Supporting Information

The experimental atomic coordinate given below are used to analysis the ferroelectric polarization.

Space group name P 1

Lattice parameters

a	b	c	alpha	beta	gamma
8.55340	8.55340	11.16200	90.0000	90.0000	120.0000

			x	y	z	Occ.	B	Site	Sym.
1	Ge	Ge1	0.00000	0.00000	0.46830	1.000	1.000	1a	1
2	Ge	Ge2	0.66667	0.33333	0.80163	1.000	1.000	1a	1
3	Ge	Ge3	0.33333	0.66667	0.13497	1.000	1.000	1a	1
4	C	C4	0.00000	0.00000	0.00200	1.000	1.000	1a	1
5	C	C5	0.66667	0.33333	0.33533	1.000	1.000	1a	1
6	C	C6	0.33333	0.66667	0.66867	1.000	1.000	1a	1
7	N	N7	0.00000	0.00000	0.87900	1.000	1.000	1a	1
8	N	N8	0.66667	0.33333	0.21233	1.000	1.000	1a	1
9	N	N9	0.33333	0.66667	0.54567	1.000	1.000	1a	1
10	I	I10	0.50485	0.49515	0.92640	1.000	1.000	1a	1
11	I	I11	0.17152	0.82848	0.25973	1.000	1.000	1a	1
12	I	I12	0.83818	0.16182	0.59307	1.000	1.000	1a	1
13	I	I13	0.50485	0.00970	0.92640	1.000	1.000	1a	1
14	I	I14	0.17152	0.34303	0.25973	1.000	1.000	1a	1
15	I	I15	0.83818	0.67637	0.59307	1.000	1.000	1a	1
16	I	I16	0.99030	0.49515	0.92640	1.000	1.000	1a	1
17	I	I17	0.65697	0.82848	0.25973	1.000	1.000	1a	1
18	I	I18	0.32363	0.16182	0.59307	1.000	1.000	1a	1
19	H	H19	0.40397	0.80795	0.51252	1.000	1.000	1a	1
20	H	H20	0.19205	0.59603	0.51252	1.000	1.000	1a	1
21	H	H21	0.37089	0.56407	0.70271	1.000	1.000	1a	1
22	H	H22	0.19318	0.62911	0.70271	1.000	1.000	1a	1
23	H	H23	0.43593	0.80682	0.70271	1.000	1.000	1a	1
24	H	H24	0.42795	0.61661	0.51361	1.000	1.000	1a	1
25	H	H25	0.59412	0.18824	0.36938	1.000	1.000	1a	1
26	H	H26	0.59412	0.40588	0.36938	1.000	1.000	1a	1
27	H	H27	0.81176	0.40588	0.36938	1.000	1.000	1a	1
28	H	H28	0.70323	0.23343	0.17919	1.000	1.000	1a	1
29	H	H29	0.76657	0.46980	0.17919	1.000	1.000	1a	1
30	H	H30	0.51356	0.28393	0.15348	1.000	1.000	1a	1

31	H	H31	0.02611	0.11554	0.81992	1.000	1.000	1a	1
32	H	H32	0.87427	0.86867	0.85460	1.000	1.000	1a	1
33	H	H33	0.09650	0.94083	0.85239	1.000	1.000	1a	1
34	H	H34	0.94870	0.85297	0.02692	1.000	1.000	1a	1
35	H	H35	0.94870	0.06320	0.07009	1.000	1.000	1a	1
36	H	H36	0.15390	0.07695	0.00200	1.000	1.000	1a	1

Analysis the ferroelectric polarization via classic point charge model method

Firstly, we expand the primitive cell to the 3×3×3 super cell, then cut off one unit cell given below to predict its ferroelectric polarization via the point charge model method. The unit cell's atomic coordinates that we choose are listed as follows:

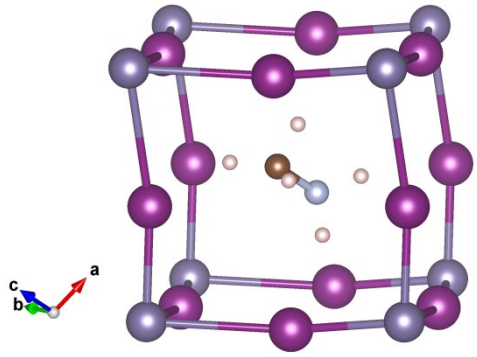


Figure S1: The primitive cell of MAGeI3.

	X	y	z
I1	0.58576	0.41424	0.62987
I2	0.58576	0.67152	0.62987
I3	0.75242	0.74757	0.46320
I4	0.75242	0.74757	0.46320
I5	0.75242	0.50485	0.46320
I6	0.32849	0.41424	0.62987
I7	0.49515	0.74757	0.46320
I8	0.66182	0.58091	0.29635
I9	0.25242	0.50485	0.46320
I10	0.41909	0.58091	0.29653
I11	0.41909	0.33819	0.29653
I12	0.25242	0.24757	0.46320

	X	Y	Z
C	0.5	0.5	0.50100
N	0.5	0.5	0.43950

	X	y	z
Ge1	0.5	0.5	0.73415
Ge2	0.16667	0.3334	0.56748
Ge3	0.33334	0.66667	0.40082
Ge4	0.66667	0.83334	0.56748
Ge5	0.66667	0.33334	0.56748
Ge6	0.33334	0.16667	0.40082
Ge7	0.5	0.5	0.23415
Ge8	0.83334	0.66667	0.40082

The equivalent charge center of Ge^{2+} and I^{-} ions can be calculated by using the

formula: $Xc = \frac{\sum q_i x_i}{\sum q_i}$, $Y_C = \frac{\sum q_i y_i}{\sum q_i}$, $Zc = \frac{\sum q_i z_i}{\sum q_i}$, x_i, y_i and z_i refer to the atomic coordinates. The q_i refers to the charge. For Ge ions, $q_i = +2e$, for I ions, $q_i = -e$. The calculated atomic coordinates of equivalent charge center of I^- ions are:

(0.501665 0.4999 0.4632)

Also the calculated atomic coordinates of equivalent charge center of Ge^{2+} ions are:

(0.501665 0.5000 0.48415)

The atomic coordinates of positive charge center of MA cation are (0.5 0.5 0.477) due to the most positive charge localized on the NH3 group. Thus, the calculated relative position r between Ge^{2+} and I^- ions is mainly along the c axis, equaling to 0.7Å. The displacement r between MA cation and I^- ions is 0.3103Å along the c axis. The volume of the unit cell is V=236 $Å^3$. Via point charge model method, $P_{Ge-I} = \frac{qr}{V} = \frac{2e \times 0.7\,Å}{236\,Å^3} = 10.37\,\mu c/cm^3$. $p_{MA-I} = \frac{qr}{V} = \frac{e \times 0.3103\,Å}{236\,Å^3} = 2.1\,\mu c/cm^3$. Here e=$1.6\times10^{-19}$C. The calculated p_{MA-I}=$2.1\,\mu c/cm^3$ via classic point charge model is accord with the results $2.4\,\mu c/cm^3$ via berry phase method. Although the P_{Ge-I} via point charge model is less than the results via berry phase method, but two methods all predict a huge ferroelectric polarization along the c axis.

Analysis spin-orbit coupling(SOC) effect

The material of $CH_3NH_3GeI_3$ regarded as solar cell candidates with high performance won't be affected by spin-orbit coupling(SOC) effects. This is because that the Ge(No.32) element at conduction band bottom(CBM) is not so heavy

compared with the traditional heavy metal, which locate after No. 53 in periodic table. Only the atomic number greater than No.53 such as Pb, Bi, Po can be affected by SOC effects markedly. Based on the above consideration, the SOC effects will not be considered in perovskite $CH_3NH_3GeI_3$.

Elastic constants tensor calculation

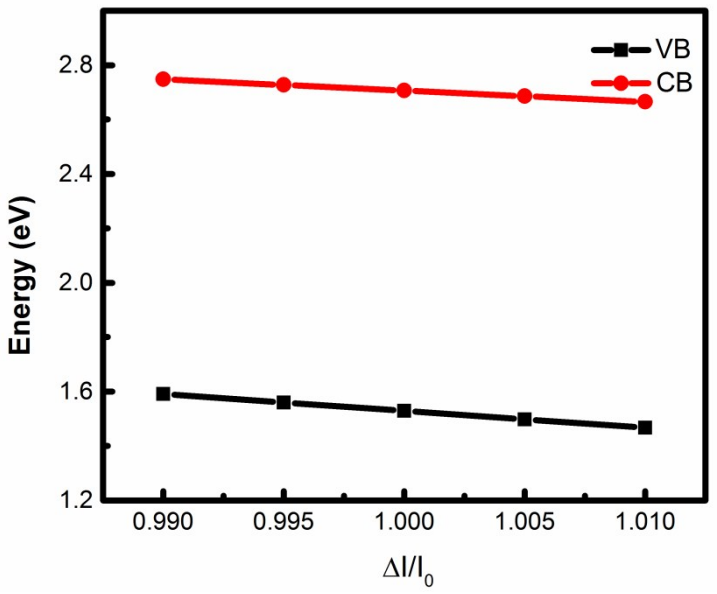
We employed more tense $12\times12\times10$ k-meshes to calculate the elastic constants tensor C_{ii} by using the optimized structure as the C_{ii} is sensitive to high-precision energy ΔE take a derivative with respect to lattice dilation Δl. The calculated C_{ii} is sixth-order tensor listed below:

Direction	XX	YY	ZZ	XY	YZ	ZX
XX	60.9849	152.3917	38.4627	20.6224	63.2060	-21.3717
YY	152.3917	114.6264	114.6710	-60.3804	-140.9847	-21.5302
ZZ	38.4627	114.6710	150.4557	11.8469	34.5352	-19.7120
XY	20.6224	-60.3804	11.8469	14.1335	-24.2668	9.3426
YZ	63.2060	-140.9847	34.5352	-24.2668	-14.3295	-18.9308
ZX	-21.3717	-21.5302	-19.7120	9.3426	-18.9308	-50.1378

Deformation potential calculation

The deformation potential constant E^i of the VBM for hole or CBM for electron along [1 0 0], [0 1 0] and [0 0 1] direction are defined as energy change ΔE as the function of deformation of lattice $\Delta l / l_0$. Here $\Delta l / l_0$ are expressed as: $0.990 l_0$, 0.995

l_0,1.000l_0, 1.005l_0 and 1.010l_0. We only listed calculated deformation potential constant E^i as below due to highest carrier mobility along [0 0 1] direction.



Appendix:

The code for calculating the ferreoelectric polarization

```
      parameter (natom=20)
       double precision
ionw(natom,3),ionw0(natom,3),iondw(natom,3),iondw0(natom,3),polax,polay,polaz
       double precision  x(natom,3),x2(natom,3),xx(natom,3),xx2(natom,3)
       double precision pol(3),pold(3)
       double precision  polat(3),polae(3),polai(3),polai0(3)
       double precision  polatc(3),polaec(3),polaic(3),polaic0(3)
       double precision  b2(3,3),c2(3,3),IS(4),JS(4)
       character(2) ch
       double precision A1(3,3),a2(3,3),latticea,latticeb,latticec,alfa,beta,seta,volum
```

```
      natom1=3; natom2=3; natom3=3; natom4=9; natom5=18
      val1=4.0; val2=4.0; val3=5.0; val4=7.0; val5=1.0;

    pol(1)=0.6136;        pol(2)= -0.37472;     pol(3)= 5.85605
!!!!!!!!!!!!!!!   read cell file "cell"
    open(10,file='CONTCAR')
    open(11,file='POSCAR')
    read(10,*)
    read(10,*)cons2
    READ(11,*)
    READ(11,*)CONS1
    do i=1,3
     read(10,*)(a2(i,j),j=1,3)
     READ(11,*)(A1(I,J),J=1,3)
    enddo
    read(10,*)
    read(10,*)
    read(10,*)
    read(11,*)
    read(11,*)
    read(11,*)
```

```
      do i=1,natom
         read(10,*)(xx(i,j),j=1,3)
         read(11,*)(x(i,j),j=1,3)
      enddo
      close(10)
      close(11)

      A1=A1*CONS1
      a2=a2*cons2
      latticea=sqrt(a2(1,1)*a2(1,1)+a2(1,2)*a2(1,2)+a2(1,3)*a2(1,3))
      latticeb=sqrt(a2(2,1)*a2(2,1)+a2(2,2)*a2(2,2)+a2(2,3)*a2(2,3))
      latticec=sqrt(a2(3,1)*a2(3,1)+a2(3,2)*a2(3,2)+a2(3,3)*a2(3,3))
      alfa=acosd((a2(2,1)*a2(3,1)+a2(2,2)*a2(3,2)+a2(2,3)*a2(3,3))/latticeb/latticec)
      beta=acosd((a2(1,1)*a2(3,1)+a2(1,2)*a2(3,2)+a2(1,3)*a2(3,3))/latticea/latticec)
      seta=acosd((a2(1,1)*a2(2,1)+a2(1,2)*a2(2,2)+a2(1,3)*a2(2,3))/latticea/latticeb)
      volum=latticea*latticeb*latticec*dsqrt(1-cosd(alfa)**2-cosd(beta)**2-
cosd(seta)**2 &
              +2*cosd(alfa)*cosd(beta)*cosd(seta))

!!!!!!!!!!!      ions location polariztion
        do i=1,natom
          if (i<=natom1) then
```

```
        iondw0(i,:)=(x(i,:))*val1
        iondw(i,:)=(xx(i,:))*val1
  elseif (i<=natom1+natom2) then
        iondw0(i,:)=(x(i,:))*val2
        iondw(i,:)=(xx(i,:))*val2
    elseif (i<=natom1+natom2+natom3) then
        iondw0(i,:)=(x(i,:))*val3
        iondw(i,:)=(xx(i,:))*val3
    elseif (i<=natom1+natom2+natom3+natom4) then
        iondw0(i,:)=(x(i,:))*val4
        iondw(i,:)=(xx(i,:))*val4
    elseif (i<=natom1+natom2+natom3+natom4+natom5) then
        iondw0(i,:)=(x(i,:))*val5
        iondw(i,:)=(xx(i,:))*val5
    endif
enddo


do i=1,natom
      polai0(:)=polai0(:)+iondw0(i,:)
      polai(:)=polai(:)+iondw(i,:)
enddo
```

```
!!!!!!!!!!!!!!!!!!    transvert cartesian to fractional coordinates
      b2=a2
      call BRINV(b2,3,L,IS,JS)

         do j=1,3
            do k=1,3
               polae(j)=polae(j)+pol(k)*b2(k,j)
            enddo
         enddo
!!!!!!!!!!!!!!!!!!!!!!!!!!

!        polat(:)=dmod(-polae(:)+polai(:)-polai0(:),1.0)
!        write(*,*)-polae(:)
!        write(*,*)polai(:)
        polat(:)=dmod(-polae(:)+polai(:),1.0)

        polai(:)=dmod(polai(:),1.0)

        polat(1)=polat(1)-1.0
        polat(2)=polat(2)-1.0
        polat(3)=polat(3)-1.0
```

```
write(*,'(a,3f10.3)')"e+ion fractional",(polat(i),i=1,3)


polatc(:)=0.0
   do j=1,3
      do k=1,3
         polatc(j)=polatc(j)+polat(k)*a2(k,j)
         polaec(j)=polaec(j)+polae(k)*a2(k,j)
         polaic(j)=polaic(j)+polai(k)*a2(k,j)
      enddo
   enddo

   polatc(:)=polatc(:)*16.0/volum
   polaec(:)=polaec(:)*16.0/volum
   polaic(:)=polaic(:)*16.0/volum


write(*,'(a,3f10.4)')"p[elc]=",(-polaec(j),j=1,3)
write(*,'(a,3f10.4)')"p[ion]=",(polaic(j),j=1,3)
write(*,'(a,3f10.4,a)')"P[e+i]",(polatc(j),j=1,3),"        C/m^2"


open(11,file='pol.dat')
write(11,'(3f10.5)')(polatc(j),j=1,3)
close(1)
```

```
      end

!!!!!!!!!!!!!!!!!!!!!!!!!!!! SUBROUTINE BRINV

      SUBROUTINE BRINV(A,N,L,IS,JS)
      DIMENSION A(N,N),IS(N),JS(N)
      DOUBLE PRECISION A,T,D
      L=1
      DO 100 K=1,N
        D=0.0
        DO 10 I=K,N
        DO 10 J=K,N
          IF (ABS(A(I,J)).GT.D) THEN
            D=ABS(A(I,J))
            IS(K)=I
            JS(K)=J
          END IF
10      CONTINUE
        IF (D+1.0.EQ.1.0) THEN
          L=0
          WRITE(*,20)
          RETURN
```

```
      END IF
20    FORMAT(1X,'ERR**NOT INV')
      DO 30 J=1,N
        T=A(K,J)
        A(K,J)=A(IS(K),J)
        A(IS(K),J)=T
30    CONTINUE
      DO 40 I=1,N
        T=A(I,K)
        A(I,K)=A(I,JS(K))
        A(I,JS(K))=T
40    CONTINUE
      A(K,K)=1/A(K,K)
      DO 50 J=1,N
        IF (J.NE.K) THEN
          A(K,J)=A(K,J)*A(K,K)
        END IF
50    CONTINUE
      DO 70 I=1,N
        IF (I.NE.K) THEN
          DO 60 J=1,N
            IF (J.NE.K) THEN
```

```
                        A(I,J)=A(I,J)-A(I,K)*A(K,J)
                      END IF
60                  CONTINUE
                  END IF
70              CONTINUE
                DO 80 I=1,N
                  IF (I.NE.K) THEN
                    A(I,K)=-A(I,K)*A(K,K)
                  END IF
80              CONTINUE
100         CONTINUE
            DO 130 K=N,1,-1
              DO 110 J=1,N
                T=A(K,J)
                A(K,J)=A(JS(K),J)
                A(JS(K),J)=T
110           CONTINUE
              DO 120 I=1,N
                T=A(I,K)
                A(I,K)=A(I,IS(K))
                A(I,IS(K))=T
120           CONTINUE
```

```
130     CONTINUE
        RETURN
        END
```