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Structural changes and self-activated photoluminescence in reductively annealed Sr_3AlO_4F

Robert Green [a], Maxim Avdeev [b], Thomas Vogt [b,c,*]

[a] Department of Chemistry, Allen University Columbia, Columbia, SC 29204, USA
[b] Bragg Institute, Australian Science and Technology Organization, PMB 1, Menai, NSW 2234, Australia
[c] Department of Chemistry & Biochemistry & NanoCenter, University of South Carolina, Columbia, SC 29208, USA

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ABSTRACT

White light emission of self-activated photoluminescence (PL) in Sr_3AlO_4F under 254 nm 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 Sr_3AlO_4F 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.

1. 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. $CaCu_3Ti_4O_{12}$, 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 Sr_3AlO_4F 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 Sr_3AlO_4F and Sr_3GaO_4F were structurally characterized in the late 1990s [8]. 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 Sullivan [17]. The most important phosphors for this application are based on substituting alio- and isovalent Ce^{3+} and Eu^{2+} activators into the Sr_3AlO_4F host lattice.

Experiments established that Sr_3AlO_4F can exhibit self-activating photoluminescence when excited with 254 nm light after being annealed in a reducing (5% H_2/95% Ar) atmosphere [18]. In addition to heating these materials in a reducing atmosphere, the color emitted by self-activating Sr_3AlO_4F 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 atmosphere [18]. The measurements of the decay times

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* Corresponding author at: Department of Chemistry & Biochemistry & NanoCenter, University of South Carolina, SC 29208, USA.
E-mail address: tvogt@mailbox.sc.edu (T. Vogt).

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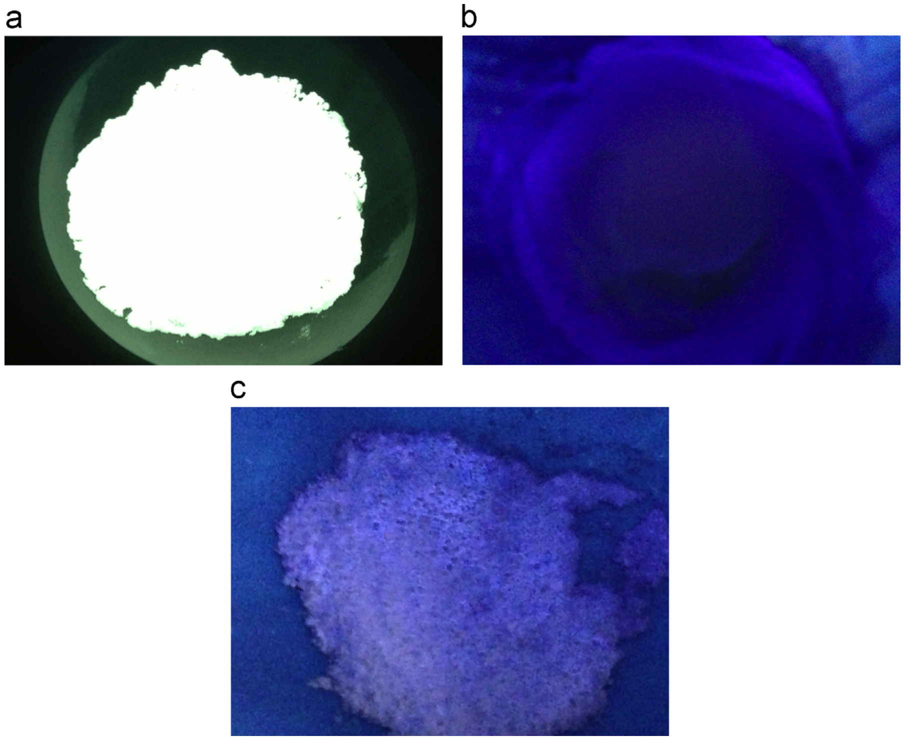

Fig. 1. Photoluminescence of (a) $Sr_3AlO_4F_{(r)}$, (b) $Sr_3AlO_4F_{(air)}$, and (c) SrF_2 powders when activated with UV lamp at λ=254 nm.

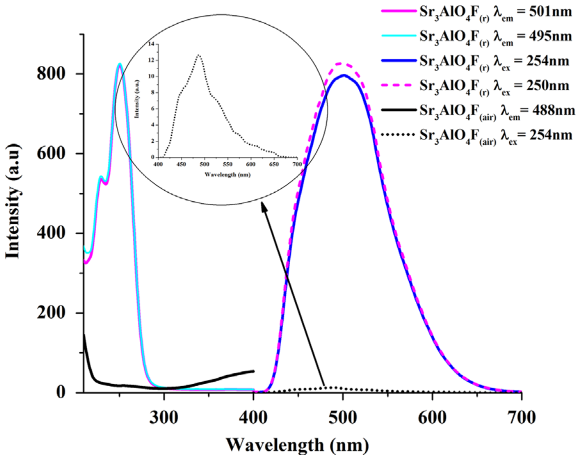

Fig. 2. Photoluminescence emission and excitation spectra of $Sr_3AlO_4F_{(air)}$ and $Sr_3AlO_4F_{(r)}$ samples.

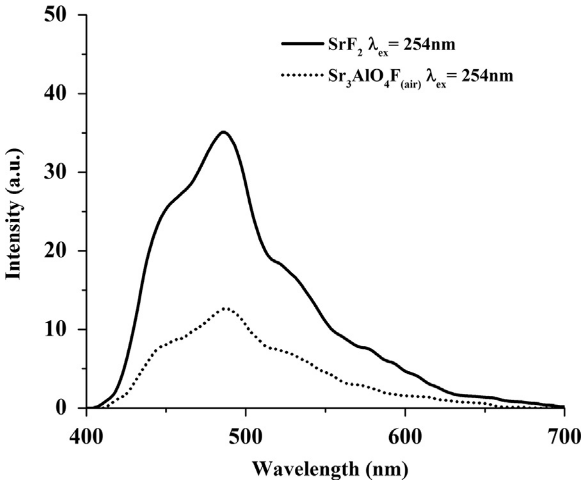

Fig. 3. Comparison of photoluminescence of $Sr_3AlO_4F_{(air)}$ and SrF_2 under UV light with λ_{ex}=254 nm.

of Sr_3AlO_4F 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 work [18] to make the Sr_3AlO_4F(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 Sr_3AlO_4F 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 Sr_3AlO_4F 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 Sr_3AlO_4F structures using the bond valence method [10] and comparing the sum of the individual