

## Electronic supplementary information

Table S1. Crystal structure refinement data.

Empirical formula	$\text{Sr}_5(\text{PO}_4)_3\text{Cu}_{0.476}\text{O}_{0.83}\text{H}_x$ , $x < 0.1$
Formula weight, $\text{g mol}^{-1}$	766.6
Temperature, K	293
Wavelength, Å	0.71073
Space group	$P63/m$ (No. 176)
$a$ , Å	9.7993(4)
$c$ , Å	7.2938(3)
$V$ , Å <sup>3</sup>	606.56(6)
$Z$	2
X-ray density, $\text{g cm}^{-3}$	4.197
Absorption coefficient, $\text{mm}^{-1}$	23.118
$2\theta$ range, deg.	3.68 – 32.86
Limiting indices	$-14 \leq h \leq 14$ , $-14 \leq k \leq 14$ , $-10 \leq l \leq 10$
Number of variable parameters	44
Independent reflections	789
Independent reflections with $I > 3\sigma(I)$	523
$R_1$ (all data), $R_1 [I > 3\sigma(I)]^{\text{a)}$	0.054, 0.026
$wR_1$ (all data), $wR_1 [I > 3\sigma(I)]^{\text{b)}$	0.028, 0.025
$\Delta F_{\text{max}}$ , $\Delta F_{\text{min}}$ , $\text{e Å}^{-3}$	1.49, -1.97

---

$$\text{a) } R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad \text{b) } wR_1 = \frac{\sum w(|F_o| - |F_c|)}{\sum w|F_o|}$$

Table S2. Atomic parameters.

Atom	Sr(1)	Sr(2)	P	O(1)	O(2)	O(3)	O(4)	Cu
Site	4f	6h	6h	6h	12i	6h	2a	2b
SOF	1	1	1	1	1	1	0.83(4)	0.476(7)
<i>x</i>	2/3	0.24697(6)	0.59937(17)	0.6654(5)	0.7365(4)	0.5383(5)	0	0
<i>y</i>	1/3	-0.01423(6)	0.63235(16)	0.5183(5)	0.0855(4)	0.1205(5)	0	0
<i>z</i>	-0.00016(9)	1/4	-1/4	-1/4	0.0783(5)	1/4	1/4	0
$U_{eq}$	0.0116(1)	0.0128(2)	0.0093(4)	0.0144(15)	0.0194(11)	0.0193(16)	0.030(4)	0.0124(7)
$U_{11}$	0.0117(2)	0.0129(2)	0.0101(6)	0.0173(218)	0.0148(13)	0.017(2)	0.015(3)	0.0119(9)
$U_{22}$	0.0117(2)	0.0087(2)	0.0073(5)	0.0177(17)	0.0170(14)	0.0088(17)	0.015(3)	0.0119(9)
$U_{33}$	0.0114(3)	0.0144(2)	0.0122(6)	0.021(2)	0.0162(16)	0.030(3)	0.062(8)	0.0136(13)
$U_{12}$	0.0059(1)	0.0038(2)	0.0056(4)	0.0120(15)	0.0003(11)	0.0054(17)	0.0074(16)	0.0059(4)
$U_{13}$	0	0	0	0	0.0054(11)	0	0	0
$U_{23}$	0	0	0	0	-0.0011(11)	0	0	0

Table S3. Selected interatomic distances in Å and angles in deg.

Sr(1)-O(1)	2.575(4)	3x	P-O(2)	1.533(3)	2x
Sr(1)-O(2)	2.890(5)	3x	P-O(3)	1.542(6)	
Sr(1)-O(3)	2.576(4)	3x	Cu-O(4)	1.8235	2x
Sr(2)-O(1)	2.783(5)		Cu-O(3)	3.140(5)	6x
Sr(2)-O(2)	2.522(3)	2x	O(1)-P-O(2)	111.3(2)	2x
Sr(2)-O(2)	2.693(3)	2x	O(1)-P-O(3)	110.0(3)	
Sr(2)-O(3)	2.474(5)		O(2)-P-O(3)	107.2(2)	2x
Sr(2)-O(4)	2.4927(7)		O(2)-P-O(2)	109.6(2)	
P-O(1)	1.546(6)				

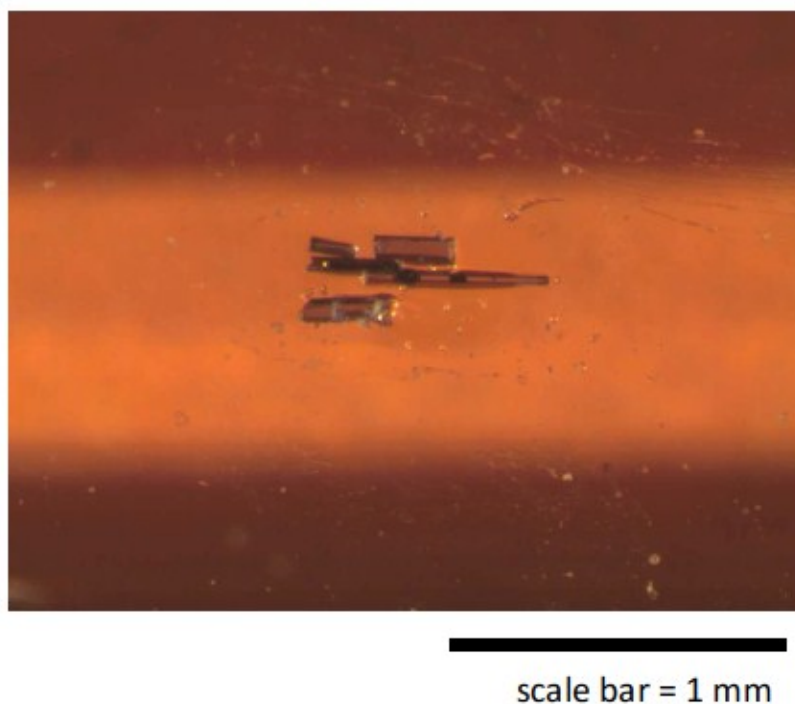


Fig. S1. Optical image of the single crystals of Cu-doped strontium hydroxyapatite fixed on the sample holder parallel to magnetic field.

### Analysis of the anharmonicity of $\nu_1(\text{OCuO})$

The anharmonicity of  $\nu_1(\text{OCuO})$  was analyzed using equation (1) for the vibration energy of a two-atomic molecule with the Morse potential [1].

$$E/hc = \nu_0(n + 1/2) - \nu_0\gamma(n + 1/2)^2, \quad (1)$$

where  $E/hc$  – energy of the vibrational level,  $\nu_0$  – wavenumber of basic harmonic vibration,  $\gamma$  – unharmonicity coefficient,  $n$  – number of the level. The Raman band energy is a difference between  $n = k + 1$  and  $n = 0$  levels, where  $k$  is the overtone number. The dependence of the Raman band position on  $n$  is shown in Fig. S2. The fitting yields  $\nu_0 = 660.6(2) \text{ cm}^{-1}$ ,  $\gamma = 0.00284(5)$ .

For a two-atomic molecule the depth of the energy well  $D_e = hc\nu_0/(4\gamma)$  and dissociation energy  $E_{\text{dis}} = \Delta E - hc\nu$ , where  $\nu$  – wavenumber of basic vibration. For  $[\text{OCuO}]$  this corresponds to breaking of two Cu-O bonds. Taking this into account, the dissociation energy of Cu-O bond in  $[\text{OCuO}]^-$  can be calculated as  $E_d = 1/2E_{\text{dis}} = 346(6) \text{ kJ/mol}$ .

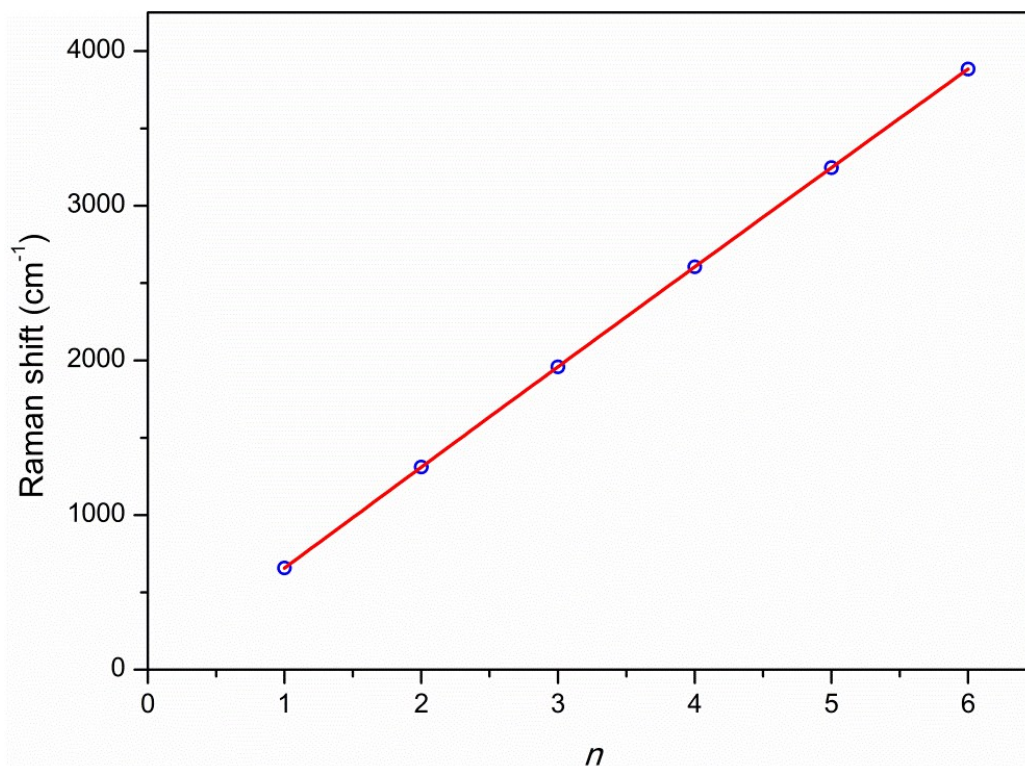


Fig. S2. The dependence of the Raman shift of the  $\nu_1(\text{OCuO})$  basic and overtone bands on the energy level number  $n$ . Circles – experimental points, line – fitting.

## References

1. P. M. Morse, *Phys. Rev.* 1929, **34**, 57-64.