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Synthesis, crystal structure, and properties of novel perovskite oxychalcogenides, Ca_2CuFeO_3Ch (Ch = S, Se)

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1. Introduction

The recent discovery of high-temperature superconductivity in an oxypnictide La(O,F)FeAs with a relatively simple LaOAgS structure [1] has triggered a burst of interest in search of novel representatives of known and novel structure types bearing [Fe₂As₂] and other antifluorite layers [2–4]. Most of this work has hitherto been done by analogy with the structures and compositions of oxychalcogenides, a family intimately related, both structurally and chemically, to the target pnictides. To the moment, the oxychalcogenides have been studied much more thoroughly as promising transparent semiconductors and ionic conductors (see the review [2] and references therein). It should be noted, however, that most structures of the oxychalcogenides and oxypnictides have been in their turn obtained by filling empty tetrahedral voids in the structures of layered oxyhalides, especially perovskite-derived, as has been pointed out earlier [2,5,6]. For instance, the structures of the most promising superconductors, i.e. Ln(O,F)FeAs [1], Sr₂VFeO₃As [3], and Sr₃Sc₂Fe₂O₅As₂ [4], are, in fact, the "filled-up" versions of the LnOCl (PbFCl) [6], Ca₂FeO₃Cl [7], and Sr₃Fe₂O₅Cl₂ [7,8] (Fig. 1). Thus oxyhalides may prove to be a good source of new charge reservoirs, both for new oxychalcogenides and oxypnictides. Even a cursory survey of the oxide halide family shows that whereas Ca²⁺ is a typical constituent of perovskite blocks therein (mostly together with Cu^{2+} or Fe^{3+} at the *B*-site [8–10]), this alkaline earth cation had

ABSTRACT

Two new perovskite oxychalcogenides, Ca_2CuFeO_3S and Ca_2CuFeO_3Se , have been synthesized in evacuated quartz tubes. They crystallize in *P4/nmm* space group with lattice parameters *a* = 3.8271(1), *c* = 14.9485(2) Å and *a* = 3.8605(1), *c* = 15.3030(2) Å for Ca_2CuFeO_3S and Ca_2CuFeO_3Se , respectively. They appear to be the first layered chalcogenide perovskites involving calcium and are structural analogs of the corresponding Sr and Ba compounds. The new compounds exhibit semiconducting properties with energy gap decreasing from the oxysulfide to the oxyselenide. Possibility of introducing Ca^{2+} into structures of known layered oxychalcogenides and oxypnictides is discussed.

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not yet been used to contribute to the chalcogenides. Two series of calcium-containing superconducting oxypnictides, $Ca_{n+1}(Sc,Ti)$ - $_nO_{3n-1}Fe_2As_2$ [11] and $Ca_{n+1}(Mg,Ti)_nOFe_2As_2$ [12,13], have been prepared recently, but most promising structure types, Sr_2VFeO_3As (Sr_2CuGaO_3S) and $Sr_3Sc_2Fe_2O_5As_2$ ($Sr_3Fe_2Cu_2O_5S_2$), remain yet unaddressed. The calcium-bearing oxyhalides were as yet obtained only among compounds of Cu and Fe. As both Fe^{3+} and Cu^{2+} are redox-incompatible with the pnictide anions, the search for new calcium-bearing compounds has been conducted among oxychal-cogenides. In the present paper, we report preparation, crystal structures and physical properties of the novel calcium compounds, Ca_2CuFeO_3S and Ca_2FeO_3Se , with the Sr_2CuGaO_3S -type [14] structure. They are structural analogs of the corresponding Sr-containing compound Sr_2CuFeO_3S , first reported by Zhu and Hor [15].

2. Experimental

2.1. Synthesis

The starting chemicals were CaO (calcined at 1100 °C for 48 h), CuO (obtained by thermal decomposition of Cu(NO₃)₂·3H₂O at 400 °C for 2 h), Fe (freshly reduced by hydrogen at 400 °C for 1 h), sulfur (melted *in vacuo* for 15 min to remove traces of water), selenium and tellurium (which were used as purchased). All chemicals were of analytically or extra pure grade. The studies were initially aimed at both possible stoichiometries, i.e. Ca₂CuFeO₃Ch and Ca₃Cu₂Fe₂O₅Ch₂. Thus, mixtures of CaO, CuO, Fe, and chalcogen in 2:1:1:1 or 3:2:2:2 ratios were thoroughly ground, pressed into pellets (at ca. 8 ton/cm² for 60 s), sealed in





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Fig. 1. The crystal structures (left to right) of (a) Sr₃Fe₂O₅Cl₂ and Sr₃Fe₂Cu₂O₅S₂; (b) Sr₂FeO₃Cl and Sr₂CuFeO₃S illustrating the "filling" concept.

evacuated quartz tubes (at the residual pressure of ca. 0.05 Torr), and annealed twice at 675 °C for 36 h for the Ca₂CuFeO₃Ch compositions, or 750 °C for 48 h for the Ca₃Cu₂Fe₂O₅Ch₂-aimed samples, with one intermediate re-grinding and re-pelletizing. The sulfide samples were pre-annealed at 400 °C for one day to ensure complete reaction of sulfur.

2.2. Characterization

Powder X-ray diffraction data were collected on a STOE STADI/P diffractometer (Cu K α_1 radiation, Ge-111 monochromator, transmission geometry) between $2\theta = 5-110^{\circ}$ at steps of 0.02° and counting time of 10 s. Ritveld refinements of both samples were performed with the TOPAS package [16] using pseudo-Voigt peak shape function. The structure of the Sr₂CuGaO₃S [14] was used for the starting coordinate values. Preferred orientation along [0 0 1] was corrected using a March-Dollase function.

Magnetic measurements were performed using a Quantum Design PPMS ac-susceptometer. In this standard method an alternating magnetic field is applied to the sample via copper drive coil, and a detection coil set (two counterwound copper coils connected in series) inductively responds to the combined sample moment and excitation field. The sample was placed inside one of the detection coils. Amplitude and frequency of the applied ac-field were 1 Oe and 137 Hz, respectively. The samples were cooled down in zero dc-field.

Resistivity measurements were performed using the standard 4-probe technique with a help of Stanford Research SR830 lock-in amplifier and SR560 preamplifier. Due to high sample resistance, we applied ac-currents as small as 10 nA. For low temperature measurements, a Dewar insert with CuFeCu thermocouple and a Lakeshore 340 temperature controller were used. For high temperature measurements, we used a high temperature insert, an oven, and a Cu–Constantan–Cu thermocouple. The temperature resolution of these thermocouples was ~10 μ V/K and ~20 μ V/K, respectively.

3. Results and discussion

3.1. New compounds and their properties

The X-ray diffraction data indicated formation of two target products, Ca_2CuFeO_3S and Ca_2CuFeO_3Se , brown in color. These phases are isostructural to Sr_2CuGaO_3S with two squarepyramidal oxide layers alternating with Cu_2Ch_2 (Ch = S, Se) block. A single phase was obtained for Ca_2CuFeO_3S . Some minor impurity peaks originating from $CuFeSe_2$ [17] were found in the X-ray diffraction pattern of Ca_2CuFeO_3Se and this phase was also included in the refinement. Details of the Rietveld refinements of both samples are listed in Table 1. Refined atomic positions are given in Table 2. The resulting bond distances are collected in Table 3 together with the data for related and isostructural compounds for comparison. Final Rietveld refinement plots are presented in Fig. 2.

In the $Ca_3Cu_2Fe_2O_5Ch_2$ -aimed samples, only $Ca_2Fe_2O_5$, CaCh (Ch = S, Se), and Cu₂Ch (Ch = S, Se) were observed after synthesis. In the case of samples containing tellurium no target compounds were observed. Attempts were also made to prepare analogous Ca₂CuMO₃Ch (M = Cr, Mn) and Ca₂AgFeO₃Ch compounds (under similar conditions), but yet also without success.

Temperature dependences of magnetic susceptibility of the synthesized samples are presented in Fig. 3(a) and (b). The two panels show two components (in-phase M' and out-of phase M'') of the ac-signal. For both samples, the in-phase component M' exhibits extrema and inflection as a function of temperature, whereas the out-of-phase component, which shows energy losses in the sample, exhibits several peaks. Obviously, there is an *anti*ferromagnetic transition with a Néel temperature T_N of ca. 150 K, also there are at least two transitions at lower temperatures (around 50 K and 30 K). Their nature is yet to be clarified by additional studies. If we compare our results to those for a similar compound Sr_2CuFeO_3S [18], we find a more complex behavior in our case.

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Table 1

Crystallographic data for Ca₂CuFeO₃S and Ca₂CuFeO₃Se.

Compound	Ca ₂ CuFeO ₃ S	Ca ₂ CuFeO ₃ Se		
Formula weight	559.225	653.012		
Crystal system	Tetra	Tetragonal		
Space group	P4/nmr	P4/nmm (#129)		
Cell parameters				
a, A	3.8269(1)	3.8596(1)		
<i>c</i> , A	14.9482(3)	15.2985(2)		
<i>V</i> , Å ³	218.91(1)	227.89(1)		
Calculated density (g/cm ³)	4.24	4.76		
Diffractometer	STOE			
Radiation	Cu Kα ₁ (λ	Cu K α_1 (λ = 1.54056 Å)		
29 range	5-110	5-110		
No. of reflexions	116	121		
No. of data points	10,499	10,499		
No. of structural parameters	13	17		
No. of overall parameters	37	46		
Analyzing package	Тора	Topas [13]		
Reliability factors				
R _n	0.014	0.011		
R	0.015	0.014		
xwp x ²	1 3 3	1 37		
X	1.55	1.57		

Table 2

Refined atomic coordinates for the Ca₂CuFeO₃Ch compounds.

Compound	Ca ₂ CuFeO ₃ S		Ca ₂ CuFeO ₃ Se	
Atom	z	B (Å ²)	z	$B(Å^2)$
Ca1 (0.75, 0.75, z) Ca2 (0.75, 0.75, z) Fe (0.25, 0.25, z) Cu (0.25, 0.75, 0) Ch (0.25, 0.25, z) O1 (0.25, 0.75, z) O2 (0.25, 0.25, z)	0.1890(3) 0.4130(2) 0.3099(2) 0 0.0981(3) 0.2889(3) 0.4392(6)	$\begin{array}{c} 0.52(8)\\ 0.52(9)\\ 0.51(6)\\ 1.53(5)\\ 0.5(1)\\ 1.0^{a}\\ 1.0^{a}\\ \end{array}$	0.1981(1) 0.4163(1) 0.3167(1) 0 0.1044(1) 0.2961(2) 0.4406(3)	$\begin{array}{c} 0.66(4) \\ 1.28(5) \\ 0.71(4) \\ 1.48(3) \\ 0.92(3) \\ 1.10(7)^{\rm b} \\ 1.10(7)^{\rm b} \end{array}$

^a Fixed.

^b Constrained to be equal.

Table 3

Selected bond lengths for Ca_2FeO_3Cl , Ca_2CuFeO_3S , Sr_2CuFeO_3S , and Ca_2CuFeO_3Se .

Compound	Ca ₂ FeO ₃ Cl [7]	Ca ₂ CuFeO ₃ S	Sr ₂ CuFeO ₃ S [15]	Ca ₂ CuFeO ₃ Se
$\begin{array}{c} \text{Ae1-O1}\times 4\\ \text{Ae2-O1}\times 4\\ \text{Ae2-O2}\times 4\\ \text{Fe-O1}\times 4\\ \text{Fe-O2}\times 1\\ \text{Cu-Ch}\times 4 \end{array}$	2.293 2.397 2.960 1.959 1.854	2.428(3) 2.664(3) 2.734(1) 1.9389(7) 1.933(9) 2.411(2)	2.512(7) 2.758(8) 2.774(2) 1.984(2) 1.91(1) 2.456(6)	2.444(2) 2.666(3) 2.7542(7) 1.9553(4) 1.895(5) 2.5055(6)



Fig. 2. (a) Observed (blue), calculated (red) and difference (gray) Rietveld plots for Ca₂CuFeO₃S. The vertical bars indicate the reflection positions. (b) Observed (blue), calculated (red) and difference (gray) Rietveld plots for Ca₂CuFeO₃Se. The vertical bars indicate the reflection positions. CuFeSe₂ was included in the refinement as impurity phase (content = 3.2%). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



Fig. 3. Temperature dependence of ac-susceptibility of (a) Ca_2CuFeO_3S and (b) $Ca_2CuFeO_3Se.$

Temperature dependences of the resistivity for the two samples are shown in Fig. 4(a) and (b). The Ca₂CuFeO₃S sample with an extremely high resistance was measured only in the temperature range from 260 K to 340 K. Its $\rho(T)$ dependence shows an approximately temperature activated type behavior, with activation energy about 0.17 eV. The deviation from the logarithmic law, obviously, indicates a change in type of conductivity The Ca₂CuFeO₃Se sample had a lower resistance and its $\rho(T)$ dependence was measured in the wider range 14–300 K. As seen from inset of Fig. 4(b), its *R*(*T*) dependence may be approximated with $R \propto \exp[(T_0/T)^{1/4}]$, which is typical for variable-range hopping transport.

3.2. Crystal chemistry

The two new compounds, Ca₂CuFeO₃S and Ca₂CuFeO₃Se, belong to the "42262" (Sr₂CuGaO₃S \equiv Sr₄Cu₂Ga₂O₆S₂) structure type. Upon comparison of structural data for Ca₂CuFeO₃S and Ca₂FeO₃Cl, one can see that the *a* cell parameters do not change significantly. It is also the case when passing from Sr₂FeO₃Cl to Sr₂CuFeO₃S. This indicates that the [Ae₂FeO₃]⁺ (Ae = Ca, Sr) block is relatively rigid, and the *a* cell parameters are more or less transferable within the structures involving them. This is not so much true for the Ca–O distances which change essentially from Ca₂FeO₃Cl to Ca₂CuFeO₃S. The bond length distribution in Ca₂FeO₃Cl, however, is broader as compared to both Sr₂CuFeO₃S and Ca₂CuFeO₃Ch. The reason may appear from differences in the strength of Ae–X and Ae–Ch bonds; unfortunately, there are no



Fig. 4. (a) Temperature dependence of resistivity of Ca_2CuFeO_3S . The inset shows a linear section of R(T) dependence in $\ln r - 1/T$ coordinates typical for temperature activation transport mechanism. (b) Temperature dependence of resistivity of Ca_2CuFeO_3Se . The insert shows a linear section of R(T) dependence in $\ln r - 1/T^4$ coordinates typical for variable-range hopping transport.

other data which permit direct comparison of Ae_2MO_3X and Ae_2CuMO_3Ch for the same couple of Ae and M. There is a small elongation of all Ca–O distances when passing from the sulfide to the corresponding selenide, as well as elongation of Cu–S distance when passing from Ca_2CuFeO_3S to Sr_2FeCuO_3S . This can be explained by increase of the *a* cell parameter when passing from Ca to Sr, or from S to Se.

A close look at Table 2 reveals a characteristic feature for the compounds bearing $[Cu_2X_2]$ anti-fluorite slabs (X = chalcogen or pnicogen), the unusually large thermal parameter for the Cu⁺ cations which suggests slight non-stoichiometry at this site. This issue has been addressed for a long time, and recently proven to occur due to reversible copper extraction resulting from oxidation by moist air [2]. The high thermal parameters of Cu in the Ca₂CuFeO₃Ch structures most likely illustrate the same phenomenon.

Our results confirm that the chemistry of layered perovskite oxide chalcogenides and pnictides is indeed not restricted to compounds of Sr and Ba, and calcium appears to be, at least within some structure types, just their smaller analog akin to the oxide halide family [8]. Considering the tendency of increasing the T_C of superconducting iron pnictides with decrease of cell dimensions in the *ab* plane (e.g. in the LnOFeAs family [19]), existence of calcium compounds is likely to provide another tool for chemical compression of the superconducting layers, al least in layered

perovskites. With calcium, we succeeded as yet in preparation of only Fe^{III} compounds, and this oxidation state is not directly transferable to pnictides due to redox incompatibility of Fe^{III} and Pn^{-III} [20]. Further studies of calcium compounds involving cations stable to reduction, e.g. Ga^{III}, are evidently necessary before we see whether isostructural Ca oxide pnictides can exist.

Unfortunately, the direct relationships between composition and structures are vet unknown as evidenced by the fact that the suggested Ca₃Ch₂Fe₂O₅Ch₂ compounds were not obtained. Though the differences in the *a* cell parameters between Ca₂FeO₃Cl and Ca₃Fe₂O₅Cl₂ are marginal, the double anionic layers in the former compound may be stuffed with Cu⁺ while in the latter, not as yet. Unless proper synthetic conditions have not been found, there seems to be a rather delicate interplay between the "42262" (Sr₂CuGaO₃S) and "32252" (Sr₃Cu₂Fe₂O₅S₂) structures both in the oxide chalcogenide and oxide pnictide families, the possibility of formation depending on the nature of both perovskite and antifluorite layers. Among compounds of Sr and Ba, for instance, the "42622" structure was observed with trivalent cations of Ga (CuS), In (CuS), Sc (FeAs, CrAs), V (FeAs), Cr (CuS, FeAs), Mn (CuS), and Fe (CuS) while the 32522 structure has been found for Sc (CuS, FeP, FeAs) and Fe (CuS, CuSe, AgS, and AgSe) [3,4,14,18,20–25]. In cases where both structures are formed, the differences in the *a* cell parameters are not so great as to suggest that the anti-fluorite layers should be strained too much to contribute to one structure but not to the other. Evidently, more thorough investigations of both structure types are necessary to discover the trends in relative stability of the structures in question. However, Ca²⁺ (and probably Eu²⁺) can be employed more widely to partially substitute for Sr²⁺ in the structures of existing FeAs superconductors as a "chemical press", to increase the transition temperature.

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