**STRUCTURAL CHANGES AND SELF-ACTIVATED PHOTOLUMINESCENCE IN
REDUCTIVELY ANNEALED $\text{Sr}_3\text{AlO}_4\text{F}$**

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Abstract

White light emission of self-activated photoluminescence (PL) in $\text{Sr}_3\text{AlO}_4\text{F}$ under 254nm light is only observed after annealing in a reducing atmosphere of 5% H_2 /95% Ar. High-resolution neutron powder diffraction reveals that the FSr_6 octahedrons and AlO_4 tetrahedrons in this anti-perovskite structure are closer packed in reduced than in air-annealed samples which show no PL. Careful analysis of temperature-dependent neutron powder diffraction data establishes smaller isotropic displacement parameters for Sr(1) and O in $\text{Sr}_3\text{AlO}_4\text{F}$ annealed in a reducing atmosphere indicating that the denser packing of the polyhedral sub-units leads to a slightly deeper potential for the Sr(1) and O atoms. Both the air- and reductively-annealed samples have identical thermal expansion within the temperature range between 3 and 350 K. The Debye temperatures were calculated using the atomic displacement parameters and show no significant differences between the air and reductively annealed samples making the Debye temperature a bad proxy for self-activated PL.

Graphical Abstract

Annealing $\text{Sr}_3\text{AlO}_4\text{F}$ under reducing conditions results in an intense self-activated photoluminescence which is correlated with a denser packing of FSr_6 and AlO_4 polyhedra.

Keywords: $\text{Sr}_3\text{AlO}_4\text{F}$, photoluminescence, neutron powder diffraction

1.0 Introduction

Subtle details and minute changes to a material's structure and composition can have a major impact on its physical and chemical properties. Establishing meaningful structure-property relationships often calls for devising initial heuristic rules relying on the best structural models available. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, a material displaying a colossal dielectric constant over a range of temperature and frequencies has been investigated thoroughly over the past decade ¹⁻². A recent study using room temperature high-resolution synchrotron x-ray powder diffraction investigated Bragg peak asymmetries and concluded that the best agreement with the experiment is found for a two-phase cubic model pointing to a very subtle heterogeneous disorder ³ which might be related to earlier proposed models of off-center displacements of the Ca ions ⁴ and/or antisite Ca-Cu defects noticed in electron microscopy studies ⁵. Recent temperature-dependent x-ray pair distribution and EXAFS investigations uncovered in ZrW_2O_8 , a paradigmatic material with negative thermal expansion between 0.3 and 1000 K, found translational-rotational motions of polyhedral units which decrease void volume by moving WO_4 units into empty space without a substantial transverse motion of corner-lined atoms, a generally accepted model of NTE materials with linear oxygen-metal linkages ⁶⁻⁷.

In this work we investigate another nonlinear structure-property relationship and show that post-synthetic reductive annealing of the ordered oxyfluoride $\text{Sr}_3\text{AlO}_4\text{F}$ results in intense self-activated photoluminescence but only minute changes within its anti-perovskite structure. We advocate the careful use of temperature-dependent neutron

diffraction to probe and confirm minute structural changes as they allow relative comparison of static *and* dynamic features of a crystal structure.

The layered oxyfluorides $\text{Sr}_3\text{AlO}_4\text{F}$ and $\text{Sr}_3\text{GaO}_4\text{F}$ were structurally characterized in the late 1990s⁸. Since then, members of this structural family have been explored as phosphors for solid-state lighting by Park *et al*⁹, Chen *et al*¹⁰, Bin Im *et al*¹¹, Setlur *et al*¹², Shang *et al*¹³, Ning *et al*¹⁴, Zheng *et al*¹⁵, Sun *et al*¹⁶ and progress has been summarized by Sullivan¹⁷. The most important phosphors for this application are based on substituting alio- and isovalent Ce^{3+} and Eu^{2+} activators into the $\text{Sr}_3\text{AlO}_4\text{F}$ host lattice.

Experiments established that $\text{Sr}_3\text{AlO}_4\text{F}$ can exhibit self-activating photoluminescence when excited with 254nm light after being annealed in a reducing (5% H_2 /95% Ar) atmosphere¹⁸. In addition to heating these materials in a reducing atmosphere, the color emitted by self-activating $\text{Sr}_3\text{AlO}_4\text{F}$ can be tailored by substitutions on the Sr(1), Sr(2) and Al sites in the host structure as well as by varying the gas flow rate and annealing temperature in the reducing atmosphere¹⁸. The measurements of the decay times of $\text{Sr}_3\text{AlO}_4\text{F}$ as well as the intensity of the photoluminescent intensity varies strongly with the synthesis conditions such as annealing temperature and the flow rate of the 5% H_2 /95%Ar gas. The decay times indicate a multiexponential decay with a fast and slower component after annealing in a reducing gas environment. This points to the existence of two distinct defect cluster responsible for the self-activating PL. The intensity of this emission increases at annealing temperatures of 900 °C. We have therefore chosen to use the same synthesis conditions, annealing temperature and flow rates based on our previous work¹⁸ to make the $\text{Sr}_3\text{AlO}_4\text{F(r)}$ and maximize the PL emission and therefore the presence of defect clusters responsible for it. The structural

changes caused by a reducing atmosphere have not been studied in detail. We investigated what occurs structurally when $\text{Sr}_3\text{AlO}_4\text{F}$ is annealed in a reducing 5% H_2 /95% Ar atmosphere using room temperature and temperature-dependent high-resolution neutron diffraction data as the atomic scattering factors are independent of the neutron's momentum transfer and more reliable displacement parameters can be obtained.

One way to describe $\text{Sr}_3\text{AlO}_4\text{F}$ is as an ordered and layered oxyfluoride structure with an anti-perovskite structure where FSr_6 octahedrons form a ReO_3 network which creates large cavities in which AlO_4 tetrahedrons can be accommodated. In another description we have alternating ionic Sr_2F^{3+} and covalent SrAlO_4^{3-} layers which create different coordination environments for the two distinct Sr atoms. The Sr atoms located in the SrAlO_4 layer will be designated as Sr(1) and are 10-coordinated by two fluorine atoms located opposite to each other and eight oxygen atoms connected to nearby AlO_4 tetrahedrons. The Sr(2) atoms in the Sr_2F layer are 8-coordinated and each Sr(2) atom is bonded to two F atoms as well as three oxygen atoms above and below the plane.

Structural analysis of $\text{Sr}_3\text{AlO}_4\text{F}$ structures using the bond valence method¹⁰ and comparing the sum of the individual bond valences to the formal charges of the atoms/ions in the structure reveal that Sr(1) is significantly “underbonded” as its valence sum of 1.30 indicates⁸. This explains why larger ions such as Ba^{2+} can readily be substituted into this site. Prodjosantoso *et al.* showed by structural refinements of x-ray powder diffraction data that the smaller Ca^{2+} ions preferentially occupy the Sr(2) sites, while the larger Ba^{2+} ions have a tendency to occupy the Sr(1) sites¹⁹.

2. Materials and Methods

The $\text{Sr}_3\text{AlO}_4\text{F}$ samples were synthesized using the solid-state method, where the solid starting materials SrCO_3 (Sigma-Aldrich, 99.995%), Al_2O_3 (Sigma-Aldrich, 99.95%), and SrF_2 (Sigma-Aldrich, 99.995%) were mixed thoroughly in an agate mortar and pestle followed by heating in 24 hour cycles at 700 °C, 800 °C and 900 °C. These samples were annealed in air for 48 hours at 1050 °C. Initial structural information was determined by data collected by a Rigaku Miniflex diffractometer with Cu- α radiation ($\lambda = 1.5406\text{\AA}$) over a range of 3° - $149^\circ 2\theta$. Once the diffraction pattern did not exhibit any discernable impurities, it was heated for 3 hours at 900°C in a 5% H_2 /95%Ar atmosphere. This caused the materials to show self-activated photoluminescence. Photoluminescence data was collected using a Perkin Elmer LS 55 fluorescence spectrometer, which uses a xenon flash tube as its source. The excitation and emission slit widths were set at 15 nm and 20 nm, respectively since a fiber optic attachment was used. The $\text{Sr}_3\text{AlO}_4\text{F}$ samples were sealed in a vanadium container using an indium wire to ensure no oxidation during the collection of neutron powder diffraction data. Initial room temperature data were collected with neutrons having $\lambda = 1.300\text{\AA}$ using a Ge 337 monochromator at the Echidna high-resolution powder diffractometer located at the OPAL research reactor of the Australian Nuclear Science and Technology Organization (ANSTO). In order to minimize systematic errors and allow for relative comparison, both samples were initially measured at room temperature using the same instrumental configuration one after the other. Temperature dependent neutron diffraction data of the air and reductively annealed $\text{Sr}_3\text{AlO}_4\text{F}$ samples were also collected on Echidna collected

using neutrons with $\lambda = 1.6215 \text{ \AA}$ and varying the temperature from 3 - 350 K. Both samples were measured using the same experimental setup.

The GSAS suite of programs was used to analyze the neutron diffraction data presented. We refined the lattice parameters, atomic coordinates, isotropic displacement parameters, scale factor, pseudo-Voigt peak profiles and background parameters²⁰. The parameters reported in Vogt *et al*⁸ were used as starting model.

3. Results and Discussion

3.1 Photoluminescence of $\text{Sr}_3\text{AlO}_4\text{F}$

$\text{Sr}_3\text{AlO}_4\text{F}$ samples show strong self-activated photoluminescence (PL) only when annealed in a 5% H_2 /95% Ar atmosphere. When samples were annealed in pure Ar gas or air, the samples do not show any PL. The self-activated photoluminescence in $\text{Sr}_3\text{AlO}_4\text{F}$ can be tailored by varying the temperature and gas flow rate in the reducing step¹⁸. In this study, the samples were tempered for three hours in a 5% H_2 /95% Ar atmosphere in a tube furnace at 900 °C, which resulted in a fine powder that has a bright white color when excited by 254 nm light as shown in Figure 1.

Figure 1: Photoluminescence of a) $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$, (b) $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$, and (c) SrF_2 powders when activated with UV lamp at $\lambda = 254 \text{ nm}$.

The corresponding PL spectrum of $\text{Sr}_3\text{AlO}_4\text{F}$ after annealing in a reducing atmosphere (5% H_2 /95% Ar) is shown in Figure 2 and reveals a broad-band emission between 430-650 nm. The excitation spectra has a maximum intensity near 250 nm and a lower intensity shoulder near 230 nm. The maximum emission is near 495 nm when excited with 250 nm light. However, the PL spectra in Figure 2 also show that the sample annealed in air, $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$, has a minute PL emission intensity. This small PL emission is due to a SrF_2 impurity. When compared to the PL spectra of pure SrF_2 shown in Figure 3, both emission spectra show peaks near 488 nm, confirming the presence of SrF_2 as an impurity. Work by us and others has shown SrF_2 to always be present as a small impurity in $\text{Sr}_3\text{AlO}_4\text{F}$ and other related systems as corroborated by Im *et al* in $\text{Sr}_{2.975}\text{Ba}_x\text{Ce}_{0.025}\text{AlO}_4\text{F}$ ¹¹ and Setlur *et al* in $(\text{Sr}_{0.5925}\text{Ca}_{0.4}\text{Ce}_{0.0075})_3\text{Al}_{0.6}\text{Si}_{0.4}\text{O}_{4.4225}\text{F}_{0.5775}$ ¹². The $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ samples also had small traces of this impurity, however, the high PL intensity of the $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ phase masks the PL of SrF_2 . The main phase of the $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ sample annealed in air shows no self-activated PL as depicted in Figure 3. The observed PL can be completely accounted for by SrF_2 .

Figure 2: Photoluminescence emission and excitation spectra of $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ samples.

Figure 3: Comparison of photoluminescence of $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and SrF_2 under UV light with $\lambda_{\text{ex}} = 254\text{ nm}$.

3.2 Room Temperature High-Resolution Neutron Powder Diffraction

The two Rietveld refinements of the room temperature neutron diffraction data show a slight change of the lattice parameters as well as site coordinates in the unit cell between $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$. Using the GSAS suite of programs, the same 42 variables were refined against the neutron diffraction data for both $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$. Plots based on the refined models for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ agree well with the experimental data and are shown in Figures 4 and 5 respectively. These plots also show that a 2-phase refinement was needed to fit the diffraction data for both the air-annealed and reduced samples, with SrF_2 as a second phase. The phase fraction of SrF_2 is 0.3 wt.% in the $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and 0.14 wt.% in the $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ sample.

Comparing the unit cell parameters of $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ with $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ shows a 0.11% smaller a -parameter while the c -parameter is 0.016 % larger. The unit cell volume decreases by ≈ 0.2 % from $513.84(2) \text{ \AA}^3$ in $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ to $512.76(2) \text{ \AA}^3$ in $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$. The site coordinates and refined displacement parameters of $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ are given in Table 1 and 2, respectively. In addition to these tables, selected distances and angles are given for both refined models in Table 3, where the difference normalized to the estimated standard deviation Δ_{esd} is used to assess the significance of the changes in distances and bond angles. This value is calculated by:

$$\Delta_{\text{esd}} = (d_{(\text{r})} - d_{(\text{air})}) / \sigma \quad (1)$$

, where $d_{(\text{air})}$ represents a refined parameter for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$, $d_{(\text{r})}$ is a refined structural parameter for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$, and σ represents the standard deviation of the structural parameter. For the following a Δ_{esd} value greater than 5σ is considered to be a significant change and (-) values indicates a decrease and (+) values indicate an increase when

comparing air and reductively annealed samples. The change in lattice parameters is significant as indicated by a $\Delta_{\text{esd}} = -76\sigma$ for the decrease in the a -parameter and 7.5σ for the increase in the c -parameter after $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ is annealed in a reducing atmosphere.

The associated bond distances and angles of $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ listed in Table 3 show that there is a minute but significant elongation of the Sr(1)-F bonds commensurate with the expansion of the lattice parameter along c . This in turn causes a minute distortion of the F-Sr₆ octahedron within the $\text{Sr}_3\text{AlO}_4\text{F}$ structure. The greatest change in bond distances was found between Sr(1) and Al ($\Delta_{\text{esd}} = -63\sigma$) and provides a measure for the separation of the F-Sr₆ and AlO₄ subunits in $\text{Sr}_3\text{AlO}_4\text{F}$. A smaller separation and an increase of the tilt angle from $17.86(6)^\circ$ to $17.97(6)^\circ$ ($\Delta_{\text{esd}} = 3.7\sigma$), indicates that the AlO₄ tetrahedron are packed more efficiently within the ReO₃-type lattice made by corner-sharing F-Sr₆ octahedron after being annealed in a 5% H₂/95% Ar atmosphere. The representative changes in the structure between $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ are illustrated in Figure 6.

Figure 4: Rietveld refinement plot of neutron diffraction data of $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$. The red green and pink profiles represent the observed, calculated and difference plots, respectively. The black vertical lines represent the peaks in the $\text{Sr}_3\text{AlO}_4\text{F}$ phase, while the red vertical lines represent the peaks in the SrF_2 phase.

Figure 5: Rietveld refinement plot of neutron diffraction data of $\text{Sr}_3\text{AlO}_4\text{F}_{(r)}$. The red green and pink profiles represent the observed, calculated and difference plots, respectively. The black vertical lines represent the peaks in the $\text{Sr}_3\text{AlO}_4\text{F}$ phase, while the red vertical lines represent the peaks in the SrF_2 phase.

Table 1: Refined lattice parameters and atomic positions for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$

Atom	Wyckoff position	x	y	z	Occupancy	$U_{\text{iso}} \times 100$
Sr(1)	$4a$	0	0	0.25	1	1.49(5)
Sr(2)	$8h$	0.1695(2)	0.6695(2)	0	1	0.56(3)
Al	$4b$	0	0.5	0.25	1	0.61(7)
F	$4c$	0	0	0	1	1.13(5)
O	$16l$	0.1418(1)	0.6418(1)	0.6483(1)	1	1.08(2)

Crystallographic data: Space group = $I4/mcm$, $a = 6.7873(1) \text{ \AA}$, $c = 11.1542(2) \text{ \AA}$,
Vol. = $513.84(2) \text{ \AA}^3$. $\chi^2 = 1.730$, $R_{\text{wp}} = 7.18 \%$, $R_p = 5.52 \%$.

Table 2: Refined lattice parameters and atomic positions for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$

Atom	Wyckoff position	x	y	z	Occupancy	$U_{\text{iso}} \times 100$
Sr(1)	$4a$	0	0	0.25	1	1.33(5)
Sr(2)	$8h$	0.1689(1)	0.6689(1)	0	1	0.54(3)
Al	$4b$	0	0.5	0.25	1	0.38(7)
F	$4c$	0	0	0	1	1.10(5)
O	$16l$	0.1416(1)	0.6416(1)	0.6484(1)	1	0.97(2)

Crystallographic data: Space group = $I4/mcm$, $a = 6.7797(1) \text{ \AA}$, $c = 11.1557(2) \text{ \AA}$,
Vol. = $512.76(2) \text{ \AA}^3$. $\chi^2 = 1.550$, $R_{\text{wp}} = 6.90 \%$, $R_p = 5.33 \%$

Figure 6: Structural changes in FSr_6 octahedrons, a lattice parameter and the separation of FSr_6 and AlO_4 subunits between air and reductively annealed Sr_3AlO_4 samples expressed in Δ_{esd} .

Table 3: Changes between distances and angles in $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$. In bold are changes larger than 5σ .

$\text{Sr}_3\text{AlO}_4\text{F}$	$\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ (Å)	$\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ (Å)	Δ_{esd} ($N\sigma$)
	NPD	NPD	
<i>a</i> -parameter (Å)	6.7873(1)	6.7797(1)	-76σ
<i>c</i> -parameter (Å)	11.1542(2)	11.1557(2)	7.5σ
Volume (Å ³)	513.84(2)	512.76(2)	-56σ
Sr(1)-O (x8) (Å)	2.8503(7)	2.8478(7)	-3.6σ
Sr(1)-F (x2) (Å)	2.78854(6)	2.78898(6)	7.3σ
Sr(2)-O (x2) (Å)	2.453(2)	2.458(2)	2.5σ
Sr(2)-O (x4) (Å)	2.690(1)	2.685(1)	-5σ
Sr(2)-F (x2) (Å)	2.5211(4)	2.5199(4)	-3σ
Sr(1)-Al (Å)	3.39365(6)	3.38986(6)	-63σ
Al-O (x4) (Å)	1.771(1)	1.768(1)	-3σ
O-Al-O	114.20(4)°	114.25(4)°	1.3σ
O-Al-O	100.37(8)°	100.29(8)°	-σ
F-Sr(2)-F	144.28(6)°	144.06(6)°	-3.7σ
Sr(2)-Sr(1)-Sr(2)	100.667(8) °	100.757(8) °	11.4σ

On the basis of these two room temperature refinements we cannot have confidence in differences of Sr(1)/Sr(2)-O distances. Furthermore, the bond valence sum values for all atoms of $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ listed in Supplementary Table 1 reveal that they are essentially the same and in good agreement with the values published by Vogt *et al.*⁸. The calculation of the atomic discrepancy factors and global instability indices (*G*) listed in Supplementary Table 2 also show that there are no significant changes based on metrics relying on bond lengths.

3.3 Temperature-Dependent Structural Studies

While our initial room temperature neutron diffraction experiments described above clearly point to the existence of a more dense structure and minute distortions in $\text{Sr}_3\text{AlO}_4\text{F}$ after annealing under reducing conditions we decided that a high-resolution temperature-dependent structural investigation could possibly reveal more subtle differences between $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$. Under-bonding of atoms as indicated by a BVS of 1.3 for Sr(1) can often be a proxy for low energy optical modes (“rattling modes”) as found in clathrates and skutteridites²¹⁻²² and result in temperature-dependent distortions and even phase transitions.

We therefore determined the structures of $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ between 3K and 350K. The refined lattice parameters as a function of temperature are given in Supplementary Table 3 and are shown in Figures 7a and b. The observation that in $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ the a lattice parameter is smaller and the c lattice parameter larger holds for the whole temperature range. Furthermore, as the temperature increases from 3K to 350K the a parameter expands by 0.51 %, while the c parameter expands only by 0.13 % in both $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$. Intriguingly, the lattice parameters for both samples have identical thermal expansion coefficients even though $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ is packed more efficiently. The Sr(1)-Al distance indicating this more efficient packing also reveals similar temperature-dependent changes (Figure 7e).

The temperature-dependent changes of the Sr(1)-O and Sr(1)-F (Figure 7f and 7g) distances are due to the opposite behavior of the a - and c -lattice parameter.

(a)

(b)

(c)

(d)

(e)

(f)

(g)

Figure 7: Plots of lattice parameters, selected bond distances and thermal expansion coefficients between 3 and 350 K for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$. The errors are smaller than the symbols.

Careful analysis of the temperature-dependence of the Al-O bonds points to an average increase by $0.001 \text{ \AA}$ ($\approx 0.1\%$ and $\Delta_{\text{esd}} = 1.6\sigma$) of this distance in the $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ sample.

The refinement of multiple independent structural models at different temperatures provides us with more confidence that this very small expansion is significant. The same holds for the changes in Sr(1)/Sr(2)-O distances. The Al-O expansion combined with the contraction of the a parameter and Sr(1)-O bonds causes the tilt angles to slightly increase in the $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ sample. Figure 8a and b shows the changes in the Al-O bond length and the tilt angles between $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$, respectively with the latter revealing a decreasing trend as the temperature increases.

Figure 8: Plots of Al-O distance (a) and tilt angles (b) as a function of temperature for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ from 3 – 350 K. The errors are smaller than the symbols.

In $\text{Sr}_3\text{AlO}_4\text{F}$, the octahedrons rotate by approximately 18° about the c-axis (Figure 6b)^{19, 23-24}. The direction of the rotation alternates from one layer to the next and is described using the Glazer notation as $a^0a^0c^-$. As larger species are accommodated in the cavity created by the corner-sharing FSr_6 octahedrons the tilt angle will become smaller²⁵⁻²⁶. These temperature-dependent studies provide us with more confidence that minute structural changes occur. They do not affect the overall stability of the $\text{Sr}_3\text{AlO}_4\text{F}$ structure as indicated by the bond valence sum and the global instability index G as shown in Supplemental Table 4.

3.4 Isotropic displacement parameters

The isotropic displacement parameters for each atom in $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ increase as a function of temperature. Comparing the displacement parameters for the individual atoms of the $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ samples significant general trends can be seen: the values for the Sr(2), and F atoms are the same, whereas the ones for Sr(1) and O shows consistently smaller values in the $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$

sample. While the bond valence sum values which are based on inter-atomic distances do not show any changes after annealing in a reducing environment the isotropic displacement values clearly reveal that they are smaller in $\text{Sr}_3\text{AlO}_4\text{F}_{(x)}$ over the whole temperature range. A simple way of describing these dynamic changes is that the more efficient packing of the AlO_4 tetrahedrons within the cavities of the ReO_3 framework made up of FSr_6 octahedrons leave less space for the $\text{Sr}(1)$ atoms to “rattle”.

This analysis shows that parametric studies of materials increase the confidence when very subtle distortions are being investigated. Furthermore, displacement parameters can provide insights into dynamical behavior related to minute structural changes.

Figure 9: Plots of isotropic displacement parameters (U_{iso}) values as a function of temperature for $Sr_3AlO_4F_{(air)}$ and $Sr_3AlO_4F_{(r)}$ from 3K-350K. The errors are smaller than the symbols

Figure 9e shows a plot of the refined U_{iso} values for the Al which indicates that above 300K an enhanced displacement exists which could give rise to further structural distortions at higher temperatures.

The thermal displacement parameters can be used to calculate the Debye temperature in both the $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ samples using the equation:

$$\Phi_{D,i} = \sqrt{\frac{3\hbar TN_A}{A_i k_B U_{\text{iso},i}}}$$

,where i represents individual atoms in $\text{Sr}_3\text{AlO}_4\text{F}$ and A_i is the atomic weight of the atom²⁷⁻²⁸. The refined U_{iso} values for each atom at their respective position is substituted in the equation to calculate an individual Debye temperature. The Debye temperature for the bulk material is calculated by summing up the individual Debye temperatures multiplied by the Wyckoff multiplicities (M_i)

$$\Phi_D = \frac{\sum M_i \Phi_{D,i}}{\sum M_i}$$

In an effort to identify suitable Ce^{3+} activated PL phosphors for white light LEDs Brgoch *et al* calculated the Debye temperature for $\text{Sr}_3\text{AlO}_4\text{F}$ to be 465 K using DFT²⁹. Using the refined U_{iso} values from the neutron diffraction data, the Φ_D for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ at 3 K are 196 K and 207 K, respectively. When the temperature increased to 25 K, the Φ_D values increased to 525 K and 581 K for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$. As

the temperature increases toward 350 K, the Φ_D increases above 1100K in $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ samples. According to Brgoch *et al* the combination of a high quantum yield, Debye temperature and wide band gap are necessary to limit thermal quenching in Ce^{3+} containing host structures ²⁹.

Figure 10: Plots of Debye temperature (Φ_D) values as a function of temperature for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ from 3K-350K

The Φ_D calculated from the refined U_{iso} values based on neutron diffraction data show that $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ have very similar values making Φ_D not a good proxy for self-activated PL. This is not surprising as the mechanisms of activated and self-activated photoluminescence are quite different. It appears that in self-activated photoluminescence subtle but distinct changes in atomic displacement parameters which are indicative of changes of the curvature of atomic potentials are the first heuristic hints of a non-linear property-structure correlation. Investigations on the concentration quenching of the PL observed in Ce^{3+} activated $\text{Sr}_3\text{AlO}_4\text{F}$ phosphors by Setlur et al³⁰ suggest O^{2-} substitution of F^- sites. This would provide a mechanism for local charge compensation for the aliovalent substitution of Sr^{2+} . If this type of substitution would also

occur in non-activated phosphors to compensate for an excess positive charge in a cation defect cluster it would explain why SrF_2 appears as an impurity in all sample preparations based on stoichiometric weigh-in and why the amount of impurity is higher in air-annealed samples. However, we have no direct experimental evidence for this mechanism based on our structural investigations.

4. Conclusion

These structural studies were done to gain insight about the effect that annealing in a reducing atmosphere has on the structure of $\text{Sr}_3\text{AlO}_4\text{F}$ materials. It is apparent that the reducing atmosphere has a significant impact on the self-activated photoluminescence in $\text{Sr}_3\text{AlO}_4\text{F}$, resulting in a bright white light emission when excited by 254 nm light. Structurally this is concomitant with a significant contraction of the a lattice parameter and a minute elongation of the c axis. Within the $\text{Sr}_3\text{AlO}_4\text{F}$ structure the FSr_6 octahedrons reveal small distortions, commensurate with the expansion of the c lattice parameter. The contraction of the a lattice parameter in $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ is concomitant with a significant decrease of the separation between the FSr_6 octahedrons and AlO_4 tetrahedrons. The smaller isotropic displacement parameter for Sr(1) and O indicates that the denser packing of the polyhedral units results in a slightly deeper potential for the Sr(1) and O atoms in this material. Both the air- and reductively-annealed samples have identical thermal expansion within the temperature range of 3 to 350 K. The Debye temperatures were calculated using the atomic displacement parameters and show no significant differences between the samples making the Debye temperature a bad proxy for self-activated PL. We have no model for the intense self-activated photoluminescence in the reduced materials only the experimental observation of densification and minute

changes in the atomic displacement parameters of an under-bonded Sr(1) atom and oxygen linking the two polyhedral subunits.

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Figure 1: Photoluminescence of a) $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$, (b) $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$, and (c) SrF_2 powders when activated with UV lamp at $\lambda = 254\text{nm}$.

Figure 2: Photoluminescence emission and excitation spectra of $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ samples.

Figure 3: Comparison of photoluminescence of $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and SrF_2 under UV light with $\lambda_{\text{ex}} = 254\text{ nm}$.

Figure 4: Rietveld refinement plot of neutron diffraction data of $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$. The red green and pink profiles represent the observed, calculated and difference plots, respectively. The black vertical lines represent the peaks in the $\text{Sr}_3\text{AlO}_4\text{F}$ phase, while the red vertical lines represent the peaks in the SrF_2 phase.

Figure 5: Rietveld refinement plot of neutron diffraction data of $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$. The red green and pink profiles represent the observed, calculated and difference plots, respectively. The black vertical lines represent the peaks in the $\text{Sr}_3\text{AlO}_4\text{F}$ phase, while the red vertical lines represent the peaks in the SrF_2 phase.

Figure 6: Structural changes in FSr_6 octahedrons, a lattice parameter and the separation of FSr_6 and AlO_4 subunits between air and reductively annealed Sr_3AlO_4 samples expressed in Δ_{esd} .

Figure 7: Plots of lattice parameters, selected bond distances and thermal expansion coefficients between 3 and 350 K for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$. The errors are smaller than the symbols.

Figure 8: Plots of Al-O distance (a) and tilt angles (b) as a function of temperature for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ from 3K-350K. The errors are smaller than the symbols.

Figure 9: Plots of isotropic displacement parameters (U_{iso}) values as a function of temperature for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ from 3K-350K. The errors are smaller than the symbols

Figure 10: Plots of Debye temperature (Φ_D) values as a function of temperature for $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{air})}$ and $\text{Sr}_3\text{AlO}_4\text{F}_{(\text{r})}$ from 3 – 350 K

Table 1: Refined lattice parameters and atomic positions for Sr₃AlO₄F_(air)

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	<i>U</i> _{iso} x 100
Sr(1)	4 <i>a</i>	0	0	0.25	1	1.49(5)
Sr(2)	8 <i>h</i>	0.1695(2)	0.6695(2)	0	1	0.56(3)
Al	4 <i>b</i>	0	0.5	0.25	1	0.61(7)
F	4 <i>c</i>	0	0	0	1	1.13(5)
O	16 <i>l</i>	0.1418(1)	0.6418(1)	0.6483(1)	1	1.08(2)

Crystallographic data: Space group = *I4/mcm*, *a* = 6.7873(1) Å, *c* = 11.1542(2) Å, Vol. = 513.84(2) Å³. χ^2 = 1.730, *R*_{wp} = 7.18 %, *R*_p = 5.52 %.

Table 2: Refined lattice parameters and atomic positions for Sr₃AlO₄F_(r)

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	<i>U</i> _{iso} x 100
Sr(1)	4 <i>a</i>	0	0	0.25	1	1.33(5)
Sr(2)	8 <i>h</i>	0.1689(1)	0.6689(1)	0	1	0.54(3)
Al	4 <i>b</i>	0	0.5	0.25	1	0.38(7)
F	4 <i>c</i>	0	0	0	1	1.10(5)
O	16 <i>l</i>	0.1416(1)	0.6416(1)	0.6484(1)	1	0.97(2)

Crystallographic data: Space group = *I4/mcm*, *a* = 6.7797(1) Å, *c* = 11.1557(2) Å, Vol. = 512.76(2) Å³. χ^2 = 1.550, *R*_{wp} = 6.90 %, *R*_p = 5.33 %

Table 3: Changes between distances and angles in Sr₃AlO₄F_(air) and Sr₃AlO₄F_(r). In bold are changes larger than 5σ.

Sr ₃ AlO ₄ F	Sr ₃ AlO ₄ F _(air) (Å)	Sr ₃ AlO ₄ F _(r) (Å)	Δ_{esd} (Nσ)
	NPD	NPD	
<i>a</i> -parameter (Å)	6.7873(1)	6.7797(1)	-76σ
<i>c</i> -parameter (Å)	11.1542(2)	11.1557(2)	7.5σ
Volume (Å ³)	513.84(2)	512.76(2)	-56σ

Sr(1)-O (x8) (Å)	2.8503(7)	2.8478(7)	-3.6σ
Sr(1)-F (x2) (Å)	2.78854(6)	2.78898(6)	7.3σ
Sr(2)-O (x2) (Å)	2.453(2)	2.458(2)	2.5σ
Sr(2)-O (x4) (Å)	2.690(1)	2.685(1)	-5σ
Sr(2)-F (x2) (Å)	2.5211(4)	2.5199(4)	-3σ
Sr(1)-Al (Å)	3.39365(6)	3.38986(6)	-63σ
Al-O (x4) (Å)	1.771(1)	1.768(1)	-3σ
O-Al-O	114.20(4)°	114.25(4)°	1.3σ
O-Al-O	100.37(8)°	100.29(8)°	-σ
F-Sr(2)-F	144.28(6)°	144.06(6)°	-3.7σ
Sr(2)-Sr(1)-Sr(2)	100.667(8) °	100.757(8) °	11.4σ

References

- [1] A. P. Ramirez, M.A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt, S. M. Shapiro Solid State Comm. 115 (2000) 217.
- [2] C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, A. P. Ramirez, Science 293 (2001) 673.
- [3] W. Sławiński, R. Przeniosło, D. Wardecki, I. Sosnowska, A. Hill, A. N. Fitch, M. Bieringer, Mat. Res. Express 1 (2014) 016306.
- [4] E. S. Božin, V. Petkov, P. W. Barnes, P. M. Woodward, T. Vogt, S. D. Mahanti, S. J. L. Billinge, *J. Phys: Cond. Mat.* 16 (2004) S5091.
- [5] T. -T. Fang, C. P. Liu, Chem. Mat. 17 (2005) 5167.
- [6] T. A. Mary, J. S. O. Evans, T. Vogt, A. W. Sleight, Science 272 (1996) 90.
- [7] F. Bridges, T. Keiber, P. Juhas, S. J. L. Billinge, L. Sutton, J. Wilde, G. R. Kowach, G. R. Phy. Rev. Lett. 112 (2014) 045505.
- [8] T. Vogt, P. M. Woodward, B. Hunter, A. K. Prodjosantoso, B. J. Kennedy, J. Solid State Chem. 144 (1999) 228.
- [9] S. Park, T. Vogt, J. Lumin. 129 (2009) 952.
- [10] W. Chen, H. Liang, X. Ding, Y. Liu, Q. Su, Appl. Phys. B 102 (2011) 699.
- [11] W. B. Im, S. Brinkley, J. Hu, A. Mikhailovsky, S. P. DenBaars, R. Seshadri, Chem. Mat. 22 (2010) 2842.
- [12] A. A. Setlur, E. V. Radkov, C. S. Henderson, J. -H. Her, A. M. Srivastava, N. Karkada, M. S. Kishore, N. P. Kumar, D. Aesram, A. Deshpande, Chem. Mat. 22 (2010) 4076.
- [13] M. Shang, G. Li, X. Kang, D. Yang, D. Geng, J. Lin, ACS Appl. Mat. & Int. 3 (2011) 2738.
- [14] L. Ning, Y. Wang, Z. Wang, W. Jin, S. Huang, C. Duan, Y. Zhang, W. Chen, H. Liang, H. J. of Phys. Chem. A 118 (2014) 986.
- [15] X. Zheng, H. Luo, J. Liu, P. Liu, X. Yu, J. Mat. Chem. C 1 (2013) 7598.

- [16] J. Sun, G. Sun, Y. Sun, L. Han, Opt. Mater. (2014)
- [17] E. Sullivan, T. Vogt, ECS J. Solid State Sc. Tech. 2 (2013) R3088.
- [18] S. Park, T. Vogt, J. Phys. Chem. C 114 (2010) 11576.
- [19] A. K. Prodjosantoso, B. J. Kennedy, T. Vogt, P. M. Woodward, J. Solid State Chem. 172 (2003) 89.
- [20] A. C. Larson, R. B. Von Dreele, *General Structure Analysis System. LANSCE, MS-H805, Los Alamos, New Mexico* **1994**
- [21] B. C. Sales, B. C. Chakoumakos, R. Jin, J. R. Thompson, D. Mandrus, Phys. Rev. B 63 (2001) 245113.
- [22] V. Petkov, T. Vogt, Solid State Comm. 127 (2003) 43.
- [23] E. Sullivan, M. Avdeev, T. Vogt, J. of Solid State Chem. 194 (2012) 297.
- [24] R. Green, T. Vogt, J. of Solid State Chem. 194 (2012) 375.
- [25] P. M. Woodward, Acta Cryst. B53 (1997) 32.
- [26] R. H. Mitchell, *Perovskites: modern and ancient*; Almaz Press Thunder Bay: 2002.
- [27] B. T. M. Willis, A. W. Pryor, *Thermal vibrations in crystallography*; Cambridge University Press Cambridge: 1975.
- [28] N. C. George, A. Birkel, J. Brgoch, B. -C Hong, A. A. Mikhailovsky, K. Page, A. Llobet, R. Seshadri, Inorg. Chem. 52 (2013) 13730.
- [29] J. Brgoch, S. P. DenBaars, R. Seshadri, J. Phys. Chem. C 117 (2013) 17955.
- [30] A. A. Setlur, D. G. Porob, U. Happek, M. G. Brik, J. of Lumin. 133 (2013) 66

Graphical Abtsract:

When annealing $\text{Sr}_3\text{AlO}_4\text{F}$ under reducing conditions an intense self-activated photoluminescence is correlated with a denser packing of FSr_6 and AlO_4 and smaller atomic displacement parameters of Sr(1) and oxygen (blue). Flourine atoms are shown by small black circles.