Crystal, magnetic, and electronic structures, and properties of new BaMnPnF ($Pn = \text{As, Sb, Bi}$)

Bayrammurad Saparov$^1$, David J. Singh$^1$, Vasile O. Garlea$^2$ & Athena S. Sefat$^1$

$^1$Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA, $^2$Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

New BaMnPnF ($Pn = \text{As, Sb, Bi}$) are synthesized by stoichiometric reaction of elements with BaF$_2$. They crystallize in the $P4/nmm$ space group, with the ZrCuSiAs-type structure, as indicated by X-ray crystallography. Electrical resistivity results indicate that $Pn = \text{As, Sb, and Bi}$ are semiconductors with band gaps of 0.73 eV, 0.48 eV and 0.003 eV (extrinsic value), respectively. Powder neutron diffraction reveals a G-type antiferromagnetic order below $T_N = 338(1)$ K for $Pn = \text{As}$, and below $T_N = 272(1)$ K for $Pn = \text{Sb}$. Magnetic susceptibility increases with temperature above 100 K for all the materials. Density functional calculations find semiconducting antiferromagnetic compounds with strong in-plane and weaker out-of-plane exchange coupling that may result in non-Curie Weiss behavior above $T_N$. The ordered magnetic moments are $3.65(5)$ $\mu_B$/Mn for $Pn = \text{As}$, and $3.66(3)$ $\mu_B$/Mn for $Pn = \text{Sb}$ at 4 K, as refined from neutron diffraction experiments.

The recent discovery of high temperature superconductivity in F-doped LaFeAsO$^1$ (1111 family) initiated an extensive research into analogous materials. This research led to the discoveries of superconductivity in doped BaFe$_2$As$_2$-$\delta$ (122 family), LiFeAs$^3$ (111 family), and FeSe$^6$ (11 family), among others. All these families feature two dimensional (2D) structures with FeAs or FeSe layers, which contain edge-shared FeAs$_4$ or FeSe$_4$ tetrahedra. Fe atoms are formally divalent; hole-, electron-, or isovalent-doping inside or outside of layers can result in superconductivity.

Among the Fe-based superconductors (FeSCs), the highest superconducting transition temperatures ($T_C$) are reported for the 1111 family$^{6,7}$. In the search for non-Fe-based oxypnictides, varieties of physical properties are found such as diamagnetism in LaZnAsO$^8$, itinerant ferromagnetism in LaCoAsO$^{9,10}$, semiconducting antiferromagnetism in $LnMnFhO^{11}$ ($Ln = \text{La-Sm}; Pn = \text{P, As}$) and superconductivity in $LaNiAsO^{12}$ ($T_C \approx 3$ K). Interestingly, although such oxyselenides have been studied in detail, reports on non-oxide 1111 fluoroarsenides with ZrCuSiAs-type structure, i.e. BFeAsF ($B = \text{alkaline-earth metal}$), are relatively scarce.

For the 1111 fluopnictides BFeAsF, rare-earth substitution at the alkaline-earth metal ($B$) site is found to give the highest $T_C$ of 56 K for Sr$_{0.5}$Sm$_{0.5}$FeAsF and Ca$_{0.25}$Nd$_{0.75}$FeAsF$^{13,14}$. The only known non-Fe transition-metal-based 1111 fluoroarsenides are BaMnPF$^{15}$, ACuCHF and AAgCHF ($A = \text{Sr, Ba, Eu}; Ch = \text{S, Se, Te}$)$^{16,17}$. However, it should be noted that Cu and Ag in ACuCHF and AAgCHF are nominally monovalent, and therefore, BaMnPF is the only known 1111 fluopnictide containing divalent non-Fe transition metal. Other known 1111 fluoroarsenides, include those of group 12 metals, namely SrZnPF, BaZnPF, BaZnSbF and BaCdSbF$^{15,18}$. According to literature on the properties of 1111 fluopnictides, SrCuCHF$^{19,20}$, BaCuCHF$^{21}$ and EuCuCHF$^{20}$ ($Ch = \text{S, Se}$ and Te) are $p$-type semiconductors with Seebeck coefficients ranging from $+10$ to $+620$ $\mu$V/K, BaZnPF$^{15}$ and BaCdSbF$^{18}$ are also semiconductors with band gaps of $E_g = 0.5$ eV and 0.25 eV, respectively. Moreover, BaMnPF is a semiconducting antiferromagnet with a temperature independent magnetic susceptibility up to 300 K$^{15}$.

Considering the fact that doped BFeAsF fluopnictides are among the highest $T_C$ ($56$ K) FeSCs, there is an incentive to explore for superconductivity in similar 1111 structures, and even non-Fe-based analogs. This is the report of the synthesis of new 1111 ZrCuSiAs-type BaMnPnF ($Pn = \text{As, Sb, Bi}$) (Figure 1) and a comprehensive study of their crystal, magnetic, and electronic structures. We report nuclear structures from powder and single crystal X-ray diffraction, and magnetic structures from neutron powder diffraction. In addition, we present thermodynamic and transport properties from temperature dependent electrical transport data, temperature- and field-dependent magnetization data. Moreover, we report density functional theory (DFT) electronic structure calculations.
tetrahedral angles are 110.65(1)°. The unit cell contains transition metal pnictide layers of [MnPn]- that are made of MnPnI4 tetrahedra.

**Results**

**Synthesis, crystal chemistry, and stability.** Three new compounds of BaMnAsF, BaMnSbF and BaMnBiF are synthesized using the solid-state sintering method. The compounds crystallize in the primitive ZrCuSiAs-type tetragonal P4/nmm (No. 139, Pearson symbol P8̅2), and are isotypic to the lighter BaMnPnF (Figure 1)⁹.

EDS results confirm the presence of small crystallites with BaMnSbF and BaMnBiF compositions after the first heating step, which allows for collection of single-crystal x-ray diffraction data (Table 1). There are four crystallographically unique atoms in the asymmetric unit cell, all located in special positions (Tables 2, 4, S1).

From single crystal X-ray data (Table 3), Mn-Sb and Mn-Bi bond distances in [MnPn]- layers are 2.7767(5) Å in BaMnSbF and 3.1595(4) Å in BaMnBiF. The Mn-Mn distances are 2.8479(11) Å, respectively; the Mn-Mn distances are 5.64(2) Å in BaMnSbF and 5.32(1) Å in BaMnBiF. The tetragonal angles are 110.65(1)° and 105.04(5)° in MnBi4 tetrahedra. The interlayer distances shown by the distance between barium and pnictogen atoms in adjacent layers are dpn-Ba = 3.6489(6) Å in BaMnSbF and dpn-Ba = 3.6711(1) Å in BaMnBiF. For comparison, MnAs4 tetrahedra in BaMnAsF are characterized by the distances dpn-Mn = 2.60460(4) Å and dpn-Mn = 3.0221(1) Å, and bond angles 109.0789(8)° and 110.259(2)°, from the room temperature PXRD data (see Table S1). The bond distances and angles in BaMnPnF are very close to those reported for the related BaMnPnI4 ternary phases ¹²⁻²⁶, which also contain anionic [MnPn]- layers.

PXRD patterns along with Rietveld refinements results for BaMnAsF, BaMnSbF and BaMnBiF are illustrated in Figures 2 to 4. There are no Bragg peaks in the 20 range of 5–20° for Pn = As and Sb, and so the low angle regions are not shown for them. The broad background below 20 ~ 25° in Pn = Sb and Bi (Figure 3–4) are caused by the polycarbonate cover. X-ray diffraction refinement detects a small amount of BaF2 crystalline impurity (less than 1% by mass) in Pn = As and Bi products, whereas no impurity peaks are observed in the Pn = Sb compound.

All BaMnPnF samples have MnO impurities if ground in air during sample sintering stages. Even in the final product form, ground-in-air BaMnSbF shows signs of oxidation in the PXRD data, while BaMnBiF burns in air. The extreme air sensitivity of ground BaMnBiF limits its full characterization through neutron diffraction experiments. Notwithstanding these facts, the heating of pellets under ambient conditions up to 130 °C and subsequent PXRD measurements demonstrate that BaMnPnF are air-stable in pellet form.

The refined room temperature lattice parameters from the PXRD data are a = 4.2739(1) Å and c = 9.5875(2) Å for BaMnAsF (Rp = 8.54%, wRp = 11.52%), a = 4.4791(1) Å and c = 9.8297(2) Å for BaMnSbF (Rp = 4.59%, wRp = 6.03%), and a = 4.5384(1) Å and c = 9.8929(2) Å for BaMnBiF (Rp = 4.05%, wRp = 5.40%). The refinement of PXRD data on BaMnAsF and BaMnSbF show (Figures 2b,

---

**Table 1** | For BaMnPnF (Pn = Sb, Bi), selected single crystal X-ray diffraction data and structure refinement parameters

| Empirical formula | BaMnSbF | BaMnBiF |
|-------------------|---------|---------|
| **Temperature, K** | 173(2)  | 173(2)  |
| **Radiation, Å**  | Mo Kα, 0.71073 | Mo Kα, 0.71073 |
| **Crystal system** | Tetragonal | Tetragonal |
| **Space group, Z** | P4/nmm (No. 129), 2 | P4/nmm (No. 129), 2 |
| **a, Å**          | 4.4682(6) | 4.5198(14) |
| **c, Å**          | 9.817(3)  | 9.875(7)  |
| **V, Å³**         | 196.00(6) | 201.74(16) |
| **ρcalc, g cm⁻³** | 5.643   | 6.198   |
| **μ, mm⁻¹**       | 19.736   | 56.034   |
| **θmin – θmax, °**| 2.07–28.20 | 2.06–28.50 |
| **R₁, (%)**       | 0.0248  | 0.0388  |
| **wR₂, (%)**      | 0.0644  | 0.0963  |
| **Goodness-of-fit on F²** | 1.23  | 1.11  |
| **Largest peak and hole, e⁻ Å⁻³** | 3.35 and –0.95 | 3.18 and –1.79 |

---

**Table 2** | For BaMnPnF (Pn = Sb, Bi), atomic coordinates and equivalent isotropic (Ueq) displacement parameters, at 173 K, from single crystal X-ray diffraction refinements

| Atom | Wyckoff site | x    | y    | z    | Ueq (Å²) |
|------|--------------|------|------|------|----------|
| Ba   | 2c           | 0.25 | 0.25 | 0.3539(1) | 0.0113(3) |
| Mn   | 2a           | 0.25 | 0.75 | 0.0205(4)  |
| Sb   | 2c           | 0.25 | 0.25 | 0.0108(3)  |
| F    | 2b           | 0.25 | 0.75 | 0.013(1)    |

---

**Table 3** | For BaMnPnF (Pn = Sb, Bi), selected bond distances (Å) and angles (°), at 173 K, from single crystal X-ray diffraction

| BaMnSbF | BaMnBiF |
|---------|---------|
| F–Ba [×4] | 2.6549(5) | F–Ba [×4] | 2.6572(12) |
| Mn–Sb [×4] | 2.7767(5) | Mn–Bi [×4] | 2.8479(11) |
| Mn–Mn | 3.1595(4) | Mn–Mn | 3.1960(10) |
| Ba–Sb | 3.6489(6) | Ba–Bi | 3.6714(14) |
| Sb–Mn–Sb | 110.65(1) | Bi–Mn–Bi | 111.73(3) |
| Ba–Mn–Sb | 107.14(3) | Bi–Mn–Sb | 105.04(5) |
| Ba–F–Ba | 114.60(3) | Ba–F–Ba | 116.53(7) |
| Ba–F–Ba | 106.97(1) | Ba–F–Ba | 106.06(3) |
Table 4 | Refined structural parameters for BaMnAsF and BaMnSbF at 4 K from neutron powder diffraction, in P4/nmm

| Atom  | Wyckoff site | x   | y   | z   | B (\AA^2) |
|-------|--------------|-----|-----|-----|-----------|
| BaMnAsF | \(a = 4.2642(1) \text{ Å}, c = 9.5586(3) \text{ Å}\) | | | | |
| Ba    | 2c           | 0.25| 0.25| 0.3386(5) | 0.09(8) |
| Mn    | 2a           | 0.25| 0.75| 0     | 0.12(7) |
| As    | 2c           | 0.25| 0.25| 0.8459(3) | 0.12(6) |
| F     | 2b           | 0.25| 0.75| 0.5   | 0.29(6) |
| BaMnSbF | \(a = 4.4636(1) \text{ Å}, c = 9.7885(4) \text{ Å}\) | | | | |
| Ba    | 2c           | 0.25| 0.25| 0.3546(4) | 0.05(7) |
| Mn    | 2a           | 0.25| 0.75| 0     | 0.29(8) |
| Sb    | 2c           | 0.25| 0.25| 0.8316(4) | 0.15(7) |
| F     | 2b           | 0.25| 0.75| 0.5   | 0.48(6) |

3b) that there are no structural anomalies upon cooling and the unit cell volumes contract uniformly. A survey of the Inorganic Crystal Structure Database (ICSD)\textsuperscript{16} and the Pearson’s Handbook\textsuperscript{17} reveals new features about the BaMnPnF family. First, they are the only reported compounds in each of the corresponding Ba-Mn-Pn-F (Pn = As, Sb, Bi) phase diagrams so far. Second, BaMnBiF can also be considered to be the first bismuthide with the ZrCuSiAs-type structure, considering that Bi in BiCuSeO\textsuperscript{27} serves as a cation. Third, together with BaMnPF, the new compounds are the first phases with Mn and F to adopt the ZrCuSiAs structure type. Fourth, the cell volumes of BaMnSbF and BaMnBiF (see Table 1) are the largest within this structure type along with that of BaCdSbF\textsuperscript{18}. As expected from the large unit cell volumes and lattice parameters of BaMnSbF and BaMnBiF, the bond distances are also longer than those reported for other compounds that adopt this structure type\textsuperscript{11}.

The thermal behaviors of BaMnAsF and BaMnSbF are studied through TGA/DTA (Figure S1). Both BaMnAsF and BaMnSbF are stable up to 1300 K (~1030 °C), after which they decompose. Additionally, pellets of BaMnAsF and BaMnSbF are separately vacuum sealed inside silica tubes and heated to 1500 K with periodic visual monitoring. This is done because the DTA on BaMnAsF (Figure S1) shows two peaks upon heating, and it is not immediately clear if the first peak corresponds to the melting of the compound. No visual change occurs to the pellets up to ~1430 K, after which molten liquid is clearly visible in both samples. These molten pieces contain MnAs and MnSb binaries according to the EDS results.

**Physical properties.** For BaMnPnF, temperature dependence of electrical resistivity results are plotted in Figure 5. The compounds show semiconducting behavior, with room temperature resistivity values of \(\rho_{300K}(\text{BaMnAsF}) = 3.6 \times 10^7 \Omega \text{ cm}, \rho_{300K}(\text{BaMnSbF}) = 2.4 \times 10^8 \Omega \text{ cm}\). Similarly, BaMnPF is also reported as a semiconductor\textsuperscript{13}. The semiconducting behavior supports the charge-balanced nature of the compounds according to [Ba\textsuperscript{3+} F \{Mn\textsuperscript{2+} Pn\textsuperscript{3+}\}].

The calculated band gaps for BaMnAsF and BaMnSbF are two orders of magnitude larger than those reported for the narrow gap semiconductors of BaMn\textsubscript{2}Pn\textsubscript{2}, with band gaps of 6–54 meV\textsuperscript{24–26}. Such a difference may be attributed to the fact that BaMnPnF contains an additional insulating [BaF\textsuperscript{+}] layer in the structure, which reduces the band dispersion in the c-axis direction. Further comparisons can be made with the isostructural quaternary phases based on manganese. Most of LnMnPnO (Ln = rare-earth metal) compositions have been reported to be semiconductors with varying band gaps\textsuperscript{13}, with exceptions such as metallic PrMnSO\textsubscript{4}\textsuperscript{13}.

Temperature- and field-dependent magnetization results for BaMnAsF are plotted in Figure 6a. ZFC and FC \(\chi(T)\) data overlap for BaMnAsF, and are measured up to ~800 K. There is an upward tail in \(\chi(T)\) below ~15 K, which is probably due to paramagnetic impurities, above which magnetic susceptibility increases slowly with rising temperature. There is another change in the slope of \(\chi(T)\) at ~550 K, above which \(\chi(T)\) starts to plateau. \(M(H)\) plots both at 5 K and 100 K are linear. \(\chi(T)\) and \(M(H)\) data, coupled with resistivity data, suggest that BaMnAsF is likely a local moment antiferromagnet.

![Figure 2](https://www.nature.com/scientificreports/)

**Figure 2** | For BaMnAsF, (a) Rietveld refinement (red line) of powder X-ray diffraction data (black dots), shown along with Bragg positions for 111 tetragonal I4/mmm phase (pink tick marks) and BaF\textsubscript{2} impurity (turquoise tick marks); (b) temperature-dependence of refined lattice parameters (dash lines are guide to the eye).
Field dependence of magnetization (not shown) for BaMnSbF and BaMnBiF suggest presence of ferromagnetic impurities. From a linear fit to the $M(H)$ data at 5 K, saturation magnetization values of $M_{\text{sat}}(\text{BaMnSbF}) = 0.039 \mu_B/\text{mol Mn}$ and $M_{\text{sat}}(\text{BaMnBiF}) = 0.006 \mu_B/\text{mol Mn}$ are obtained. Assuming that the sources of the ferromagnetic impurities are MnSb or MnBi binaries, the $M_{\text{sat}}$ values correspond to 1.2% (molar) MnSb, or 0.13% MnBi impurity concentrations. Consequently, in order to find intrinsic behavior for BaMnSbF and BaMnBiF compounds, magnetic susceptibility measurements were performed under two applied fields (20 kOe and 30 kOe), then subtracted from each other according to $\chi = \Delta M/\Delta H$; the resulting $\chi(T)$ plots are shown in Figure 6b, c. Although there are low temperature upturns below $\sim100$ K, $\chi(T)$, similar to BaMnAsF, increase slowly with rising temperature.

The long range antiferromagnetic order found from neutron diffraction results (see next section) at $T_N = 338(1)$ K for BaMnAsF, and $T_N = 272(1)$ K for BaMnBiF do not manifest clearly in the magnetic susceptibility data (Figure 6). Magnetic susceptibility data without a feature at $\chi \propto \Delta M/\Delta H$; the resulting $\chi(T)$ plots are shown in Figure 6b, c. Although there are low temperature upturns below $\sim100$ K, $\chi(T)$, similar to BaMnAsF, increase slowly with rising temperature.

Neutron powder diffraction. Results of the neutron powder diffraction (NPD) experiments are summarized in Table 4, and Figures 7 and 8, and S2 to S4. Rietveld refinement of the NPD data at 4 K gives lattice parameters of $a = 4.2642(1)$ Å and $c = 9.5586(3)$ Å for BaMnAsF ($R_{\text{Bragg}} = 3.54\%$, $R_p = 2.4\%$), and $a = 4.4636(1)$ Å and $c = 9.7885(4)$ Å for BaMnBiF ($R_{\text{Bragg}} = 4.85\%$, $R_p = 3.2\%$). Magnetic peaks can be indexed by a wave vector $k = (0 0 1/2)$, giving a magnetic structure (Figure 8a) with antiferromagnetic (AF) coupling between nearest-neighbor Mn ions in the [MnPt] layers. The adjacent [MnP] layers are also antiferromagnetically coupled, leading to a G-type AF order and a magnetic unit cell twice the size of the chemical unit cell. The NPD data at 4 K yield ordered moment values of $3.65(5) \mu_B/\text{Mn}$ for BaMnAsF and $3.66(3) \mu_B/\text{Mn}$ for BaMnBiF, which are lower than the value of 5.00 $\mu_B/\text{Mn}$ expected for the $S = 5/2$ (high spin) Mn$^{2+}$ ions, assuming $\mu = gS\mu_B$ with $g = 2$.

Although lower than expected, the ordered moment values of $3.65(5) \mu_B/\text{Mn}$ for BaMnAsF, and $3.66(3) \mu_B/\text{Mn}$ for BaMnBiF suggest local moment antiferromagnetism in these compounds. In comparison, the ordered moment values are 0.2–1.0 $\mu_B/\text{Fe}$ in the delocalized spin-density-wave (SDW) antiferromagnets of $\text{AFE}_2\text{As}_2$ and $\text{LnFeAsO}_3$. Reduced moments and G-type ordering have also been reported for $\text{BaMn}_2\text{As}_2$ and $\text{BaMn}_2\text{Bi}_2$, $\text{BaFe}_2\text{As}_2$ and $\text{LaFeAsO}_3$.

Electronic structure calculations. All three compounds are found to be strongly magnetic with substantial Mn moments, in spite of the strong covalency between Mn and pnictogens. We perform calculations for both ferromagnetic (F) and in-plane nearest-neighbor...
anti-ferromagnetic (AF) spin configurations for the materials and consider additional magnetic configurations for BaMnAsF. In all cases, the AF configuration was lower in energy than the F configuration. The energy differences between the two configurations are 0.48 eV/f.u for BaMnAsF, 0.37 eV/f.u for BaMnSbF, and 0.33 eV/f.u for BaMnBiF. These energies are extremely high and indicate high magnetic ordering temperatures. For comparison, the prototypical ferromagnet, bcc Fe (T_C ~ 1043 K), has a F – AF energy difference of ~0.4 eV in density functional calculations.38

The qualitative reasons for these high energies may be seen in the electronic structures. The calculated densities of states for BaMnAsF for the in-plane AF order are shown in Figure 9, with the corresponding band structures in Figure 10 (the plots for BaMnSbF and BaMnBiF are provided in Figures S5–S6). The fluorine and barium atoms are fully ionic, and the resulting ionic [BaF] layers form insulating barriers between the [MnPn] layers in the crystal structure as is seen in the relatively weak dispersion of the occupied bands along the c-axis (T-Z) in Figure 10. As may be seen, the band structures with this magnetic order are semiconducting. The calculated gaps are 0.70 eV, 0.56 eV and 0.42 eV for BaMnAsF, BaMnSbF and BaMnBiF, respectively. The values for BaMnAsF and BaMnSbF are close to those found from transport data, which is the expected behavior of a material where the gap is between different transition metal d-manifolds and where Mott-Hubbard type Coulomb correlations are not large. This is in contrast to simple semiconductors where DFT gaps are underestimates and especially Mott-Hubbard insulators where DFT calculations give either no gaps or gaps much smaller than experiment. The inferred relative weakness of Mott-Hubbard correlation effects in these materials is reminiscent of the FeSCs, although it should be noted that this does not mean that the FeSCs are uncorrelated.

We find very strong covalency between the spin polarized Mn d orbitals and the pnictogen p orbitals in all three compounds. This is seen in the electronic densities of states for the nearest neighbor antiferromagnetic state (Figure 9). As may be seen from the projections the hybridization is strongly spin dependent, providing an explanation for the high energy scale associated with magnetic order. This is further seen by comparing the calculated electronic structures for the F and AF order. Figure 11 compares the Mn d projection of the spin resolved density of states (DOS) for BaMnAsF with these two orders. There is a strong reconstruction of the electronic structure when going to the less favorable F order. In fact, this reconstruction is so strong that the semiconducting gap is closed and because of this the magnetization is reduced from the nominal value of 5 \( \mu_B \)/Mn to lower values of 4.0 \( \mu_B \), 4.3 \( \mu_B \) and 4.4 \( \mu_B \) for BaMnAsF, BaMnSbF and BaMnBiF, respectively (calculated based on the total spin magnetization in the cell, not the moments in LAPW spheres). As discussed e.g. by Goodenough,32, cases where the covalency and electronic structure are strongly affected by magnetic order are cases where high exchange couplings can be expected.

In general local moment magnetism has two ingredients: (1) moment formation and (2) the interactions between the moments.

![Figure 5](image1.png)  
**Figure 5** | Temperature dependence of electrical resistivity, \( \rho(T) \), for polycrystalline pellets of (a) BaMnAsF and BaMnSbF, and (b) BaMnBiF. Insets illustrate lines (in red) corresponding to Arrhenius fit for the temperature region.

![Figure 6](image2.png)  
**Figure 6** | Temperature dependence of magnetic susceptibility, \( \chi(T) \), for (a) BaMnAsF, (b) BaMnSbF and (c) BaMnBiF. For BaMnAsF, inset shows a linear field-dependence of magnetization, \( M(H) \), at 5 K and 100 K. Note that (b) and (c) are derived using magnetization data under 20 kOe and 30 kOe assuming \( \chi = \Delta M/\Delta H \), in order to eliminate ferromagnetic impurities (see text).
that lead to order. While divalent Mn can occur in different spin states depending on the strength of the hybridization with ligands, here we find a near high spin case for all the magnetic orderings considered with similar spin moments in the Mn LAPW spheres for the F and AF cases (as well as the other cases for BaMnAsF). However, the energy associated with moment formation is not so much smaller than the ordering energy. For BaMnAsF in particular, non-spin-polarized calculations (no moments) yield an energy 1.27 eV/f.u. higher than the nearest neighbor AF order, i.e. less than three times higher than the F order (0.48 eV/f.u.).

Consistent with this, we find very weak magnetic interactions in the c-axis direction. For BaMnAsF, we calculated the energy for doubled cells along c-axis for the F and in-plane AF cases with and without alternation of spins along the c-axis. The energy differences were below 1 meV per formula unit implying that this is a very highly two dimensional magnetic system.

In the case of BaMnAsF, we also considered other AF in-plane configurations. These were for the order observed in the Fe-pnictides consisting of chains of like spin Mn atoms (the so-called SDW order) and the double stripe pattern found in FeTe43 (see Ref. 43 for a depiction of these orders). On a per formula unit basis, we find that the SDW type ordering and the double stripe ordering are 0.12 eV and 0.21 eV higher than the nearest neighbor AF order, respectively. Therefore, in agreement with the NPD data, we conclude that the nearest neighbor in-plane order is the probable ground state.

As mentioned, our calculations included spin orbit. In this case the energy depends on the spin orientation through the magnetocrystalline anisotropy. While this energy is small compared to the ordering energy, it is relevant to the magnetic behavior. For BaMnAsF, we did calculations with the moments oriented in the a-axis direction as well along the c-axis direction. For the other cases discussed, the calculations are done with the moments along the c-axis. With the experimental crystal structure the uniaxial c-axis direction is favored by 1.0 meV/f.u.. While this is a small energy, if correct, the result implies that there will not be a strong Kosterlitz-Thouless type reduction in the ordering temperature due to the near 2D character of the material. To summarize, the calculations find that these materials are local moment antiferromagnetic semiconductors with moderate band gaps and strong spin-dependent hybridization between the Mn d states and the pnictogen p states. The materials are rather two dimensional both electronically and magnetically. The strong hybridization leads to reconstructions of the band structure with changes in

Figure 7 | (a) Rietveld plots of the neutron powder diffraction data for BaMnAsF collected at 4 K using 1.54 Å and 2.41 Å wavelengths. The two most prominent magnetic reflections, indexed as (1 0 1/2) and (1 0 3/2), are indicated by arrows. (b) Trends in lattice parameters for BaMnAsF as obtained from the NPD data. Dashed lines are intended as a guide to the eye. 

Figure 8 | (a) The magnetic structure for BaMnAsF and BaMnSbF. Temperature dependence of (1 0 0.5) magnetic peak for (b) BaMnAsF and (c) BaMnSbF. Insets of (b) and (c) show evolution of (1 0 1/2) and (1 0 3/2) magnetic peaks with lowering temperature in low Q region.
magnetic order. This in turn underlies very high magnetic energy scales consistent with high \( T_N \) that are confirmed in neutron diffraction.

**Discussion**

Three new 1111 fluoropnictides with the ZrCuSiAs-type structure, namely BaMnAsF, BaMnSbF and BaMnBiF, are synthesized by reacting elements with BaF\(_2\). The initial reactions of these components give small plate crystallites that are suitable for structure refinements using single crystal X-ray diffraction. Subsequent two-step annealing procedure results in approximately single-phase products (<2% impurity content from PXRD and magnetization results). For BaMnPnF, the unit cell volumes and bond distances are much larger compared to the isostructural Mn-based oxypnictides.

Temperature dependence of electrical resistivity suggest that BaMnPnF are semiconductors with band gaps of \( E_g(\text{BaMnAsF}) = 0.73 \, \text{eV} \), \( E_g(\text{BaMnSbF}) = 0.48 \, \text{eV} \), and \( E_g(\text{BaMnBiF}) = 0.003 \, \text{eV} \). These values are comparable to the theoretical gaps of 0.70 eV for BaMnAsF and 0.56 eV for BaMnSbF, but not 0.42 eV for BaMnBiF. The large discrepancy in the band gap for BaMnBiF derived from the resistivity data is likely due to the influence of doping. Based on electronic structure calculations, BaMnPnF are strongly magnetic with a preferred G-type antiferromagnetic ground state. Neutron powder diffraction (NPD) results give evidence for the G-type antiferromagnetic order below \( T_N = 338(1) \, \text{K} \) for BaMnAsF, and \( T_N = 272(1) \, \text{K} \) for BaMnSbF. However, temperature dependence of magnetization \( \chi(T) \) data on these polycrystalline pellets show no anomalies at \( T_N \) and \( \chi(T) \) increase with increasing temperature above \( T_N \). Similar featureless \( \chi(T) \) data and non-Curie-Weiss behavior was recently reported for LaMnPO\(_3\), and increasing \( \chi(T) \) above ordering temperatures are observed for BaMn\(_2\)As\(_2\), BaMn\(_2\)Bi\(_2\), BaFe\(_2\)As\(_2\) and LaFeAsO. Such behavior may be indicative of strong exchange coupling among Mn moments in BaMnPnF. Another important feature of BaMnPnF phases is a strong hybridization between Mn and Pn states, which is responsible for reduced ordered moment values of 3.65(5) \( \mu_B/\text{Mn} \) for BaMnAsF, and 3.66(3) \( \mu_B/\text{Mn} \) for BaMnSbF, as determined from the NPD data at 4 K. The observed semiconducting antiferromagnetic behavior of BaMnPnF (Pn = As, Sb and Bi) is similar to the reported behavior in Mn-based oxypnictides LnMnPnO (Ln = La-Sm; Pn = F, As)\(^{11}\).

In conclusion, further studies of transition-metal-based ZrCuSiAs-type compounds in general, and BaMnPnF in particular, are warranted. Although electronic structures of BaMnPnF are not similar to that of the superconducting Fe-based 1111 compounds, recent reports show that 1111 phases may demonstrate interesting variation of electrical and magnetic properties with doping and under applied pressure; for example, antiferromagnetic insulator LaMnAsO turns ferromagnetic metal when doped with hydrogen\(^{24}\). Another Mn-based compound, LaMnPO, transforms from an AF insulator to an AF correlated metal under pressure\(^{21}\). In addition, there is continued interest in 1111 phases due to the recent discovery of a high thermoelectric efficiency in BiCuSeO, which is further enhanced by introduction of Cu defects\(^{27}\).

**Methods**

**Synthesis.** Dendritic Ba, Mn and As pieces, and Sb and Bi granules with purities greater than 99.9% are used as received from Alfa Aesar. Ultrapure BaF\(_2\) powder, from Ventron Alfa Inorganics, is dried at 200 °C for 3 h before using. Reactants in the stoichiometric ratio of Ba: BaF\(_2\); Mn : Pn = 1 : 1 : 2 : 2 are weighed inside a helium-filled glovebox and put into alumina crucibles. The alumina crucibles are then transferred into silica tubes and sealed under vacuum. The reaction mixtures are heated to 1000 °C (300 °C h\(^{-1}\); dwell 6 h), then to 900 °C (100 °C h\(^{-1}\); dwell 6 h), and subsequently to 300 °C (30 °C h\(^{-1}\)) after which the furnaces are switched off. This initial sintering step produced multi-phase reaction products, along with μm-size crystallites of 1111 phase in Pn = Sb and Bi, which are extracted for structural determinations using single crystal X-ray diffraction. The products are reground and pelletized inside the glovebox. The pellets are then placed inside alumina crucibles, enclosed in silica tubes, vacuum sealed, then annealed for a second time at 900 °C (dwell 60 h). The third sintering step is the repeat of the latter annealing procedure. This only results in marginal improvement of phase purity as judged by slightly lower BaF\(_2\) impurity levels compared to the second sintering step.

**Characterization.** X-ray diffraction. For BaMnPnF (Pn = As, Sb, Bi), powder X-ray diffraction (PXRD) data are collected on a PANalytical X’Pert PRO MPD X-ray Diffractometer using monochromated Cu-K\(_{α1}\) radiation. Scans are performed in 5–65° (2θ) range, with a step size of 1°/60 and 20–100 seconds/step counting time. Low temperature data collections are carried out using an Oxford Phenix closed cycle cryostat. Due to the air sensitivity of finely ground powders of Pn = Sb and Bi, the powders are loaded in a protective holder with a polycarbonate cover, inside the
5. Hsu, F.-C. et al. Scien. Rep. 8, 15049 (2018).

Elemental analysis. Energy-dispersive X-ray spectroscopy (EDS) measurements are carried out using a Hitachi TM3000 scanning electron microscope equipped with a Bruker Quantax 70 EDS system. Data acquisition is carried out with an accelerating voltage of 15 kV in 2–3 min scanning time. EDS results confirm elemental compositions of 1:1:1:1 for BaMnAsF, BaMnSbF, and BaMnBiF.

Physical property measurements. For BaMnPFn (P = As, Sb), DC magneto-transport measurements are carried out using a Quantum Design Magnetic Property Measurement System. Temperature dependence of magnetization experiments are carried out on polycrystalline pellets under applied fields of 10 kOe, 20 kOe and 30 kOe. Both zero field cooled (ZFC) and field cooled (FC) data are collected. Magnetization measurements as a function of field are carried out at 5 K, 100 K and 300 K. Four-probe electrical resistivity measurements are carried out on a Quantum Design Physical Property Measurement System.

Thermal analysis. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on BaMnPF (P = As, Sb) are performed using a Pyris Diamond TG/DTA from Perkin Elmer, under a stream of ultra-high purity argon gas. The measurements are carried out on 20–25 mg pellet pieces in the temperature interval of 323–1573 K (20 K min−1).

Neutron powder diffraction. Neutron powder diffraction experiments on BaMnPFn (P = As and Sb) are carried out using the HB-2A neutron powder diffractometer at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL). Measurements are performed using two different wavelengths of λ = 1.363 Å and 2.410 Å provided by the (115) and (113) reflections of a vertically focusing Ge monochromator; this allows for the optimization of the instrument resolution function for specific Q ranges. The data are collected by scanning the detector array consisting of 44° He tubes in two segments to cover the total 2θ range of 6°–150° in steps of 0.05°; overlapping detectors for the given step average the counting efficiency of each detector. For the measurements, 4 g powder samples are confined inside vanadium containers. For below room temperature measurements, samples are loaded inside a JANIS top-loading cryogenic pulse refrigerator, while high temperature experiments up to 800 °C, samples are loaded in an ILL vacuum furnace equipped with Nb heating elements. Rietveld refinements are performed using the FULLPROG program11. Spin configurations compatible with the crystal symmetry are generated by group-theory analysis using the program SARAh12. In Pn = As compound, impurity phases of BaF2 (As, Sb, Bi), BaF2 (P, As) and BaSb (P, As and Sb) are observed. BaF2 (As, Sb) peaks at 2θ > 16° are indexed as 27 reflexions in the hexagonal Pn3n lattice, BaSb (P, As and Sb) with 14 reflexions in the hexagonal P63/mmc lattice.

Electronic structure calculations. First principles calculations are performed using the experimental crystal structure data. The calculations are done within DFT using the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof19 and the general potential linearized augmented plane wave (LAPW) method22 as implemented in the WIEN2k code22. Well-converged basis sets and Brillouin zone samplings are employed, along with LAPW sphere radii of 2.4 Bohr for Ba, Mn, As and Sb and 1.9 Bohr for F. Local orbitals are added to the basis to include semi-core states and spin-orbit is included in the calculations.
Acknowledgements
This work was supported by the Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. Work at the High Flux Isotope Reactor, Oak Ridge National Laboratory, was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy. We thank R. Custelcean for his help with the single crystal X-ray diffraction measurements.

Author contributions
B.S. conceived the experiments, prepared the samples, carried out PXRD and SXRD experiments, electrical resistivity and magnetic susceptibility measurements, and wrote the paper. D.J.S. performed electronic structure calculations. V.O.G. carried out NPD experiments. A.S.S. initiated the project, assisted with the magnetic susceptibility measurements, supervised the experiments, analyzed the data and wrote the paper. All authors reviewed the manuscript.

Additional information
Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Saparov, B., Singh, D.J., Garlea, V.O. & Sefat, A.S. Crystal, magnetic, and electronic structures, and properties of new BaMnPnF (Pn = As, Sb, Bi). Sci. Rep. 3, 2154; DOI:10.1038/srep02154 (2013).

This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported license. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-nd/3.0
CORRIGENDUM: Crystal, magnetic, and electronic structures, and properties of new BaMnPnF ($Pn = \text{As, Sb, Bi}$)

Bayrammurad Saparov, David J. Singh, Vasile O. Garlea & Athena S. Sefat

The labels and title of the x-axis of Figure 9 are omitted in this Article. The correct Figure 9 appears below as Figure 1.