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Letter to the editor

CaFeO₂Cl and Ca₂FeO₃Cl with higher space group symmetry, a reevaluation

The structures of CaFeO₂Cl and Ca₂FeO₃Cl, which were published by Ackerman in 1991 with the non-centrosymmetric space groups (8) *Am* and (75) *P4*, respectively, can be described with the centrosymmetric space groups (12) *C2/m* and (129) *P4/nmm*, respectively. Ca₂FeO₃Cl is found to be isotypic with Sr₂FeO₃F.

CaFeO₂Cl: Ackerman [1] described the structure of monoclinic CaFeO₂Cl with the non-centrosymmetric space group No. 8. Having selected a monoclinic unit cell with a unique *b* axis ($\beta \geq 90^\circ$), he had a choice between two different space group settings: *A1m1* and *C1m1* (standard setting). A change from one setting to the other requires an interchange of the *a* and *c* axes (also an interchange of *x* and *z* positional atom coordinates) and a sign change of the *b* axis (and *y* positional atom coordinates). In the abstract and main text, Ackerman cites as space group *Am* (*A1m1*). However, in the heading of Table III, he refers to *Cm* (*C1m1*), although both unit cell and positional atom coordinates in the table apply to the nonstandard setting *Am* (*A1m1*). This mix-up is the reason that CaFeO₂Cl data in inorganic databases (e.g., Inorganic Crystal Structure Database, version 2002, collection code ICSD 69869) are erroneous. Interatomic distances calculated with these data do not agree with the numerical values reported in Ackerman's publication.

We started with Ackerman's structure data in setting *A1m1* ($a=8.712$, $b=3.828$, $c=9.999$, $\beta=103.53^\circ$) and changed the setting to *C1m1* ($a=9.999$, $b=3.828$, $c=8.712$, $\beta=103.53^\circ$). Interatomic distances, calculated with these transformed data, agree with the values listed in the publication. In a second step we applied an origin shift of 0.13700. Allowing for minimal shifts of the positional atom coordinates within error limits, we could group all atoms in pairs, such that $x_2 = -x_1$, $y_2 = y_1 = 0$ and $z_2 = -z_1$. With these modified parameters the CaFeO₂Cl structure can be described with the centrosymmetric space group (12) *C2/m*, as shown in Table 1.

Ca₂FeO₃Cl: Interatomic distances for Ca₂FeO₃Cl, calculated with the positional coordinates given in Table V of Ackerman's paper, agree only partially with the numerical values listed in his Table VI or the values

Table 1

Structure data for CaFeO₂Cl in centrosymmetric space group (12) *C2/m* and Pearson code *mS20*. $a=9.999$ Å, $b=3.828$ Å, $c=8.712$ Å, $\beta=103.53^\circ$

		<i>x</i>	<i>y</i>	<i>z</i>
Ca	in 4(<i>i</i>)	0.6079	0	0.2935
Fe	in 4(<i>i</i>)	0.1372	0	0.0001
O(1)	in 4(<i>i</i>)	0.0253	0	0.1633
O(2)	in 4(<i>i</i>)	0.6815	0	0.0539
Cl	in 4(<i>i</i>)	0.3354	0	0.3755

No compound isotypic with CaFeO₂Cl could be found in the Literature.

described in his Figs. 6, 7, and 8. The reasons are printing errors and a mix-up of labels. For example, the Fe(1)–O(3) distance, calculated with the data in Table V, has the value of 1.69 Å, which does not agree with 1.856 Å listed in Table VI (wrongly labeled as Fe(3)–O(3)). Further, the six atoms that are coordinated to Fe(1) are O(3), 4x(O)1, and Cl(1) if one uses data from Table V, but they are O(4), 4xO(1), and Cl(1) according to Table VI and Fig. 6.¹

With these many inconsistencies and uncertainties, it might appear hopeless to come to any reliable conclusions. But we succeeded to show that Ca₂FeO₃Cl is isotypic with a chemically related compound. First, we made small corrections of the positional atom coordinates in Table V to obtain distance values that agree approximately with numerical values listed in Table VI. This also required an interchange of the coordinates for O(3) and O(4). The modified positional atom coordinates are presented in Table 2. These are not the final data.

Applying to the revised and standardized data an origin shift of 0.250.250.2093 and making small shifts of the *z* coordinates in the third place after the decimal points, one can group the Wyckoff sites in pairs. For each pair the numerical values of the *xyz* triplets are

¹ Additional printing errors in Ackerman's publication: In Table V, the compound formula in the title is incorrect. In Table VI, an Fe(3) atom is mentioned twice but does not exist. In Table VII, the "a" value is misprinted. In Table X, the coordinates for O(2) atoms are listed, but not the table O(2). In Fig. 1, the coordinate frame does not agree with a right-handed coordinate system.

Table 2

Revised positional atom coordinated for $\text{Ca}_2\text{FeO}_3\text{Cl}$ in the old space group (75) $P4$ (to be compared with data in Ackerman's Table V)

		<i>x</i>	<i>y</i>	<i>z</i>
$a = 3.848 \text{ \AA}$, $c = 13.650 \text{ \AA}$				
Fe(1)	in 1(<i>a</i>)	0	0	0.0000
Fe(2)	in 1(<i>b</i>)	1/2	1/2	0.4186
Ca(1)	in 1(<i>a</i>)	0	0	0.5500
Ca(2)	in 1(<i>a</i>)	0	0	0.3024
Cl(1)	in 1(<i>a</i>)	0	0	0.7813
Cl(2)	in 1(<i>b</i>)	1/2	1/2	0.6342
Ca(3)	in 1(<i>b</i>)	1/2	1/2	0.8680
Ca(4)	in 1(<i>b</i>)	1/2	1/2	0.1134
O(1)	in 2(<i>c</i>)	0	1/2	0.9757
O(2)	in 2(<i>c</i>)	0	1/2	0.4484
O(3)	in 1(<i>b</i>)	1/2	1/2	0.2824
O(4)	in 1(<i>a</i>)	0	0	0.1395

Table 3

Comparison of the standardized structure data for $\text{Ca}_2\text{FeO}_3\text{Cl}$ in centrosymmetric space group (129) $P4/nmm$ and Pearson code tP14 with the standardized data for $\text{Sr}_2\text{FeO}_3\text{F}$

		<i>x</i>	<i>y</i>	<i>z</i>
$\text{Ca}_2\text{FeO}_3\text{Cl}$				
$a = 3.848 \text{ \AA}$, $c = 13.650 \text{ \AA}$				
Ca(1)	in 2(<i>c</i>)	1/4	1/4	0.5945
Ca(2)	in 2(<i>c</i>)	1/4	1/4	0.8410
Fe	in 2(<i>c</i>)	1/4	1/4	0.2907
O(1)	in 4(<i>f</i>)	3/4	1/4	0.2637
O(2)	in 2(<i>c</i>)	1/4	1/4	0.4265
Cl	in 2(<i>c</i>)	1/4	1/4	0.0736
$\text{Sr}_2\text{FeO}_3\text{F}$				
$a = 3.8660 \text{ \AA}$, $c = 13.1724 \text{ \AA}$				
Sr(1)	in 2(<i>c</i>)	1/4	1/4	0.60471
Sr(2)	in 2(<i>c</i>)	1/4	1/4	0.87773
Fe	in 2(<i>c</i>)	1/4	1/4	0.27249
O(1)	in 4(<i>f</i>)	3/4	1/4	0.24640
O(2)	in 2(<i>c</i>)	1/4	1/4	0.41710
F	in 2(<i>c</i>)	1/4	1/4	0.06520

identical except for the sign, which is an indication that the structure is centrosymmetric. An analysis of all the symmetry elements leads to space group (129) $P4/nmm$. The new final structure data are listed in Table 3.

$\text{Ca}_2\text{FeO}_3\text{Cl}$ is found to be isotopic with $\text{Ba}_2\text{InO}_3\text{X}$ where $X = \text{F}$, Cl , Br [2] and $\text{Sr}_2\text{FeO}_3\text{F}$ [3], which had already been published the first time with the correct centrosymmetric space group (129) $P4/nmm$. To recog-

nize the correspondence between relative unit cell dimensions and positional atom coordinates of $\text{Ca}_2\text{FeO}_3\text{Cl}$ and $\text{Sr}_2\text{FeO}_3\text{F}$ it is necessary to compare structure data which have been standardized with STRUCTURE TIDY [4]. As shown in Table 3, there are small differences in the relative unit cell dimensions and in the numerical values of the positional atom coordinates for $\text{Ca}_2\text{FeO}_3\text{Cl}$ and $\text{Sr}_2\text{FeO}_3\text{F}$. But this is to be expected due to the size differences between Ca and Sr as well as between Cl and F ions.

Ackerman did not deposit his experimental diffraction data. Thus, unfortunately, we do not have the possibility of refining the CaFeO_2Cl and $\text{Ca}_2\text{FeO}_3\text{Cl}$ structures with the positional atom coordinates listed in Tables 1 and 3, respectively.

$\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cl}_2$: The third oxyhalogenoferrate structure in Ackerman's paper, another anion substitution variant of a Ruddlesden–Popper phase, is described with the correct space group (139) $I4/mmm$ and Pearson code tI24. However, the structure of this compound was already known. The structure of $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cl}_2$ was first by Leib and Müller-Buschbaum [5].

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