Electrical properties and thermal expansion of strontium aluminates

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ABSTRACT

Strontium aluminate ceramics, including $Sr_3Al_2O_6$, $SrAl_2O_4$ and $Sr_4Al_{14}O_{25}$, synthesized by glycine–nitrate combustion and sintered at 1773 K in air, were characterized by thermal analysis, dilatometry and electrical measurements in controlled atmospheres. All studied strontium aluminates are semiconductors with electrical conductivities as low as $10^{-6}-4\times10^{-5}$ S/cm at 1273 K in dry air. Electrical measurements in controlled atmospheres in combination with ion transference number determination demonstrated that $SrAl_2O_4$ is a mixed conductor with predominant ionic conductivity and increasing n-type and p-type electronic contributions under highly reducing and oxidizing conditions, respectively. While the behavior of electrical conductivity of $Sr_3Al_2O_6$ in dry atmospheres was qualitatively similar to that of $SrAl_2O_4$, a significant increase of conductivity in wet atmospheres was attributed to a protonic contribution to electrical conduction, in correlation with thermogravimetric data and the tendency of this material to form a hydrogarnet at low temperatures. The average thermal expansion coefficients of strontium aluminates, $(8.5–11.1)\times10^{-6}$ K^{-1} at 333–1373 K, increase with increasing strontium content in the sequence $Sr_4Al_{14}O_{25} < SrAl_2O_4 < Sr_3Al_2O_6$ and are essentially independent of oxygen partial pressure.

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1. Introduction

Available phase diagrams [1,2] show the existence of five compounds in the SrO–Al_2O_3 pseudo-binary system including $4SrO·Al_2O_3$ ($Sr_4Al_2O_7$), $3SrO·Al_2O_3$ ($Sr_3Al_2O_6$), $SrO·Al_2O_3$ ($SrAl_2O_4$), $SrO·2Al_2O_3$ ($SrAl_4O_7$) and $SrO·6Al_2O_3$ ($SrAl_{12}O_{19}$), where $Sr_4Al_2O_7$ exists only in a narrow temperature range from ~1398–1403 to 1963–2017 K. In more recent years, an additional compound $4SrO·7Al_2O_3$ ($Sr_4Al_{14}O_{25}$), which was not shown in the original phase diagrams, was synthesized and reported by a number of authors [3–5]. It was suggested that $Sr_4Al_{14}O_{25}$ may be metastable at temperatures below ~1373 K and that $Sr_4Al_{14}O_{25}$ and $SrAl_4O_7$ compete with each other for crystallization [5,6]. Other new compounds, $12SrO·7Al_2O_3$ [7] and $10SrO·3Al_2O_3$ [8], were reported to exist, but their stabilities are uncertain.

Strontium aluminates have been studied intensively for application as long-persistence phosphors and thermoluminescence pigments ([9–12] and references therein). When doped with rare-earth metal cations such as Eu^{2+}, they show photoluminescent characteristics that are superior as compared to predecessors such as copper-activated zinc sulfide. Other potential applications of strontium aluminates include heterogeneous catalysts [13],

oxygen resistive sensors [14] and dense electrochemical membranes with mixed ionic–electronic conductivity for oxygen separation and partial oxidation of methane [15–18]. Strontium aluminates are often observed as secondary phases in mixed-conducting perovskites, such as lanthanum-strontium ferrite, as a result of either aluminum substitutions into the perovskite lattice or additions of alumina as a sintering aid (e.g. Refs. [19–21]). In recent works, $SrAl_2O_4$ was intentionally added to mixed-conducting perovskite matrices as a component of composite membranes [15–18]. Such additions of strontium aluminate phase were found to improve thermomechanical properties and the stability of the membrane materials under operation conditions. Nevertheless, data on the electrical conductivity and thermomechanical behavior of Sr–Al–O compounds, factors that are important for their use as components of composite mixed conductors or sensors, are very scarce. The present work, thus, focused on the studies of electrical properties and thermal expansion of strontium aluminates with high and intermediate strontium content including $Sr_3Al_2O_6$, $SrAl_2O_4$ and $Sr_4Al_{14}O_{25}$.

2. Experimental

The precursor powders of $Sr_3Al_2O_6$, $Sr_4Al_{14}O_{25}$ and $SrAl_2O_4$ were prepared by the glycine–nitrate process (GNP), a self-combustion technique using nitrates of metal components as oxidant and glycine as a fuel and chelating agent. Appropriate amounts of $Sr(NO_3)_2$ (⩾99.0%, Sigma–Aldrich), $Al(NO_3)_3·9H_2O$ (⩾98%,

Sigma–Aldrich) and glycine (Sigma–Aldrich) were dissolved in distilled water under continuous stirring. In the case of the composition $Sr_4Al_{14}O_{25}$, small amount of H_3BO_3 (Sr:Al:B cation ratio = 1:3.5:0.1) was added into the solution as a flux. The aqueous solutions were heated on a hot plate until auto-ignition. The obtained combustion products were ground and annealed at 1273 K for 2 h in order to remove organic residues. The disc-shaped samples were compacted uniaxially (40 MPa) and sintered at 1773 K in air for 10 h using Pt foil as a substrate. A solid-state synthesis route was also attempted for preparation of $Sr_4Al_{14}O_{25}$ starting from decomposition of a nitrate mixture with subsequent calcinations at elevated temperatures (see discussion below).

Sintered samples were polished and machined to produce disc-shaped samples (diameter ~12 mm, thickness ~1.5 mm) for electrical measurements and rectangular bars (~2 × 2 × 13 mm) for dilatometric studies. Experimental density was calculated from the weight and geometric dimensions of the samples. The powdered samples for X-ray diffraction (XRD) and thermal analysis were prepared by grinding the sintered ceramics.

XRD patterns were recorded at room temperature using a Rigaku D/Max-B diffractometer (Cu Kα, $2\Theta = 10–80°$, step 0.02°, exposition 3s). Differential thermal analysis (DTA) was performed employing Setaram LabSys analyzer in air flow at 5 K/min. Thermogravimetric analysis (Setaram SetSys 16/18 instrument, sensitivity 0.4 μg, initial sample weight ⩾0.3 g) was carried out at heating/cooling rate of 2 K/min in a flow of dry air, nitrogen and $10\%H_2–N_2$ mixture or in wet nitrogen. Thermal expansion was studied using vertical Linseis L75 dilatometer at 3 K/min if a flow of air or $10\%H_2–N_2$. Total electrical conductivity (σ) was determined by impedance spectroscopy (Agilent 4284A precision LCR meter) using disk–shaped samples with applied porous Pt electrodes. The measurements were performed as function of temperature at 973–1273 K in controlled dry or wet atmosphere (oxygen, air, argon and $10\%H_2–N_2$ mixture). The average ion transference numbers under air/O_2 and air/$10\%H_2–N_2$ gradients were determined at 1023–1223 K by the modified electromotive force (EMF) technique taking electrode polarization into account [22,23].

The terms of "dry" and "wet" atmosphere refer to a gas passed through silica–gel dryer or humidified by a bubbling through distilled water at room temperature, respectively. Oxygen partial pressure, $p(O_2)$, and relative humidity in a gas flow were monitored by yttria-stabilized zirconia oxygen sensor and Jumo humidity transducer, respectively. Representative $p(O_2)$ values in argon, wet $10\%H_2–N_2$ and dry $10\%H_2–N_2$ at 1223 K correspond to $5 × 10^{-5}$ atm, $5 × 10^{-17}$ atm and $5 × 10^{-20}$ atm, respectively. Relative humidity in dry and wet atmosphere was ⩽0.3 % ($p(H_2O) ⩽ 10^{-4}$ atm) and ~93–95% ($p(H_2O) ~ 3 × 10^{-2}$ atm).

3. Results and discussion

XRD analysis confirmed that calcination of powder compacts at ⩾1573 K yields single-phase $Sr_3Al_2O_6$ ceramics. Fig. 1A shows
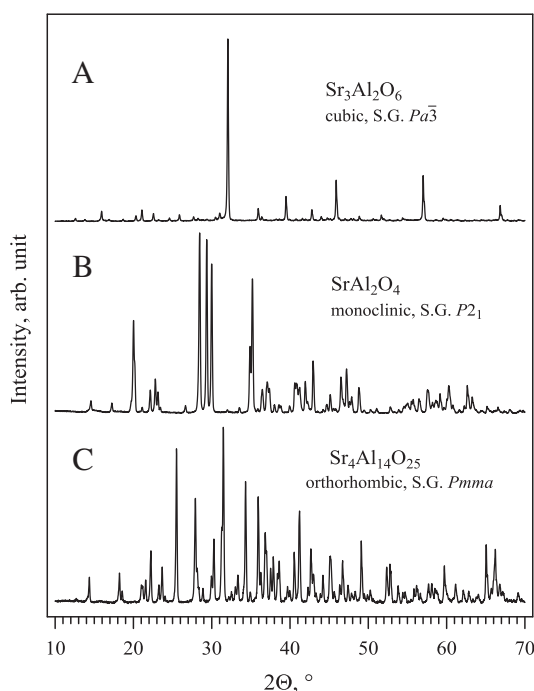

Fig. 1. XRD patterns of (A) $Sr_3Al_2O_6$, (B) $SrAl_2O_4$ and (C) $Sr_4Al_{14}O_{25}$ ceramics sintered at 1773 K for 10 h in air.

the XRD pattern of $Sr_3Al_2O_6$ sample sintered at 1773 K. All reflections can be indexed in S.G. $Pa\overline{3}$ characteristic for cubic $Sr_3Al_2O_6$ (JCPDS PDF # 81-0506 and Refs. [24,25]). Alonso et al. [24] suggested that the $Sr_3Al_2O_6$ structure can be described as a superlattice derivative of perovskite-type structure with A-site and oxygen deficiency, 1:3 ordering in B sublattice, and overall formula expressed as $Sr_{7/8}\square_{1/8}(Sr_{1/4}Al_{3/4})O_{9/4}\square_{3/4}$. The density of sintered ceramics was 86% of the theoretical (Table 1).

$SrAl_2O_4$ ceramics sintered at 1773 K were found to be single-phase (Fig. 1B) with the tridymite-type monoclinic structure (S.G. $P2_1$), as expected (JCPDS PDF # 76-7488 and Refs. [26–28]), and a density of 94% of theoretical (Table 1). This strontium aluminate is known to undergo reversible first-order transition from low-temperature monoclinic to high-temperature hexagonal modification at ~923–950 K [27,28]. This transition is indicated by a thermal effect in DTA curves (Fig. 2A) and was shown in the present work to correspond to ~940 K. More recent and detailed structural studies [26] demonstrated that the behavior of $SrAl_2O_4$ is more complex; in fact, it undergoes two reversible phase transitions on heating from monoclinic (S.G. $P2_1$) to an intermediate hexagonal modification (S.G. $P6_3$) and then to a high-temperature hexagonal polymorph (S.G. $P6_322$). The latter transition is second order in nature and is not visible by DTA, but is indicated by a discontinuity in the differential dilatometric curve (i.e. in thermal expansion coefficient) at ~1153 K (Fig. 2B).

Synthesis of $Sr_4Al_{14}O_{25}$ ceramics required more efforts compared to the other two compositions. Initially, the same GNP procedure was attempted, without additions of any other components into nitrates–glycine aqueous solution. Sintering of thus prepared precursor compacts at 1773 K yielded a mixture of $SrAl_2O_4$ and $SrAl_{12}O_{19}$ phases (Table 2). Calcinations of the precursor powder at a lower temperature (1473 K) resulted in a mixture of aluminates – $SrAl_2O_4$, $SrAl_4O_7$ and $SrAl_{12}O_{19}$; increasing the calcination time led to appearance of only minor traces of the target $Sr_4Al_{14}O_{25}$ phase.

Capron et al. reported previously the successful synthesis of $Sr_4Al_{14}O_{25}$ by spray-drying the aqueous solution of nitrates and subsequent calcinations [5]. Therefore, the second attempt was focused on a solid-state reaction route starting from thermal decomposition of the aluminum and strontium nitrates mixture followed by calcination/sintering at elevated temperatures. Unfortunately, thermal treatment at 1573 K yielded again a mixture of different phases including the target phase, while the product of sintering at 1773 K comprised only $SrAl_2O_4$ and $SrAl_{12}O_{19}$ phases (Table 2).

Following the typical procedures for preparation of strontium aluminate-based phosphors (for instance, Refs. [4,12,29,30]), a small amount of H_3BO_3 was added into nitrates–glycine solution during GNP in the next synthesis attempt. Sintering of synthesized precursor compacts at 1773 K readily yielded single-phase $Sr_4Al_{14}O_{25}$ ceramics (Fig. 1C) with orthorhombic structure (S.G. $Pmma$), in agreement with JCPDS PDF # 89-8206 and [3,4]; the density of samples was 92% of theoretical (Table 1).

It is generally accepted that additions of B_2O_3 (melting point 723 K [31]) or H_3BO_3 (decomposes to B_2O_3 on heating) to strontium aluminates precursors as a flux agent provide a low-melting-point medium facilitating solid-state diffusion and promoting grain growth, with generally a positive effect on luminescent properties [29,30,32–34]. The effect of boron additions on the defect chemistry of $Sr_4Al_{14}O_{25}$ and other strontium aluminates is however not univocal. For the case of $SrAl_2O_4$, some reports suggest incorporation of boron into the aluminum sublattice [34–36], while no clear evidence of boroaluminate solid solution formation is found in other works [32]. Often, the effect of B_2O_3 additions is ascribed mainly to the formation of fusible vitreous strontium borates [32,33]. In general, it seems however that the