

MS15-05 Negative linear compressibility and complex high-P structure in Zn[Au(CN)₂]₂. Julien Haines^a, Jadna Catafesta^{a,b}, Andrew Cairns^c, Jérôme Rouquette^a, Claire Levelut^b, Andrew Goodwin^c, Arie van der Lee^d, Vladimir Dmitriev^e ^aInstitut Charles Gerhardt Montpellier, UMR 5253 CNRS-Université Montpellier 2, France, ^bLaboratoire Charles Coulomb, UMR 5221 CNRS-Université Montpellier 2, France, ^cDepartment of Inorganic Chemistry, Oxford University, UK, ^dInstitut Européen des Membranes, UMR CNRS 5635, Université Montpellier 2, France, ^eESRF, Grenoble, France
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The structure of the framework material zinc dicyanoaurate is built up of tetrahedrally-coordinated Zn cations linked by linear [NC-Au-CN]⁻ complex anions, which form a six-fold interpenetrated β-quartz-type network. This material exhibits strong negative linear thermal expansion along the *c* direction due to framework flexibility [1]. *In situ*, single-crystal and powder x-ray diffraction under high pressure in diamond anvil cells indicate that the *c* lattice parameter increases by 8% from ambient pressure up to 1.8 GPa, which is the highest negative linear compressibility (NLC) known for any material. Structural data obtained from single crystal x-ray diffraction indicate that the NLC mechanism is linked to the closing of N-Zn-N angles and the bending of Au-C-N-Zn linkages. A large number of superlattice reflections are observed above 2 GPa, indicating that the unit cell is doubled in all three directions. This phase transition is accompanied by a strong decrease in NLC. Systematic absences indicate that the space group changes from *P*6₂22 to *P*6₄22 or vice versa depending on the absolute configuration of the initial crystal corresponding to an instability at one of the *L* points in the Brillouin zone. The resulting unit cell has the following lattice parameters at 3.6 GPa: *a*=14.485(2)Å, *c*=45.796(6)Å with 528 atoms per unit cell. The ZnAu₂ sublattice of the new, high-pressure form was solved by direct methods and followed by the use of difference Fourier maps to locate the C and N atoms. A significant change occurs in the Au sublattice with the Au-Au interatomic vector becoming canted with respect to *c*. This provides an additional compression mechanism, which reduces the need for the structure to expand along *c*. These results provide a detailed structural mechanism for the exceptional and unusual mechanical properties of this material.

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MS16-01 Light-emitting lanthanide based organic-inorganic hybrids. Santiago García-Granda,^a Zakariae Amghouz,^a José R. García,^a Rafael Valiente,^b Rute A. S. Ferreira,^c Luís Mafra,^c Luis D. Carlos,^c João Rocha,^c and Abraham Clearfield,^d. ^aDepartments of Physical and Analytical and Organic and Inorganic Chemistry, University Oviedo-CINN, 33006 Oviedo, Spain, ^bMALTA Consolider Team, Department of Applied Physics, University Cantabria, 39005 Santander, Spain, ^cDepartments of Chemistry & Physics, CICECO, University Aveiro, 3810-193 Aveiro, Portugal, ^dDepartment of Chemistry, Texas A&M University, College Station, TX 77842-3012, USA
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Three series of novel organic-inorganic hybrids materials based on trivalent lanthanides (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), formulated as [LnNa(Tart)(BDC)(H₂O)₂] (**S1**), [LnNa(Tart)(biBDC)(H₂O)₂] (**S2**), and [Ln(HBDP)] (**S3**) (H₂Tart = Tartaric acid; H₂BDC = Terephthalic acid; H₂biBDC = Biphenyl-4,4'-dicarboxylic acid; H₄BDP = 1,4-phenylbis(phosphonic acid)), were obtained as single phases under hydrothermal conditions [1-5]. The compounds have been studied by single-crystal and powder X-ray diffraction, X-ray powder thermogravimetry, thermal analyses (TG-MS and DSC), vibrational spectroscopy (FTIR), scanning and transmission electron microscopy (SEM-EDX and TEM), and elemental analysis. The X-ray powder thermogravimetry study reveals that the dehydration of **S1** and **S2** is accompanied by phase transformation, while the spontaneous rehydration process is characterized by different kinetics. However, **S3** exhibits an unusual very high thermal stability. The catalytic activity has been investigated for **S1** to behave as Lewis acid catalysts and the results show a quite positive activity. All the investigated materials show paramagnetic behavior and the observed values of the magnetic susceptibilities follow a Curie-Weiss law. Photoluminescence studies of the investigated materials show room temperature tunable UV-VIS-IR light emission through an effective Ln³⁺ sensitization via aromatic ligands.

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