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Reply to the Correspondence on “K₂Sb(P₂O₇)F: Cairo Pentagonal Layer with Bifunctional Genes Reveal Optical Performance”

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Abstract: In their Correspondence, Sergey V. Krivovichev and Luca Bindi argue that the novel excellent nonlinear optical material antimony pyrophosphate, K₂Sb(P₂O₇)F, reported in our Research Article published in this journal belongs to the fresnoite Ba₂[TiO(Si₂O₇)] group and its structure is not novel in terms of either topology or local coordination geometry around Sb³⁺ cations. We clarify that the statements regarding structural features of our original paper are valid in context.

We would like to thank Prof. Krivovichev and Prof. Bindi for their interest in our recent work,^[1] and appreciate their concerns regarding the crystallographic structure of our reported novel excellent nonlinear optical (NLO) material, K₂Sb(P₂O₇)F. In our original paper “K₂Sb(P₂O₇)F: Cairo Pentagonal Layer with Bifunctional Genes Reveal Optical Performance”, we developed an effective strategy to explore new high-performance bifunctional optical materials with both strong second harmonic generation (SHG) responses and large birefringence by introducing the bifunctional [SbO₄F]^{6−} group in the phosphate groups and reported the first antimony phosphate fluoride material, K₂Sb(P₂O₇)F. The title compound not only displays a sharply enhanced birefringence (0.157@546 nm), achieving approximately an order of magnitude enhancement compared to those of the newly reported UV phosphates, but also exhibits a strong SHG response (4.0 × KDP). Also, a solvent-free synthesis method has been introduced to grow Sb^{III}-based inorganic crystals, which provides us with a very useful synthetic route for the

growth of easily hydrolyzed crystalline compounds. Simultaneously, we point out that a new bifunctional gene, the square-pyramidal SbO₄F group, was discovered, and that a unique two-dimensional arrangement of the Cairo pentagonal tiling unit [Sb(P₂O₇)F]^{2−} was observed in inorganic compounds for the first time. However, in the correspondence, Prof. Krivovichev and Prof. Bindi argue that, since K₂Sb(P₂O₇)F belongs to the mineral fresnoite-type structure, the structural characteristics of K₂Sb(P₂O₇)F are not novel.^[2] Specifically, they think that the SbO₄F group has been described earlier^[3] and the topology of the [Sb(P₂O₇)F]^{2−} layer in K₂Sb(P₂O₇)F as “a unique two dimensional arrangement of Cairo pentagonal tiling units” is by far not new.^[4]

Our group has been working on developing new design and synthesis strategies to explore novel functional materials. Recently, we have been focusing on synthesizing new high-performance Sb^{III}-based inorganic NLO materials. A series of new Sb^{III}-based NLO materials such as CsSbF₂SO₄ and RbSbSO₄Cl₂ have been successfully discovered by systematic studies.^[5] K₂Sb(P₂O₇)F has been discovered in the same way. Thus, we always emphasize the functional groups in our work.

First, the correspondence indicates that SbO₄F square pyramids with distorted configurations have been described earlier.^[3] Yes, as a structural group, the SbO₄F group has been reported earlier. However, the SbO₄F group as a bifunctional group with both high anisotropies and large hyperpolarizabilities has never been reported. In the title, the abstract, the introduction, and the conclusion of our original paper we always stated that “a new bifunctional gene, the square-pyramidal SbO₄F group, was discovered”. In our work, we emphasized that the SbO₄F group was discovered for the first time as a new bifunctional group to design NLO materials, not as a structural group.

Second, the correspondence indicates that since K₂Sb(P₂O₇)F belongs to the mineral fresnoite-type structural group, the structural characteristics of K₂Sb(P₂O₇)F are not novel. Furthermore, the topology of the [Sb(P₂O₇)F]^{2−} layer in K₂Sb(P₂O₇)F as “a unique two dimensional arrangement of Cairo pentagonal tiling units” is by far not new. As previously mentioned, our work focused on the functions of the materials, not the crystallography and mineralogy. Hence, we unwittingly ignored the structure of the mineral fresnoite,

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Ba₂[TiO(Si₂O₇)]. Our conclusion about Cairo pentagonal tiling units is based on Ref. [19] in our original paper, “Periodic Tiling of Pentagons: The First Example of a Two-Dimensional (5₄³)-net” reported by Prof. Michael J. Zaworotko and co-workers in 2001.^[6] Also, the Cairo pentagonal tiling [Sb(P₂O₇)F]²⁻ layer is really reported for the first time in inorganic compounds. In our work, we want to emphasize the superior NLO properties of K₂Sb(P₂O₇)F compared to that of the classical NLO material KBe₂BO₃F₂ (KBBF) by optimizing the structural mode. Although the topology of pentagonal tiling is common in inorganic crystal chemistry, no example has yet been put forward where novel NLO materials have been designed using the Cairo pentagonal tiling layered structure.

Indeed, inorganic crystal chemistry and structural mineralogy are sometimes helpful for the exploration of new functional materials. However, materials with the same structures exhibit very different performance, for example, the birefringence for Ba₂TiO(Si₂O₇) is tiny, but K₂Sb(P₂O₇)F exhibits a very large birefringence (0.157@546 nm). Hence, we think that understanding the mechanism responsible for the excellent functional properties is more important for designing and synthesizing new superior functional materials. Furthermore, we believe that the statements regarding the structural features of our original paper are valid in context.

Conflict of interest

The authors declare no conflict of interest.

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