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## On the Symmetry of the $n=1$ Ruddlesden-Popper Phase $\text{Ca}_2\text{FeO}_3\text{Cl}$

Single crystals of  $\text{Ca}_2\text{FeO}_3\text{Cl}$  have been obtained as a by product during single crystal growth experiments of calcium ferrates from a  $\text{CaCl}_2$  flux. The reddish-brown optically uni-axial crystals adopt the tetragonal space group  $P4/nmm$  with  $a = 3.8381(4)$  Å and  $c = 13.685(2)$  Å and  $Z = 2$  formula units per cell. The structure has been determined from a single crystal diffraction data set collected at room conditions and refined to final residual  $R(|F|) = 0.053$  for 163 observed independent reflections with  $I > 2\sigma(I)$ .  $\text{Ca}_2\text{FeO}_3\text{Cl}$  belongs to the structure family of the Ruddlesden-Popper series with  $n = 1$ , which is also referred to as the  $\text{K}_2\text{NiF}_4$ -type. Main building units are layers of perovskite type corner connected  $\text{FeO}_5\text{Cl}$ -octahedra perpendicular to  $[001]$ . The two crystallographically independent calcium ions are located between the octahedral layers and are coordinated by nine ligands each: Ca1 ( $4 \times \text{O} + 5 \times \text{Cl}$ ) and Ca2 ( $9 \times \text{O}$ ). Following prior studies  $\text{Ca}_2\text{FeO}_3\text{Cl}$  crystallizes in space group  $P4$ . However, the present investigation shows clearly that this assignment is incorrect and that the compound has been described in an unnecessarily low symmetry.

Keywords: ruddlesden-popper phase, symmetry

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### Introduction

The crystal chemistry of the members of the so called Ruddlesden-Popper ( $RP$ ) series has been studied extensively during last ten years (see BEZNOSIKOV & ALEKSANDROV 2000 and the references cited in there). The general formula for these compounds is  $\text{A}_{n+1}\text{B}_n\text{X}_{3n+1}$ , where A and B are different cations and X represents the anions. So far stoichiometric phases have been reported for  $n = 1-3$ . The member with  $n = 1$  is also referred to as the  $\text{K}_2\text{NiF}_4$ - or  $\text{K}_2\text{MgF}_4$ -structure type. Besides the electronic and magnetic properties of the  $RP$ -phases containing transition metals the discovery of superconductivity in the  $\text{K}_2\text{NiF}_4$ -type structure of  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  (AL-MAMOURI et al. 1994) has triggered new detailed studies on this class of materials. Several  $\text{K}_2\text{NiF}_4$ -type phases with Fe(III) occupying the B-position have been reported in the literature. Examples are  $\text{CaLaFeO}_4$  (NGUYEN-TRUTH-DINH et al. 1980) or  $\text{SrLaFeO}_4$  (SOUBEYROUX et al. 1980), crystallizing in the space group  $I4/mmm$  which corresponds to the maximal topological symmetry for a  $RP$ -phase with  $n = 1$ . A substitution of 25% of the oxygen atoms by chlorine or bromine results in a symmetry reduction within the tetragonal crystal system (space group  $P4$ ) as described by ACKERMANN (1991) for the oxyhalides  $\text{Ca}_2\text{FeO}_3\text{Cl}$ ,  $\text{Sr}_2\text{FeO}_3\text{Cl}$  and  $\text{Sr}_2\text{FeO}_3\text{Br}$ . In the course of our own investigations we observed the structural symmetry  $P4/nmm$  for  $\text{Ca}_2\text{FeO}_3\text{Cl}$  which contradicts the findings of the previous study. The present paper reports these results and gives evidence that  $\text{Ca}_2\text{FeO}_3\text{Cl}$  has been described in an unnecessarily low space group symmetry.

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### Experimental details

Single crystals of  $\text{Ca}_2\text{FeO}_3\text{Cl}$  were obtained as a by-product in growth experiments aimed on the synthesis of dicalcium ferrate from a  $\text{CaCl}_2$  flux. Starting materials were precursors prepared at  $1150^\circ\text{C}$  from  $\text{CaCO}_3$  (Merck, 99%) and  $\text{Fe}_2\text{O}_3$  (Fluka, 99.9%) in the molar ratio 2:1. The sintered pellets were re-ground in an agate mortar: Dried  $\text{CaCl}_2$  (Merck, purum) was added and the compounds were mixed again; the nutrient to flux weight ratio was 1:3. A sample of 4g was placed in a 50 ml platinum crucible with a crimped platinum cover. The mixture was heated from  $100^\circ\text{C}$  to  $1050^\circ\text{C}$  in 9.5 h in a resistance heated furnace; it was held at this temperature for 6h in order to homogenize the melt, then cooled down to  $900^\circ\text{C}$  at a rate of  $5^\circ\text{C}/\text{h}$ . Subsequently the melt was cooled to  $400^\circ\text{C}$  with  $100^\circ\text{C}/\text{h}$ , where the crucible was removed from the furnace.

The product of the synthesis contained red-brown crystals of two different phases :  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and  $\text{Ca}_2\text{FeO}_3\text{Cl}$ . Due to the different optical characters (optically bi- and uni-axial, respectively), the crystal could be easily distinguished using a polarizing microscope.

Diffraction data for  $\text{Ca}_2\text{FeO}_3\text{Cl}$  were collected on a small platy specimen, about  $120 \times 120 \times 30 \mu\text{m}^3$  in size, on a Stoe-IPDS imaging plate single crystal diffractometer. The diffraction symmetry was consistent with the Laue group  $4/mmm$ . In order to study the systematic absent reflections in detail undistorted sections of the reciprocal space were calculated using the Stoe SPACE program. The analysis of the precession-type pictures unambiguously showed the absence of reflections  $(hk0)$  with  $h+k \neq 2n$ , implicating the tetragonal space group  $P4/nmm$ . An analytical absorption correction based on eleven indexed faces was applied. Data reduction included Lorentz and polarization corrections and was performed with the Stoe XRED-software package. Parameters of the data collection and of the subsequent structure refinement are summarized in Table 1.

Table 1: X-ray data collection and refinement parameters for  $\text{Ca}_2\text{FeO}_3\text{Cl}$ .

(A)	Crystal - cell data
$a$ (Å)	3.8381(4)
$c$ (Å)	13.685(2)
$V$ (Å <sup>3</sup> )	201.6(1)
Space group	$P4/nmm$
$Z$	2
Formula	$\text{Ca}_2\text{FeO}_3\text{Cl}$
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	3.61
$\mu$ (mm <sup>-1</sup> )	6.79
(B)	Intensity measurements
Crystal shape	Fragment of a plate
Crystal dimensions	$0.12 \times 0.12 \times 0.03$ mm
Diffractometer	Stoe IPDS
Monochromator	Graphite
X - ray radiation	Sealed tube MoK $\alpha$ (0.71073 Å)
X-ray power	50 KV, 40 mA
$\theta$ - range	$3.0^\circ - 28.1^\circ$

Reflection range	$ h  \leq 5;  k  \leq 5; -17 \leq l \leq 18$
Detector distance	60 mm
No. of exposures	180
Data collection time per exposure	3 min.
Rotation width per frame	$2.0^\circ$
Measured reflections	3343
Unique reflections in $4/mmm$	190
Observed reflections ( $I > 2 \sigma(I)$ )	163
$R_{\text{int}}$ for $4/mmm$	0.077
(C)	Refinement of the structure
Parameters used in the refinement	21
$R1$ ( $F_o > 4 \sigma(F_o)$ )	0.053
wR2 ( $F_o > 4 \sigma(F_o)$ )	0.166
Weighting parameter a, b	0.065, 2.535
Goodness of Fit	1.392
Final $\Delta\rho_{\text{min}}$ ( $e / \text{\AA}^3$ )	2.26
Final $\Delta\rho_{\text{max}}$ ( $e / \text{\AA}^3$ )	-1.31
$R1 = \Sigma   F_o  -  F_c   / \Sigma  F_o $	$wR2 = (\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w(F_o^2)^2))^{1/2}$
$w = 1 / (\sigma^2(F_o^2) + (aP)^2 + bP)$	$P = (2F_c^2 + \max(F_o^2, 0)) / 3$

Structure solution was initiated with the program SIR92 (ALTOMARE et al. 1992) using direct methods. The phase set with the maximum combined figure of merit resulted in an  $E$ -map, the most intensive peaks of which could be interpreted as the positions of the Ca-, Fe- and Cl-atoms. The structure was completed by difference Fourier calculations. This initial model was refined with the program SHELXL-93 (SHELDRICK 1993). X-ray scattering factors for neutral atoms were taken from the International Tables for Crystallography, Vol. C (WILSON 1995). Anisotropic displacement parameters for all atoms and a Larson-type extinction correction were included in the final full matrix least-squares cycles based on  $F^2$ . The refinements converged to a residual of  $R_1 = 0.053$  for 21 parameters. The largest parameter shift in the final cycle was  $< 0.001$ . Resulting fractional atomic coordinates, equivalent isotropic and anisotropic displacement parameters as well as selected interatomic distances and angles are listed in Tables 2 - 4. Crystal structure drawings were prepared with the program ATOMS (DOWTY 2000).

Table 2: Atomic coordinates and equivalent isotropic displacement factors.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Atom	Wyckoff-site	x	y	z	$U(\text{eq})$
Fe1	2c	0.25	0.25	0.7932(2)	0.0169(9)
Ca1	2c	0.75	0.75	0.6589(3)	0.0199(10)
Ca2	2c	0.75	0.75	0.9055(3)	0.0228(11)
Cl	2c	0.75	0.75	0.5760(3)	0.0256(12)
O1	4f	0.25	0.75	0.7679(6)	0.0208(21)
O2	2c	0.25	0.25	0.9307(11)	0.0255(32)

Table 3: Anisotropic displacement parameters ( $\text{\AA}^2$ ). The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$ 

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Fe	0.0137(11)	0.0137(11)	0.0235(15)	0	0	0
Ca1	0.0181(14)	0.0181(14)	0.0238(18)	0	0	0
Ca2	0.0213(14)	0.0213(14)	0.0258(20)	0	0	0
Cl	0.0263(18)	0.0263(18)	0.0243(23)	0	0	0
O1	0.0190(47)	0.0117(42)	0.0319(48)	0	0	0
O2	0.0186(48)	0.0186(48)	0.0396(80)	0	0	0

Table 4: Selected bond distances ( $\text{\AA}$ ) and bond angles (deg.)

Fe1	- O2	1.882(15)
	- O1	1.950(2) x 4
	- Cl	2.972(5)
Ca1	- O1	2.430(6) x 4
	- Cl	2.941(2) x 4
	- Cl	3.216(2)
Ca2	- O2	2.242(15)
	- O1	2.689(7) x 4
	- O2	2.736(2) x 4
O - Fe - O		
	O2 - Fe - O1	100.2(3) x 4
	O2 - Fe - Cl	180.00
	O1 - Fe - O1	159.5(4) x 2
	O1 - Fe - O1	88.19(1) x 4
	O1 - Fe - Cl	79.76(3) x 4

### Description of the structure and discussion

$\text{Ca}_2\text{FeO}_3\text{Cl}$  belongs to the  $\text{K}_2\text{NiF}_4$ -type which in turn is a special case of the structure family of the Ruddlesden-Popper phases. It can be considered as built by blocks of  $\text{CaFe}(\text{O},\text{Cl})_3$  perovskite-type units. Each unit cell contains two blocks stacked along the  $c$ -axis with a relative shift of  $\frac{1}{2} \mathbf{a} + \frac{1}{2} \mathbf{b}$  from one to another, interleaved with the adjacent layers of CaO and CaCl and connected by Ca-O and/or Ca-Cl bonds (cf. Fig. 1).

Concerning the oxygen atoms of the  $\text{FeO}_5\text{Cl}$  octahedra four basal (O1) and a single terminal (O2) ligand with bond distances of 1.950  $\text{\AA}$  and 1.882  $\text{\AA}$ , respectively, can be distinguished. As can be seen from Table 4 the Fe-Cl bond length has a significantly larger value of about 2.97  $\text{\AA}$ , resulting in a pronounced distortion of the corner sharing octahedra. A calculation of the bond valence for the chlorine atom using the parameters given by BROWN & ALTERMATT (1985) for the Fe-Cl bond pair results in a low value of 0.099 v.u. Therefore, it is questionable whether the Fe atom should be regarded as bonded to chlorine. Alternatively, the structure could be described as consisting of infinite layers of  $\text{FeO}_5$  pyramids with the central iron atom shifted from the plane defined by the four basal oxygen

ligands along [001]. Because of the deviation of the O1-Fe-O1 bond angle ( $159.5^\circ$ ) from the ideal value of  $180^\circ$ , the corner shared  $\text{FeO}_4$  plane is not regular. The two crystallographically independent Ca ions reside in the vacancies between the octahedral layers are coordinated by nine ligands each (Ca1:  $4\text{O1} + 5\text{Cl}$ ; Ca2:  $4\text{O1} + 5\text{O2}$ ). Concerning the bond valence sums (BVS) both calcium atoms differ considerably. Whereas the corresponding value for Ca2 is 2.048 v.u.(almost identical with the expected value of +2), the Ca1 atom is strongly underbonded (BVS = 1.544 v.u.). This indicates that Ca2 fits less well in its void compared with Ca1 and is subject to a tensional stress.

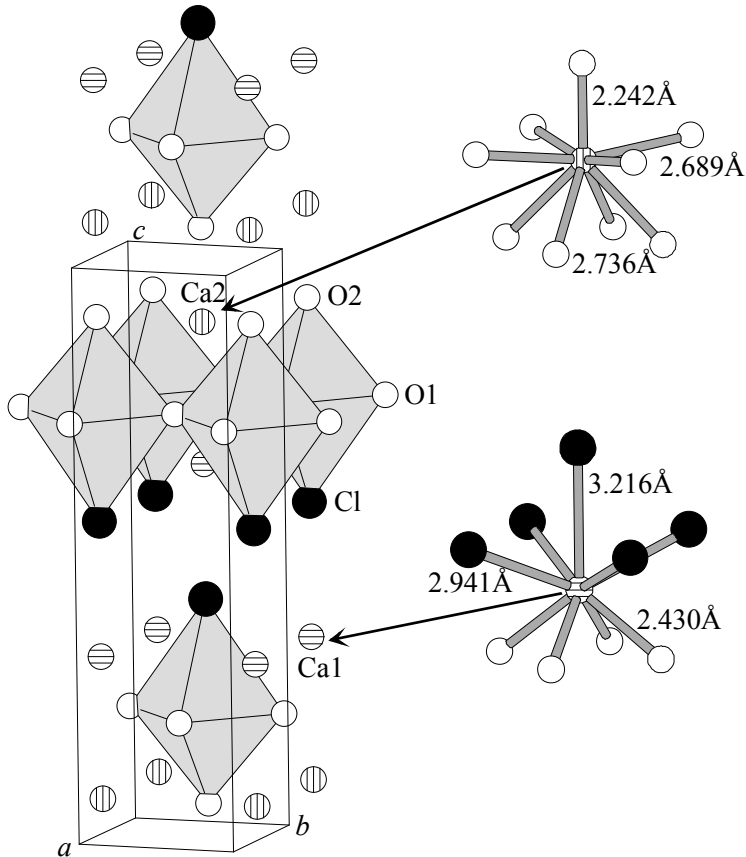


Fig. 1: Side view of the crystal structure of  $\text{Ca}_2\text{FeO}_3\text{Cl}$ , showing the coordination environments of the Ca- and Fe atoms.

A first structural characterization of  $\text{Ca}_2\text{FeO}_3\text{Cl}$  has been given by ACKERMANN (1991). Although the basic structural features were the same as in the present paper, it was suggested that the oxychloride crystallizes in the acentric space group  $P4$ . Concerning our own diffraction data we could not observe any violations of the systematic extinction rule for a  $n$ -glide plane perpendicular to [001]. The internal residuals for merging the data set in the two tetragonal Laue groups  $4/m$  and  $4/mmm$  were almost identical ( $R_{\text{int}}(4/m) = 0.076$ ;

$R_{\text{int}}(4/mmm) = 0.077$ ). The combination between the diffraction symmetry and the systematic absences implicates space group type  $P4/nmm$ . However, there are two further indications that suspicion has to be attached to a structure model in  $P4$ : (I) A careful analysis of the atomic coordinates given by ACKERMANN (1991) shows, that after shifting the origin by [0.25 0.25 0.209] six pairs of atoms can be found which are independent in the description in  $P4$ , but are symmetrically equivalent in  $P4/nmm$ . The shifts in the positional coordinates necessary to achieve the higher symmetry are less than 0.1 Å for all atoms. (II) A comparison between the bond distances for  $\text{Ca}_2\text{FeO}_3\text{Cl}$  obtained from a re-calculation using the atomic positions of the paper by ACKERMANN and those listed in the corresponding bond distance table of the same paper revealed pronounced discrepancies. Actually, the description in  $P4$  results in a single Fe-O<sub>term.</sub> bond length of 1.692 Å which is about 0.2 Å - 0.3 Å off the accepted range for Fe<sup>[6]</sup>. Furthermore, the estimated standard deviations (e.s.d.'s) given in the paper of ACKERMANN are very large, especially compared with the results of our refinements in  $P4/nmm$ . Large distortions of observed bond distances from accepted values as well as unusually high e.s.d.'s are typical warning signs frequently encountered when a structure is refined in an unnecessarily low space group symmetry (BAUR & TILLMANN 1986) and can be attributed to correlations between related parameters.

Due to the polar character of the space group proposed for  $\text{Ca}_2\text{FeO}_3\text{Cl}$  in the previous investigation, ABRAHAMS (1999) predicted that this compound may show ferroelectricity. The revised centrosymmetric model in space group  $P4/nmm$  precludes the existence of a ferroelectric effect in  $\text{Ca}_2\text{FeO}_3\text{Cl}$ .

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