

New Modification of PbF(IO₃)

Subjects: [Crystallography](#)

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New crystals of PbF(IO₃) polytype modification are synthesized hydrothermally and demonstrate strong SHG optical response. They are phase-matchable at the fundamental wavelength of 1064 nm. The crystal structure was solved in two space groups, orthorhombic *C2ma* and monoclinic *Pn*, of which monoclinic is true and is described with a twinning by mirror plane introduced in structural refinements taken into account. Orthorhombic symmetry was used in comparison with the related structures and deviation close similarity in the selected suggested family MX(IO₃), M = Bi, Ba, Pb, X= O, F, (OH) with series of members. These compounds were also characterizing as similar to Aurivillius phases with fluorite-like layer and perovskite-like layer substituted by (IO₃) groups. The optical nonlinearity of the iodates of the Aurivillius family and structurally related iodates is determined by the polar orientation of the iodate groups, which make an overwhelming contribution to the optical nonlinearity. From crystal chemistry point of view, the heavy atoms in these structures are located in the second cation environments in relation to the iodate groups and indirectly affect the nonlinearity. In particular, large Ba-cations without single electron pairs provoke a symmetric variant of the Aurivillius type structure, in contrast to the acentric Bi³⁺ and Pb²⁺ cations known in polar iodates with strong second-order optical nonlinearity. There is wide diversity in the extended series of related compounds which includes variation of fluorite-like layers (single or double), perovskite-like layers presented by octahedral or more complicate polyhedral, or by IO₃ (BrO₃) groups, or by Cl-atoms, or by NH₄-groups. This allows the development of future search for new promising phases.

compound

1. SHG, Orthorhombic Model, Ambient Conditions Data

The SHG output from 100 mcm PbF(IO₃) powder is approximately 2 times larger in relation to analogous KDP (KH₂PO₄) powder, which is close to other metal iodate fluorides (**Figure 1**).

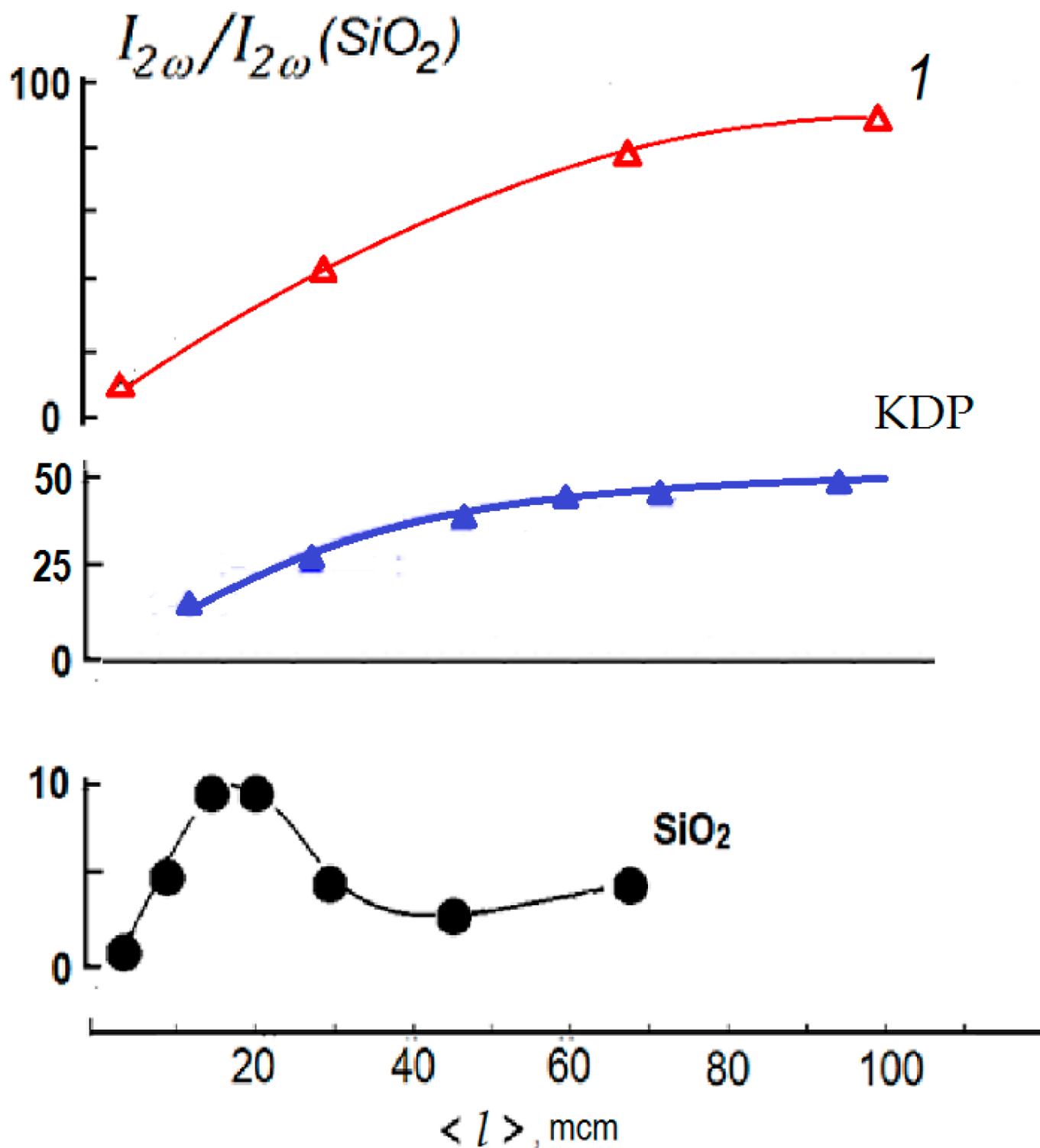


Figure 1. Powder SHG response of two experiments of PbF(IO₃) shown as 1 in comparison with a-quartz and KH₂PO₄ in dependence on average grain size in the powders.

The orthorhombic symmetry was tested with the unit cell $a = 6.0438(2)$, $b = 5.7840(2)$, $c = 11.0731(3)$ determined by the CrysAlis program. The unit cell dimensions correlate with the unit cell of BiO(IO₃) [1], $a = 5.658$, $b = 11.039$, $c = 5.748$, which correspond to the $Pca2_1$ space group. The polar space group $C2ma$ ($Abm2$ in the standard setting) was selected for the new lead fluoride iodate in contrast with the centrosymmetric $Cmma$ suggested by the

CrysAlis program (C-lattice was confirmed by the extinction of reflections), which was impossible because of the optical nonlinearity. The search of the model by direct methods in SHELXS [2] allowed researchers to find two heavy atoms: Pb and I, coordinated by O atoms, whose positions were found from the residual density with R~5%. The heavy atoms were on the mirror plane, which doubled the O atoms up to split umbrella-like IO₃⁻ groups with short O-O distances, which required half occupations of O positions and a disordered model. It was necessary to introduce an absorption correction, which was done using numerical Gaussian integration over a multifaceted crystal model [3]. The refinement of the model in SHELXL [2] gave satisfactory atomic displacement parameters, interatomic distances (except splitting), and R-factor. One of the O atoms was an F atom; based on the temperature displacement parameters, it was the atom at the center of the Pb tetrahedra (anion-centering polyhedra) presented in previously determined structures (see below) also by an F atom or by an (OH) group. The model was neutral, based on Pauling's balance of valences. The resulting chemical formula is PbF(IO₃), Z = 2.

The monoclinic cell, as a second variant of the indexing, was $a = 4.1867(1)$, $b = 11.0837(3)$, $c = 4.1870(1)$, and $\beta = 92.518(3)$ Å (mineralogical setting) and has not been previously defined. This unit cell correlates with the orthorhombic, with c_{orth} equal to b_{mon} , and the choice of two orthorhombic C vectors as the a, c -axis of the new monoclinic cell (Figure 2).

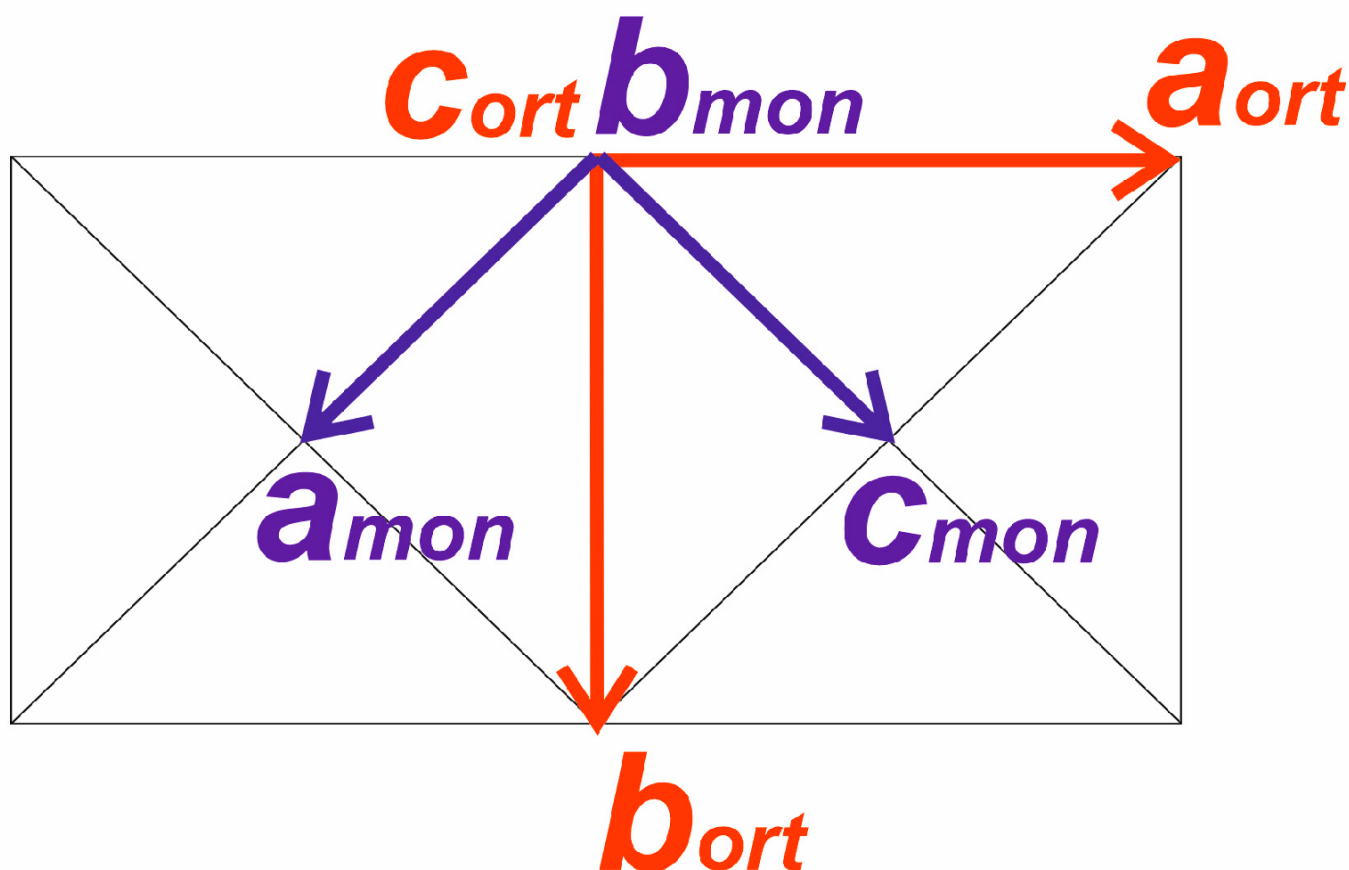
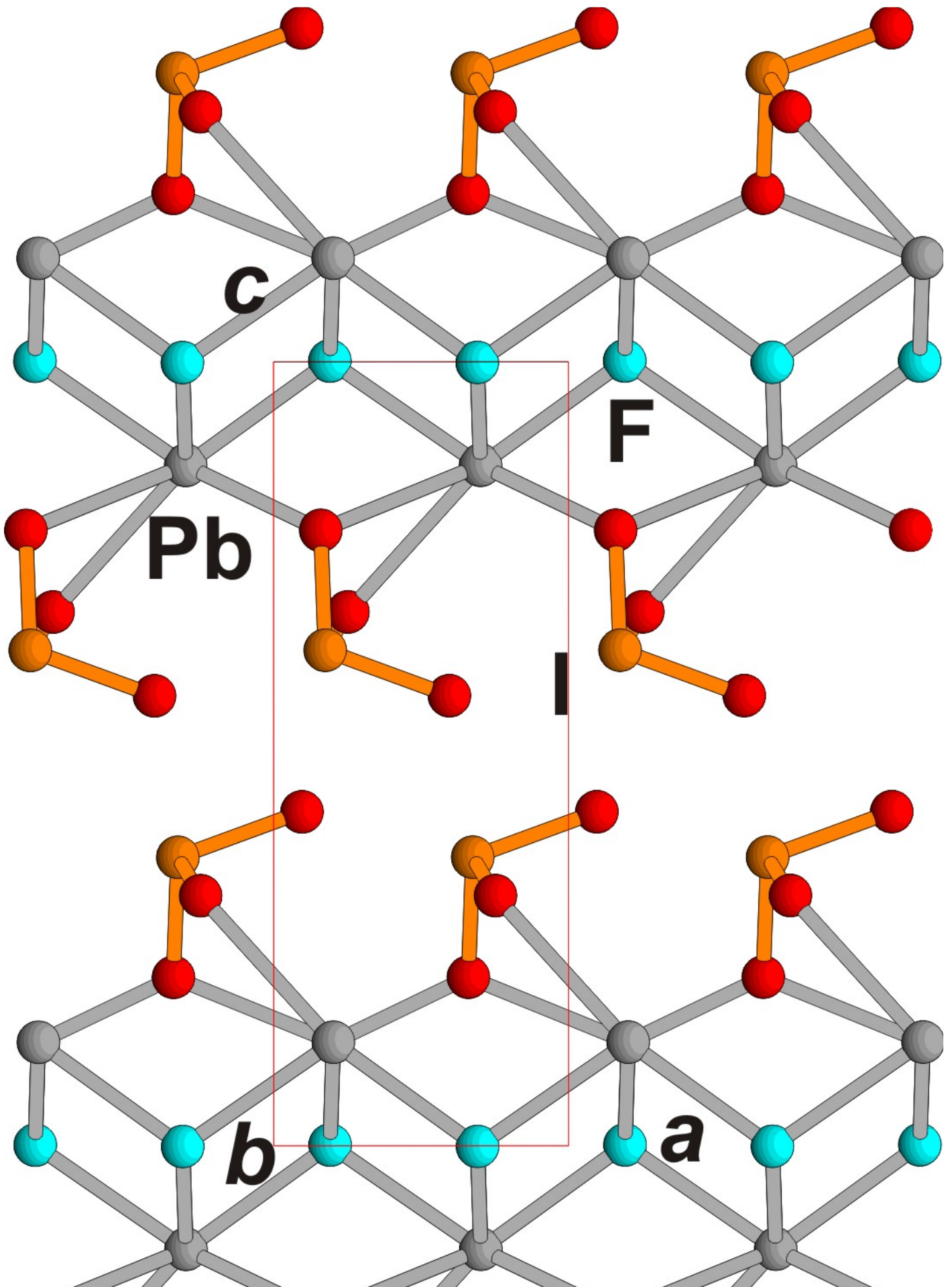


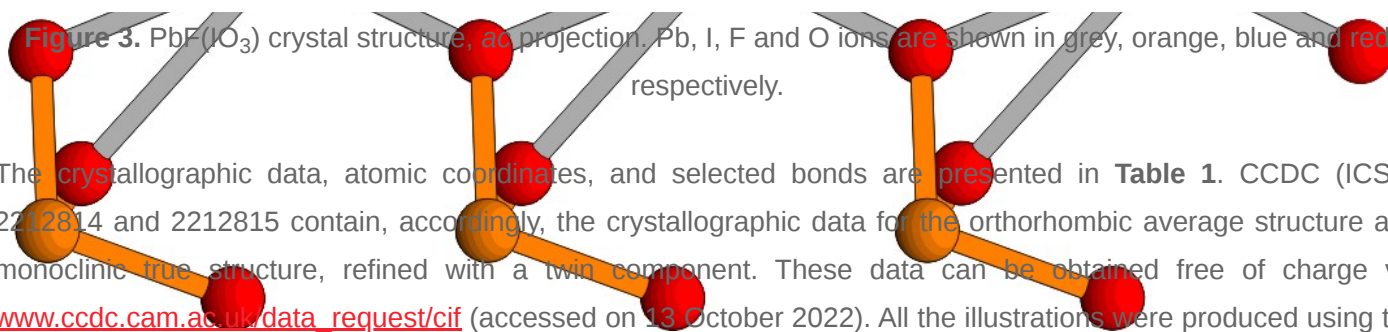
Figure 2. Monoclinic *P*-lattice (blue) selected from the orthorhombic *C*-lattice (red).

As before, the space group suggested by CrysAlis was P12/n1, and acentric P1n1 was used in the calculations. The next calculations for the monoclinic version of the structure were carried out using the low-temperature data, as the low-temperature experiment showed a definite monoclinic cell.

2. Monoclinic Model, Low-Temperature Data

The monoclinic cell parameters at of 150 K $a = 4.1581(4)$, $b = 4.1548(4)$, $c = 11.042(1)$ Å, $\gamma = 92.470$ (5) showed contraction because of cooling compared with the cell at ambient conditions. The polar acentric space group P11n (standard setting) was consistent with a strong SHG signal, extinctions, and unit cell angles. A semi-empirical absorption correction was then applied, based on symmetrically equivalent reflections in the SADABS program [4]. The direct methods in SHELXS [2] gave, again, two positions for the heavy atoms Pb and I, and a series of O⁻ atoms obtained in the difference Fourier synthesis on the distances typical for the (IO₃)⁻ group. As before in the orthorhombic model, the doubling of O⁻ atoms in the umbrella-like IO₃⁻ groups appeared and required an explanation. It was supposed that the mirror plane is a twin element in a monoclinic group, which leads to overestimating the symmetry as orthorhombic (see room temperature experiment). Three O⁻ atoms forming the normal umbrella coordination of I -atoms were selected and refined in SHELXL [2]. Twinning was introduced by matrix 010/100/001 for the diagonal vertical mirror plane, which reduced the R-factor. The components of the twin were refined, BASF = 0.58, and the additional peaks, corresponding to the doubled by twinning O⁻ atoms, disappeared from the residual electron density. The final formula was the same PbF(IO₃), Z = 2. The structural model was finally refined using the least squares procedure in an anisotropic approximation for the atomic displacements for all the atoms, correction of the anomalous scattering, and with the refinement of the weighting scheme using SHELXL [2]. The substitution of O for F lowered the R-factor and confirmed the presence of the F -atom by the anisotropic displacement parameters (**Figure 3**). The true structure of the new modification is monoclinic with twinning by the mirror plane. If this mirror plane is considered as a real symmetry element, the structure of the merohedral twin is described as orthorhombic C2ma and corresponds to the structure determined on the base of the ambient conditions data.





The crystallographic data, atomic coordinates, and selected bonds are presented in **Table 1**. CCDC (ICSD) 2212814 and 2212815 contain, accordingly, the crystallographic data for the orthorhombic average structure and monoclinic true structure, refined with a twin component. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (accessed on 13 October 2022). All the illustrations were produced using the ATOMS ^[5] and CORELDRAW programs.

Orthorhombic symmetry for new compound was used in comparison with the related structures and deviation close similarity in the selected suggested family MX(IO₃), M = Bi, Ba, Pb, X= O, F, (OH) with series of members: orthorhombic PbF(IO₃), monoclinic PbF(IO₃), BiO(IO₃), Ba(OH)(IO₃) and BaF(IO₃). All of them have polytypic nature with sheets composed of central pseudo-tetragonal anion-centered layer (MX) similar to layer in PbO lithargite structure and attached from its both sides (IO₃) groups. The central layer has also description as fluorite-like layer. These compounds were also characterizing as similar to Aurivillius phases with fluorite-like layer and perovskite-like layer substituted by (IO₃) groups.

The new crystals demonstrate disorder presented as twinning. It is proved that in the experiment researchers obtained the simplest structure in the whole polytype family which has the smallest unit cell and the lowest symmetry in contrast with previously determined polytype and other members of the family. Researchers analyzed the reason of formation of different polytypes. Despite the fact that new modification of PbF(IO₃) was synthesized under hydrothermal conditions, and the previously known one was obtained during unconventional low-temperature solid-phase technology, the conditions for obtaining both phases are similar. Both syntheses proceeded at a temperature of 270°C in autoclaves of approximately equal capacity. HIO₃ and NH₄NO₃, which were used to obtain the previous modification, decompose at a temperature of about 200°C to form water, thus the reaction proceeded in an aqueous solution. The main difference in the formation of two polytypes is the reaction rate and the amount of solvent. The synthesis of the phase described proceeds with a large amount of solvent at a lower reaction rate, which contributed to the formation of simpler polytype structure. The growth conditions of previously obtained PbF(IO₃) modification favor to synthesis of the most complicate polytype in the family.

The optical nonlinearity of the iodates of the Aurivillius family and structurally related iodates is determined by the polar orientation of the iodate groups, which make an overwhelming contribution to the optical nonlinearity. From crystal chemistry point of view, the heavy atoms in these structures are located in the second cation environments in relation to the iodate groups and indirectly affect the nonlinearity. In particular, large Ba-cations without single electron pairs provoke a symmetric variant of the Aurivillius type structure, in contrast to the acentric Bi³⁺ and Pb²⁺ cations known in polar iodates with strong second-order optical nonlinearity.

There is wide diversity in the extended series of related compounds which includes variation of fluorite-like layers (single or double), perovskite-like layers presented by octahedral or more complicate polyhedral, or by IO₃ (BrO₃) groups, or by Cl-atoms, or by NH₄-groups. This allows the development of future search for new promising phases.

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