

Articles

Absence of Ligand-Mediated Symmetry Reduction in a Solid Solution: $\text{Cu}(\text{NC}_5\text{H}_5)_4[(\text{NbOF}_5)_{1-x}(\text{WO}_2\text{F}_4)_x]$ ($0 \leq x \leq 1$)

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ABSTRACT: Organic chromophores crystallizing in nonpolar space groups ($P\bar{1}$) have been converted to polar structures ($P1$) by solid solution symmetry reduction to produce materials with measurable SHG signals. Here, the inorganic compound $\text{Cu}(\text{NC}_5\text{H}_5)_4\text{NbOF}_5$ is used to demonstrate that solid solution symmetry reduction depends on molecular recognition of the guest species at crystal growth faces. In the solid solution $\text{Cu}(\text{NC}_5\text{H}_5)_4[(\text{NbOF}_5)_{1-x}(\text{WO}_2\text{F}_4)_x]$ ($0 \leq x \leq 1$) the $[\text{WO}_2\text{F}_4]^{2-}$ guest molecular ions disrupt the local symmetry, but owing to the lack of recognition of guest anions at the crystal growth surfaces, the full three-dimensional structure retains the host's symmetry.

Introduction

The introduction of a carefully selected guest molecule into a centrosymmetric structure composed of noncentrosymmetric molecules can reduce crystal symmetry and allow expression of interesting physical properties, such as second-harmonic generation (SHG).^{1–3} For example, substitution of *p,p'*-dinitrobenzylideneaniline guest molecules into a *p*-(dimethylamino)benzylidene-*p'*-nitroaniline host destroys the inversion center of the pure crystals. Incorporation of *p,p'*-dinitrobenzylideneaniline causes the next host molecule to reverse orientation and attach to the crystal face through the methyl group and avoid an unfavorable interaction between two adjacent nitro groups. Crystals of this host–guest solid solution display a measurable SHG signal, in contrast to the complete absence of SHG in the purely centrosymmetric host.¹

The reduction of crystal symmetry through cocrystallization with guest molecules is not a general phenomenon. In order for symmetry reduction to occur, guest molecule occlusion must occur through a specific subset of surface sites. If the guest occupancy were random, only local distortions in symmetry would occur,

leaving the full solid solution symmetry the same as that of the host.

The centrosymmetric host structure of $\text{Cu}(\text{py})_4\text{MX}_6$ ($\text{py} = \text{NC}_5\text{H}_5$) is ideal to demonstrate the absence of symmetry reduction in a situation where no molecular recognition occurs at the crystal growth surface. $\text{Cu}(\text{py})_4\text{MX}_6$ contains neutral, one-dimensional, nonintersecting chains of alternating $[\text{Cu}(\text{py})_4]^{2+}$ cations and $[\text{MX}_6]^{2-}$ anions. Both metal ion sites occupy an inversion center. $\text{Cu}(\text{py})_4\text{MX}_6$ can be formed with both acentric ($[\text{NbOF}_5]^{2-}$,⁴ $[\text{WO}_2\text{F}_4]^{2-}$,⁵ and $[\text{TaOF}_5]^{2-}$ ⁶) and centric ($[\text{TiF}_6]^{2-}$,⁶ $[\text{ZrF}_6]^{2-}$ ⁶) anions. The anions selected for this study were $[\text{NbOF}_5]^{2-}$ and $[\text{WO}_2\text{F}_4]^{2-}$.⁷ Octahedrally coordinated Nb(V) and W(VI) cations have similar ionic radii (0.64 and 0.60 Å, respectively),⁸ allowing their oxide fluoride anions to substitute for one another in a crystal with minimal lattice strain. In addition, and perhaps more importantly, the $[\text{NbOF}_5]^{2-}$ and $[\text{WO}_2\text{F}_4]^{2-}$ anions strongly favor trans cation coordination,⁶ as required by the $\text{Cu}(\text{py})_4\text{MX}_6$ structure. Owing to this similarity in both size and coordination preference, the compounds $\text{Cu}(\text{py})_4\text{NbOF}_5$ and $\text{Cu}(\text{py})_4\text{WO}_2\text{F}_4$ and the solid solution $\text{Cu}(\text{py})_4[(\text{NbOF}_5)_{1-x}(\text{WO}_2\text{F}_4)_x]$ ($0 \leq x \leq 1$) are readily formed over a wide range of overlapping synthetic conditions.⁴

Experimental Section

Caution! $(\text{HF})_x$ pyridine is toxic and corrosive.

Materials. CuO (99%, Aldrich), Nb_2O_5 (99.99%, Aldrich), WO_3 (99%, Aldrich), pyridine (py) (99.8%, anhydrous, Aldrich), and $(\text{HF})_x$ pyridine (pyridinium poly(hydrogen fluoride), 70%

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HF by weight, Aldrich) were used as received. Reagent amounts of deionized H₂O were used in the syntheses.

Synthesis. One point in the composition space was selected for all reactions. This composition consisted of 0.0596 g (7.5×10^{-4} mol) of CuO, 7.5×10^{-4} mol of $0.5\text{Nb}_2\text{O}_5 + \text{WO}_3$, 0.197 g (7.5×10^{-4} mol) of (HF)_xpyridine, 0.094 g (5.25×10^{-3} mol) of H₂O, and 1.5 g (1.26×10^{-2} mol) of solvent pyridine. The mole fraction of WO₃ was varied from 0 to 1 in 0.1 increments for Nb_{1-x}W_x. For example, at the 0.1 WO₃ level 0.089 g (6.75×10^{-4} mol) of $0.5\text{Nb}_2\text{O}_5$ and 0.017 g (7.5×10^{-5} mol) of WO₃ were combined in the reaction. Reactants were placed in fluoro-(ethylene-propylene) Teflon "pouches".⁹ The pouches were sealed and placed into a 2000 mL autoclave (Parr) with 600 mL of deionized water. The autoclave was sealed and heated at 150 °C for 24 h and then slowly cooled to room temperature over an additional 24 h. The pouches were removed from the autoclave, opened in air, and products recovered by filtration.

Density. Density was determined using flotation pycnometry at 25 °C. Two crystals from each reaction were suspended in a mixture of tetrahydrofuran ($\rho = 0.884$ g/mL) and dibromomethane ($\rho = 2.477$ g/mL). The ratio of tetrahydrofuran to dibromomethane was varied until the crystal was neutrally buoyant. The solution was placed in a vial of known volume and weighed to determine the density of the solution and crystal.

Refractive Index. The refractive indices (n_D) of the compounds were determined by the Becke line test.¹⁰ Single crystals with well-defined faces are placed in a solution of known refractive index (Cargille, Inc.). Differences in refractive index, either positive or negative, were determined by observing the behavior of the bright line on the periphery of the crystal under polarized light.

Powder Diffraction. Phase identification and purity were checked by powder X-ray diffraction (XRD) on a Rigaku X-ray powder diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å) and a nickel filter.

Results

The significant difference in the densities of Cu(py)₄NbOF₅ ($\rho = 1.69$ g/cm³) and Cu(py)₄WO₂F₄ ($\rho = 2.00$ g/cm³) allows flotation pycnometry density measurements to determine the extent of [WO₂F₄]²⁻ substitution in Cu(py)₄[(NbOF₅)_{1-x}(WO₂F₄)_x] ($0 \leq x \leq 1$) to within 1–3%. Density measurements have the added advantage that they are performed on a single crystal, whereas measurements requiring bulk amounts of sample could mistakenly allow for mixtures containing differing mixed anion compositions. The densities of at least two crystals were determined for each [WO₂F₄]²⁻ substitution level.

It is also possible to monitor a solid solution by measuring the lattice constants at each substitution level. The unit cell dimensions increase from $a = 10.450(2)$ Å, $b = 13.396(3)$ Å, $c = 16.067(7)$ Å for Cu(py)₄WO₂F₄ to $a = 10.561(3)$ Å, $b = 13.546(6)$ Å, $c = 16.103(4)$ Å for Cu(py)₄NbOF₅. However, this method requires higher quality single crystals and is experimentally more time-consuming than the flotation pycnometry experiments. Therefore, density measurements were used to determine the experimental guest anion substitution level.

It is possible for guest anions to localize in small domains as opposed to a completely random dispersion. Crystals will not uniformly extinguish plane-polarized light if such domains exist. For each guest anion substitution level, all single crystals examined did not show multiple domains when examined under polarized light, indicating a random distribution within the crystal.

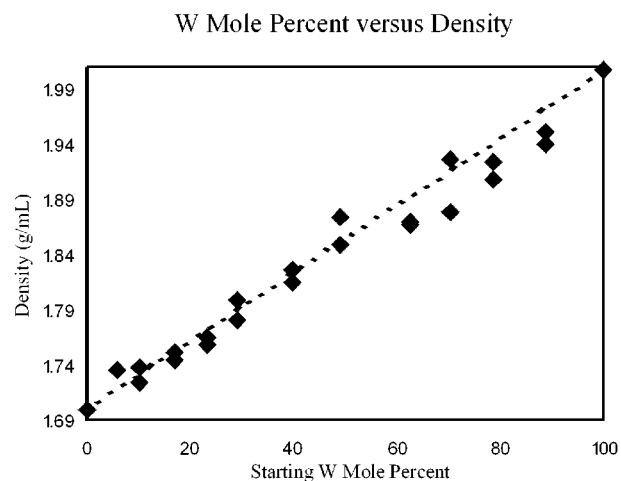


Figure 1. Density versus starting W mole percent for Cu(py)₄[(NbOF₅)_{1-x}(WO₂F₄)_x] ($0 \leq x \leq 1$).

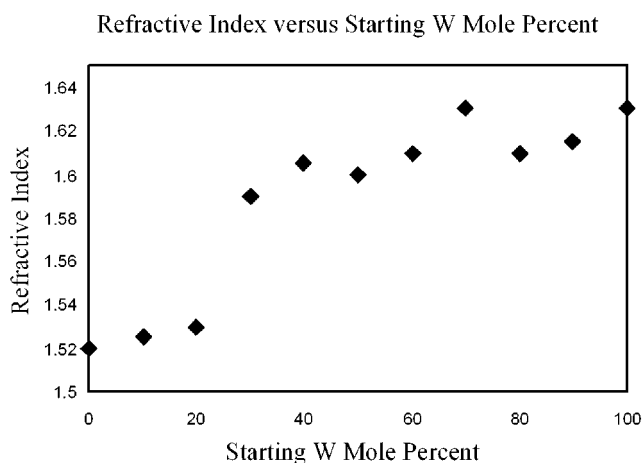


Figure 2. Refractive index versus starting W mole percent for Cu(py)₄[(NbOF₅)_{1-x}(WO₂F₄)_x] ($0 \leq x \leq 1$).

A plot of tungsten mole percent in the initial Nb₂O₅·WO₃ mixture versus the measured density of the resulting crystals (Figure 1) shows a steady increase in density as the amount of tungsten in the reaction mixture is increased, indicating a solid solution has formed.

A plot of refractive index versus starting W mole percent (Figure 2) shows an increase in the refractive index of the samples as the amount of tungsten present is increased, also suggesting that a solid solution is formed. An unexplained discontinuity is observed at approximately 30% W.

The measured SHG signals, using the Kurtz powder technique,^{11,12} for the Cu(py)₄[(NbOF₅)_{1-x}(WO₂F₄)_x] ($0 \leq x \leq 1$) compounds are included in the Supporting Information. All samples tested gave signals below the level of the NaCl blank standard. Ground Cu(py)₄[(NbOF₅)_{1-x}(WO₂F₄)_x] ($0 \leq x \leq 1$) powders stick together in clumps rather than form free-flowing powders. Air pockets trapped in mixtures of this powder and the index matching fluid used in the powder SHG experiments can cause increased scattering and a reduced SHG signal at the detector. Nevertheless, the signals are low enough to be considered zero, indicating all the

solid solution compositions retain the centrosymmetric symmetry of the host structure.

Discussion

The lack of symmetry reduction in $\text{Cu}(\text{py})_4[(\text{NbOF}_5)_{1-x}(\text{WO}_2\text{F}_4)_x]$ ($0 \leq x \leq 1$) demonstrates that molecular recognition at the surface of the growing crystal is essential to symmetry reduction in solid solutions.¹³ In the *p,p'*-dinitrobenzylideneaniline (guest)/*p*-(dimethylamino)benzylidene-*p'*-nitroaniline (host) solid solution discussed earlier, molecules in the host structure line up "head to tail" to maximize the favorable interactions between methyl group hydrogens and nitro groups.¹⁴ Chains of head to tail molecules alternate between the [010] and [0 $\bar{1}$ 0] directions in the crystal. Thus, the molecules are presented at two symmetry equivalent sites on the (010) face of the growing crystal: one site with methyl groups exposed to the solution and one site with the nitro group exposed. Host molecules have an equal probability of crystallizing on either site. However, the *p,p'*-dinitrobenzylideneaniline guest molecule preferentially adsorbs to the surface at sites with exposed methyl groups to avoid close contact between the nitro groups of the host and guest molecules. For this reason, one site remains populated exclusively by host molecules, while the other becomes a mixture of host and guest molecules. Upon incorporation of a *p,p'*-dinitrobenzylideneaniline guest molecule the orientation of the next host molecule to incorporate into the structure is reversed because the second terminal nitro group on the guest forces the *p*-(dimethylamino)benzylidene-*p'*-nitroaniline to attach to the crystal growth face through the methyl group, and the crystal's symmetry is reduced from $P\bar{1}$ to $P1$.

In the $\text{Cu}(\text{py})_4[(\text{NbOF}_5)_{1-x}(\text{WO}_2\text{F}_4)_x]$ ($0 \leq x \leq 1$) solid solution, no guest anion orientation is preferred. At the (110) surface of the growing crystal, the anions coordinate to a $[\text{Cu}(\text{py})_4]^{2+}$ cation in a random orientation through their most nucleophilic ligands, the oxide and trans fluoride ligands on the $[\text{NbOF}_5]^{2-}$ anion (see Figure 3). Either ligand is able to coordinate to the $[\text{Cu}(\text{py})_4]^{2+}$ cation, resulting in "up" (fluoride ligand coordinates to the surface) and "down" (oxide ligand coordinates) orientations. In order for symmetry reduction to occur in the $\text{Cu}(\text{py})_4[(\text{NbOF}_5)_{1-x}(\text{WO}_2\text{F}_4)_x]$ ($0 \leq x \leq 1$) solid solution, the $[\text{WO}_2\text{F}_4]^{2-}$ anions would have to substitute exclusively for $[\text{NbOF}_5]^{2-}$ anions in either "up" or "down" orientations. However, the most nucleophilic ligands on the $[\text{WO}_2\text{F}_4]^{2-}$ anion are the two oxide and their two trans fluoride ligands. Again, either the fluoride or the oxide ligand can coordinate to the $[\text{Cu}(\text{py})_4]^{2+}$ cation on the growing crystal, resulting in "up" and "down" orientations analogous to those of the $[\text{NbOF}_5]^{2-}$ anions. The orientation of one oxide fluoride anion does not dictate the orientation of the next anion to attach to the crystal, and either orientation is possible for the host and the guest molecular ion. The original symmetry of the host crystal is preserved, owing to the random orientation of the oxide fluoride anions, and is reflected in the physical properties of the solid solution.

The requirements for ligand-mediated molecular recognition symmetry reduction are not met, and $\text{Cu}(\text{py})_4[(\text{NbOF}_5)_{1-x}(\text{WO}_2\text{F}_4)_x]$ ($0 \leq x \leq 1$) retains the symmetry of the centrosymmetric host structure upon the addition

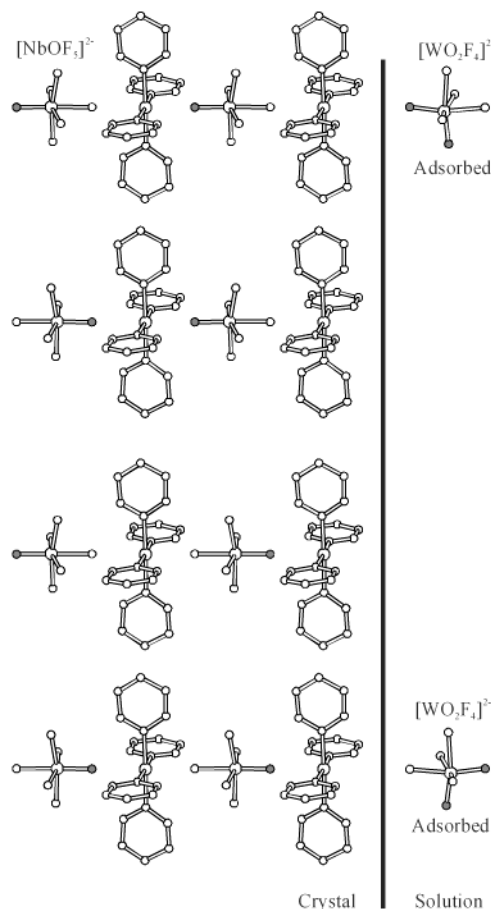


Figure 3. Crystal growth at the (110) face of $\text{Cu}(\text{py})_4[(\text{NbOF}_5)_{1-x}(\text{WO}_2\text{F}_4)_x]$ ($0 \leq x \leq 1$). The guest $[\text{WO}_2\text{F}_4]^{2-}$ anions substitute randomly over the symmetry-related anion sites. Shaded circles represent oxygen atoms.

of $[\text{WO}_2\text{F}_4]^{2-}$, because the orientation of $[\text{NbOF}_5]^{2-}$ and $[\text{WO}_2\text{F}_4]^{2-}$ within the crystal remains random. The average guest population for each lattice site still reflects the symmetry of the host.

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Supporting Information Available: Lists of density and refractive index data in tabular format, a packing diagram of the $\text{Cu}(\text{py})_4\text{MX}_6$ structure type, and composition space diagrams for $\text{CuO}:\text{MO}_x(\text{HF})_x\text{pyridine}/\text{H}_2\text{O}$ ($\text{MO}_x = 0.5\text{Nb}_2\text{O}_5, \text{WO}_3$). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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