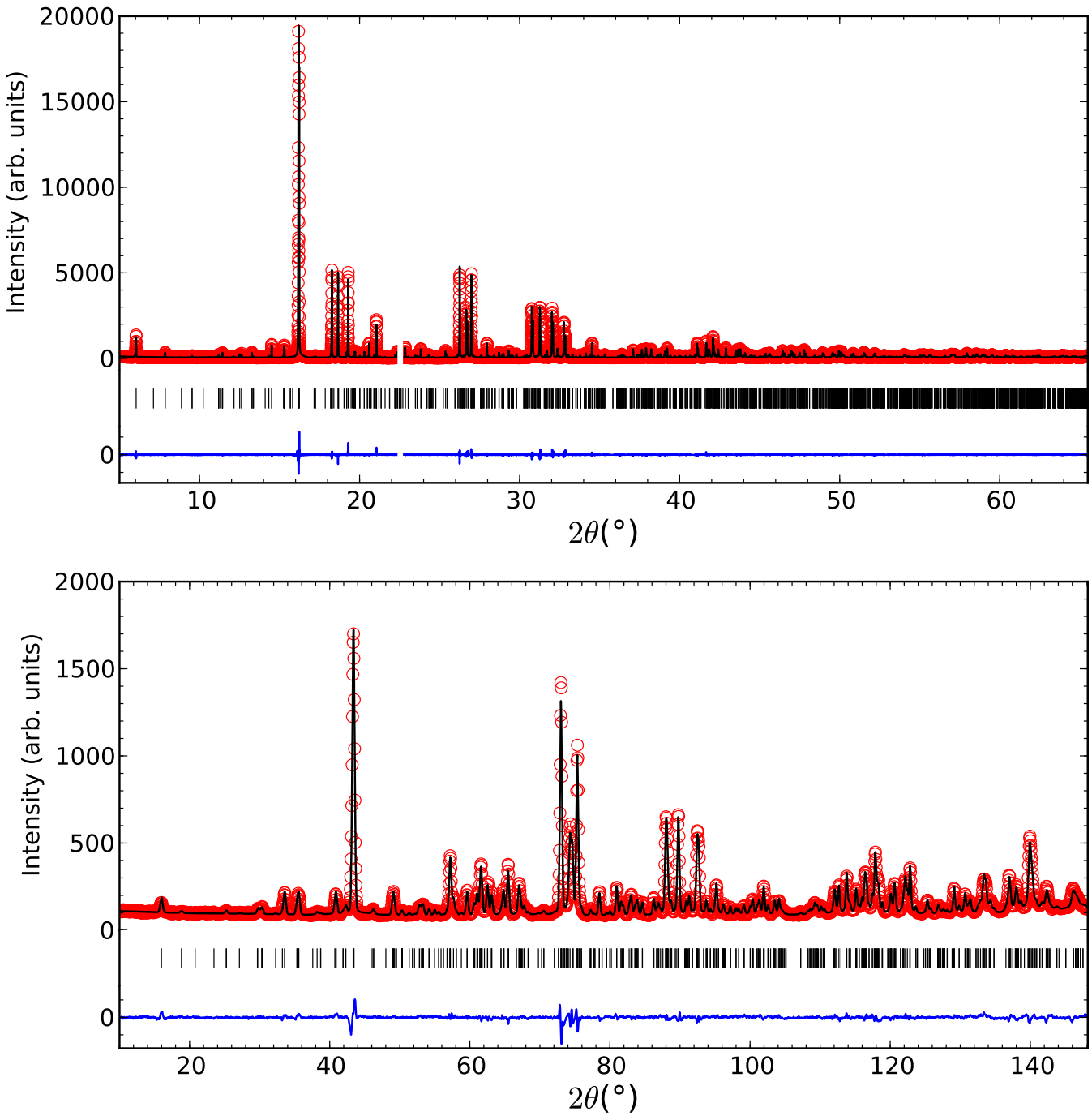

Figure S1
Observed, calculated and difference XPD (top) and NPD (bottom) patterns obtained after simultaneous Rietveld refinement of the 3D model of the member $n = 3$. Vertical markers indicate the positions of Bragg reflections. In the XPD pattern an unidentified peak has been removed excluding certain region.

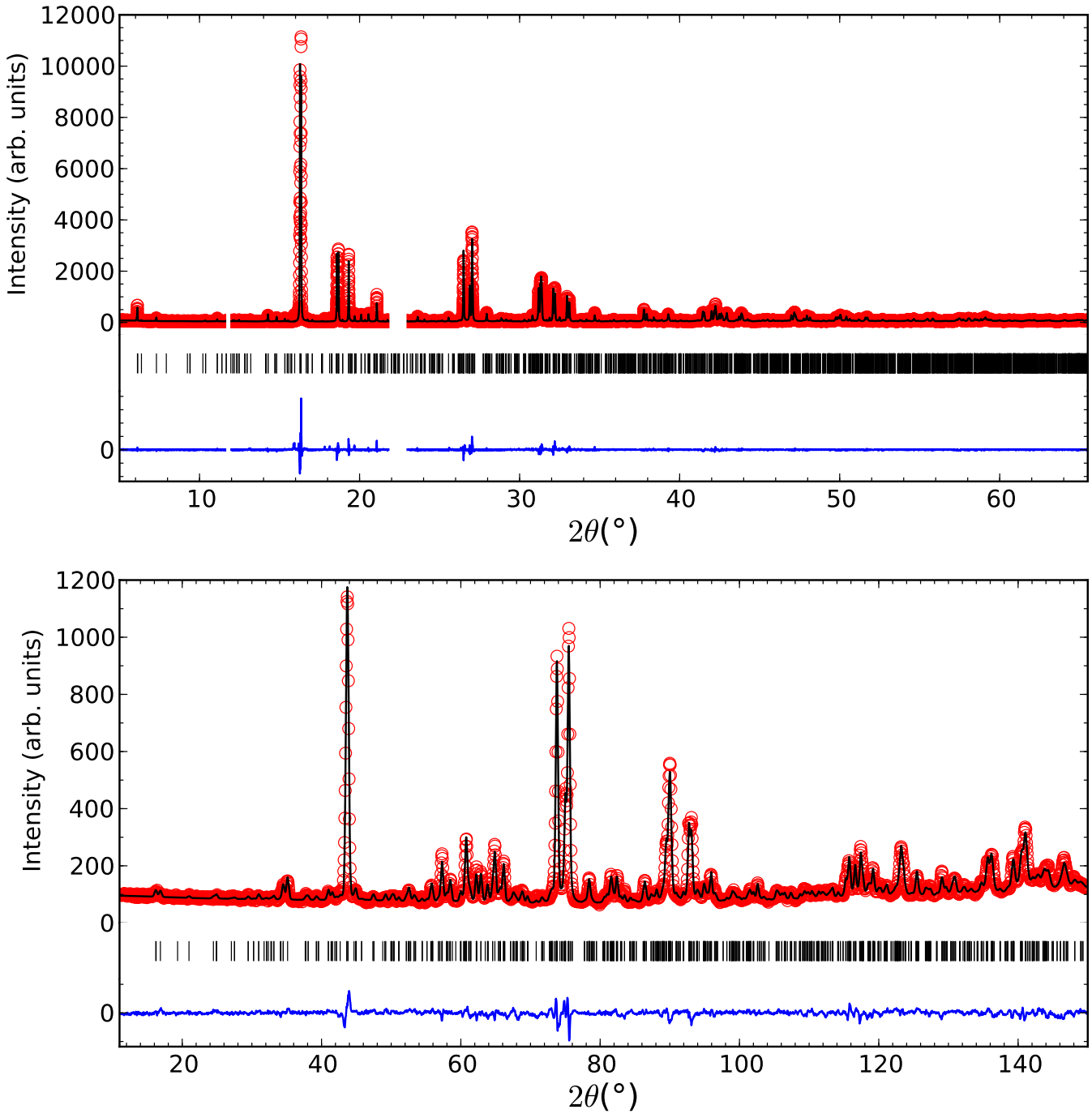

Figure p!
Observed, calculated and difference XPD (top) and NPD (bottom) patterns obtained after simultaneous Rietveld refinement of the structure of the member $n = 5$. Vertical markers indicate the positions of Bragg reflections. In the XPD pattern two regions have been excluded because of unidentified peaks.

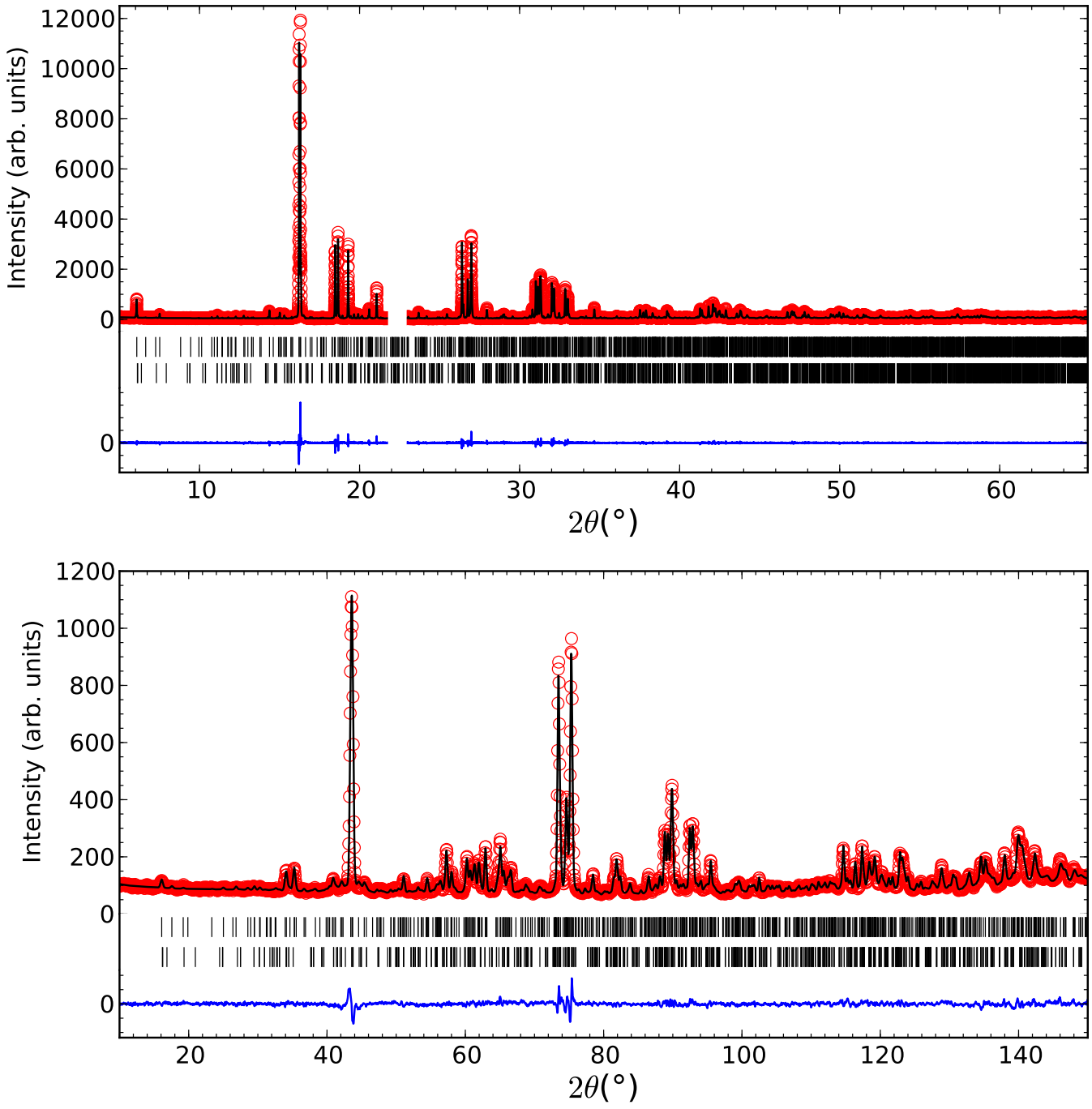

Figure p
Observed, calculated and difference XPD (top) and NPD (bottom) patterns obtained after simultaneous Rietveld refinement of the model I for the member $n = 4$. Vertical markers indicate the positions of Bragg reflections. In the XPD pattern a region has been excluded because of an unidentified peak.

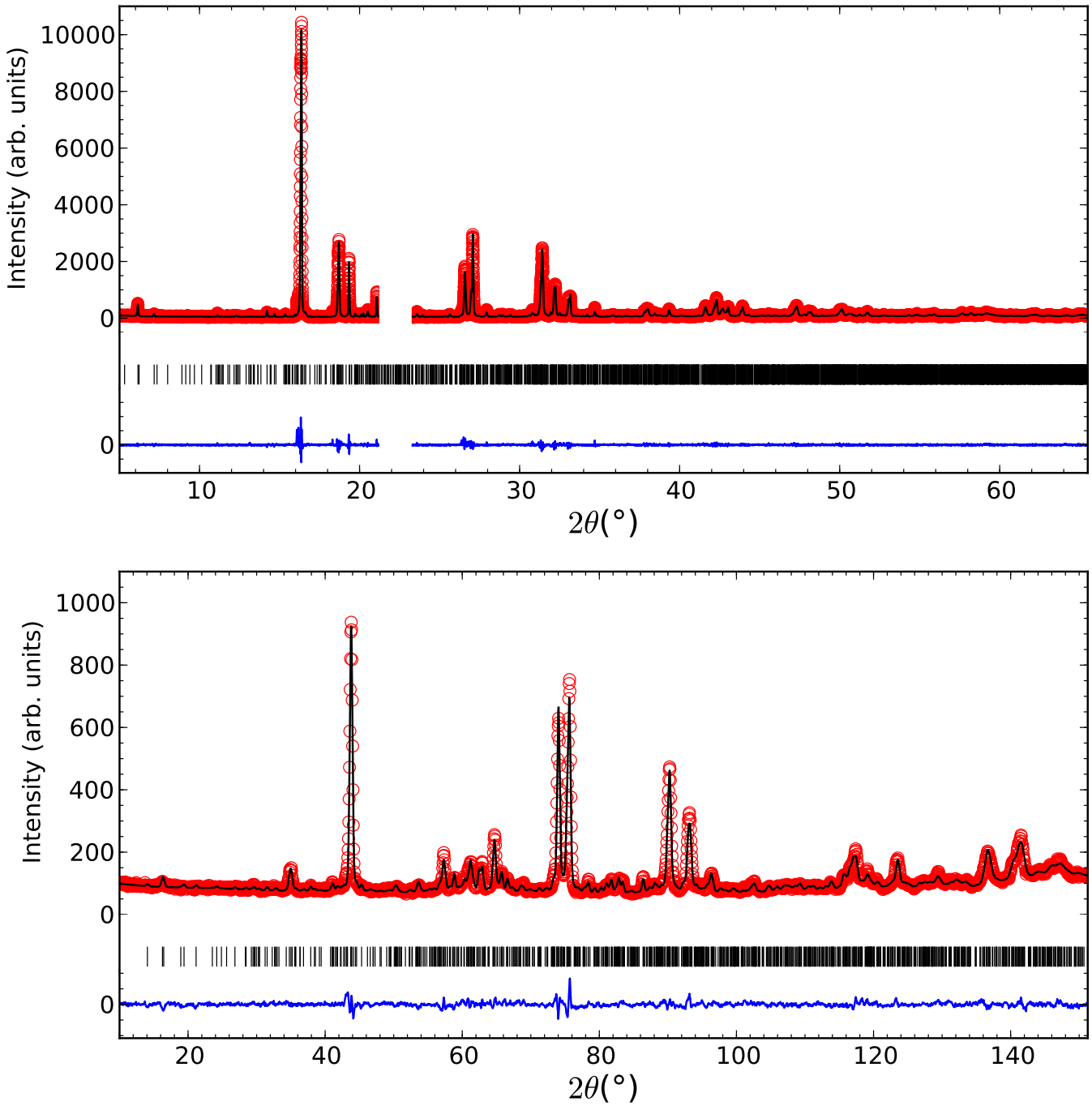

Figure p
Observed, calculated and difference XPD (top) and NPD (bottom) patterns obtained after Rietveld refinement of the structure of the member $n = 6$. Vertical markers indicate the positions of Bragg reflections.

IUCr macros version 2.1.4: 2010/12/07

S1. Superspace model based on fluorite structure

As explained above, the compounds of the family $Bi_{2(n+2)}Mo_nO_{6(n+1)}$ can also be described as different distortions of the fluorite-type structure of the compound δ-Bi_2O_e. That is, it is also possible to build a superspace model for this series of compounds starting from the end member corresponding to $n = 0$.

The phase δ-Bi_2O_3 exhibits a face-centred cubic structure similar to fluorite but with an oxygen deficiency of 25 %. The average structure of this superspace model can be obtained by including the corresponding proportion of Mo atoms at cationic positions, which remain fully occupied. Obviously, the occupancy factors of the O atoms are modified to obtain an adequate balance of charge.

The superspace model is constructed through the embedding of the 3D atomic distribution of the member with $n = 3$. The average unit cell and the modulation vector are the same that were chosen for the superspace model based on the Aurivillius structure. Thus, the description obtained for the Bi and Mo atoms is also the same. Since the superspace group is $F2(\alpha 0\gamma)$, the O atoms are distributed in two different average positions after the embedding of the 3D structure, $(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$ and $(\frac{1}{4}\,\frac{3}{4}\,\frac{1}{4})$; each O atom of the 3D structure is associated with the closest average position. This process leads to two domains with different occupancies. The first one is fully occupied, while the other presents an occupancy factor Occ(O2)$= \frac{11}{13} = 1 - \frac{2}{13}$. Taking into account this occupancy, this structure could be explained as a fluorite-type structure with some vacancies at one of the oxygen average positions.

To describe the real structure the positional modulations $\mathbf{u}(\bar{x}_4)$ of the atomic domains were calculated from the embedding of the 3D structure. In the case of the O1 atom, which is defined continuously throughout the internal space, this displacive modulation is represented by a truncated sum of harmonic functions

$$\mathbf{u}(\bar{x}_4) = \sum_n [\mathbf{A}_n \sin(2\pi n\bar{x}_4) + \mathbf{B}_n \cos(2\pi n\bar{x}_4)] \qquad (1)$$

The rest of atoms are only defined within a limited region of the internal space. Therefore, their positional modulations are expressed as a finite sum of some special functions (see Eq. 10 in the main text). In the case of Mo atomic domain, these special functions $S_n(\bar{x}_4)$ are Legendre polynomials of several orders, whereas orthogonalized harmonic functions have been employed for the Bi and O2 atoms. The parameters of the positional modulation of each atomic domain have been calculated from the embedding of the 3D model and checked by refining the superspace model through the Rietveld method, employing simultaneously the XPD and NPD data. The agreement between observed and calculated patterns is similar to that obtained with the 3D refinement (Fig. S1). Reliability factors are indicated in Table S1.

Table S1
Background corrected reliability factors obtained with the XPD and NPD patterns of the $n = 3$ member using the superspace model based on fluorite structure.

	XPD	NPD
R_p	0.1255	0.1084
R_{wp}	0.1452	0.1111
S	1.23	1.99
R_B(all)	0.0358	0.0442
R_F(all)	0.0211	0.0285
No. of parameters	76	73

As in the case of the superspace model based on Aurivillius structure, the positional modulations of the different atomic domains are very wavy, especially for the O1 and O2 atoms. As an example, the positional modulations along *z* axis for this two atoms are represented in Fig. S5. Although the average position is $z = \frac{1}{4}$ for both atomic domains, atoms are scattered and far from a simple harmonic behaviour, as can be seen in Fig. S5.

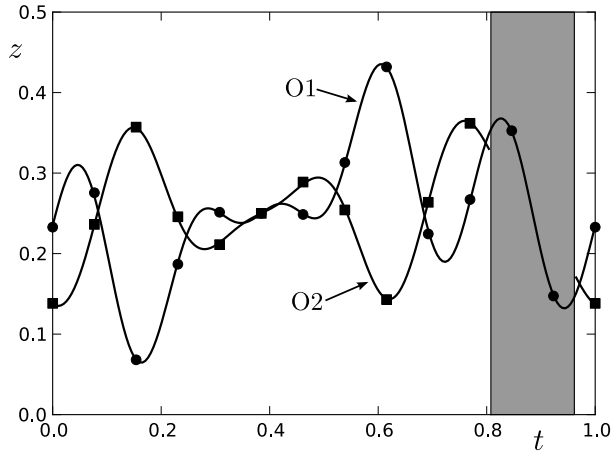

Figure S5
Positional modulation along *z* coordinate for O1 and O2 atomic domains. Discrete points indicate positions of O atoms of the 3D structure and continuous lines represent refined positional modulation of the atomic domains. The shaded region is the range in which O2 atom is not defined. Two atoms overlap at $t = \frac{5}{13}$.

Keeping the same superspace group $F2(\alpha 0\gamma)$, this model can be generalized, varying the width of the corresponding crenel functions according to the composition of each compound. As in the case of the superspace model based on Aurivillius, the occupancy of Bi and Mo at each average position are given by $\frac{2(n+2)}{3n+4}$ and $\frac{n}{3n+4}$ respectively. Since all atomic domains of the superspace structure present the same multiplicity ($m = 4$), the total amount of O atoms distributed in both average positions has to be $\frac{6(n+1)}{3n+4}$. As the O1 atom is fully occupied, the occupancy of the O2 atom is $\frac{6(n+1)}{3n+4} - 1 = \frac{3n+2}{3n+4}$. The occupancy factor of each atom determines the width of the corresponding crenel function (Table S2). The general expression for the modulation vector $\mathbf{q}_o$ has already been given in Eq. 4 of the main text. Since this is a superspace model for a commensurate structure, a value of the *t* parameter for this general model is required to determine the corresponding 3D structure and space group.

IUCr macros version 2.1.4: 2010/12/07

The value $t = 0$ or any of its equivalent lead to the corresponding 3D space group $C2$ with a Mo atom located at a twofold axis, as it is expected.

Table S2

Distribution of the atomic domains for the superspace model based on fluorite. The O1 atom is fully occupied and the rest are represented by crenel functions whose widths depend on parameter n. The superspace group is $F2(\alpha 0\gamma)$ with the average unit cell defined by the vectors $\{\mathbf{a}_F, \mathbf{b}_F, \mathbf{c}_F, \}$. The corresponding modulation vector is give by Eq. 4 of the main text.

Atom	Average position	x_4^0	Δ
Bi	(0 0 0)	$\frac{1}{2}$	$\frac{2(n+2)}{3n+4}$
Mo	(0 0 0)	0	$\frac{n}{3n+4}$
O1	$(\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4})$	–	–
O2	$(\frac{1}{4}\ \frac{3}{4}\ \frac{1}{4})$	$\frac{1}{2}$	$\frac{3n+2}{3n+4}$

IUCr macros version 2.1.4: 2010/12/07