

Electronic Supplementary Information for the Paper

PbMnTeO₆: a chiral quasi 2D magnet with all cations in octahedral coordination and the space group problem of trigonal layered A²⁺M⁴⁺TeO₆

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For elemental analysis of PbMnTeO₆, an electron microprobe (INCA ENERGY 450/XT) was used with an X-Act ADD detector based on an electron microscope VEGA II LMU (Tescan) operated at the accelerating voltage of 20 kV. The data were averaged on five measurements at various points of the sample (Table S1) and yielded the following gross formula: Pb_{0.96(1)}Mn_{0.97(7)}Te_{1.00(3)}O_{4.9(5)}. Within experimental uncertainties, the cationic composition is stoichiometric and agrees with the previously reported Pb_{0.99(8)}Mn_{1.04(7)}Te_{0.98(1)}O_x.¹

Table S1. Results of the EDX analysis of PbMnTeO₆

Element	Pb	Mn	Te	O
Weight %	43.61	11.28	27.71	17.4
	44.01	12.9	29.39	13.71
	43.56	11.39	27.54	17.52
	43.47	10.8	27.09	18.64
	43.2	11.61	27.56	17.63
Average	43.57	11.59	27.86	16.98
Esd	0.29	0.79	0.89	1.9
Recalculated to atomic fractions and normalized to 1 Te	0.963(6)	0.966(66)	1.000(32)	4.86(54)

Neutron diffraction data

Table S2. Details of the neutron diffraction experiment and structure refinement of PbMnTeO₆, space group *P312*

Wavelength, Å	1.494	<i>Z</i>	1
Step size, °	0.050	Molar weight	485.74
Angular range, °	3.55-164.50	Density (calc.), g/cm ³	6.634
Number of <i>h k l</i>	124	<i>R</i> _p , %	4.17
Temperature, K	300	<i>R</i> _{wp} , %	5.47
Space group	<i>P312</i> (149)	<i>R</i> _e , %	4.38
<i>a</i> , Å	5.10112(2)	χ^2	1.455
<i>c</i> , Å	5.39564(4)		
<i>V</i> , Å ³	121.59		

Table S3. Atomic coordinates, thermal displacement parameters and site occupancy factors of PbMnTeO_6 , space group $P312$

Atom	x/a	y/b	z/c	U_{iso}	SOF
Pb	0	0	0	0.0110(4)	1
Mn1	2/3	1/3	1/2	0.0090(19)	0.906(6)
Te1	1/3	2/3	1/2	0.0082(11)	0.906(6)
Mn2	1/3	2/3	1/2	0.0082(11)	0.094(6)
Te2	2/3	1/3	1/2	0.0090(19)	0.094(6)
O	0.3815(2)	0.0019(4)	0.30184(17)	0.0085(2)	1

Preparation and properties of PbGeTeO_6

PbGeTeO_6 was prepared similar to PbMnTeO_6 , by solid-state reactions from reagent-grade PbO_2 , GeO_2 and TeO_2 in three steps: at 500 °C (1h), 730 °C (15 h) and 700 °C (5 h) with intermediate regrinding and pressing. Phase purity of the product is illustrated by its XRD pattern (Fig. S1). Lattice parameters were refined with corundum as internal standard: $a=5.0885(2)$; $c=5.4484(1)$ Å. Another single-phase sample was prepared by a slightly different route with essentially same lattice constants: $a=5.0885(2)$; $c=5.4487(1)$ Å.

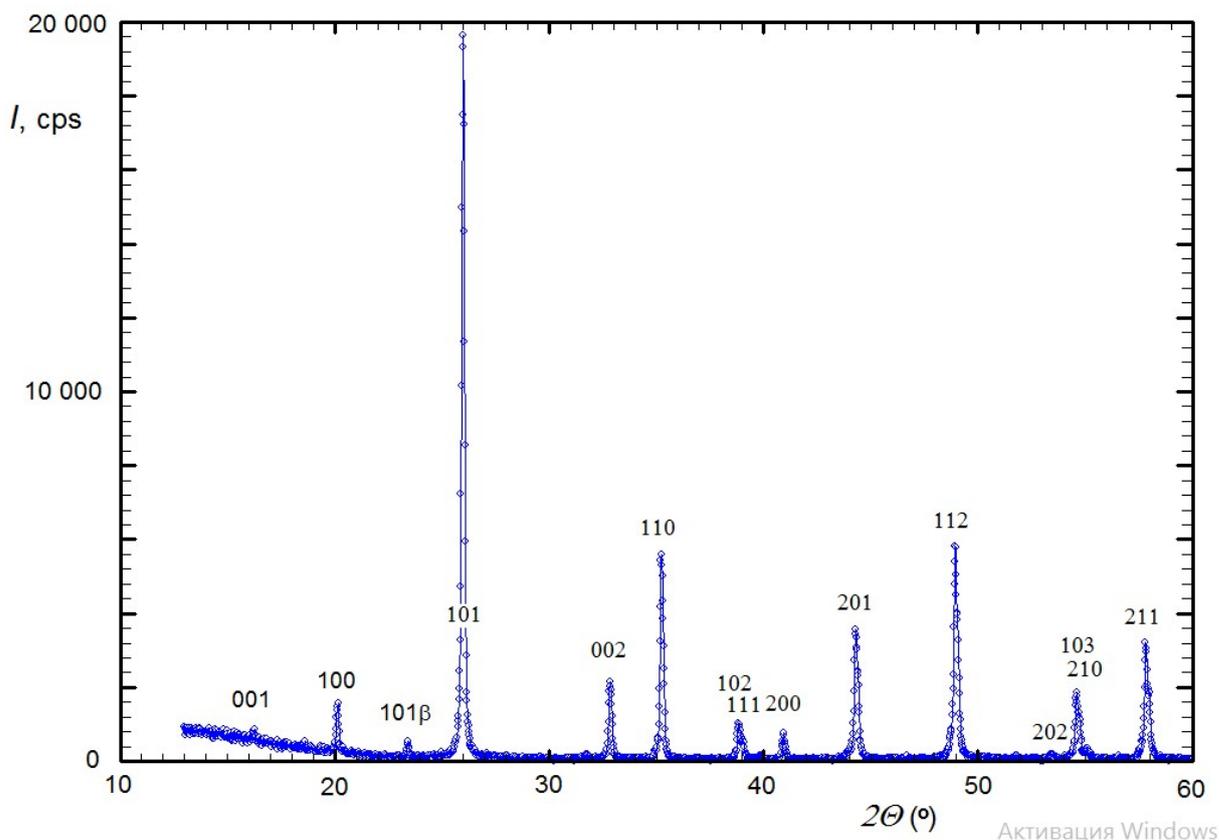


Fig. S1. XRD pattern of PbGeTeO_6 (low angle part)

Dense PbGeTeO_6 ceramics was prepared by uniaxial hot pressing for 1 h at $700\text{ }^\circ\text{C}$ in surrounding coarse-grained corundum. Then, the outer contaminated layer was eliminated using a diamond saw and two discs were cut, with diameter of 12.5 mm and thickness of 1.2 mm. Their apparent density, 6.52 g/cm^3 , constitutes 95% of the X-ray density (6.84 g/cm^3).

XRD of the disc surface revealed considerable grain orientation indicated by enhanced intensity ratio of reflections 0 0 2 and 1 1 0, as compared with the powder mixed with coffee eliminating grain orientation (Fig. S2). This means preferred orientation of the three-fold axis, suggested to be polar, perpendicular to the disc, thus making favourable conditions for discovery of dielectric anomalies, if any.

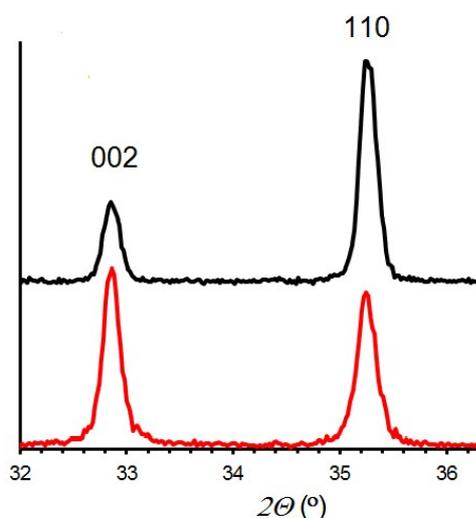


Fig. S2. Comparison of reflections from planes parallel (002) and perpendicular (110) to the layers of the PbGeTeO_6 crystal structure. Top (black): powder mixed with coffee; bottom (red): ceramic disc

The discs were electroded by firing silver paste. One of them was used for study of temperature dependence of dielectric properties: permittivity and loss tangent (Fig. S3). The measurements were made with a semi-automatic bridge Tesla BM-484 at a fixed frequency of 1592 Hz. No signs of expected ferroelectric phase transition could be found between room temperature and $300\text{ }^\circ\text{C}$, and at higher temperatures, rapid growth of conductivity and losses precluded meaningful measurements. In addition, absolute values of relative permittivity, in the range 20-50, were too low for ferroelectric ceramics. Another disc was tested for ferroelectric hysteresis using a standard Sawyer-Tower circuit at room temperature. Here, again, meaningful results could not be obtained: instead of characteristic hysteresis loop, only oval loops could be observed typical of conducting samples.

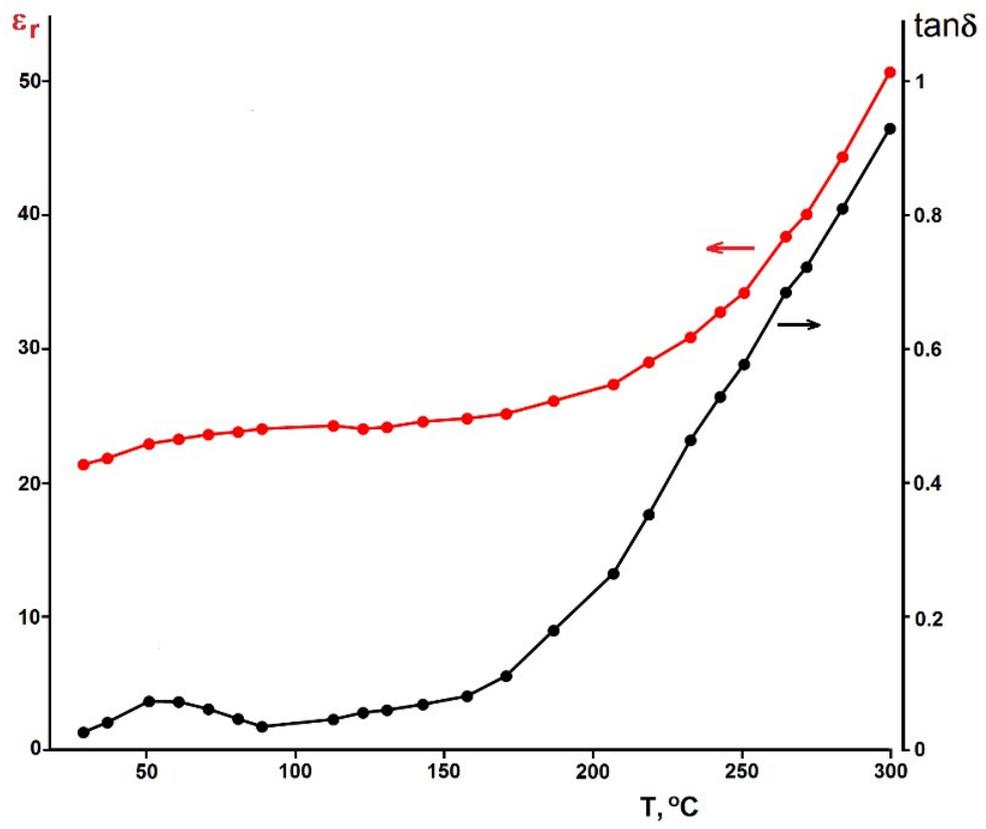


Fig. S3. Temperature dependence of the relative dielectric permittivity (red) and loss tangent (black) of dense PbGeTeO₆ ceramics at 1592 Hz.