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Supporting Information for

Alkali-Earth Metal Lead (II) Oxyhalide $Ba_{27}Pb_8O_8Cl_{54}$ Exhibiting Interesting $[Pb_4Ba_4O_4]^{8+}$ Species

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Experimental details

1. Synthesis

Single crystals of $Ba_{27}Pb_8O_8Cl_{54}$ were grown through a high temperature solid state reaction. The mixtures of $BaCl_2{\cdot}2H_2O$ (3 mmol, 0.679 g) and PbO (6 mmol, 1.338 g) were put into a platinum crucible, heated up to 800 °C and held at this temperature for 72 h. Then the mixtures were cooled to 300 °C at a rate of 3 °C h^{-1} and cooled to room temperature by switching off the furnace. A colorless block shaped crystal with dimensions of 0.1 × 0.2 × 0.2 mm^3 was selected for single crystal structure determination. Polycrystalline powder samples of $Ba_{27}Pb_8O_8Cl_{54}$ were obtained by grinding the single crystal samples selected under a microscope.

2. Structure determination

Single crystal X−ray diffraction data were recorded on a Xcalibur Ecos diffractometer equipped with a graphite−monochromated Mo−K_α (λ = 0.71073 Å) radiation at 293 K. The structure was solved with direct method by SHELXS−97 and refined by the full matrix least squares on F^2 by SHELXL−97, respectively. The detailed crystallographic data were summarized in Table S1. The atomic coordinates, occupancy and equivalent displacement parameters are given in Table S2. The important bond lengths and angles are listed in Table S3.

3. Property Characterization

Powder X−ray Diffraction

The powder X−ray diffraction pattern of the as−obtained polycrystalline powder was performed at room temperature on a Bruker D8 Focus diffractometer with Cu K_α (λ = 1.5418 Å) radiation. The scanning step width of 0.1º and a fixed counting time 0.2 s/step were applied to record the patterns in the 2θ range of 10 – 70º.

Element Analysis

Elemental analysis of compositions of the single crystal was performed on an energy−dispersive

X−ray (EDX)−equipped Hitachi S−4800 scanning electron microscopy (SEM) instrument.

Diffuse reflectance spectroscopy

A Cary 5000 UV−vis−NIR spectrophotometer with a diffuse reflectance accessory was used to measure the spectrum of $Ba_{27}Pb_8O_8Cl_{54}$ and $BaSO_4$ (as a reference) in the range 200 nm (6.2 eV) to 800 nm (1.55 eV).

Infrared spectrum: Infrared (IR)

Spectroscopy was collected on a Varian Excalibur 3100 spectrometer in the 400 – 4000 cm^{-1} range. The $Ba_{27}Pb_8O_8Cl_{54}$ and KBr samples with mass ratio about 1:100 were mixed thoroughly.

Raman Spectroscopy.

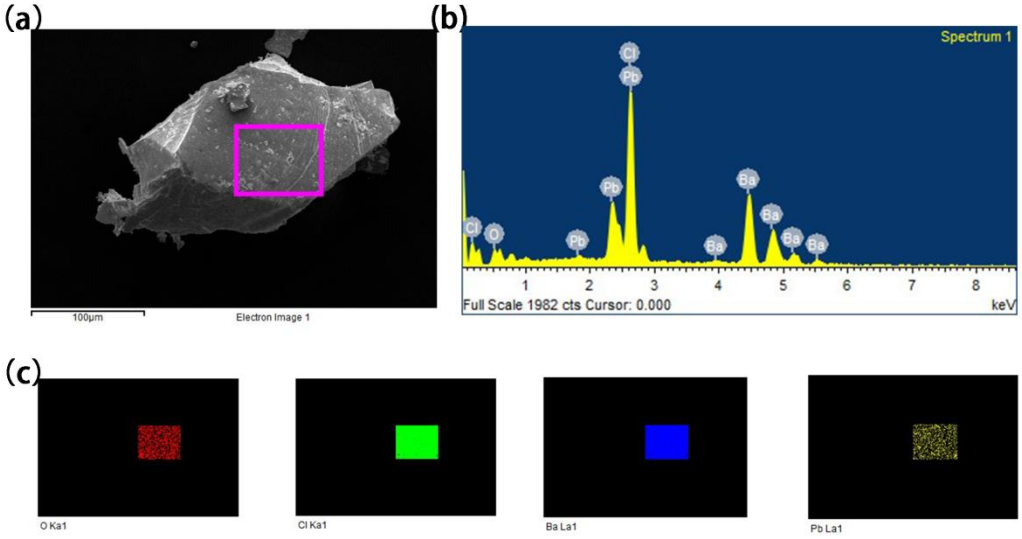
The unpolarized Raman scattering spectrum was recorded from ground powder sample at room temperature with an in Via-Reflex instrument with a line of 532 nm of solid state laser. The spectral resolution was 2 cm^{-1}, and the scanning range was 100−1200 cm^{-1}.

4. Computational methods

The first–principles calculations for $Ba_{27}Pb_8O_8Cl_{54}$ were performed by CASTEP, a plane–wave pseudopotential total energy package based density functional theory (DFT). The functional developed by Perdew–Burke–Emzerhoff (PBE) functional within the generalized gradient approximation (GGA) form were adopted to describe the exchange–correlation energy. The optimized norm–conserving pseudopotentials in the Kleinman–Bylander form for all the elements are used to model the effective interaction between atom cores and valence electrons. And Ba $4d^{10}5s^25p^66s^2$, Pb $5d^{10}6s^26p^2$, O $2s^22p^4$ and Cl $3s^23p^5$ electrons were treated as valence electrons, allowing the adoption of a relatively small basis set without compromising the computational accuracy. The high kinetic energy cutoff 700 eV and dense 2×2×2 Monkhorst–Pack k–point meshes in the Brillouin zones were chosen for $Ba_{27}Pb_8O_8Cl_{54}$. Our tests showed that the above computational set ups are sufficiently accurate for present purposes. It is well known that the energy band gaps calculated by standard DFT method are smaller than the measured values, due to the discontinuity of exchange–correlation energy. The scissor operators were adopted to shift all

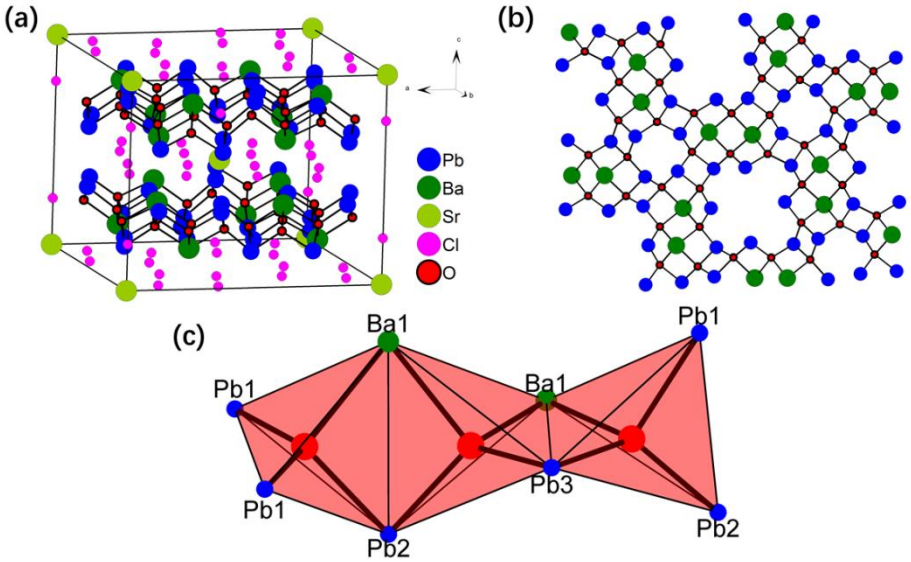
the conduction bands to match the calculated band gaps with the measured values.

5. Figure S1



(a) Scanning electron microscopy (SEM) image of $Ba_{27}Pb_8O_8Cl_{54}$; (b) Elemental analysis of $Ba_{27}Pb_8O_8Cl_{54}$ by EDX spectroscopy. (c) Elemental distribution of the as-grown crystal (from left to right: O, Cl, Ba Pb).

6. Figure S2



(a) unit cell of $Ba_8SrPb_{24}O_{24}Cl_{18}$; (b) $[BaPb_3O_3]$ layer; (3) $OBaPb_3$ and OBa_2Pb_2 tetrahedra.

7. Table S1 Crystallographic data and structure refinement for $Ba_{27}Pb_8O_8Cl_{54}$.

Empirical formula	$Ba_{27}Pb_8O_8Cl_{54}$

Formula weight	7409.19
Space group	$Fm\ \bar{3}m$
a/Å	22.5847(2)
b/Å	22.5847(2)
c/Å	22.5847(2)
α/°	90.00
β/°	90.00
γ/°	90.00
V/Å^3	11519.7 (3)
Z	4
ρ_{calc} g/cm^3	4.271
μ/mm^{-1}	21.967
F(000)	12600.0
Radiation	MoKα (λ = 0.71073 Å)
2θ range for data collection/°	5.982 to 52.674
Index ranges	−28 ≤ h ≤ 28, −28 ≤ k ≤ 28, −27 ≤ l ≤ 28
Reflections collected	34227
Independent reflections	694 [R_{int} = 0.1056, R_{sigma} = 0.0187]
Data/restraints/parameters	649/0/36
GOF on F^2	1.142
Final R indexes [I>=2σ (I)]	R_1 = 0.0385, wR_2 = 0.0939
Final R indexes [all data]	R_1 = 0.0389, wR_2 = 0.0943

8. Table S2 Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for $Ba_{27}Pb_8O_8Cl_{54}$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	Wyckoffsite	U(eq)
Pb1	6955.2(2)	8044.8(2)	8044.8(2)	32f	18.4(2)
Ba1	5000	5000	5000	4b	17.5(6)
Ba2	5000	6648.7(3)	6648.7(3)	48i	22.3(3)
Ba3	5000	5000	8131.3(6)	24e	15.9(3)
Ba4	6396.4(3)	6396.4(3)	8603.6(3)	32f	20.9(3)
Cl1	5752(3)	7500	7500	48g	46.9(18)
Cl2	4183.6(11)	5816.4(11)	5816.4(11)	32f	22.2(9)
Cl3	5846.2(8)	5846.2(8)	7418.0(11)	96k	22.2(6)
Cl4	5000	6199.3(15)	8800.7(15)	48h	28.0(9)
Cl5	5000	5000	10000	4a	170(20)
O1	7047(4)	7047(4)	7953(5)	32f	22(3)

9. Table S3 Selected bond lengths (Å) and angles (°) for $Ba_{27}Pb_8O_8Cl_{54}$.

Pb1−O1×3	2.273(6)	O1−Pb1−O1×3	79.1(5)
Ba4−O1	2.545(91)	Ba4−O1−Pb1	117.851(37)