Comment on "Octahedral Distortion and Displacement-Type Ferroelectricity with Switchable Photovoltaic Effect in a $3d^3$-Electron Perovskite System"

Alexei A. Belik

Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science, Namiki 1-1, Tsukuba, 305-0044, Japan

In a recent Letter [1], Zhou et al. prepared $Hg_{0.75}Pb_{0.25}MnO_3$ and reported that it crystallizes in a new polar structure (space group *Ama*2; $a = 7.8029$ Å, $b = 5.3312$ Å, $c = 5.2709$ Å) for perovskite-related materials. Many claims of Ref. [1] depend on the structural model proposed, such as, an unusually large octahedral distortion (Fig. 1 [1]), displacement-type ferroelectricity (Figs. 2b, 2e, 3 [1]), and calculated polarization of 26.5 μC/cm^2. Ref. [1] claimed that laboratory powder X-ray diffraction data (LPXRD) (Fig. 2a [1]) could not be fit by any previously known perovskite-related structural models. Therefore, the structure was solved (including space group determination) from LPXRD.

We believe that there are serious concerns about the structural model proposed in [1]: 1) heavy (Hg,Pb) and Mn are actually located at centrosymmetric crystallographic positions (after an origin shift) resulting in about 99 % contribution of light O atoms to the calculated polarization, 2) MnO_6 octahedra are extremely distorted with O–Mn–O angles of 150.7° and 155.3° (×2), 3) a large common atomic displacement parameter for the O sites is obtained, and 4) the structure solution in *Ama*2 is not unique. Without the access to raw PXRD data, we obtained an "experimental" PXRD pattern of Ref. [1] by calculations using the reported structural parameters and RIETAN 2000 program [2]. Then, we could perfectly fit the "experimental" PXRD pattern by the Rietveld method using the $GdFeO_3$-type model in space group *Pnma* ($a = 5.3312$ Å, $b = 7.8029$ Å, $c = 5.2709$ Å [3]) as illustrated in Fig. 1. We note that any direct or indirect subgroups of *Pnma* (including polar $Pn2_1a$ to match with the observation of SHG signals) could also fit the PXRD pattern if *Pnma* could. This fact shows that claims of Ref. [1] about inability to find a known structural model are not correct, and the PXRD pattern can be explained equally well by other *known* structural models including centrosymmetric *Pnma*.

*Ama*2 and *Pnma* (or its polar pairs) space groups have different reflection conditions. [Space group *Ama*2 has reflection conditions: $k + l = 2n$ for hkl, $0kl$; $h = 2n$ and $l = 2n$ for $h0l$; $k = 2n$ for $hk0$; $h = 2n$ for $h00$; $k = 2n$ for $0k0$; $l = 2n$ for $00l$. Space group *Pmnb* (a different setting of *Pnma* to keep the same order of lattice parameters) has reflection conditions: $h + l = 2n$ for $h0l$; $k = 2n$ for $hk0$; $h = 2n$ for $h00$; $k = 2n$ for $0k0$; $l = 2n$ for $00l$]. Therefore, these space groups should be distinguishable by electron diffraction, which is one of the best methods to directly determine space groups. Electron diffraction was used in Ref. [1] but its full potentials have not been utilized to independently and unbiasedly determine a set of possible space groups as a non-representative pattern along only one zone axis was reported. Fits of LPXRD in the *Ama*2 and *Pnma* models are very similar to each other (see the difference curve). But there are

still small differences in weak reflections as reflection conditions are different (the inset of Fig. 1). Weak reflections between 37.5° and 40.0° and near 44.5° and 52.3° should be observed in the *Pnma* and related models. However, experimental weak reflections exactly in these regions were omitted from the analysis in Ref. [1] as they were considered originating from unknown impurities [3: Figure S2].

In conclusion, we showed that the well-known $GdFeO_3$-type *Pnma* model (and its subgroups) can equally well explain the observed LPXRD instead of a completely new, polar model. There is evidence that weak reflections belonging to $Hg_{0.75}Pb_{0.25}MnO_3$ were omitted from the analysis in Ref. [1] resulting in incorrect space group determination and the whole structure solution as a result (especially, oxygen localization). The structure should be reinvestigated with single-crystal X-ray or neutron powder diffraction.

References

[1] B.W. Zhou, J. Zhang, X. B. Ye, G. X. Liu, X. Xu, J. Wang, Z. H. Liu, L. Zhou, Z. Y. Liao, H. B. Yao, S. Xu, J. J. Shi, X. Shen, X. H. Yu, Z.W. Hu, H. J. Lin, C. T. Chen, X. G. Qiu, C. Dong, J. X. Zhang, R. C. Yu, P. Yu, K. J. Jin, Q. B. Meng, and Y.W. Long, Octahedral Distortion and Displacement-Type Ferroelectricity with Switchable Photovoltaic Effect in a $3d^3$-Electron Perovskite System, Phys. Rev. Lett. **130**, 146101 (2023).

[2] F. Izumi and T. Ikeda, A Rietveld-analysis program RIETAN-98 and its applications to zeolites, Mater. Sci. Forum, **321–324**, 198 (2000).

[3] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett, which includes Tables with the structural parameters and a zoomed difference curve.

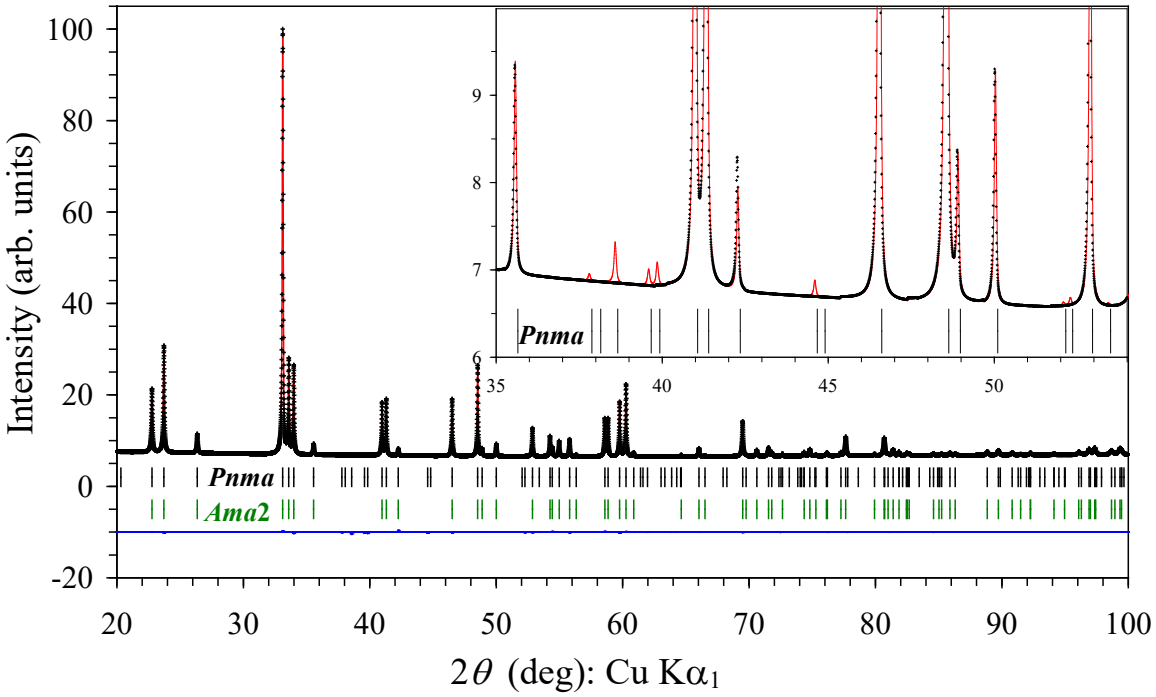

FIG. 1. Black crosses: "experimental" PXRD pattern of $Hg_{0.75}Pb_{0.25}MnO_3$ obtained by calculations (as described in the text). Red line: the calculated PXRD pattern in space group *Pnma* based on the Rietveld fitting [3] using black crosses as "experimental" data. Blue line: the difference curve between the black crosses and the red line. Possible Bragg reflection positions are shown by tick marks for *Pnma* (the first black row) and *Ama*2 (the second green row). The inset shows a zoomed part between 35° and 54°.

TABLE SI. Structure parameters of $Hg_{0.75}Pb_{0.25}MnO_3$ from Table S1 of Ref. [1] used to generate "experimental" data.

Site	WP	*g*	*x*	*y*	*z*	*B* (Å^2)	*z* (shifted)
Hg	4*b*	0.75	0.25	0.4708	0.0145	1.68	0.0005
Pb	4*b*	0.25	0.25	= *y*(Hg)	= *z*(Hg)	= *B*(Hg)	= *z*(Hg)
Mn	4*a*	1	0	0	0.014	0.35	0
O1	8*c*	1	0.046	0.204	0.270	3.63	0.256
O2	4*b*	1	0.25	0.528	0.417	3.63	0.403

WP: Wyckoff position. *g* is the occupation factor.

Space group *Ama*2 (No 40); $Z = 4$. $a = 7.8029$ Å, $b = 5.3312$ Å, $c = 5.2709$ Å, and $V = 219.263$ Å^3.

The "experimental" data were generated with RIETAN 2000 [2] between 5° and 150° with a step of 0.005° for the CuKα_1 radiation (close to the experimental conditions of Ref. [1]). The Split pseudo-Voigt function was used for profiles (with FWHM parameters, $U = 7.01761\times10^{-2}$, $V = -6.16392\times10^{-2}$, and $W = 1.94284\times10^{-2}$; Decay parameters, eta_L0 = 0.999822, eta_L1 = 0, eta_H1 = 0.769485, eta_H2 = 0; and no asymmetry). Total intensities were normalized to 100.

Additional comments about this structural model and other reported results in Ref. [1]:

1. As the cell origin of polar structures can be fixed at any arbitrary values (along polar axes), *z*(Mn) can be fixed at 0. With such a shift, *z*(Hg/Pb) will be 0.0005 and *z*(O1) will be 0.256, that is, very close to centrosymmetric positions (see the last column in Table SI). Therefore, heavy cations, which give the largest contributions to X-ray diffraction intensities, are actually located at centrosymmetric positions even in the *Ama*2 model (this is consistent with Fig. 2e of Ref. [1]). Oxygen atoms actually contribute more than 99 % to its calculated polarization of 26.5 μC/cm^2, and the O2 atom gives the major contribution.

2. The atomic displacement parameter for the oxygen sites was quite large and constrained to be the same for the two sites during the refinement procedure. These facts mean that one atomic displacement parameter would converge to an unphysical value if refined independently. This fact, in turn, should give doubts about the correctness of its localization.

3. According to the interpretation of Fig. S4 in [1], a 0.25-mm-thick sample experienced the electrical breakdown at the voltage of 8 V. The breakdown electrical field was as low as 320 V/cm. This field is much smaller than the electrical field of about 10^4-10^5 V/cm that is usually applied to insulating ferroelectrics to switch the direction of their spontaneous polarization. A field of 320 V/cm is unlikely to switch any polarization. This fact also means that the $Hg_{0.75}Pb_{0.25}MnO_3$ sample in [1] was quite conductive. This fact, in turn, could result in artefacts

in the reported piezoresponse force microscopy results. Artefacts of piezoresponse force microscopy were widely discussed recently in connection with halide perovskites (see, for example, Energy Environ. Sci., **12**, 2537 (2019)).

TABLE SII. Structure parameters of $Hg_{0.75}Pb_{0.25}MnO_3$ refined by the Rietveld method using the generated "experimental" data.

Site	WP	*g*	*x*	*y*	*z*	*B* (Å^2)
Hg	4*c*	0.75	0.02940(1)	0.25	0.99883(5)	1.690(1)
Pb	4*c*	0.25	= *x*(Hg)	0.25	= *z*(Hg)	= *B*(Hg)
Mn	4*b*	1	0	0	0.5	0.380(3)
O1	4*c*	1	0.46714(18)	0.25	0.10490(12)	4.69(3)
O2	8*d*	1	0.29443(15)	0.04327(8)	0.75926(17)	4.10(2)

WP: Wyckoff position. *g* is the occupation factor.

Space group *Pnma* (No. 62); $Z = 4$. $a = 5.3312$ Å, $b = 7.8029$ Å, $c = 5.2709$ Å, and $V = 219.263$ Å^3.

Note that the obtained structural parameters in the *Pnma* model are, of course, highly biased toward the initial *Ama*2 model (as it was used to generate the "experimental" data), such as, atomic displacement parameters and bond lengths. Real experimental powder X-ray diffraction data of $Hg_{0.75}Pb_{0.25}MnO_3$ should be used to get unbiased structural parameters in the *Pnma* model.

Note that the electron diffraction pattern reported on Fig. 2c of Ref. [1] is a typical electron diffraction pattern of the *Pnma* model along the [010] zone axis with the double diffraction (the appearance of the 100 and 001 reflections and alike, forbidden in *Pnma*, is due to the double diffraction).

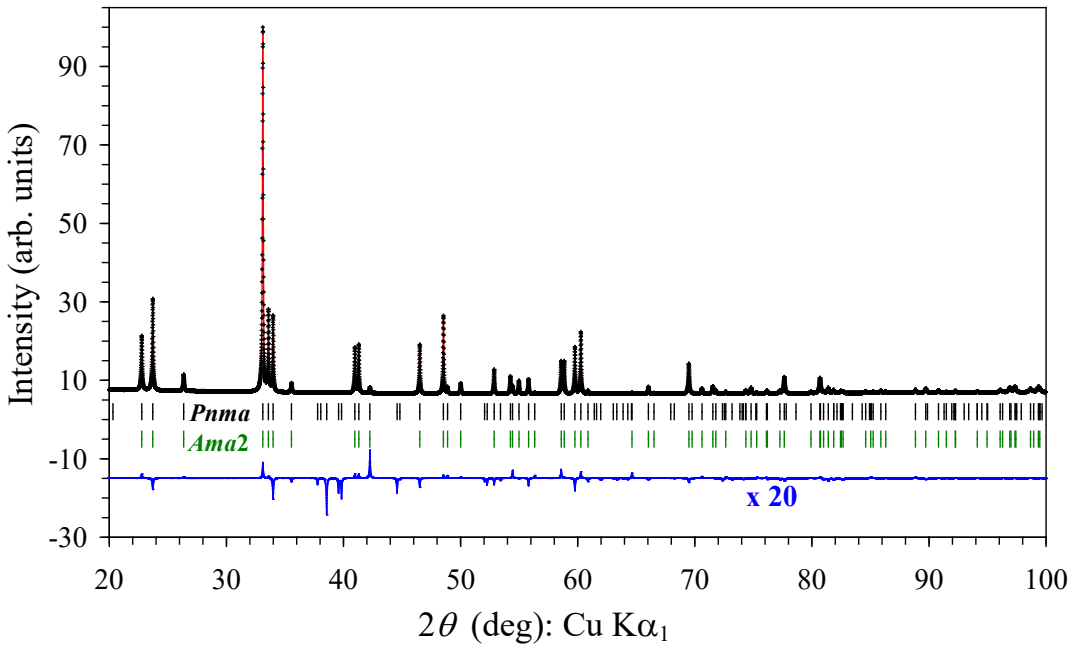

FIG. S1. The same figure as FIG. 1. in the main text. The difference blue curve was only multiplied by 20.

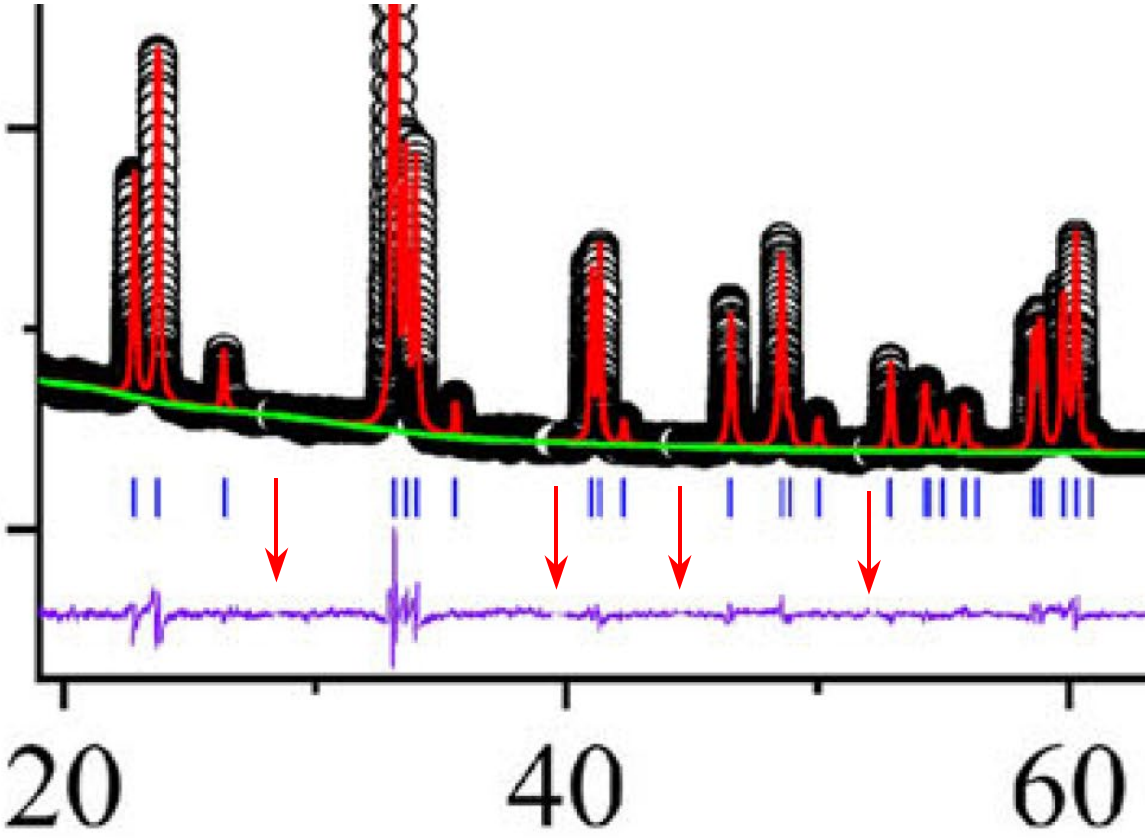

FIG. S2. A zoomed part of Fig. 2a of Ref. [1], where the red arrows show the regions excluded from the analysis in Ref. [1]. They could also be seen as the visible white parts of the circles showing the experimental data – the width of the visible white parts is proportional to the width of the excluded regions.