

Preparation and structural properties of new series of mixed-anion compounds: rare earth fluorosulfides

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Received 12 May 2000; received in revised form 25 July 2000; accepted 9 August 2000

Abstract

Rare earth fluorosulfides with the following compositions: LnSF and Ln₂AF₄S₂ have been prepared by solid state routes. These structures can be described as a stacking of fluoride-based slabs ([Ln₂F₂]⁴⁺ in LnSF and [Ln₂AF₄]⁴⁺ in Ln₂AF₄S₂) and double layers [S₂]⁴⁻. The fluoride blocks are related to fluorite-type structure. The relative compactness of the fluoride blocks leads to a relaxation of the Ln–S bond lengths. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Colour pigments; Fluorosulfides; Diffuse reflectance; Electronic transitions

1. Introduction

One of the main goals of the investigations carried out these last decades in Bordeaux in the field of solid state fluorine chemistry has been the search for new compounds exhibiting outstanding properties (see for example, contributions in “Inorganic Solid Fluorides” (1985) [1] and “Advanced Inorganic Fluorides” (2000) [2]).

Among these series, mixed-anion compounds containing fluoride ion aroused constant interest. Fluoride ions, because of their high electronegativity and large reactivity are able, indeed, to modify the nature of the structural arrangements and the charge density carried by polarizable cations. When the size of the anions is similar, they are often randomly distributed. This is the case for many examples taken from results obtained in the laboratory

- oxyfluorides of transition elements, such as for instance, FeOF of the rutile type-structure [3], Sr₂FeO₃F of the K₂NiF₄-type structure [4], Na₅W₃O₉F₅ of the chiolite-type structure [5], Na₃M(O, F)₆ of the cryolite type [6];
- fluoronitrides, such as Fe₄N₃F₃, with the spinel-type structure [7];
- fluorohydrides, such as CsCaF₂H, with the perovskite structure [8].

When the anions differ in polarizability the resulting structures often show strong anisotropy, leading to 2D or 1D character; this is the case of fluorohalides, such as EuFCl [9] of the PbFCl type, Ba₆Mn₂ZnF₁₂Cl₆ [10], Ba₂MM'F₇Cl [11], whose structures are related to 2D BaMF₄, Ba₁₂Cl₅F₁₉ or Ba₇Cl₂F₁₂ [12], with structures related to BaF₂ fluorite-type structure.

In the structure of EuFCl (PbFCl), sheets of more or less distorted tetrahedra [Eu₄F], disposed on a tetragonal symmetry alternate with a double layer of non-metal Cl. Numerous compounds adopt a structure deriving from the PbFCl type which can be described as a succession of [Pb₂F₂]²⁺ sheets and [Cl₂]²⁻ layers. In BaCuFS [13] for instance, the structure contains fluorite-like (Ba₂F₂)²⁺ layers alternating with anti-fluorite (Cu₂S₂)²⁻ type layers. Rare earth fluorosulfides LnSF (Ln = La–Er) have been prepared several years ago [14,15] and adopt also the PbFCl-type structure. However, the crystal structure had been partially described and the results were questionable [16].

Numerous rare earth sesquisulfides Ln₂S₃ in their high temperature γ form exhibit interesting chromatic properties and can be used as colour pigments [17,18]. Crystal field, exchange energy and nephelauxetic effect are determining factors for the electronic transition at the origin of the colour in these compounds. While most of rare-earth fluorides or oxyfluorides are colourless or lightly coloured, we have prepared, by two different routes, strongly coloured rare earth fluorosulfides. Powder X-ray diffraction analysis (Rietveld) has been undertaken in order to determine

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accurately the unit-cell parameters and the atomic positions in LnSF phases. New phases with $\text{Ln}_2\text{AF}_4\text{S}_2$ ($A = \text{Ca}, \text{Sr}$) chemical formula have been also prepared and the structure determined on single crystal and powder has been described by considering the LnSF and the fluorite-type structures. Four examples (CeSF , SmSF , $\text{Ce}_2\text{SrF}_4\text{S}_2$, $\text{Sm}_2\text{CaF}_4\text{S}_2$) will be considered in this paper.

2. Experimental

2.1. Sample preparation

Polycrystalline samples were synthesised by solid state reactions from stoichiometric mixtures of rare earth fluorides, binary fluorides AF_2 ($A = \text{Ca}, \text{Sr}$), and rare earth sulfides (α -form). The starting materials were mixed under a dry argon atmosphere in a glove box because of their sensitivity to oxygen and moisture. Ln_2S_3 - α (orthorhombic, SG: Pnma) were previously prepared from stoichiometric mixtures of pure rare earth metal and sulphur, slowly heated in sealed quartz tubes at 400°C during 24 h and at 700°C for 24 h. For LnSF, the reactions were carried out in a carbon crucible placed in a sealed quartz tube at 900°C for 24 h. For $\text{Ln}_2\text{AF}_4\text{S}_2$, the conditions of synthesis were the same as LnSF but the temperature of annealing was equal to 1100°C . In these last conditions single crystals of $\text{Sm}_2\text{CaF}_4\text{S}_2$ composition were obtained.

Another method of synthesis of LnSF phases was to heat the oxyfluoride LnOF at 700°C for 12 h under the following gas mixture: 75% Ar/12.5% CS_2 /12.5% H_2S . The oxyfluorides were prepared from Ln_2O_3 and LnF_3 powders mixed in stoichiometric proportions and annealed at 700 and 800°C , respectively, under Ar.

2.2. X-ray diffraction analysis

Weissenberg and precession photographs of $\text{Sm}_2\text{CaF}_4\text{S}_2$ single crystal showed a tetragonal symmetry belonging to the Laue class $4/mmm$ with systematic extinctions consistent with space group $I4/mmm$. Intensity data were collected on an Enraf Nonius CAD4 four-circle diffractometer using graphite monochromated $\text{Mo K}\alpha$ radiation. Intensity treatment and refinement calculations were performed using the SHELXL93 program [19]. The quality of the acquisition and refinement was based on the conventional reliability factors R_{int} and R_1 , wR_2 , respectively.

Complementary studies of LnSF and $\text{Ln}_2\text{AF}_4\text{S}_2$ phases were carried out by the Rietveld method. Powder X-ray diffraction profiles were recorded on a Philips PW 1050 in Bragg–Brentano geometry, using graphite monochromated $\text{Cu K}\alpha$ radiation. Data were collected over $10^\circ \leq 2\theta \leq 120^\circ$ in 0.020° with integration times of 40 s. The refinements were performed with the FULLPROF program package [20]. The background level was optimised with a polynomial function and the peak shape was fitted by a pseudo-Voigt

function. The reliability factors were the usual ones in the Rietveld method (R_B , R_p and R_{wp}) [21].

3. Structure determination

The $P4/nmm$ space group corresponding to the PbFCl -type structure is compatible with X-ray patterns of the LnSF phases ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}$). The a and c unit-cell constants of CeSF and SmSF are reported in Table 1. The lattice parameters decrease as the rare earth size diminishes. The rare earth and the sulphur atoms occupy the 2c site and the fluorine atoms are in 2a site. The experimental and calculated X-ray diffraction patterns are illustrated for CeSF in Fig. 1. The Rietveld refinements lead to satisfactory R values ($R_B = 3.06\%$; $R_p = 6.02\%$; $R_{\text{wp}} = 8.55\%$). The atomic positions and isotropic thermal displacements of LnSF ($\text{Ln} = \text{Ce}, \text{Sm}$) are given in Table 2. These new data differ from previous results obtained by Batsanov et al. [16] and Dagron et al. [15]. In order to confirm these results obtained on LnSF, EXAFS experiments have been undertaken on CeSF at the CeL_{III} edge. The spectra have been collected on station 7.1 of the CCLRC Daresbury synchrotron radiation source with beam currents between 150 and 250 mA. They were recorded on a transmission mode using a $\text{Si}(111)$ monochromator crystal and 50% of harmonic rejection. X-ray absorption spectra at the CeL_{III} -edge were reduced to normalised XAFS $\chi(k)$ using DARESBUURY software and weighted $k^3\chi(k)$ data analysed using the EXCURV suite of programs. Good quality spectra were obtained up to $k = 11 \text{ \AA}^{-1}$. A gaussian window were used for the Fourier transform. Atomic environments for cerium in CeSF have been refined to obtain the radial distance and the Debye–Waller factors associated with each of the Ce–F, Ce–S bonds and Ce–Ce shell (Fig. 2). Results are reported in Table 3a. Finally four Ce–F distances at 2.56 Å and five Ce–S distances at 2.92 Å have been refined. These results are in good agreement with those obtained from X-ray diffraction data refinement (Table 3b) The four Ln–F distances vary from 2.56 Å for Ce to 2.50 Å for Sm (Table 3c). As far as the Ln–S distances are concerned, the Ln–S bond values become smaller as the rare earth size decreases. Moreover, the four larger Ln–S bond lengths decrease more rapidly than the unique and smaller Ln–S distance and only one Ln–S bond length is found in the case of samarium. Our results reject, definitively, previous data on LnSF phases that

Table 1
Unit-cell constants of CeSF and SmSF

Compounds	Cell parameters (Å)
CeSF	$a = 3.9917(2)$
	$c = 6.9473(6)$
SmSF	$a = 3.8723(2)$
	$c = 6.8755(4)$

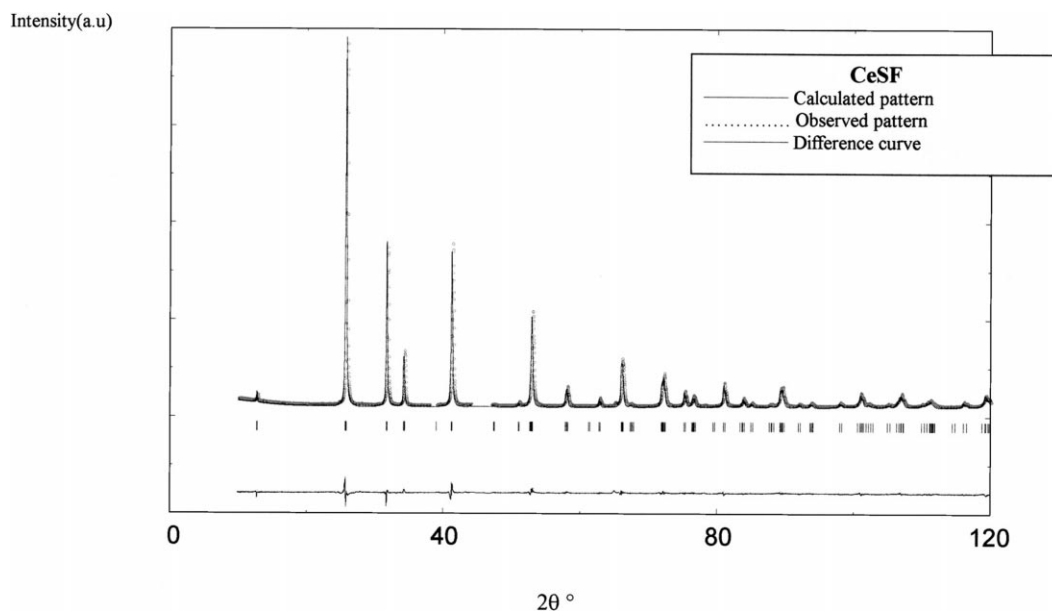


Fig. 1. Observed (dots), calculated (full line) X-ray diffraction patterns and difference curve of CeSF.

Table 2
Atomic positions, isotropic thermal displacements and reliability factors of LnSF phases (Ln = Ce, Sm)

Atoms	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
CeSF, (<i>R</i> _B = 0.036, <i>R</i> _p = 0.060, <i>R</i> _{wp} = 0.085)					
Ce	2c	1/4	1/4	0.2316(3)	0.65(4)
S	2c	1/4	1/4	0.648(2)	0.7(2)
F	2a	3/4	1/4	0	0.8(4)
SmSF (<i>R</i> _B = 0.047, <i>R</i> _p = 0.098, <i>R</i> _{wp} = 0.136)					
Sm	2c	1/4	1/4	0.2296(4)	0.24(6)
S	2c	1/4	1/4	0.6487(1)	0.2(2)
F	2a	3/4	1/4	0	0.7(4)

mentioned lower unit-cell parameters, shorter Ln–F bond distances and larger Ln–S distances.

The crystal structure of LnSF is shown on Fig. 3. The rare earth is at the center of a distorted square antiprism with four F atoms in one base and four S atoms in the other. A fifth Ln–S bond smaller than the other ones appears parallel to the *c*-axis. Such co-ordination is very typical of Sillén-phases. The structure can be described as a succession of various sheets of rare earth, fluorine and sulphur, the sequence being [S–Ln–F–Ln–S]–[S–Ln–F–Ln–S].

The rare earth and fluorine atoms form [Ln₂F₂]⁴⁺ layers where Ln₄F tetrahedra share four edges with four

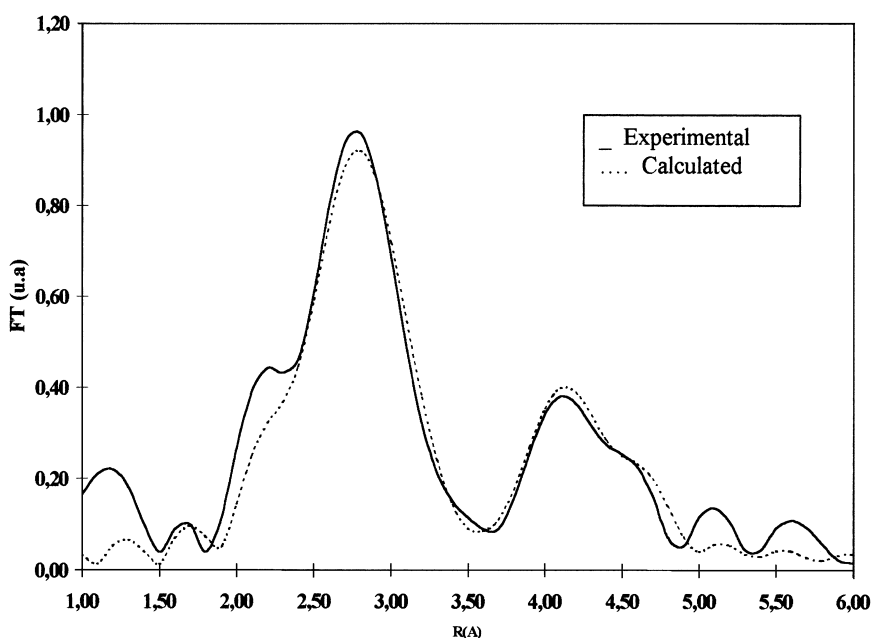


Fig. 2. Fourier transform of experimental and calculated XAFS spectra of CeSF at Ce L_{III} edge.

Table 3

Interatomic distances in CeSF taken from XAFS analysis (a) and Rietveld refinement (b) Interatomic distances in SmSF determined from XRD analysis (c)

	Ln–F (Å)	σ^2 (Å ²)	Ln–S (Å)	σ^2 (Å ²)	Ln–Ln (Å)	σ^2 (Å ²)
(a) Interatomic distances from XAFS analysis						
CeSF	2.56×4	0.017	2.92×5 4.02×1	0.012 0.012	3.97×4 4.27×4	0.013 0.021
(b) Rietveld refinement from XRD analysis						
CeSF	$2.564(2) \times 4$		$2.91(2) \times 1$ $2.940(3) \times 4$ $4.04(1) \times 1$		$3.992(1) \times 4$ $4.280(3) \times 4$	
(c) Interatomic distances from XRD analysis						
SmSF	$2.498(2) \times 4$		$2.87(2) \times 1$ $2.867(4) \times 4$			

neighboring tetrahedra in a tetragonal arrangement. In order to equilibrate charges, the $[\text{Ln}_2\text{F}_2]^{4+}$ fluorite-like layers alternate with double $[\text{S}_2]^{4-}$ layers along the *c*-axis.

In order to identify new phases with various successions of layers deriving from fluorite-type structure and Sillén-type phases, the $\text{Ln}_2\text{S}_3\text{--AF}_2$ (*A* = Ca, Sr) systems have been studied. In the experimental diffraction patterns, besides the peaks attributable to the ALn_2S_4 sulphides, new diffraction lines which were characteristic of one phase crystallising in tetragonal symmetry (Bravais mode: I) have been identified. The *a* parameter was almost identical to that of LnSF phase and the *c* value equal to $a(\text{AF}_2) + 2c(\text{LnSF})$, i.e. around 19 Å. $\text{Ln}_2\text{AF}_4\text{S}_2$ phases were discovered during the investigation of the $\text{AF}_2\text{--LnSF}$ systems.

The structure of a single crystal corresponding to $\text{Sm}_2\text{CaF}_4\text{S}_2$ composition has been solved in the $I4/mmm$ space group. Atoms have been placed by considering

conventional Patterson methods associated with a difference Fourier synthesis. The reliability factor $R_{\text{int}} = 0.0548$, $R_1 = 0.0151$ and $wR_2 = 0.0331$ are rather small. The atomic positions of heavy elements Sm and Ca have been firstly determined and correspond to $4e(0, 0, z)$ and $2b(0, 0, 1/2)$ positions. However, the isotropic thermal displacement is too small for the 2*b* site and too high for the 4*e* site, leading to consideration that there is a lack of electronic density for the Ca site (2*b*) and on the contrary, an excess of density in the case of the Sm site (4*e*). Finally, the 4*e* and 2*b* positions have been found to be partially occupied by Sm and Ca. Another 4*e* site is fully occupied by S atoms. On the other hand, the 16*n* site $(0, y \approx 0, 40, z)$ is half occupied by fluorine atoms. It can be noted that the 8*g* positions $(0, 1/2, z)$, close to the previous 16*n* ones, could not be taken into account because the isotropic thermal displacement was too high for this site.

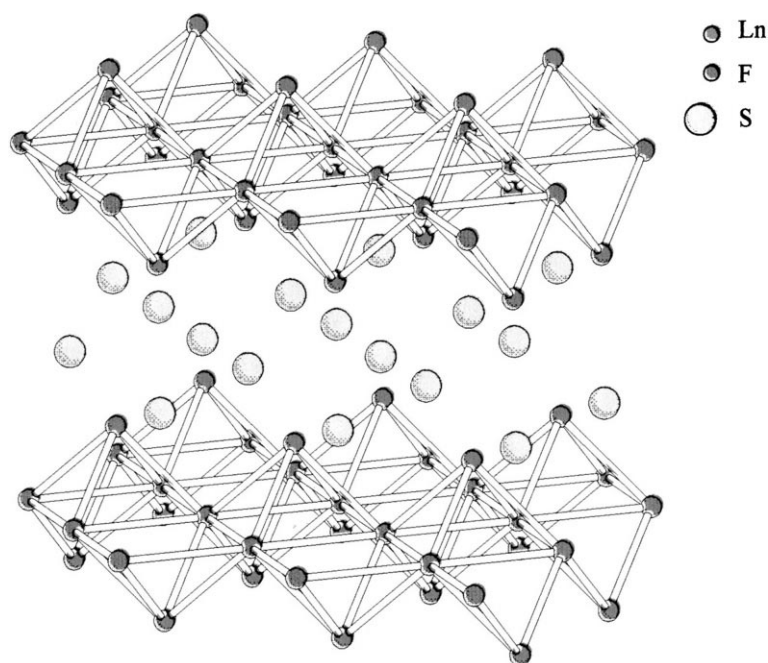


Fig. 3. Crystal structure of LnSF phases.

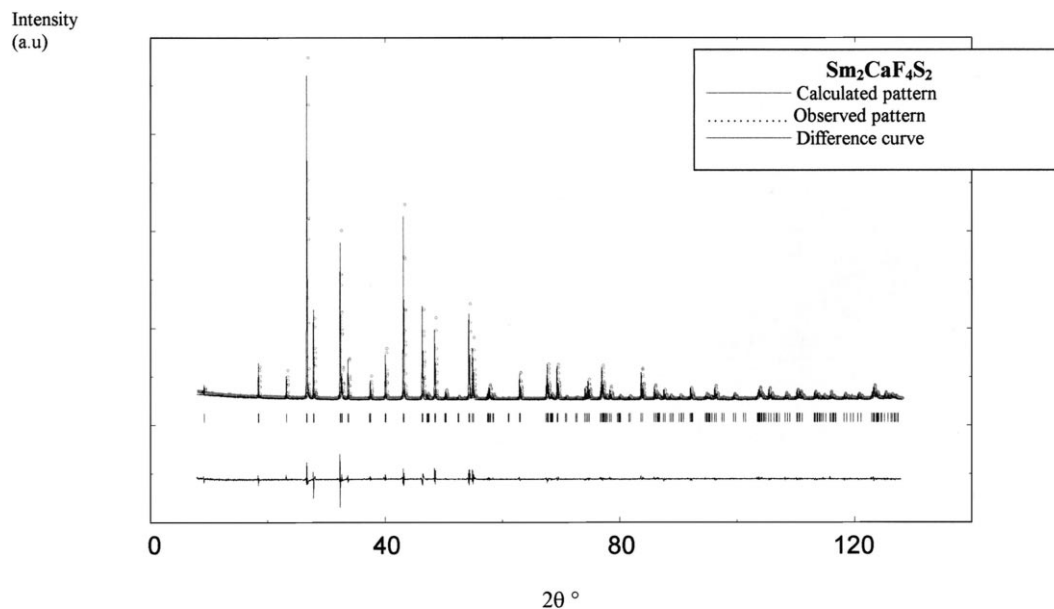


Fig. 4. Observed (dots), calculated (full line) X-ray diffraction patterns and difference curve of $\text{Sm}_2\text{CaF}_4\text{S}_2$.

In order to confirm this structural hypothesis, a Rietveld analysis have been performed on the powder X-ray diffraction pattern of $\text{Sm}_2\text{CaF}_4\text{S}_2$ compound (Fig. 4). The reliability factors are rather small ($R_B = 0.063$, $R_p = 0.163$, $R_{wp} = 0.188$). Thus, the occupancies of 4e and 2b sites corresponding to Sm and Ca atoms, determined on the basis of powder data, are in excellent agreement with the results obtained from single crystal analysis. The following formula can be written: $[\text{Sm}_{1.7}\text{Ca}_{0.3}] (4e) [\text{Ca}_{0.7}\text{Sm}_{0.3}] (2b) \text{F}_4\text{S}_2$. The structure of another compound of this type: $\text{Ce}_2\text{SrF}_4\text{S}_2$ has been determined on the basis of powder X-ray diffraction analysis (Rietveld). The atomic positions and isotropic thermal displacements of $\text{Ce}_2\text{SrF}_4\text{S}_2$ are compared with those of $\text{Sm}_2\text{CaF}_4\text{S}_2$ in Table 4. In this case, the following formula can be proposed: $[\text{Ce}_{1.6}\text{Sr}_{0.4}] (4e) [\text{Sr}_{0.6}\text{Ce}_{0.4}] (2b) \text{F}_4\text{S}_2$. The cell parameters of $\text{Ce}_2\text{SrF}_4\text{S}_2$ and $\text{Sm}_2\text{CaF}_4\text{S}_2$

phases are reported in Table 5. This evolution is in good agreement with the respective ionic radii of cations. The structure of $\text{Ln}_2\text{AF}_4\text{S}_2$ is represented in Fig. 5: the $[\text{Ln}_2\text{F}_2]^{4+}$ layers present in LnSF structure are replaced in these phases by larger sheets with $[\text{Ln}_2\text{AF}_4]^{4+}$ formulae. These sheets (Fig. 5) are always separated by double layers of sulphur atoms with $[\text{S}_2]^{4-}$ formula. In $[\text{Ln}_2\text{AF}_4]^{4+}$ blocks, Ln(A) (4e site) is at the vertex of a pyramid whose base is constituted by four F atoms, as in $[\text{Ln}_2\text{F}_2]^{4+}$ layers for LnSF compounds. Each F atom is shared by four pyramids. 8 F atoms in $[\text{Ln}_2\text{AF}_4]^{4+}$ blocks form a distorted cubic site which is occupied once over two by A(Ln) (2b site) atoms along a (and b) axis. When the center of the cube is empty, Ln(A) atoms in 4e site are present above and below the cube at the vertex of pyramids whose bases are constituted by the F atoms of the upper and lower faces of the cube. Conversely,

Table 4

Atomic positions and isotropic thermal displacements of $\text{Sm}_2\text{CaF}_4\text{S}_2$ and $\text{Ce}_2\text{SrF}_4\text{S}_2$ [Rietveld analysis on polycrystalline samples]

Atoms	Site	x	y	z	$B_{\text{eq}} (\text{Å}^2)$	Occupancies
$\text{Sm}_2\text{CaF}_4\text{S}_2$						
Sm1	4e	0	0	0.1564(1)	0.12(5)	0.86
Ca1	4e	0	0	0.1564(1)	0.12(5)	0.14
Sm2	2b	0	0	1/2	0.2(1)	0.28
Ca2	2b	0	0	1/2	0.2(1)	0.72
S	4e	1/2	1/2	0.1943(4)	0.3(2)	1
F	16n	0	0.391(4)	0.0638(8)	0.8(4)	0.5
$\text{Ce}_2\text{SrF}_4\text{S}_2$						
Ce1	4e	0	0	0.1586(3)	0.5(2)	0.80
Sr1	4e	0	0	0.1586(3)	0.5(2)	0.20
Ce2	2b	0	0	1/2	0.6(2)	0.39
Sr2	2b	0	0	1/2	0.6(2)	0.61
S	4e	1/2	1/2	0.1888(8)	1.3(4)	1
F	16n	0	0.384(8)	0.064(2)	1.4(9)	0.5

Table 5
Unit-cell constants of $\text{Ln}_2\text{AF}_4\text{S}_2$

Compounds	Cell parameters (Å)	
	<i>a</i>	<i>c</i>
$\text{Ce}_2\text{SrF}_4\text{S}_2$	4.0782(2)	19.637(1)
$\text{Sm}_2\text{CaF}_4\text{S}_2$	3.91594(5)	19.2530(5)

when A(Ln) atoms (2b site) are present inside the cube, there is no Ln(A) (4e site) above and below the cube. This arrangement in the $[\text{Ln}_2\text{AF}_4]^{4+}$ blocks is characteristic of the fluorite-type structure.

Thus, in $\text{Ln}_2\text{AF}_4\text{S}_2$, the A(Ln) (2b site) is eight-fold coordinated to fluorine, whereas Ln(A) (4e site) is four-fold coordinated to F^- ions and five-fold coordinated to sulphur as in LnSF . In $\text{Ce}_2\text{SrF}_4\text{S}_2$ and $\text{Sm}_2\text{CaF}_4\text{S}_2$ (Table 6), Ln(A)–F distances in both (4e) and (2b) sites are identical and are comparable to A–F bond lengths in AF_2 [$\text{Sr–F} = 2.47 \text{ \AA}$

Table 6
Co-ordination polyhedra of rare earths and alkaline earths in $\text{Ln}_2\text{AF}_4\text{S}_2$

$\text{Ce}_2\text{SrF}_4\text{S}_2$	$\text{Sm}_2\text{CaF}_4\text{S}_2$
Distances (Å)	
Ce(Sr) [4e site]–F: $2.43(3) \times 4$	Sm(Ca) [4b site]–F: 2.352×4
Ce(Sr) [4e site]–S(1): $2.944(4) \times 4$	Sm(Ca) [4b site]–S(1): 2.863×4
Ce(Sr) [4e site]–S(2): $2.99(2) \times 1$	Sm(Ca) [4b site]–S(2): 2.876×1
Sr(Ce) (2b site)–F: $2.44(2) \times 8$	Ca (Sm) [2e site]–F: 2.350×8

(SrF_2); $\text{Ca–F} = 2.36 \text{ \AA}$ (CaF_2)]. This result still shows that the $[\text{Ln}_2\text{AF}_4]^{4+}$ blocks have got the characteristics of the fluorite-type structure and explains the occurrence of a cationic disorder between rare earth and alkaline earth. Moreover, in order to keep equal distances between cations (Ln and A) and fluorine in $[\text{Ln}_2\text{AF}_4]^{4+}$ blocks, F^- ions are preferentially located in the 16n (0, $y \sim 0.4$, z) position, which is half occupied, rather than the 8g (0, $1/2$, z) position

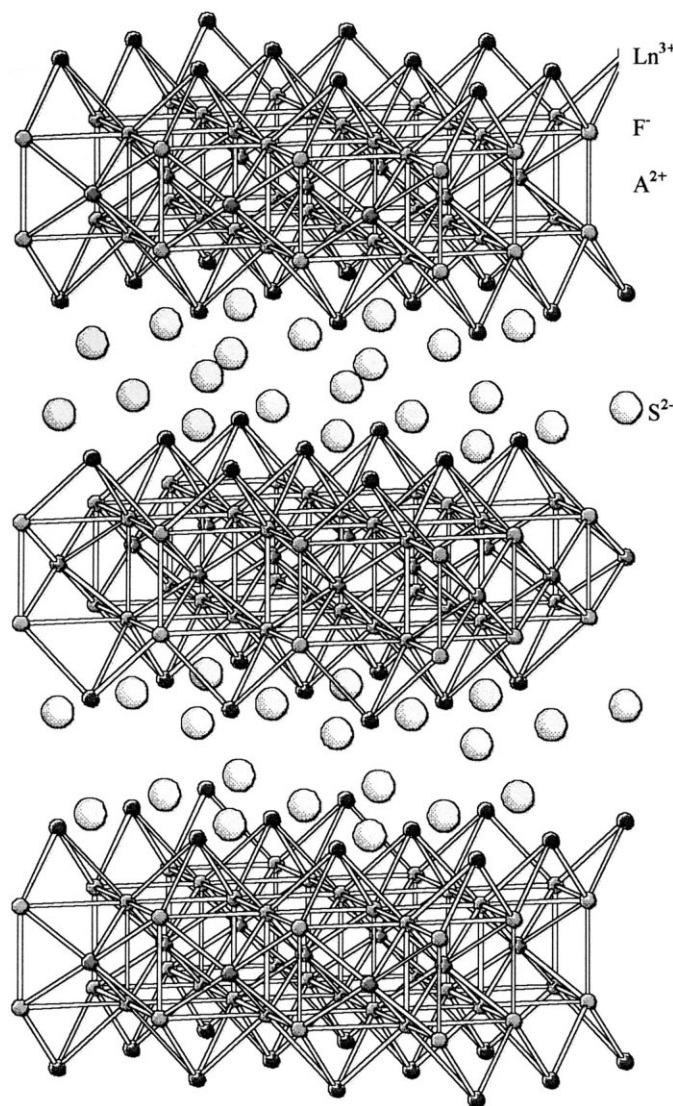


Fig. 5. Crystal structure of $\text{Ln}_2\text{AF}_4\text{S}_2$ phases.

which would be totally filled. When comparing the Ln–F and Ln–S bond distances in LnSF and Ln₂AF₄S₂, one should notice that in Ln₂AF₄S₂ the Ln(A)–F distances are shorter than in LnSF (compare, for instance, the couples Ce₂SrF₄S₂–CeSF and Sm₂CaF₄S₂–SmSF, (Tables 3 and 6)). Thus, the [Ln₂AF₄]⁴⁺ sheets are more compact than the [Ln₂F₂]⁴⁺ layers in LnSF. This leads to a more or less pronounced relaxation of Ln(A)–S distances in Ln₂AF₄S₂. For instance, in Ce₂SrF₄S₂ there are four short Ce(Sr)–S bond lengths equal to those found in CeSF (Ce–S = 2.94 Å). In addition, there is a longer one (Ce–S = 2.99 Å), longer than that identified in CeSF (Ce–S = 2.91 Å). This last Ce(Sr)–S chemical bond which appears along the c-axis is characteristic of the relaxation of [Ce₂SrF₄]⁴⁺ and [S₂]^{4–} sheets. In Sm₂CaF₄S₂, no relaxation is observed because all Sm(Ca)–S distances are equal to those found in SmSF.

4. Conclusion

LnSF and Ln₂AF₄S₂ phases adopt bi-dimensional structures as most of compounds containing mixed anions which differ by their size. Sulphur atoms are the most polarizable and are present in double layers [S₂]^{4–}. The size of this slab depends on the compactness of the fluoride-based sheets [Ln₂F₂]⁴⁺ in LnSF and [Ln₂AF₄]⁴⁺ in Ln₂AF₄S₂. The difference between these two phases results from the size of fluoride blocks which are related to fluorite-type structure. In these compounds, the nephelauxetic effect or the reduction of the electrostatic interaction, and the crystal field are stronger with sulphur than fluorine. The electronic transitions at the origin of the colour in most of these compounds are the result of a charge transfer mechanism from 3p (S) band to rare earths (4f, 5d) bands. The correlation between structural features and colour of the pigments will be the subject of a forthcoming paper.

References

- [1] P. Hagenmuller (Ed.), *Inorganic Solid Fluorides*, Academic Press, 1985.
- [2] T. Nakajima, A. Tressaud, B. Žemva (Eds.), *Advanced Inorganic Fluorides*, Elsevier, Amsterdam, 2000.
- [3] P. Hagenmuller, J. Portier, J. Cadiou, R. de Pape, C. R. Acad. Sci. 260 (1965) 4768.
- [4] L. Fournès, N. Kinomura, F. Ménil, C. R. Acad. Sci. 290 (1980) 235.
- [5] J. Ravez, M. Elaammani, J.P. Chaminade, *Solid State Commun.* 32 (1979) 749.
- [6] M. Hamadene, J. Grannec, J. Ravez, A. Laïdoudi, *J. Fluorine Chem.* 78 (1996) 141.
- [7] B. Tanguy, M. Pezat, A. Wold, P. Hagenmuller, C. R. Acad. Sci. 280 (1975) 1347.
- [8] M. Pezat, J. Sénégas, G. Villeneuve, H.H. Park, A. Tressaud, *J. Solid State Chem.* 77 (1988) 389.
- [9] B. Tanguy, M. Pezat, C. Fontenit, J. Portier, C. R. Acad. Sci. 280 (1975) 1019.
- [10] J. Darriet, M. Ducau, M. Feist, A. Tressaud, *Eur. J. Solid State Inorg. Chem.* 29 (1992) 435.
- [11] J. Fontpeyrine, J. Darriet, J.J. Maguer, J.M. Greneche, G. Courbion, T. Roisnel, J. Rodriguez-Carvajal, *J. Solid State Chem.* 131 (1997) 198.
- [12] B. Es-Sakhi, J.M. Tallon, A. Garcia, C. Fouassier, L. Struye, P. Willems, P. Leblans, 2000, in press.
- [13] W.J. Zhu, Y.Z. Huang, F. Wu, C. Dong, H. Chen, Z.X. Zhao, *Mater. Res. Bull.* 29 (5) (1994) 505.
- [14] J. Flahaut, *J. Solid State Chem.* 9 (1974) 124.
- [15] M.C. Dagon, F. Thevet, *Ann. Chim.* 6 (1971) 67.
- [16] S.S. Batsanov, V.S. Filatkina, G.N. Kustova, *Izv. Akad. Nauk SSSR, Ser. Khim.* 6 (1971) 1190.
- [17] R. Mauricot, P. Gressier, M. Evain, R. Brec, *J. Alloys Comp.* 223 (1995) 130.
- [18] H. Laronze, A. Demourgues, A. Tressaud, L. Lozano, J. Grannec, F. Guillen, P. Macaudière, P. Maestro, *J. Alloys Comp.* 275-277 (1998) 113.
- [19] G.M. Sheldrick, "SHELXL93, A Program for Refinement of Crystal Structure", University of Göttingen, Germany, 1993.
- [20] J. Rodriguez-Carvajal, FULLPROF, Vers. 3-2, LLB-CEA, Saclay, France, 1997.
- [21] H.M. Rietveld, *J. Appl. Crystallogr.* 2 (1969) 65.