Electronic Supplementary Material

Metal fluoride nanotubes featuring square-planar building blocks in a high-pressure polymorph of AgF₂⁺

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1. A brief overview of nanotubular structures

Date of discovery of carbon nanotubes has been a matter of discussion¹. Nowadays, it is known that Radushkevich et al.² were probably the first to synthesize them, but due to the low impact of the Soviet journal in which they published their findings, the subject did not gain attention until lijima's publication in 1991.³

As it has been discovered over the following years, nanotubular structures are formed not only by carbon, but also by a diverse group of chemical systems:

- 1. Elements:
 - a. Nonmetals: carbon^{2,3};
 - b. Metalloids: silicon^{4,5}, germanium^{6,7};
 - c. Metals: gold⁸, bismuth⁹.
- 2. Binary systems:
 - a. Borides: CuB₂₃¹⁰;
 - b. Carbides: SiC, TiC, NbC, Fe₃C¹¹;
 - c. Nitrides: BN¹², AlN¹³, GaN¹⁴;
 - d. Phosphides: GaP¹⁵, InP¹⁶;
 - e. Arsenides: GaAs¹⁷;
 - f. Oxides: TiO₂^{18,19}, ZrO₂²⁰, ZnO²¹, Fe₂O₃²², WO₃^{23,24}, V₂O₅^{25,26}, SiO₂²⁵, Al₂O₃²⁵, MoO₃²⁵;
 - g. Sulphides: WS₂^{27,28}, MoS₂^{29,30}, NbS₂/TaS₂³¹, ZnS³²;
 - h. Selenides: ZnSe^{33,34}, CdSe³⁵, MoSe₂³⁶;
 - i. Halogenides: NiCl₂³⁷
 - j. Compounds of rare earth elements³⁸;
 - k. Even more complex stoichiometries.³⁹

This list is by no means exhaustive, but it does show the variety of chemical combinations that can produce nanotubes or nanowires. Some are single-wall, made from neat monolayers, in others thicker layers built of several atomic sheets are found.

A rudimentary timeline of discovery of various nanotubular materials along with their impact to date is shown in Fig.S1.



Figure S1. Timeline of discoveries of the quasi-1D nanotubular forms of various materials, and the semi-log plot of the impact they made (as measured by the number of citations gained by the original works which reported them). Black – Group 14 systems, yellow – chalcogenides, blue – nitrides, red – oxides, green – halides, brown – elemental metals, mauve – lanthanide compounds.

2. Experimental methods

The sample of AgF₂ was compressed in a symmetrical diamond-anvil cell, with culets 250 μ m in diameter. Rhenium was used as gasket material. Slivers of perfluorinated ethylene propylene were used as pressure transferring medium. High-edge frequency of the first order Raman band of diamond was used as pressure gauge.⁴⁰

X-ray diffraction measurements were carried out at Advanced Photon Source in Argonne Laboratory, Argonne (IL), United States. GSE-CARS synchrotron was used as radiation source, at wavelength of 0.4113 Å (30.14 keV). "Jana2006"⁴¹ software was used for Rietveld refinement of XRD data, with pseudo-Voigt functions as profiles and Legendre polynomials as background. "VESTA"⁴² was used for drawing crystal structures. Due to its very high reactivity, samples of AgF₂ inevitably contain some amount of AgF – its primary decomposition product.

3. Crystallographic data on the new AgF₂ Pbcn structure



Fig. S3.1. Crystal structures of AgF₂. Left: ambient pressure layered structure (*Pbca* space group); right: high-pressure tubular structure (*Pbcn* space group).

Pbcn	<i>Z</i> = 8	V = 264.0 ± 1.1 Å ³	
<i>a, b, c</i> [Å]:	5.476(9)	8.33(2)	5.787(7)
$\alpha = \beta = \gamma = 90^{\circ}$			
$R_{\rm p} = 0.50\%$	$R_{\rm wp} = 0.71\%$	GOF = 0.50	
Ag1	0.20439	0.62693	-0.55926
F1	1	0.64551	-0.25
F2	1	1.20262	-0.25
F3	0.32092	0.58270	-0.89643
Ag–F [Å]:	2.084(6) 2	.086(5) 2.116(4	4) 2.118(4)





Fig. S3.2. Rietveld fit of the Pbcn AgF₂ structure (14.8 GPa).

4. Theoretical DFT calculations

Periodic density functional theory (DFT) calculations with plane-wave basis sets were performed in VASP package.⁴³ Spin-polarized calculations were performed within generalized gradient approximations (GGA)⁴⁴ with projected augmented waves (PAW)⁴⁵ and PBEsol functional.⁴⁶ The plane-wave cut-off was set to 520 eV and and a k-spacing of 0.3 Å⁻¹ was used. An antiferromagnetic (AFM) model constructed within the crystallographic cell of the layered AgF₂ form was used in all calculations. Within this model the nearest-neighbor intra-layer Ag(II) cations are oppositely polarized. The tubular AgF₂ was obtained by following the phonon soft modes of the AFM layered form. Calculations of lattice dynamics (phonon dispersions) were performed using the direct method of Parlinski, Li, and Kawazoe⁴⁷ implemented in PHONOPY program.⁴⁸ The phonon dispersion curves for the layered AgF₂ form were calculated by taking into account symmetries of the fully relaxed 2 × 2 × 2 supercell containing 96 atoms, and using the 2 x 1 x 2 supercell for the tubular form.



Fig. S4.1. The AFM model of the layered AgF_2 form used in DFT calculations. Large grey and blue balls represent $Ag(\uparrow)$ and $Ag(\downarrow)$, respectively, and small balls are F atoms.



Fig. S4.2. Phonon dispersion curves of the tubular AgF_2 form calculated at 0 GPa using 2 x 1 x 2 supercell containing 96 atoms (left) and the AFM unitcell from which the supercell was constructed (right). Large grey and blue balls represent $Ag(\uparrow)$ and $Ag(\downarrow)$, respectively, and small balls are F atoms.

5. Relationship between [CuO₂] sublattice of CuO (221 supercell) and new high-pressure for of AgF₂ (111 unit cell)



Fig.S5. Half of Cu atoms (which must be removed from CuO to obtain the $[CuO_2]$ sublattice) have been shown as small pink balls.

6. References

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