

# Trigonal structures of $ABe_2BO_3F_2$ ( $A = Rb, Cs, Tl$ ) crystals

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Several interesting fluoroberyllium borates were synthesized hydrothermally and characterized by single-crystal X-ray diffraction. The crystal structures of  $RbBe_2BO_3F_2$  (RBBF; rubidium fluoroberyllium borate) and  $CsBe_2BO_3F_2$  (CBBF; caesium fluoroberyllium borate), previously determined in the space group  $C2$ , were reinvestigated for higher symmetry and found to have more suitable solutions in the space group  $R32$ .  $TlBe_2BO_3F_2$  (TBBF; thallium fluoroberyllium borate) was synthesized as a novel compound also having this trigonal structure type. Details of the space-group determination and unique structural features are discussed. These crystal structures were compared with that of  $KBe_2BO_3F_2$ , revealing interesting structural trends within this family of compounds that are also discussed. A crystallographic explanation of the physical morphology is postulated.

## 1. Introduction

The development of borate-based deep-UV nonlinear optical (NLO) materials is an interesting avenue of research which requires the fusion of crystal structure determination and advanced crystal growth efforts. Recently the understanding of borate anionic group theory has provided a number of useful insights into the structure–property relationships of NLO materials, thus allowing the design of structures having high NLO conversion efficiencies and wide UV transparency ranges (Chen *et al.*, 2005, 2006). Crystals based on the  $[BO_3]^{3-}$  anion tend to exhibit the best combination of these properties for practical device applications (Chen *et al.*, 2005; Xue *et al.*, 2000).  $KBe_2BO_3F_2$  (KBBF) is one such material, having transparency to 153 nm and an NLO coefficient of  $d_{11} = 0.49 \text{ pm V}^{-1}$  (Chen *et al.*, 2005). The structure of KBBF was first reported in 1970 by Russian scientists who obtained a single-crystal structure solution in the monoclinic space group  $C2$  with  $R = 0.131$  (Soloveva & Bakakin, 1970). The analogous compounds  $RbBe_2BO_3F_2$  (RBBF) and  $CsBe_2BO_3F_2$  (CBBF) were examined in 1975, and their structures likewise determined in the space group  $C2$  with  $R = 0.157$  and  $0.092$  (Baidina *et al.*, 1975). The authors of these initial structural investigations noted pseudo-threefold symmetry within the monoclinic structures, but it was not until 1995 when the structure of KBBF was revisited by Chinese researchers that the space group  $R32$  was assigned (Mei *et al.*, 1995). This solution accounts for the threefold symmetry and produced an improved  $R$  value of  $0.031$ , although a similar redetermination has not yet been applied to the RBBF and CBBF analogs.

Misassignment involving the space groups  $C2$  and  $R32$  is not unusual (Cenzual *et al.*, 1990; Marsh & Spek, 2001). In particular, Marsh and Spek used the ADDSYM function of the PLATON software package to identify 144 structures in the

**Table 1**  
Experimental details.

	KBBF	TBBF	RBBF	CBBF
Crystal data				
Chemical formula	$\text{KBe}_2\text{BO}_3\text{F}_2$	$\text{BBe}_2\text{F}_2\text{O}_3\text{Tl}$	$\text{BBe}_2\text{F}_2\text{O}_3\text{Rb}$	$\text{BBe}_2\text{CsF}_2\text{O}_3$
$M_r$	153.93	319.20	200.30	247.74
Crystal system, space group	Trigonal, $R\bar{3}2$	Trigonal, $R\bar{3}2$	Trigonal, $R\bar{3}2$	Trigonal, $R\bar{3}2$
Temperature (K)	293	293	293	293
$a, c$ (Å)	4.4220 (6), 18.734 (4)	4.4387 (6), 19.942 (4)	4.4387 (6), 19.820 (4)	4.4575 (6), 21.310 (4)
$V$ (Å <sup>3</sup> )	317.25 (9)	340.27 (9)	338.17 (9)	366.68 (10)
$Z$	3	3	3	3
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.196	35.54	10.93	7.52
Crystal form, size (mm)	Hexagonal plate fragment, 0.24 × 0.24 × 0.07	Hexagonal plate fragment, 0.36 × 0.08 × 0.04	Hexagonal plate fragment, 0.50 × 0.26 × 0.24	Hexagonal plate, 0.35 × 0.32 × 0.09
Data collection				
Diffractometer	Rigaku AFC8S	Rigaku AFC8S	Rigaku AFC8S	Rigaku AFC8S
Data collection method	$\omega$ scans	$\omega$ scans	$\omega$ scans	$\omega$ scans
Absorption correction	Multi-scan†	Multi-scan†	Multi-scan†	Multi-scan†
$T_{\min}$	0.7623	0.020	0.030	0.163
$T_{\max}$	0.9210	0.241	0.073	0.510
No. of measured, independent and observed reflections	967, 166, 166	990, 163, 162	974, 162, 161	1166, 200, 200
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\text{int}}$	0.0496	0.074	0.079	0.048
$\theta_{\max}$ (°)	29.05	26.1	26.2	29.3
Refinement				
Refinement on	$F^2$	$F^2$	$F^2$	$F^2$
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.0301, 0.0734, 1.233	0.035, 0.084, 1.20	0.036, 0.081, 1.18	0.016, 0.034, 1.25
No. of reflections	166	163	162	200
No. of parameters	17	17	16	17
$(\Delta/\sigma)_{\max}$	< 0.0001	< 0.0001	< 0.0001	0.001
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.43, -0.29	2.65, -1.72	0.72, -1.00	0.39, -0.47
Extinction method	SHELXL	SHELXL	None	SHELXL
Extinction coefficient	0.011 (6)	0.013 (3)	—	0.052 (4)
Absolute structure	Flack (1983)	Flack (1983)	Flack (1983)	Flack (1983)
Flack parameter	0.04 (16)	0.00 (9)	0.15 (5)	-0.09 (7)

Computer programs used: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2000), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 1999). † Based on symmetry-related measurements.

Cambridge Structural Database reported in the space group  $C2$  that were candidates for revision in higher-symmetry space groups (Marsh & Spek, 2001). Of these, 50 were found to be more accurately described using space groups possessing additional symmetry, including two structures that were more suitable in the space group  $R\bar{3}2$ . These authors also noted two others with probable  $R\bar{3}2$  symmetry, although concerns regarding the stoichiometry and questionable intensity data in these cases require a more thorough examination. Given this propensity for misassignment and their potential interest to the optics community, we feel the title compounds are worthy of a detailed structural investigation. Recently we developed a convenient hydrothermal technique to synthesize and grow ABBF crystals (McMillen & Kolis, 2008), permitting such a study. In the present work we redetermined the structures of RBBF and CBBF in the space group  $R\bar{3}2$  and present the structure determination of  $\text{TlBe}_2\text{BO}_3\text{F}_2$  (TBBF), a novel addition to this trigonal fluoroberyllium borate family. The structure of KBBF is also included for comparative purposes

within the ABBF family and this study serves as verification of its trigonal structure (Mei *et al.*, 1995) rather than a re-determination. We offer a discussion of structural trends among these compounds that can account for the physical morphology of the crystals, and present a comparison with  $\text{NaBe}_2\text{BO}_3\text{F}_2$  (NBBF) having a monoclinic structure.

## 2. Experimental

Crystals for X-ray structure analysis were obtained through hydrothermal spontaneous nucleation in silver ampoules using powdered ABBF as the starting charge and 1 M fluoride solutions as mineralizers. A detailed discussion of this synthesis and crystal growth has been published elsewhere (McMillen & Kolis, 2008). Crystals tended to have a micaceous habit and formed as colorless hexagonal plates. Selected single crystals were ground into a fine powder and pressed into a transparent pellet with a KBr matrix for IR spectroscopic analysis. These pellets were then dried at 363 K to remove

**Table 2**

Selected distances (Å) and angles (°) in trigonal ABBF ( $A = \text{K, Rb, Cs, Tl}$ ) crystals.

	KBBF	RBBF	CBBF	TBBF
A—F ( $\times 6$ )	2.7523 (9)	2.833 (2)	2.9641 (13)	2.851 (6)
B—O ( $\times 3$ )	1.367 (2)	1.367 (5)	1.369 (3)	1.369 (11)
Be—O ( $\times 3$ )	1.638 (2)	1.639 (4)	1.644 (2)	1.626 (9)
Be—F	1.510 (5)	1.532 (9)	1.526 (5)	1.55 (2)
F—A—FA ( $\times 6$ )	73.10 (5)	76.86 (10)	82.49 (6)	77.8 (3)
F—A—FB ( $\times 6$ )	106.90 (5)	103.14 (10)	97.51 (6)	102.2 (3)
O—B—O ( $\times 3$ )	120	120	120	120
O—Be—O ( $\times 3$ )	108.01 (17)	108.8 (3)	109.21 (15)	109.9 (7)
O—Be—F ( $\times 3$ )	110.89 (16)	110.1 (3)	109.73 (15)	109.0 (8)

surface water and analyzed using a Nicolet Magna 550 FTIR spectrometer. Data were collected under flowing nitrogen from 400 to 4000  $\text{cm}^{-1}$ , and a background correction applied using a blank KBr pellet.

Diffraction-quality crystals were selected after inspection under an optical microscope with polarizing filters and mounted on the end of glass fibers using epoxy. Diffraction intensity data were collected at room temperature using a Rigaku AFC8S diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) and equipped with a Mercury CCD area detector. Data were processed using the *CrystalClear* software package (Molecular Structure Corporation & Rigaku, 2001) and corrections were applied for absorption (Jacobsen, 1999) as well as Lorentz and polarization effects. The structures were determined by direct methods and refined using full-matrix least-squares techniques (on  $F^2$ ) using the *SHELXTL* (Version 6.1) software package (Sheldrick, 2008). All atoms were refined anisotropically for all structures. Structural drawings were prepared for publication using the *DIAMOND* software package (Brandenburg, 1999). Atomic coordinates and anisotropic displacement parameters have been deposited.<sup>1</sup> Details of the data collection and structure refinements are found in Table 1.

### 3. Results and discussion

#### 3.1. Space-group determination

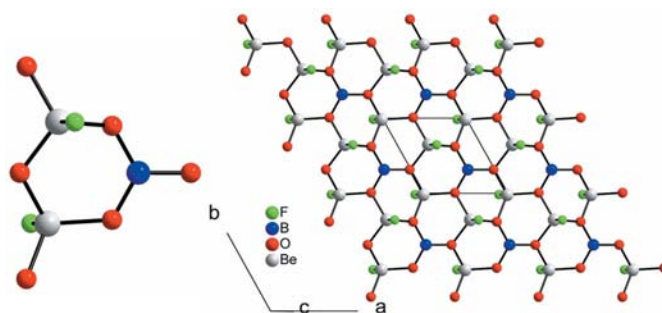
The Laue symmetry was first investigated by comparing the merging  $R$  ( $R_{\text{int}}$ ) values calculated during the transformation of the reduced cell to higher-symmetry obverse rhombohedral and C-centered monoclinic settings for identical datasets from each member of the ABBF family in this study. The  $R_{\text{int}}$  values for KBBF, RBBF, TBBF and CBBF in the monoclinic setting (0.0336, 0.0589, 0.0573 and 0.0337) are only slightly lower and not significantly different than those in the rhombohedral setting (see Table 1), suggesting that the higher-symmetry option was a suitable choice. Elements of the final refined

structures also indicated a preference for the trigonal setting. In all cases the final  $R$  factors were lower in  $R32$  (Table 1) than  $C2$  (0.0348, 0.0635, 0.0455 and 0.0207 for KBBF, RBBF, TBBF and CBBF) even though only 17 parameters were varied in  $R32$  versus 44 parameters in  $C2$ . Axial photographs of the crystals confirmed the unit-cell parameters observed in the space group  $R32$ .

From a crystal chemistry standpoint, the differences in space-group assignment are primarily apparent about the triangular planar borate groups in the structure where there are two unique O atoms in the space group  $C2$  compared with only one in the space group  $R32$ . Anomalous B—O bond distances and O—B—O angles with high degrees of uncertainty were always observed about the B atom in the monoclinic solutions (in the present study as well as previous literature). For example, in TBBF these bond distances varied from 1.29 (8) to 1.41 (4) Å with angles of 123 (3) and 114 (6)°. In the trigonal TBBF structure this borate group is not distorted, but centered on a threefold rotation axis with all B—O distances in agreement with the expected value of 1.369 (11) Å for this geometry (Hawthorne *et al.*, 2002). The triangular borate environments in trigonal RBBF and CBBF (see Table 2) are similarly improved over the distorted arrangements observed in our study and in the published monoclinic determinations (where B—O distances are 1.33 and 1.47 Å in RBBF, and 1.28 and 1.43 Å in CBBF according to Baidina *et al.*, 1975). Differences in the coordination geometries in the monoclinic and trigonal settings are less pronounced for Be and the A-site metal, but do stray slightly from the expected bond distances and angles in the monoclinic setting while again possessing higher degrees of uncertainty. Finally, the solutions for KBBF, RBBF, TBBF and CBBF in  $C2$  were checked for alternate symmetry using the ADDSYM function of *PLATON* (Spek, 2009), and in each case the transformation to  $R32$  was recommended.

#### 3.2. Structural discussion

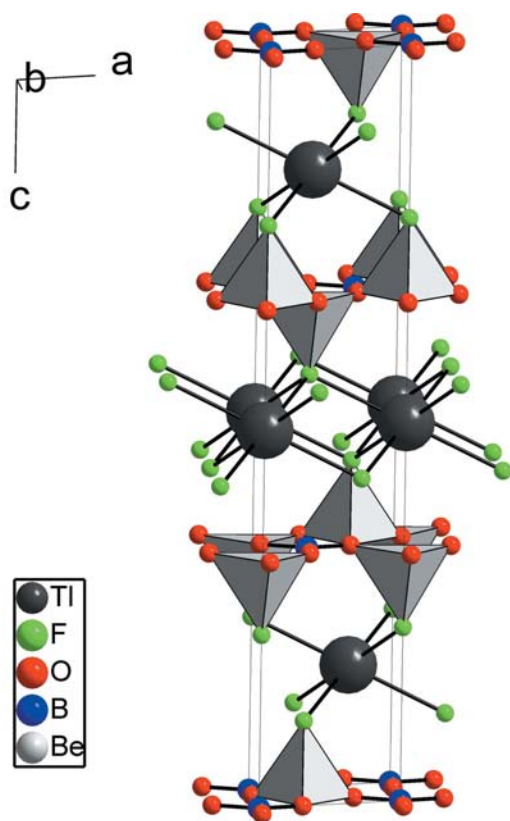
The structures of RBBF, TBBF and CBBF are isomorphous with the trigonal structure of KBBF that has been described in detail elsewhere (Mei *et al.*, 1995). The structure is based on  $[\text{Be}_2\text{BO}_6\text{F}_2]$  rings constructed by oxygen corner-sharing of two

**Figure 1**

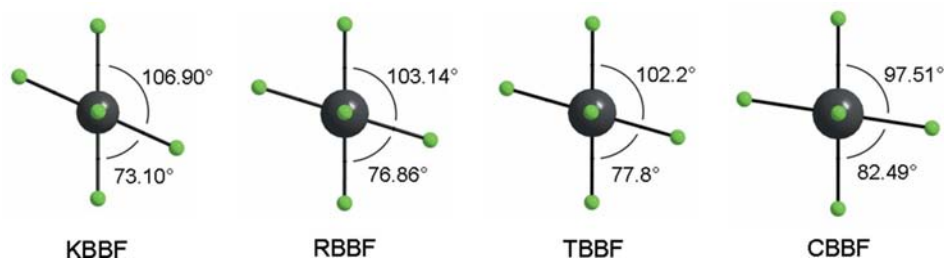
Atomic arrangement of one  $[\text{Be}_2\text{BO}_6\text{F}_2]$  unit (left) and sheet-like connectivity of  $[\text{Be}_2\text{BO}_6\text{F}_2]$  units in the  $ab$  plane of TBBF (right, viewed slightly off the  $c$  axis).

<sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: BP5022). Services for accessing these data are described at the back of the journal.

[BeO<sub>3</sub>F] tetrahedra and one [BO<sub>3</sub>] triangle, as shown in Fig. 1. Sheets of these units extend infinitely in the *ab* plane (also Fig. 1) and are connected to one another along the *c* axis by the monovalent metal that interacts with out-of-plane F atoms in each layer. This layered structure type is typified by the TBBF structure shown in Fig. 2. The micaceous nature of the crystals can be attributed to this layering since the *A*–F interactions are relatively weak compared with B–O or Be–O bonds within the [Be<sub>2</sub>BO<sub>6</sub>F<sub>2</sub>] units and provide a convenient cleavage plane for the crystals. Isomorphous substitution of monovalent Rb, Tl and Cs ions for K in the KBBF structure type results in a notable expansion of the unit-cell volume as the [Be<sub>2</sub>BO<sub>6</sub>F<sub>2</sub>]-based sheets are spread apart to accom-



**Figure 2**  
Layered structure type of ABBF crystals (off-axis view of TBBF, BeO<sub>3</sub>F units drawn as polyhedra).

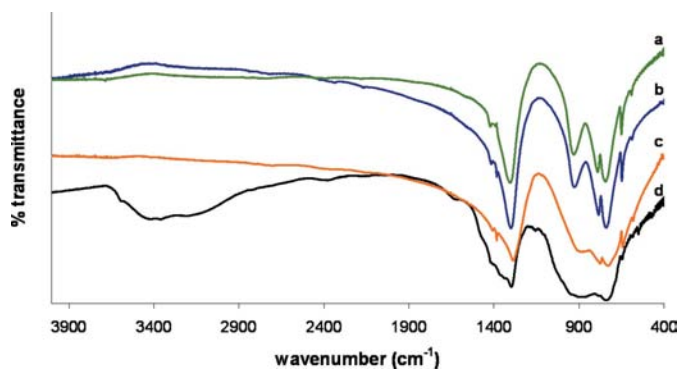


**Figure 3**  
*A*–F distorted octahedra in trigonal ABBF compounds. Metal atoms are depicted as dark gray spheres and F atoms as green spheres.

modate the larger metals. Bond distances for B–O and Be–O interactions vary little among the isomorphs (Table 2) inhibiting dramatic expansion along the *a* and *b* axes. Significant expansion of the unit cell caused by increasing *A*–F bond distances occurs primarily along the *c* axis. Comparatively, the volumetric expansion from KBBF to CBBF is accounted for by a 13.8% increase in *c*-axis length and only a 0.8% increase in the lengths of the *a* and *b* axes. These anisotropic effects can be envisioned as a compressed spring or accordion that relaxes with the isomorphous substitution of larger monovalent cations resulting in less angular distortion about the *A*–F octahedra, although an ideal octahedron is not attained even about the largest metal (Cs) in this study. These environments are shown in Fig. 3. KBBF also shows slight angular distortion about the [BeO<sub>3</sub>F] tetrahedra to additionally compensate for the small size of the potassium ion relative to the other monovalent ions studied in this structure type. It is interesting that, based on the angular distortion of the *A*–F octahedra and [BeO<sub>3</sub>F] tetrahedra, the most-studied compound in this family, KBBF, seems the least suited to the trigonal structure type it adopts. It is our empirical observation that the micaceous tendency of the alkali fluoroberyllium borate crystals decreases with increasing metal-ion size. We postulate that this is due to a better crystallographic fit (and a more fully satisfied bond valence) of the larger alkali ions between the layers, leading to an overall less-strained crystal.

While the TBBF structure fits within the general crystallographic trends observed in the ABBF family, its *c*-axis length of 19.942 Å is noticeably longer than that of RBBF (19.820 Å), even though the effective ionic radius of Tl<sup>+</sup> is slightly shorter (1.50 Å) than that of Rb<sup>+</sup> (1.52 Å) for six-coordinate geometries (Shannon, 1976). This phenomenon is not uncommon when comparing the cell parameters of Tl-containing crystals *versus* isomorphous Rb-containing crystals, and can often be attributed to the inert pair effect associated with Tl<sup>+</sup> (Kyono *et al.*, 2000; Kyono & Kimata, 2001). If such an effect is present in TBBF it does not appear to be strong enough to influence the stereochemistry about Tl, as the high symmetry of the metal site observed in the other ABBF structures is retained. Partial OH<sup>−</sup> substitution at the F<sup>−</sup> site could account for the slightly elongated Tl–F and Be–F distances observed in the present study. Structural refinements accounting for varying degrees of substitution did not result in improved *R* factors, but the presence of OH<sup>−</sup> in TBBF was verified by IR spectroscopy.

The vibrational spectra of the ABBF family are compared in Fig. 4. The materials exhibit identical spectral features with the exception of the broad OH<sup>−</sup> stretch from 3000–3500 cm<sup>−1</sup> in TBBF. While the B–O stretching vibrations of the isolated borate triangles are characterized by sharp peaks around 1300 cm<sup>−1</sup> in each spectrum, the vibrational signature of the [BeO<sub>3</sub>F] tetrahedron from 650–1000 cm<sup>−1</sup> is much less defined for



**Figure 4**  
Vibrational spectra of (a) KBBF, (b) RBBF, (c) CBBF and (d) TBBF. Spectra have been offset in % transmittance for clarity.

TBBF than for the other materials. This overall broadening especially observed in this portion of the TBBF IR spectrum may also be suggestive of partial  $\text{OH}^-$  substitution for  $\text{F}^-$  in the  $[\text{BeO}_3\text{F}]$  group.

Although  $\text{NaBe}_2\text{BO}_3\text{F}_2$  (NBBF) possesses the same sheet structure, based on  $[\text{Be}_2\text{BO}_6\text{F}_2]$  units, as the title compounds it has been shown to crystallize in the  $C2$  space group (Mei *et al.*, 1994). We also verified this monoclinic structure using our own NBBF crystals during the present study. The transition from space group  $C2$  in NBBF to the space group  $R32$  in KBBF, RBBF, TBBF and CBBF appears to be driven by the size of the monovalent metal. Owing to the smaller atomic radius of the Na ions that link the same rigid sheets in NBBF, the six-coordinate equidistant  $A-\text{F}$  bonding observed in the space group  $R32$  cannot be met and this symmetry is broken in favor of four unique four-coordinate Na ions in the space group  $C2$ . This differs even from the previously determined monoclinic structures of KBBF, RBBF and CBBF where the lone unique  $A$ -site cation is sufficiently large to interact with all six neighboring F atoms (although in these cases the symmetry in the prior literature did not require the  $A-\text{F}$  bonds to be equidistant). It was this apparent dependence on atomic radius observed during our redetermination of the RBBF and CBBF structures that initially led us to explore TBBF as a novel compound having the trigonal ABBF structure type since Tl has an atomic radius very close to that of Rb. We have begun to study the solid-solution behavior of the ABBF materials to further detail the substitutional effects within the trigonal structure type and in particular the structural transition between NBBF and KBBF, and this discussion is forthcoming elsewhere. Similarly, the synthesis and structure determination of other fluoroberyllium borates such as  $\text{AgBe}_2\text{BO}_3\text{F}_2$  (since Ag has an atomic radius between that of Na and K) may be useful in improving the understanding of this interesting structural transition.

#### 4. Conclusions

We conducted a systematic study of the single-crystal structures of a family of compounds having the general formula

$\text{ABe}_2\text{BO}_3\text{F}_2$  ( $A = \text{K, Rb, Cs, Tl}$ ) in order to better characterize the structural behavior of these interesting nonlinear optical materials. The structures of  $\text{RbBe}_2\text{BO}_3\text{F}_2$  (RBBF) and  $\text{CsBe}_2\text{BO}_3\text{F}_2$  (CBBF) have been redetermined in the trigonal space group  $R32$ . The structure of a novel member of this fluoroberyllium borate family,  $\text{TlBe}_2\text{BO}_3\text{F}_2$  (TBBF), was also determined in this work, and anomalous  $\text{Be}-\text{F}$  bond distances coupled with IR spectroscopic analysis were suggestive of partial  $\text{OH}^-$  substitution at the  $\text{F}^-$  site, which was not present in the other structures. These structures are consistent with the layered structure type published for  $\text{KBe}_2\text{BO}_3\text{F}_2$  (KBBF), but are distinguished by a notable expansion of the unit cell along the  $c$  axis for the Rb, Tl and Cs analogs. This expansion relieves the slight angular distortion present about the  $[\text{BeO}_3\text{F}]$  tetrahedra of KBBF and results in less angular distortion about the  $A-\text{F}$  octahedra as the size of the monovalent metal increases. Understanding this crystallographic trend within this fluoroberyllium borate family helps to clarify why  $\text{NaBe}_2\text{BO}_3\text{F}_2$ , based on a smaller monovalent ion, adopts a different structure type, which is described by the space group  $C2$ .

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