

or physical sensing devices. On-off switching of solid-state luminescence intensity have been achieved by adsorption and desorption of guest molecules or thermal stimuli. However, there has been few reports on the switching of luminescence mode. Here, we report the regulation of luminescence mode of organic salts of anthracene-2,6-disulfonic acid (ADS) with *sec*-butylamine by external stimuli. The organic salts yielded inclusion crystals with 1,4-dioxane, 1,4-thioxane or benzene. Whereas emission spectra of inclusion crystal with 1,4-thioxane or benzene have vibrational structure, that of inclusion crystal with 1,4-dioxane are broad and redshifted by 20 nm. This indicate that the latter exhibited excimer-like emission derived from the large π/π overlap of the anthracene moieties. Powder X-ray diffraction (PXRD) analyses indicated that the inclusion crystals with 1,4-dioxane showed supramolecular isomerization by chemical and physical stimuli. When the inclusion crystal with 1,4-dioxane was heated until 473 K, 1,4-dioxane was released completely from the crystal. The emission spectrum of the resulting crystal was similar to inclusion crystal with 1,4-thioxane or benzene. PXRD pattern and emission spectra suggest the rearrangement of ADS. By the exposure of the crystal to 1,4-dioxane, the PXRD peak shifted to the longer distance. After cooling of the crystal until 253 K, the peak in PXRD pattern and emission spectrum became similar to that of original crystal. These date confirm that the inclusion crystal with 1,4-dioxane changes the emission mode from monomer emission to excimer-like one through the reversible structure transition by external stimuli.

Keywords: solid-state dynamics, luminescence, organic crystals

P08.03.09

Acta Cryst. (2008). A64, C421

Computational studies of relationships between structure and lattice dynamics in organic crystals

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There is an increasing demand for accurate assignments of the vibrational modes in molecular organic crystals at terahertz frequencies (1 THz = 33 cm⁻¹), due to the rapidly growing number of experimental activities using terahertz time-domain spectroscopy (THz-TDS). The vibrational modes in this region are largely due to whole-molecule motions and are therefore dictated by the intermolecular interactions in the crystal. To date, a number of approaches have been developed to calculate vibrational spectra in the terahertz range, including lattice dynamics based on atom-atom model potentials [1] and on periodic electronic structure theory [2]. We have been applying the two methods to develop an understanding of relationships between structure and lattice dynamics in molecular organic crystals and to characterise observed THz-TDS spectra. Computational investigations of the vibrational modes in several series of small molecules with well-characterised crystal structures will be presented, along with the observed spectra. We find that the computational efficiency of the atom-atom approach can be exploited to rapidly investigate the effect of structural changes on lattice dynamics, while the more demanding electronic structure calculations must be used when the mixing of low-frequency molecular modes with the lattice modes becomes significant. Their combined use can be a successful approach to characterising

observed spectra and is leading to an understanding of the influence of both molecular structure and intermolecular interactions on the dynamics in molecular crystals in the terahertz region.

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Keywords: dynamics, theoretical calculations, vibrational spectra

P08.03.10

Acta Cryst. (2008). A64, C421

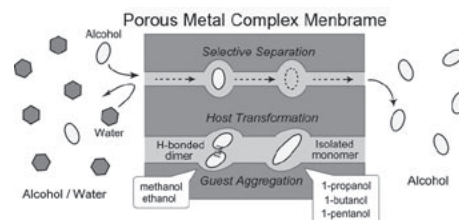
Alcohol vapor inclusion in transformable crystal hosts and application to separation membrane

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The vapor absorbency of series of alcohols from methanol to 1-pentanol was characterized on single crystal adsorbents, [M^{II}₂(bza)₄(pyz)]_n (bza = benzoate; pyz = pyrazine; M = Rh (1), Cu (2)). The crystal structures for all alcohol-inclusions were determined by single-crystal X-ray crystallography at 90 K. The crystal phase transition induced by the guest adsorption occurred in the inclusion crystals except for the 1-propanol. A hydrogen-bonded dimer of adsorbed alcohol was found in the methanol and ethanol inclusion-crystals. In contrast, an isolated monomer existed in the channel for 1-propanol, 1-butanol, and 1-pentanol inclusions. Alcohol/water separation was characterized by a pervaporation (PV) technique using microcrystals of 2 dispersed in a poly(dimethylsiloxane) membrane [1].

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Keywords: gas-solid inclusion reaction, solid-state structural changes, single-crystal applications

P08.03.11

Acta Cryst. (2008). A64, C421-422

Gas-conforming ability of [M^{III}(en)₃]Cl₃ as transformable ionic-single crystal hosts

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Single crystal of [Co(en)₃]Cl₃ shows gas adsorbency for various gases

and organic vapors accompanying the expansion of channel in its crystal structure.[1] To investigate the possibility of single crystal of tris-ethylenediamine metal complexes as ionic single-crystal hosts for vapor adsorption, a series of adsorbency of single crystals of $[M^{III}(en)_3]Cl_3$ ($M = Co, Cr, Rh, Ir$) were studied. All complexes have channels in their crystal structures, which dynamically and reversibly change their size with vapor adsorption, and show similar vapor adsorbency like the adsorption behavior of $[Co(en)_3]Cl_3$. [2]

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Keywords: gas-solid inclusion reaction, solid-state structural changes, ionic crystals

P08.04.12

Acta Cryst. (2008). A64, C422

Synthesis and properties of dioxalatocuprates (II) and ruthenium (III) aminocomplexes salts

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Double complex salts (DCS) are of great interest as precursors of bimetallic solid solutions and intermetallics. Solid solutions based on platinum group metals have high catalytic activity. Thermolysis such single-source molecular precursors under low temperature (400 °C) allows to prepare bimetallic powders with definite ratio of components and particles size about 5-10 nm. This work related to synthesis of complexes contained simultaneously ruthenium and copper and study of their metallic thermolysis products. In the field of this work the following DCS were synthesized: $[Ru(NH_3)_5Cl][Cu(C_2O_4)_2] \cdot H_2O$ (I), $[RuNO(NH_3)_4OH][Cu(C_2O_4)_2] \cdot 1.5H_2O$ (II). Obtained DCS were characterized by IR-spectroscopy, element analysis, XRD and X-ray single crystal analysis. This is crystallographic data: (I) $a = 7.6277(5)$, $b = 13.1052(8)$, $c = 14.9640(7)$ Å, $\beta = 97.852(2)$, $V = 1481.81(15)$ Å³, $P2_1/n$, $Z = 4$, $D_x = 2.148$ g/cm³; (II) $a = 7.1121(2)$, $b = 10.3941(3)$, $c = 10.6288(3)$ Å, $\alpha = 97.0340(10)$, $\beta = 107.6150(10)$, $\gamma = 92.8600(10)$, $V = 740.10(4)$ Å³, $P-1$, $Z = 1$, $D_x = 2.276$ g/cm³. Structures are build of discrete $[Ru(NH_3)_5Cl]^{2+}$, $[RuNO(NH_3)_4OH]^{2+}$, $[RuNO(NH_3)_5]^{2+}$ cations and $[Cu(C_2O_4)_2]^{2-}$ anions. Thermolysis of obtained salts under inert and reduction atmosphere was studied. The XRD investigation of thermolysis products was carried out. Decomposition of salts under helium atmosphere begin at 140 - 150°C, occur in 2 stages and finish at 520°C (I), at 300°C (II). Thermolysis products are Ru, RuO₂, CuCl, Cu₂O. Decomposition of complexes under hydrogen atmosphere also studied. Product is Ru_{0.8}Cu_{0.2}. This work was supported by the RFBR grants 07-03-01038-a, 08-03-00603-a.

Keywords: double complex salt, ruthenium, copper

P08.04.13

Acta Cryst. (2008). A64, C422

Synthesis and crystallographic study in the PbO-Bi₂O₃-V₂O₅ System: Pb_{3-x}Bi_{2/3x}V₂O₈

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PbO-Bi₂O₃-V₂O₅ System is of current interest owing to its use to generate novel ion conducting materials [1]. Pb₃V₂O₈ displays two structural phase transitions at 373 and 273 K [2]. The first order phase transitions have been studied both by neutron and X-ray powder diffraction [3]. The high temperature γ phase of Pb₃V₂O₈ adopts the palmerite structure [4, 5]. In this context, polycrystalline samples in the series Pb_{3-x}Bi_{2/3x}V₂O₈ ($x = 0.2$ to 1.5) have been synthesized by solid-state route. The compositions $x = 0.2$ to 0.7 form a solid solution with a structure similar to γ form of Pb₃V₂O₈, as confirmed by powder diffraction studies while Pb₃BiV₃O₁₂ ($x = 1.0$) was isolated from a mixture of two phases. Single crystals of both phases representing two new vanadates were grown by melt-cool technique. Pb_{2.5}Bi_{1/3}V₂O₈ ($x = 0.5$) and Pb₃BiV₃O₁₂ ($x = 1.0$), have been analysed by single-crystal X-ray diffraction. Pb_{2.5}Bi_{1/3}V₂O₈ crystallizes in a trigonal system, space group $R-3m$, with $a = 5.755(6)$ Å, $c = 20.317(4)$ Å, $V = 582.74(1)$ Å³ and $Z = 3$ whereas Pb₃BiV₃O₁₂ is cubic (eulytite), space group $I-43d$, with $a = 10.749(2)$ Å, $V = 1241.9(1)$ Å³ and $Z = 4$. It is of interest to note that this study for the first time describes the structural motifs formed by a eulytite vanadate.

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Keywords: synthesis, solid solution, powder and single crystal diffraction

P08.04.14

Acta Cryst. (2008). A64, C422-423

Photoinduced surface relief grating formation using single crystals of azobenzene derivatives

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Surface relief grating (SRG) formation by irradiation of amorphous films of azobenzene-containing polymers with two coherent laser beams has recently received a great deal of attention in view of both academic interest and potential technological applications. We have been performing studies of the photoinduced SRG formation using azobenzene-based photochromic amorphous molecular materials. Photoinduced SRG formation is believed to take place by mass transport induced by *trans*-*cis* and *cis*-*trans* isomerizations of azobenzene chromophore. Several models for the mechanism of the SRG formation have been proposed; however, the details have not been clear yet. In contrast to amorphous materials, it is of interest to