligned parallel to the tunnel would be significantly more effective than 1,10-dibromodecane/urea (corresponding to a reduction in R_γ by a factor of about 2). In this paper, we describe a new molecular material—the 1-bromoadamantane/thiourea inclusion compound—that has been *designed* specifically to give optimal properties as a dichroic filter for X-ray polarization analysis.

The main features of our design strategy were: 1) to have a guest molecule with only one C–Br bond (thus, by constraining all molecules to have the same orientation, all C–Br bonds would implicitly be aligned parallel to each other), 2) to constrain the orientation of the guest within the host structure such that the C–Br bonds of all guest molecules are parallel and do not undergo dynamic reorientation (at the temperature of the intended operation of the analyzer, ideally room temperature), and 3) to ensure that the direction of the C–Br bonds bears a straightforward relationship to the crystal morphology, such that the analyzer crystal(s) could be aligned readily during polarization analysis.

These requirements are most readily satisfied for a material in which all guest molecules are oriented such that their C–Br bonds are parallel to the host tunnel. As described above, it is difficult to envisage a material based on the urea tunnel structure that can satisfy requirements 1) and 2), and

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thiourea inclusion compounds provide a better opportunity for achieving the desired orientational characteristics of the guest molecules. While the urea tunnel is essentially cylindrical, the tunnel in conventional thiourea-inclusion compounds[9] may be considered to comprise "cages" (diameter ≈ 7.1 Å) connected by narrower "windows" (diameter ≈ 5.8 Å). Our design of the 1-bromoadamantane/thiourea inclusion compound was based on the rationale that the adamantane moiety would essentially fill the cage, with the C–Br bond constrained to project into the narrower window region between adjacent cages and thus oriented essentially parallel to the tunnel axis. It is already known[13] that adamantane forms an inclusion compound with thiourea in which the adamantane guest molecules efficiently fill the cages in the conventional thiourea tunnel structure. Furthermore, thiourea inclusion compounds usually have a needle morphology, with the host tunnel parallel to the needle axis, which would allow straightforward alignment of the crystal in polarization analysis. Herein, we describe the preparation and structural characterization of 1-bromoadamantane/thiourea, and assess the performance of this material as a dichroic filter for X-ray polarization analysis. To our knowledge, the formation of the 1-bromoadamantane/thiourea inclusion compound has not been reported previously.

The 1-bromoadamantane/thiourea inclusion compound was prepared by using standard crystallization procedures for thiourea inclusion compounds, by slowly cooling a solution containing the guest (1-bromoadamantane) and thiourea dissolved in methanol. Comparatively large needle-shaped crystals (typical dimensions $1 \times 1 \times 10\ mm^3$) were obtained. Structural properties of 1-bromoadamantane/thiourea were determined from single crystal X-ray diffraction data recorded at 200 K.[14] Differential scanning calorimetry indicates that the material does not undergo any phase transitions between this temperature and ambient temperature. Full structural details will be presented elsewhere[17] and only the salient features are discussed here. As expected, the thiourea molecules form a tunnel host structure (Figure 1a), constructed from N–H···S hydrogen bonding between the thiourea molecules. This structure differs to some extent from the conventional thiourea host structure (it is well known[9] that the host structure in thiourea inclusion compounds can exhibit variations depending on the guest molecule). Within the repeat unit (24.75 Å) along the tunnel, there are three crystallographically independent 1-bromoadamantane guest molecule sites (Figure 1b), corresponding[18] to a thiourea/guest molar ratio of 4:1. Importantly, the C–Br bond of each guest molecule lies parallel to

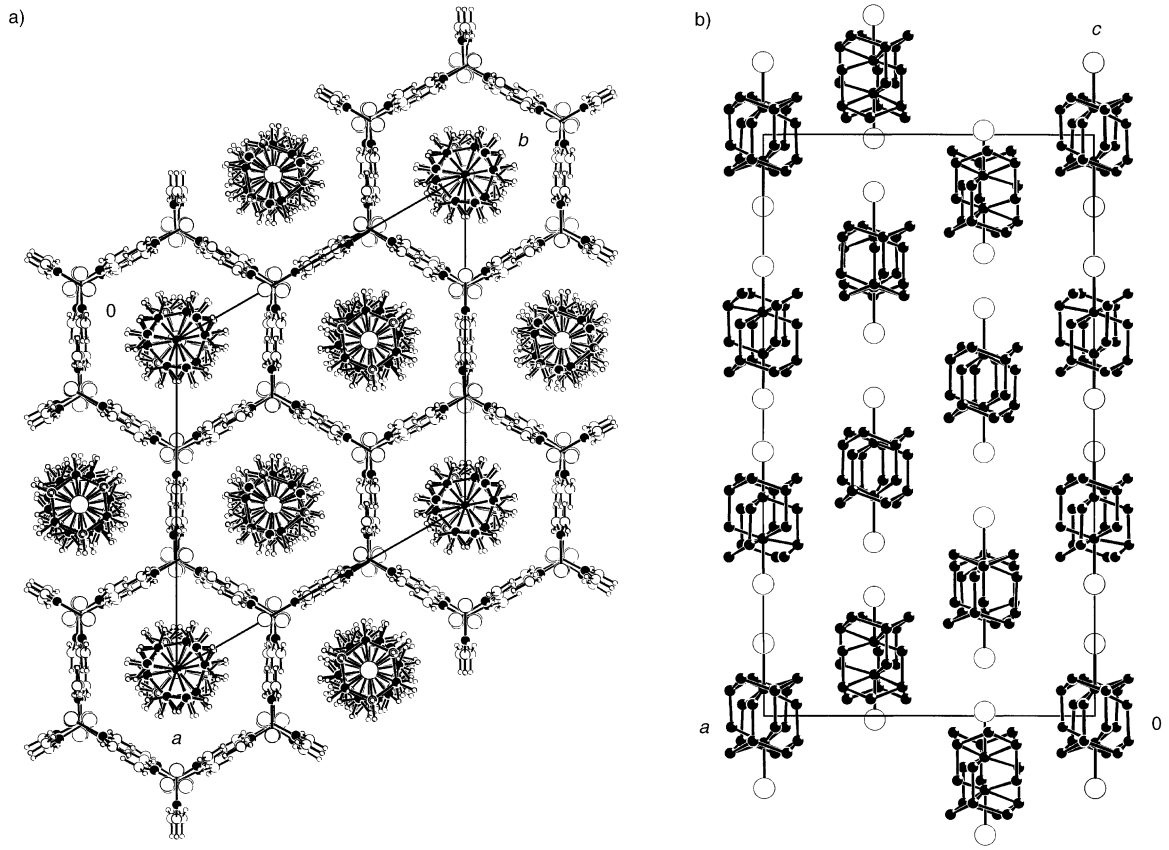

Figure 1. a) Crystal structure of 1-bromoadamantane/thiourea at 200 K viewed along the tunnel axis (*c* axis) of the thiourea host structure. In each tunnel, there are three crystallographically independent 1-bromoadamantane guest molecules, each of which is disordered between two orientations. b) The guest substructure in 1-bromoadamantane/thiourea (thiourea molecules omitted for clarity) viewed perpendicular to the tunnel axis, which is vertical. Note that the C–Br bonds of all guest molecules lie parallel to the tunnel axis. The disorder is discussed in the text. Hydrogen atoms are omitted for clarity.

the thiourea host tunnel, as required in our design strategy for an X-ray polarization analyzer. For each guest molecule, there is disorder between two orientations (with essentially equal occupancies) in which the C–Br bond lies along the positive *c* axis or the negative *c* axis. Given the spatial constraints imposed by the host tunnel, it is unlikely that the guest molecules undergo dynamic interconversion between the two orientations, and this disorder is presumably "locked in" during crystal growth.[19] Importantly, in each orientation, the C–Br bond lies parallel to the tunnel axis, and therefore the performance as a polarization analyzer should be unaffected by this disorder. Clearly (as seen in Figure 1b), the positions of the carbon atoms of the adamantane moiety are different for each orientation of the molecule.

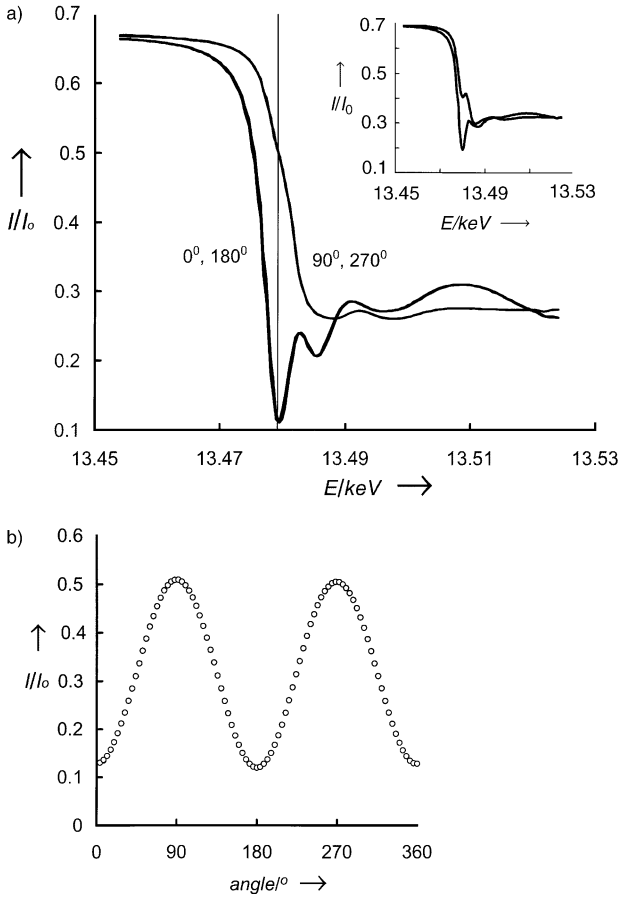

Figure 2. a) X-ray transmittance[10] (I/I_o) through a crystal of 1-bromoadamantane/thiourea as a function of energy (E) close to the Br K-edge, with the X-ray polarization parallel (0° and 180°) and perpendicular (90° and 270°) to the crystal *c* axis. The vertical line is at 13.479 keV (see text). The insert shows the corresponding data for 1,10-dibromodecane/urea.[5] One notable difference between the data for the two materials is the complete absence of a resonance at 13.479 keV for 1-bromoadamantane/thiourea when the X-ray polarization is perpendicular to the *c* axis and therefore perpendicular to the C–Br bonds. b) X-ray transmittance (I/I_o) as a function of the orientation of a crystal of 1-bromoadamantane/thiourea (defined as the angle between the tunnel axis of the crystal and the electric vector of the polarized incident X-ray beam) at the value of energy (13.479 keV) at which the ratio of absorption coefficients R_γ is minimum.

To assess the performance of 1-bromoadamantane/thiourea as a dichroic filter for polarized X-rays, dichroism spectra were measured for a single crystal on Station 16.3, at the Synchrotron Radiation Source, Daresbury Laboratory.[21,22] Figure 2a shows the X-ray transmittance[10] as a function of X-ray energy (close to the bromine K edge, 13.474 keV) for both the parallel and perpendicular orientations of the crystal, and Figure 2b shows the X-ray transmittance as a function of crystal orientation at 13.479 keV. Close to the absorption edge, the transmission of polarized X-rays through the crystal shows a very significant dependence on crystal orientation. The maximum dependence is at 13.479 keV, and corresponds to $R_\gamma = 0.32$. This represents an improvement in performance of 1-bromoadamantane/thiourea, in comparison to 1,10-dibromodecane/urea, by a factor of 2, and the value of R_γ for 1-bromoadamantane/thiourea is very close to the minimum attainable value predicted theoretically[5] (on the assumption that the only factor influencing the difference in performance of the two materials arises from the different C–Br bond orientations).

In summary, we have demonstrated the successful implementation of a crystal-design strategy to produce a material, the 1-bromoadamantane/thiourea-inclusion compound, which exhibits essentially optimal performance as a dichroic filter for X-ray polarization analysis. This material will be valuable in a range of X-ray measurements, at wavelengths close to the bromine K-edge, most notably in studies of nonresonant magnetic scattering. Investigations to assess the stability of this material[23] with respect to time and radiation exposure are in progress, and strategies for producing large platelike samples with suitable dimensions and orientational characteristics for practical applications as polarization analyzers are under development.

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[1] E. H. Land, *J. Opt. Soc. Am.* **1951**, *41*, 957.
[2] For a magnetic material, spin and orbital magnetism lead to a very weak scattering signal for which the polarization dependence is very different from classical "charge" scattering, and provides a signature of the relative contributions from spin and orbital magnetic moments.[3] The ability to determine separate spin and orbital densities in magnetic crystals is unique to nonresonant X-ray diffraction, and information of this type is vital for understanding the origin of fundamental materials properties, such as magnetic anisotropy. One reason that progress in this field has been slow is that conventional X-ray polarization analyzers are diffraction-based, tend to have low efficiency, and suffer from systematic errors arising from variations in beam divergence, analyzer crystal uniformity, and misalignment.
[3] D. Gibbs, G. Grübel, D. R. Harshman, E. D. Isaacs, D. B. McWhan, D. Mills, C. Vettier, *Phys. Rev. B* **1991**, *43*, 5663.
[4] C. Brouder, *J. Phys. Condens. Matter* **1990**, *2*, 701.
[5] S. P. Collins, D. Laundy, K. D. M. Harris, B. M. Kariuki, C. L. Bauer, S. D. Brown, P. Thompson, *J. Phys. Condens. Matter* **2002**, *14*, 123.

[6] A. E. Smith, *Acta Crystallogr.* **1952**, *5*, 224.
[7] K. D. M. Harris, J. M. Thomas, *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 2985.
[8] K. D. M. Harris, S. P. Smart, M. D. Hollingsworth, *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 3423.
[9] M. D. Hollingsworth, K. D. M. Harris, in *Comprehensive Supramolecular Chemistry, Vol. 6* (Ed.: D. D. MacNicol, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, p. 177.
[10] The ratio R_γ is defined as $\gamma_{min}/\gamma_{max}$, where γ_{min} and γ_{max} are the values of the linear absorption coefficients for the crystal orientations with lowest and highest attenuation respectively. For the materials studied here, γ_{min} and γ_{max} arise, respectively, for crystal orientations with the tunnel axis essentially perpendicular and parallel to the electric vector of the polarized incident X-ray beam. The linear absorption coefficient γ is related from the ratio of the transmitted (I) and incident (I_o) X-ray intensities as follows: $I/I_o = \exp(-\gamma t)$, where t is the sample thickness. X-ray transmittance (see Figure 2) refers to the measured ratio I/I_o.
[11] F. Guillaume, S. P. Smart, K. D. M. Harris, A. J. Dianoux, *J. Phys. Condens. Matter* **1994**, *6*, 2169.
[12] A. E. Aliev, S. P. Smart, I. J. Shannon, K. D. M. Harris, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 2179.
[13] R. Gopal, B. E. Robertson, J. S. Rutherford, *Acta Crystallogr. Sect. C* **1989**, *45*, 257.
[14] Single-crystal X-ray-diffraction data were recorded on a Bruker SMART 6000 diffractometer with a graphite-monochromated $Cu_{K\alpha 1}$ source and CCD area detector: $[SC(NH_2)_2]_{12}[C_{10}H_{15}Br]_3$; crystal size $0.32 \times 0.40 \times 0.22\ mm^3$; $T = 200$ K; $\lambda = 1.54178$ Å; Trigonal, $P321$; $a = 16.1112(1)$ Å, $c = 24.7533(2)$ Å; $V = 5564.41(7)$ Å^3; $Z = 3$. The structure was solved by using SHELXS86[15] and refined by using SHELXL 97[16] ($R_1 = 11.99\%$; w$R_2 = 32.95\%$). Note that the crystal used for the X-ray diffraction study was not needlelike, and was considerably smaller than typical crystals of this material. Powder X-ray diffraction confirms that the structure determined from this crystal is representative of the bulk material.
[15] G. M. Sheldrick, SHELXS 86, Program for the Solution of Crystal Structures, University of Göttingen (Germany), **1986**.
[16] G. M. Sheldrick, SHELXL 97, Program for the Refinement of Crystal Structures, University of Göttingen, (Germany), **1993**.
[17] M.-H. Chao, B. M. Kariuki, K. D. M. Harris, unpublished results.
[18] The thiourea/guest molar ratio of 4:1 was confirmed from the results of elemental analysis. This stoichiometry of 1-bromoadamantane/thiourea differs from that of conventional thiourea-inclusion compounds,[9] for which there are typically two guest molecules per 12 Å along the tunnel and the thiourea/guest molar ratio is 3:1.
[19] Analysis of the single-crystal diffraction data cannot distinguish whether this disorder represents (1) disorder in the orientations of individual molecules within a given tunnel, or (2) an ordered arrangement of the C–Br bond vectors within each tunnel, with the disorder in the average crystal structure arising from different tunnels having different orientations of the (ordered) C–Br bond directions. Interpretation of our disorder model in terms of situation (1) would correspond to unfavourable local interactions between Br atoms (Br···Br separations as short as 2.14–2.75 Å), and therefore we believe that situation (2) is more plausible. For comparison, the Br···Br separation for two Br atoms in van der Waals contact is ≈ 3.7 Å.[20] Bromine K-edge EXAFS spectroscopy would be informative for directly determining the Br···Br separations between neighbouring guest molecules in this structure.
[20] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.
[21] S. P. Collins, B. M. Murphy, C. C. Tang, M. C. Miller, G. Oszlanyi, *J. Phys. D* **1999**, *32*, A81.
[22] Linear polarization of incident X-ray beam $\approx 95\%$.
[23] From the investigations that we have carried out so far, the 1-bromoadamantane/thiourea inclusion compound does not undergo any thermal decomposition (e.g. by loss of the guest component) at ambient temperature, and no beam damage was observed during the X-ray studies described in this paper. The 1,10-dibromodecane/urea inclusion compound studied previously[5] also exhibited suitable characteristics with regard to stability for applications in X-ray polarization analysis.

