Sr₂GaScO₅, Sr₁₀Ga₆Sc₄O₂₅ and SrGa_{0.75}Sc_{0.25}O_{2.5}: a play in octahedra to tetrahedra ratio in oxygen-deficient perovskites.

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Supporting Information Placeholder

ABSTRACT: Three different perovskite-related phases were isolated in the SrGa_xSc_{1-x}O₃ system: Sr₂GaScO₅, Sr₁₀Ga₆Sc₄O₂₅ and SrGa_{0.75}Sc_{0.25}O_{2.5}. Sr₂GaScO₅ (x = 0.5) crystallizes in a brownmillerite type structure (S.G. *Icmm*, *a* = 5.91048(5) Å, *b* = 15.1594(1) Å and *c* = 5.70926(4) Å) with complete ordering of Sc and Ga³⁺ over octahedral and tetrahedral positions, respectively. The crystal structure of Sr₁₀Ga₆Sc₄O₂₅ (x = 0.4) was determined by the Monte Carlo method and refined using a combination of X-ray, neutron and electron diffraction data (S.G. *I4/a*, *a* = 17.517(1) Å; *c* = 32.830(3) Å). It represents a novel type of ordering of the B-cations and oxygen vacancies in perovskites. The crystal structure of SrGa_{0.75}Sc_{0.25}O_{2.5} can be described as a stacking of eight perovskite layers along the *c*-axis ...[- (Sc/Ga)O₆ - SrO₆ - (Sc/Ga)O₆ - SrO₆ -]... Similar to Sr₂GaScO₅, this structure features a complete ordering of the Sc³⁺ and Ga³⁺ cations over octahedral and tetrahedral positions, respectively, within each layer. A specific feature of the crystal structure of SrGa_{0.75}Sc_{0.25}O_{2.5} is that 1/3 of the tetrahedra have one vertex not connected with other Sc/Ga cations. Further partial replacement of Sc³⁺ by Ga³⁺ leads to the formation of the cubic perovskite phase SrGa_{0.25}Sc_{0.75}O₃ (x = 0.25) with *a* = 3.9817(4) Å. This compound incorporates water molecules in the structure forming SrGa_{0.25}Sc_{0.75}O₃·xH₂O hydrate, which exhibits proton conductivity ~2.0·10⁻² S/cm at 673K.

1. INTRODUCTION

Oxygen-deficient perovskites are known to have various important industrial applications, including high-temperature electrochemical devices, such as Solid Oxide Fuel Cells (SOFC). In SOFC, electrical energy is obtained through the conversion of chemical energy released in the Red-Ox reaction between the fuel, e.g.

hydrogen (at the anode) and oxygen (at the cathode). Depending on the utilized type of ionic conductivity, SOFC can be classified into proton or oxide-ion conductors. The former includes different high-temperature proton conducting materials like doped cerium or zirconium perovskites ABO₃, A = Sr, Ba; B = Ce; Zr, or oxygen-deficient perovskite-related niobium

and tantalum oxides like $A_{0.5}B_{0.5}O_{3-0.5}$; A = alkaline-earth; B = Nb, Ta (see, for example, a recent review¹). The latter includes various oxygen-deficient compounds, e.g. $Zr_{0.5}Y_{0.5}O_{2}$ (YSZ) and $La_{0.5}Sr_{0.5}Ga_{0.5}Mg_{0.5}O_{3}$ (LSGM) with fluorite and perovskite related structures respectively.

Among oxide-ion conductors with negligible electronic conductivity, complex oxides of the group 13 elements demonstrate the highest oxide-ion conductivity. This is related to a flexibility of the oxygen coordination environment for these elements, especially characteristic for the Ga³⁺ and In³⁺ cations. Thus the oxide-ion conductivity of LSGM outperforms traditional SOFC materials like YSZ^{2,3} and is considered as a base for the intermediate-temperature SOFC (IT-SOFC), operating at 500-700°C. However, the use of LSGM in SOFC is restricted by difficulties in obtaining single-phase material, the volatility of gallium at high temperatures and its high reactivity towards metallic Ni, often used as a component of anodes in SOFC. Another example is $BaInO_3$ with the brownmillerite structure which transforms at ~930°C to the disordered perovskite with high oxide-ion conductivity⁴. The cubic perovskite phase can be stabilized by appropriate doping, and $Ba_{0.5}Sr_{0.5}LaInO_{3-x}$ is known to exhibit oxide-ion conductivity up to 0.1 S/cm at 800°C⁵.

Perovskite-like oxides $A(B,B')O_{3-x}$, A = Sr, Ba and B = group 13 element; B' = other trivalent cation with invariable oxidation state like Sc³⁺ or small rare-earth cations, can be of interest as fast oxide-ion conductors used as electrolytes in SOFC since they possess high concentration of oxygen vacancies. In these oxides the large B' cation preferentially occupies octahedral positions, whereas the group 13 element has coordination number < 6. $BaAlScO_3$ ⁶ and $BaGaScO_3$ ⁷ have ordered structures with the hexagonal closed packing of the BaO_3 layers (so called anion-deficient hexagonal perovskites). In the $Sr(Sc,Al)O_{3-x}$ system several compounds have been reported. $SrAl_{0.5}Sc_{0.5}O_{3-x}$ has a cubic structure ($a = 7.9078(4)$ Å) with oxygen vacancies randomly distributed around two B-cation sites⁸. Y. Takeda et al.⁹ have reported the formation of the cubic $SrAl_xSc_{1-x}O_{3-x}$ perovskite with $a = 3.9554(6)$ Å and the perovskite related phases in the compositional range $SrAl_xSc_{1-x}O_{3-x}$, $0 \leq x \leq 0.15$. $SrAl_{0.5}Sc_{0.5}O_{3-x}$ exhibits low oxide-ion conductivity of ~10⁻³ S/cm at 1000°C.

In the present paper we report on the investigation of the $SrGa_xSc_{1-x}O_{3-x}$ system, where three novel oxygen-deficient perovskites have been isolated: $SrGa_{0.5}Sc_{0.5}O_{3-x}$ with the cubic perovskite structure, brownmillerite type Sr_2GaScO_7 , and $SrGaScO_3$ with a novel type of ordering of the B-cations and oxygen vacancies. The high-temperature conductivity of $SrGa_xSc_{1-x}O_{3-x}$ in various atmospheres including wet gases was also studied.

2. EXPERIMENTAL

Samples of $SrGa_xSc_{1-x}O_{3-x}$, $0.05 \leq x \leq 0.75$ were prepared by the polyacrylamid gel synthesis¹⁰. Stoichiometric mixtures of Sc_2O_3 , Ga_2O_3 , $SrCO_3$ were dissolved in a minimal amount of concentrated HNO_3 . Thereafter an aqueous solution of ammonium citrate $(NH_4)_3(cit)$ was added. The amount of citrate was calculated according to the chelate formula ML_n , where M is the metal, n its valence, and L ligand (citric acid). Finally, the pH of the solution was adjusted to 7 by adding of aqueous NH_3 . Acrylamide and N,N'-methylendiacylamide in a quantity of 6 g and 1 g per 100 ml of solution, respectively, were dissolved separately in distilled water and mixed with the citrate solution. The resulted solution was heated up to boiling whereupon a few grains of a,a'-Azobisisobutyronitrile (AIBN) were added. The solution turned into a transparent colorless gel, which was placed into furnace and slowly heated in air at a rate of 2K/min up to 1173K and kept at this temperature for 2 hours. The obtained powder was grinded, pressed in pellets and heated at 1473-1673K for 15-24 hours.

For the preparation of the Zr-doped samples $SrGa_xSc_{1-x}Zr_xO_{3-x}$, $x = 0.01-0.12$; $x = 0.01$ stoichiometric mixtures of Sc_2O_3 and Ga_2O_3 were dissolved in minimal quantity of concentrated nitric acid. The obtained solution together with stoichiometric amounts of $SrCO_3$ and $ZrO(NO_3)_2 \cdot 5.3H_2O$ were added into the melt of citric acid and heated on a hot plate in air to achieve the formation of a brown viscous mass. Further annealing was performed at 873K for 2 hours. The obtained powder was grinded, pressed in pellets, and finally heated in air at 1673K for 15 hours.

The phase purity of the compounds was checked by X-ray powder diffraction (XRPD) recorded with a Huber G670 Guinier diffractometer (CuK α radiation, image foil detector). High-temperature X-ray powder diffraction (HT XRPD) data for $SrGa_xSc_{1-x}O_{3-x}$ and room-temperature data for the Rietveld refinement of $SrGaScO_3$ crystal structure were collected in air using a Bruker D8-Advance diffractometer (CuK α radiation, Vantec PSD) in reflection mode equipped with a high-temperature camera XRK-900 (Anton Paar). XRPD pattern for the structural refinement of $SrGaScO_3$ crystal structure was collected with a PANalytical X'pert PRO MPD diffractometer using CuK α radiation, variable slits with a constant area of 4 cm² irradiated, and a step size of 0.0167°, in the 2θ range 5-125° and with a total measuring time of 30 min, yielding patterns with maximum peak intensities of ca. 50000 counts. The patterns were converted to corresponding 0.5° fixed-slit data using the PANalytical X'Pert HighScore Plus software. Neutron powder diffraction (NPD) data were collected on the GEM diffractometer at the spallation source ISIS, Rutherford Appleton Laboratory, U.K. Rietveld structure refinements were made with the GSAS program package¹¹.

Electron diffraction (ED) patterns were recorded with JEOL JEM2000FX and Philips CM20 TEMs with a LaB₆

filament, equipped with a double tilt sample holder $\pm 45^\circ$, operating at 200 kV. The sample was fixed on a copper grid with holey carbon by dipping the grid through an ethanol suspension of the sample.

Electrical conductivity measurements were performed by a.c. impedance spectroscopy using a Solartron 1260 frequency response analyzer in the frequency range 1 Hz to 1 MHz for $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$. For the electrical conductivity measurements pellets of $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ ($d = 12.4$ mm, $h = 1.5$ mm) were coated by Pt-paste (Heraeus CL 11-5100) and heated at 1273 K for 1 h.

Netsch 402C dilatometer operated in air (298–1173 K, 10 K/min) was used for the thermal expansion coefficient measurements of the SrGaScO_3 sample. For the thermal expansion measurements oxide powder was pressed into pellets 8 mm in diameter and 5–5.5 mm in height and annealed at 1473 K.

Thermogravimetric (TG) studies were carried out in argon (Linde Gas, 99.997%, 5 ppm H_2O) or nitrogen (AGA, 5 ppm H_2O) with gas flow rates of 20 mL/min from 298 to 1273 K at a heating rate of 5 or 15 K/min using NETZSCH STA 409 PC.

3. RESULTS

Three novel compounds with different perovskite-related structures were found in the SrGaScO_3 system. The formation of single-phase samples was observed for the compositions $\text{SrGa}_x\text{Sc}_{1-x}\text{O}_3$, $x = 0.25, 0.375$, and 0.5 . The color of the samples was crème-brown for $x = 0.25$, and white for 0.375 and 0.5 . The samples with $x \leq 0.25$ contained significant amount of SrGaO_3 , while for $0.25 < x < 0.35$ unidentified admixture phase(s) was observed as well. The $0.375 < x < 0.5$ samples contained a mixture of the two phases with $x = 0.375$ and 0.5 . Also the samples with $0.5 < x \leq 0.75$ were not single-phase and contained unknown admixture phase(s), together with the $x = 0.5$ phase.

3.1. SrGaScO_3 with the brownmillerite structure. Single phase samples of SrGaScO_3 were obtained by annealing at 1473 K for 15 hours followed by cooling down to room temperature with a rate of ~ 150 K/h. The XRPD pattern of SrGaScO_3 was indexed with an orthorhombic unit cell with $a = 5.91048(5)$ Å, $b = 15.1594(1)$ Å, and $c = 5.70926(4)$ Å, suggesting the formation of the brownmillerite type structure, hereinafter referred to as SrGaScO_3 . The $h+k+l=2n$ reflection condition unambiguously suggests a body-centred orthorhombic unit cell. It is well-known that depending on the relative orientation of the tetrahedral chains between the octahedral layers in brownmillerite two highly ordered structures having space groups *Ibm2* (no. 46) and *Pcmm* (no. 62) can be obtained. A random ordering of the tetrahedral layers leads to space group *Icmm* (no. 74).

Figure 1. Observed, calculated and difference between them XRPD profiles for SrGaScO_3 .

Reflection conditions do not allow distinguishing between *Ibm2* and *Icmm* space groups. The SrGaScO_3 structure was refined in both space groups using XRPD data. In both models we observed complete ordering of the B-cations over two sites in the brownmillerite structure where the large Sc occupies the octahedral position while Ga is situated in the tetrahedral one. Refinement in *Icmm* led to slightly better R-values ($R_w = 0.0796$, $R_p = 0.0618$, $\chi^2 = 2.23$) compared to *Ibm2* ($R_w = 0.0804$, $R_p = 0.0623$, $\chi^2 = 2.28$). Moreover, some interatomic distances between B-cations and oxygen atoms in *Ibm2* were unreasonably short. For example, two distances between scandium and equatorial oxygen atoms were 1.92(1) Å in comparison with a typical Sc-O distance of ~ 2.1 Å. This indicates that the correct space group for SrGaScO_3 is *Icmm*. The final refined atomic parameters are given in Table 1, main interatomic distances are given in Table 2. Experimental, calculated, and difference diffraction profiles are shown in Figure 1. As mentioned above, in the crystal structure of SrGaScO_3 there is a full order of Sc and Ga cations over octahedral and tetrahedral positions, respectively. The scandium octahedron is rather distorted with substantially elongated Sc-O axial bonds (2.250(4) Å) in comparison with equatorial ones (2.0647(4) Å). This together with disorder in the tetrahedral layers leads to distortion of the gallium tetrahedron with the Ga-O bond length varying between 1.799(4)–1.877(8) Å.

The DSC experiment on SrGaScO_3 shows a strong exothermal effect at ~ 1663 K, which can be most likely interpreted as melting. XRPD pattern of the SrGaScO_3 sample quenched from 1723 K (Figure 2) can be indexed in a cubic perovskite cell with $a = 3.99382(1)$ Å, as no additional reflections indicating neither superstructure nor splitting of the perovskite subcell reflections are observed. However, one cannot exclude the brownmillerite-like ordering of the B-cations and oxygen vacancies on the level of the micro domains in this metastable phase.

Figure 2. XRPD pattern of the SrGaScO_6 sample quenched from 1723K.

Figure 3. The compositional dependence of the unit cell parameters for $\text{SrGaSc}_{1-x}\text{Zr}_x\text{O}_6$.

In order to stabilize a disordered cubic perovskite, heterovalent substitution of Sc³⁺ by Zr according to the formula $\text{SrGaSc}_{1-x}\text{Zr}_x\text{O}_6$, $x=0.01$ was performed. The samples were annealed at 1673K and cooled to room temperature at the rate of 150K/h. A solid solution with a cubic perovskite structure was formed in a narrow composition range $x=0.03$ -0.1. For the samples with $x = 0.01$ and 0.02 SrGaScO_6 and the cubic perovskite phase were observed, whereas for the samples with $x > 0.1$ admixtures of SrZrO_6 and Sc_2O_3 were found. The compositional dependence of the unit cell parameter of $\text{SrGaSc}_{1-x}\text{Zr}_x\text{O}_6$ is shown in Figure 3. The minor increase of the unit cell parameter of the perovskite phase with the Zr content is most probably associated with an increase of the oxygen content as the ionic radii of Zr⁴⁺ ($r = 0.84 \text{ \AA}$) is slightly smaller than that of Sc³⁺ ($r = 0.87 \text{ \AA}$).

3.2. A novel oxygen-deficient perovskite SrGaScO_6 . The SrGaScO_6 sample was prepared by annealing in air at 1473K for 15 h. The XRPD pattern suggests the formation of a perovskite-related phase. However, in addition to the perovskite subcell reflections there were numerous weak superstructure reflections, which required SAED to identify the supercell. The SAED investigation revealed the material to be well crystallized without indications of disorder. A number of tilt series

were recorded and the relation between the supercell and the perovskite subcell was found to be $\mathbf{a}^* = 1/10(2\mathbf{a}^* - \mathbf{b}^*)$, $\mathbf{b}^* = 1/10(-\mathbf{a}^* + 2\mathbf{b}^*)$, $\mathbf{c}^* = 1/8\mathbf{c}^*$. The superstructure reflections can thus be indexed with a tetragonal unit cell, $a = b \approx 2\sqrt{5}a_p \approx 17.5 \text{ \AA}$ and $c \approx 8a_p \approx 33 \text{ \AA}$, with $a_p \approx 4 \text{ \AA}$ (subcell parameter). A number of SAED patterns corresponding to low index zone axes in the perovskite subcell in addition to low index zone axes in the supercell are shown in Figure 4. SAED indicates the reflection conditions hkl ; $h + k + l = 2n$, $hk0$; $h,k = 2n$, $00l$; $l = 4n$, consistent with the space group $I4/a$ (no. 88). In the Rietveld refinement of the crystal structure (see below) we have found that the composition of the phase corresponds to the formula SrGaScO_6 , which differs only slightly from the composition of the sample SrGaScO_6 . Therefore the composition of the phase will hereinafter be referred to as SrGaScO_6 .

Figure 4. SAED patterns of SrGaScO_6 . Selected low index zone axes patterns in the perovskite subcell are shown as well in the supercell. The relation between the perovskite subcell and supercell is $a = b \approx 2\sqrt{5}a_p$, $c \approx 8a_p$.

3.2.1. Refinement of the crystal structure of SrGaScO_6 . The XRPD pattern of SrGaScO_6 was fully indexed with the unit cell parameters and space group obtained from the SAED study ($a = 17.517(1) \text{ \AA}$; $c = 32.830(3) \text{ \AA}$). The structure was solved using the direct space Monte Carlo simulation program FOX⁺ applied to powder XRPD data. The multiplicity for a general site in the space group $I4/a$ is 16 and it was assumed that the unit cell contains 16 formula units of SrGaScO_6 . The solution of the structure was simplified by the fact that it contains B-cations with different crystal chemistry. Large Sc³⁺ cations are known to possess octahedral oxygen coordination. A localization of all 4 ScO_6 octahedra and all Sr atoms in the structure, accounting for ca. 80% of the total scattering power, would, in the case of an ordered structure, probably enable remaining atoms to be located subsequently. Structure optimiza-

tion was accordingly carried out using FOX, with 10 Sr atoms at general $16f$ positions and 4 ScO_6 semi-rigid octahedra introduced randomly and using the dynamical occupancy correction. Four Sr atoms were found to occupy special $8e$ positions and eight were located at $16f$ positions. After the Sr atoms were located, 6 Ga atoms were randomly introduced in $16f$ positions. Probable Sc/Ga atom positions could at this stage also be inferred from the partial structure model. The difficulty in assigning the Sc and Ga atoms to different positions was overcome during a considerably long optimization. Several O atoms of the ScO_6 octahedra atoms were located by first refining the structure model using the full XRPD data range. The obtained refined atom positions were then fixed and FOX was used to find the positions of the missing atoms.

The final refinement was performed in the GSAS program package using simultaneously both the XRPD data and TOF NPD data. In total 310 variables were refined. Final reliability factors were $\chi^2 = 3.56$; $R_p = 0.023$ for the XRPD data (4475 reflections) and $R_p = 0.0339$ for the NPD data (154.4° data bank, 7074 reflections at $1.77 < d < 0.75 \text{ \AA}$) (see Table 3). Observed, calculated, and difference XRPD and NPD profiles are given in Figure 5a and b. Final atomic coordinates and displacement parameters are given in Table 1 of the Supporting Information, selected bond distances in Table 4. The variations in bond lengths are: $1.97 - 2.28 \text{ \AA}$ (average distance $2.105 \text{ \AA}$) for the ScO_6 octahedra and $1.76 - 1.93 \text{ \AA}$ (average distance $1.831 \text{ \AA}$) for the GaO_4 tetrahedra. These values are within the ranges typical for the Sc-O and Ga-O bond lengths observed in other oxides.

Figure 5. Observed, calculated and difference between them XRPD (a) and NPD (b) profiles for $\text{Sr}_x\text{Ga}_x\text{Sc}_x\text{O}_z$.

Figure 6. The crystal structure of $\text{Sr}_x\text{Ga}_x\text{Sc}_x\text{O}_z$. Red spheres are Sr cations; Sc³⁺ cations are located in octahedra (blue) and Ga³⁺ cations in tetrahedra (yellow and green).

The crystal structure of $\text{Sr}_x\text{Ga}_x\text{Sc}_x\text{O}_z$ (Figure 6) represents the novel type of ordering of the B-cations and oxygen vacancies in perovskites. It can be described as a sequence of eight perovskite layers along to the c -axis. There are only two unique (Sc/Ga)O₆ layers in the structure, named layer 1 (Figure 7a) and 2 (Figure 7b). Other layers are related to them by the symmetry elements of the $I4/a$ space group. As in the structure of brownmillerite $\text{Sr}_2\text{GaScO}_7$, gallium and scandium cations are fully ordered in the structure with Ga³⁺ and Sc³⁺ located in tetrahedra and octahedra, respectively. However, in comparison with the brownmillerite, gallium tetrahedra and scandium octahedra are present in all layers. Each layer consists of 12 GaO_4 tetrahedra and 8 ScO_6 octahedra. The arrangement of scandium octahedra in the layers 1 and 2 is different. In the layer 1 there are units of four corner sharing ScO_6 octahedra, while in the layer 2 only pairs of corner sharing ScO_6 octahedra are present. These units are connected through the GaO_4 tetrahedra. There are two tetrahedral groups marked in green and yellow on Figure 7a and b. The first group (yellow on Figure 7) represents a pair of the tetrahedra with a common corner. They are connected with a pair of ScO_6 octahedra. Such arrangement is also observed between octahedra and tetrahedra along the direction of tetrahedral chains in the neighboring layers of the brownmillerite structure. In the second group (green on Figure 7), namely Ga_2O_4 in the layer 1 and Ga_5O_4 in the layer 2, one of the tetrahedral vertices (O6 and O15, respectively) is not connected to other Ga/Sc polyhedra. In the layer 1 the remaining oxygens of the Ga_2O_4 tetrahedra are connected with both tetrahedral and octa-

hedral units, while in the layer 2 the Ga5O_4 tetrahedra are connected with the octahedral units only. This leads to different orientation of the Ga2O_4 and Ga5O_4 tetrahedra (O15 belongs to the $(\text{Sc}/\text{Ga})\text{O}_6$ layer, while O6 belongs to the SrO layer). As a result, the oxygen content of the layer 1 is $(\text{Sc}/\text{Ga})\text{O}_{15}$, while it is $(\text{Sc}/\text{Ga})\text{O}_{16}$ for the layer 2. Therefore the sequence of layers along to c -axis can be written as $\dots[-(\text{Sc}/\text{Ga})\text{O}_{15} - \text{SrO}_{16} - (\text{Sc}/\text{Ga})\text{O}_{16} - \text{SrO}_{16}] \dots$.

Figure 7. Two unique $(\text{Sr}/\text{Ga})\text{O}_6$ layers in the crystal structure of SrGaScO_{15} with different oxygen content: $(\text{Sc}/\text{Ga})\text{O}_{15}$, layer 1 (a) and $(\text{Sc}/\text{Ga})\text{O}_{16}$, layer 2 (b). GaO_4 tetrahedra belong to two groups with all vertexes shared with other Sc/Ga polyhedra (marked green) or with some oxygen atoms not connected to other Sc/Ga polyhedra (marked yellow).

3.3. $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_{15}$ with cubic perovskite structure. The XRPD pattern of the sample with the nominal composition $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_{15}$ (Figure 8) was indexed with a cubic perovskite cell with the unit cell parameter $a = 3.9817(4)$ Å. The presence of weak ($<1\%$) reflections from SrGa_2O_7 and unidentified phases was observed on the XRPD pattern. All attempts to prepare a single-phase sample by slightly varying the cation content off the stoichiometric $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_{15}$ composition were unsuccessful. Thorough analysis of the profiles of the reflections at the XRPD pattern did not indicate the deviation from the cubic symmetry. The primitive cubic unit cell was also supported by the absence of superstructure reflections in the SAED patterns of $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_{15}$ (Figure 9a). B-cations as well as the oxygen vacancies do thus not exhibit long range order although there is short range order forming domains as seen as diffuse scattering in the $[001]$ and $[1-30]$ SAED patterns and in a corresponding a dark field image from the diffuse scattering of the former (Figure. 9b).

Figure 8. XRPD pattern of the $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_{15}$ sample.

Figure 9. a) SAED patterns of the cubic perovskite $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_{15}$ viewed along $[001]$, $[11-1]$, $[110]$ and $[1-30]$. b) Dark field image from the diffuse intensities in the $[001]$ SAED pattern.

In order to determine the thermal expansion properties of $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_{15}$, a high-temperature XRPD study was performed. Temperature variation of the unit cell parameter is shown in Figure 10. Two regions with different thermal expansion coefficients (TEC) are observed. In the low temperature region (298-498K) the TEC value is 16.1 ppm K⁻¹ while it decreases sharply down to 11.8 ppm K⁻¹ in the high-temperature region (698-1098K). The latter value is close to 11.2 ppm K⁻¹ obtained from dilatometry data for the SrGaScO_4 brownmillerite.

Figure 10. Temperature variation of the unit cell parameter of $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ determined from high-temperature XRPD data. Thermal expansion coefficients (TEC) for different temperature ranges are given.

Combined thermal analysis and mass-spectrometry studies revealed release of water from the $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ sample in the temperature range of 500-673K. The measured weight loss corresponds to the composition $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3 \cdot 0.13\text{H}_2\text{O}$. The unit cell parameter of $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3 \cdot x\text{H}_2\text{O}$ increases with increasing the water content (x). For example, the unit cell parameter of the $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ sample treated in moisturized N_2 at 488K for 3 days ($a = 3.989(1) \text{ \AA}$) is substantially larger compared to that for the sample annealed in dry Ar at 1173K for 1h ($a = 3.973(1) \text{ \AA}$). This explains the existence of two regions with different TEC values shown in Figure 10. The absorption of water by $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ seems to be the first step of the decomposition of the compound in wet air. Holding $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ at 343K for 2 days in air saturated with water vapor leads to the complete decomposition of the compound. Only reflections from SrCO_3 are observed on the XRPD pattern, indicating the formation of amorphous products containing Sc and Ga. The decomposition seems to be accelerated by the formation of the thermodynamically stable SrCO_3 due to a reaction between $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3 \cdot x\text{H}_2\text{O}$ and CO_2 present in air. However, the decomposition process is rather slow at room temperature in air with natural humidity and $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ samples can thus be stored in these conditions for a prolonged period of time.

3.3.1. Study of the proton conductivity in $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$. Since Sc-contained perovskites, like doped LaScO_3 , are known to exhibit high-temperature proton conductivity⁴⁶, we have studied high-temperature conductivity of the $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$. A water saturated sample of $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ was prepared by heating the as-prepared samples at 488 K for 3 days in a flow of N_2 saturated with water vapor at 363K, $p_{\text{sat}}=0.69 \text{ atm}$ (so called prehydrated samples). The study of the sample by thermogravimetical analysis in dry N_2 at 298-1273K (Figure 1 of the Supporting Information) shows

that starting from $\sim 500\text{K}$ it exhibits significant mass loss due to the release of water molecules from the crystal structure. The weight of the sample stabilizes at $\sim 1150\text{K}$. The composition of the prehydrated sample was calculated from TG data as $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3 \cdot 0.043\text{H}_2\text{O}$. No mass gain was observed on the cooling cycle.

Conductivity measurements were performed on the prehydrated samples in the following cycle: 1. the prehydrated samples were heated up to 1273 K in dry Ar; 2. thereupon the samples were cooled down to 423K in dry Ar; 3. finally the samples were heated up to 1273K in wet Ar and the conductivity was measured in the cooling cycle.

Complex impedance plots for prehydrated $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ samples in heating and cooling cycles in dry Ar are presented in Figure 2 of the Supporting Information with the equivalent circuit model used for the analysis of impedance data shown on the inset. At temperatures higher than 773 K it was difficult to separate bulk and grain boundary conductivities; therefore only the values of the total conductivities are presented.

The corresponding Arrhenius plots are shown on Figure 11, from which it is clear that the total conductivity of the prehydrated samples is higher in the heating cycle than in the cooling cycle in dry Ar, especially at $T < 773\text{K}$. Therefore one can conclude that within this temperature range the proton conductivity dominates due to the presence of water molecules in the crystal structure. This idea is supported by the fact that the water-free samples obtained after the heating cycle in dry Ar show much higher conductivity at $T < 773\text{K}$ in wet Ar in comparison with dry Ar (compare curves 2 and 3 on Figure 11).

Assuming proton conduction has no effect on other charge carriers contribution, the pure protonic conductivity σ_H can be calculated as the difference between the conductivity in H_2O -saturated Ar, σ_{wet} , and the conductivity of water-free sample obtained during the cooling cycle in dry Ar, σ_{dry} :

$$\sigma_H = \sigma_{\text{wet}} - \sigma_{\text{dry}}$$

The corresponding Arrhenius plot for pure protonic conductivity is shown in Figure 11.

Figure 11. Temperature dependences (Arrhenius plots) of the total conductivities of the prehydrated $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ samples in heating and cooling cycles in dry Ar. Curve 1 corresponds to the heating of the prehydrated sample in dry Ar; curve 2 corresponds to the cooling of the water-free sample in dry Ar; curve 3 corresponds to the heating of the water-free sample in wet Ar.

Figure 12. Temperature dependence (Arrhenius plot) of the proton conductivity (σ_H) for $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ calculated as the difference between the conductivity in H_2O -saturated Ar (σ_w) and the conductivity of water-free sample (σ_d).

The transference number for proton conductivity (t_H) in wet Ar can be calculated from the equation ²²:

$$t_H = \frac{\sigma_H}{\sigma_{wet}}$$

The temperature dependence of t_H is given in Figure 13. Proton conductivity dominates in the low temperature region and the substantial decrease is observed only at $T > 623$ K.

Figure 13. Proton transfer number (t_H) in wet Ar for $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$.

Higher activation energies (E_a) are observed for the high-temperature part of the total conductivity in the heating cycle in dry and the cooling cycle in wet Ar and in the whole temperature range for the cooling cycle in dry Ar (Figures 11) in comparison with the low-temperature part (e.g. for the $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ sample cooled down in wet Ar $E_a = 1.21$ eV at $T = 873$ – 1273 K while at $T = 573$ – 773 K it is only 0.71 eV). Such a high value of E_a at high temperature indicates predominant hole or oxide-ion conductivity. To reveal the nature of the high-temperature conductivity, conductivity measurements were performed for $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ in dry oxygen and dry Ar. The corresponding Arrhenius plots are given in Figures 3 of the Supporting Information. The conductivity of $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$ in dry oxygen is similar to that in dry Ar, indicating a predominance of oxide-ion conductivity in this compound under these conditions. Moreover, taking into account total conductivity values at high temperature ($8.5 \cdot 10^{-5}$ S/cm at 1273 K) and expectedly low electronic conductivity for such type of oxides, one can propose moderate oxide-ion conductivity for $\text{SrGa}_{0.5}\text{Sc}_{0.5}\text{O}_3$.

4. DISCUSSION

The $\text{A}_2(\text{B},\text{B}')\text{O}_3$ oxygen-deficient perovskites with only one type of A-cation crystallize in different structure types, depending on the stable coordination number of B-cation. One type comprises oxides with Jahn-Teller B-cations such as CaMnO_3 , SrMnO_3 and LaCuO_3 . In their crystal structures BO_4 square pyramids are connected by vertexes forming a 3D framework (Figure 14a). In the crystal structure of LaNiO_3 Ni^{2+} cations are distributed over an equal amount of corner shared squares and octahedra (Figure 14b). The brownmillerite structure type ($\text{Ca}(\text{Fe},\text{Al})\text{O}_3$) is the most widely spread among the $\text{A}_2(\text{B},\text{B}')\text{O}_3$ compounds. It contains layers of corner-shared octahedra alternating with tetrahedral layers (Figure 14c). Brownmillerites with a single type of B-cation or with several B-cations are known. In the former case the B-cation should be sta-

ble in both tetrahedral and octahedral environments like in the case of SrFeO_3 , CaFeO_3 , BaInO_3 or SrInO_3 . When different B-cations are present, they can be fully or partially ordered over the octahedral and tetrahedral positions in the brownmillerite structure due to the geometrical or/and electronic reasons. Full ordering is usually observed in compounds with Jahn-Teller cations, for example, in LaSrCuGaO_6 and M_2GaMnO_6 , $\text{M}=\text{Ca}, \text{Sr}$. Partial ordering of B-cations can be found in $\text{CaGa}(\text{Al})\text{FeO}_6$ or $\text{Sr}(\text{Ca})_x(\text{Co}, \text{Ga})_{1-x}\text{O}_6$ where the 3d-metal cations preferentially occupy octahedral positions. In the above-listed structures all corners of the BO_x polyhedra are connected with each other. To our knowledge, however, there is at least one example of the anion-deficient perovskite BaRM_2O_6 (or $\text{BaR}_x\text{M}_{2-x}\text{O}_6$, $\text{R} = \text{rare-earth elements}, \text{M} = \text{Al}, \text{Ga}$) in which structures there are tetrahedral units with some vertexes not connected to other B-cations.

Figure 14. Crystal structures of different oxygen-deficient perovskites ABO_3 : a) SrMnO_3 ; b) LaNiO_3 ; c) brownmillerite $\text{Ca}(\text{Fe}, \text{Al})\text{O}_3$.

The studied $\text{SrGa}_x\text{Sc}_{1-x}\text{O}_6$ system provides a rare example of a variation of the B/B' -cation ratio with fixed oxygen content leading to three different perovskite-related phases. The basis for such behavior is a substantial difference in the size of Sc^{3+} and Ga^{3+} ($r(\text{Sc}^{3+})=0.73\text{\AA}$; $r(\text{Ga}^{3+})=0.62\text{\AA}$ for $\text{CN}=6$ and $r(\text{Ga}^{3+})=0.47\text{\AA}$ for $\text{CN}=4$) and a strong preference of Sc^{3+} for an octahedral environment. As a consequence, the variation of the Sc/Ga ratio in $\text{SrGa}_x\text{Sc}_{1-x}\text{O}_6$ is equivalent to the variation of the octahedra/tetrahedra ratio. In SrGaScO_6 ($x=0.5$) with the brownmillerite structure the octahedra and tetrahedra are present in equal amounts, thus oxide represents an example of the structure in which a complete ordering of the B-cations occurs mainly due to coupling with the ordering of the oxygen vacancies.

One can imagine several ways of transforming an ordered brownmillerite phase into a disordered cubic perovskite. The first one includes a temperature induced phase transformation. An example of such a transformation is BaInO_3 with the brownmillerite structure which reversibly transforms to a disordered perovskite phase at $T>930^\circ\text{C}$ due to a disorder in the O-sublattice. The ordering of Ga^{3+} and Sc^{3+} in SrGaScO_6 brownmillerite prevents a disorder of oxygen vacancies without a disorder in the B-cation sublattice. A com-

plete disorder at both sublattices was achieved only by quenching the melt of this compound. Another common way to introduce disorder in the O-sublattice is an increase of the oxygen content in tetrahedral layers by the heterovalent substitution of the A- and/or B-cations. This was done for SrGaScO_6 by partial replacement of Sc^{3+} by Zr^{4+} according to the formula $\text{SrGa}_x\text{Sc}_{1-x}\text{Zr}_y\text{O}_{6-y}$. For SrGaScO_6 , a third way to transform to the cubic phase is the partial replacement of octahedral Sc^{3+} by Ga^{3+} as achieved in the cubic perovskite $\text{SrGa}_x\text{Sc}_{1-x}\text{O}_6$. The substitution introduces disorder in the octahedral layers of the brownmillerite structure due to the substantial size difference between Ga^{3+} and Sc^{3+} cations and also allows the disorder in the oxygen sublattice since Ga^{3+} , in comparison with Sc^{3+} , has a rather high flexibility of its coordination environment.

The transformation of the SrGaScO_6 brownmillerite to a cubic perovskite by substitution of Sc^{3+} by Ga^{3+} does not occur continuously and at intermediate composition the novel $\text{Sr}_x\text{Ga}_y\text{Sc}_{1-x-y}\text{O}_6$ compound with a previously unknown type of ordering of B-cations and oxygen anions was isolated. Despite the resemblance of the lattice metrics and space group ($a = b \approx 2\sqrt{5} \cdot a_c$ and $c \approx 8 \cdot a_c$; S.G. $I4/a$) to some elpasolites type-compounds like $\square\text{-KAlF}_6$, the crystal structure is different. In elpasolites, $\text{AB}_2\text{B}'\text{F}_6$, the B and B' cations are ordered in a chessboard manner due to a substantial size and charge difference. Moreover, since one of the B-cations represents a large alkaline cation, which prefers coordination numbers >6 , sometimes large displacements of the anions take place. This leads to an increase of the coordination numbers of alkaline cations to $\text{CN} = 7, 8$ like e.g. in $\square\text{-KAlF}_6$. In the crystal structure of $\text{Sr}_x\text{Ga}_y\text{Sc}_{1-x-y}\text{O}_6$ there is a complete ordering of B-cations over the octahedral (Sc^{3+}) and tetrahedral (Ga^{3+}) sites. In comparison with brownmillerite SrGaScO_6 the number of tetrahedra in $\text{Sr}_x\text{Ga}_y\text{Sc}_{1-x-y}\text{O}_6$ exceeds the number of octahedra by 50%. The oxygen stoichiometry O_{6-x} is maintained by that 1/3 of the tetrahedra in the $\text{Sr}_x\text{Ga}_y\text{Sc}_{1-x-y}\text{O}_6$ crystal structure have one vertex not connected with other Sc/Ga cations. A similar effect is also observed in the already mentioned BaRM_2O_6 (or $\text{BaR}_x\text{M}_{2-x}\text{O}_6$, $\text{R} = \text{rare-earth elements}, \text{M} = \text{Al}, \text{Ga}$) anion-deficient perovskites. In BaRM_2O_6 , the R- and M- cations, substantially different in size, are fully ordered over octahedral and tetrahedral sites. However, the arrangement of these polyhedra in BaRM_2O_6 is completely different in comparison with $\text{Sr}_x\text{Ga}_y\text{Sc}_{1-x-y}\text{O}_6$.

Sc -containing oxygen-deficient perovskites are known to exhibit proton conductivity due to the partial filling of the oxygen vacancies by water molecules and to the formation of the hydroxyl groups according to the equation:

Thus $\text{La}_{0.5}\text{Ba}_{0.5}\text{ScO}_3$ exhibits high proton conductivity $\sim 1.5 \cdot 10^{-2} \text{ S/cm}$ at 673 K . We have shown that

$\text{Sr}_{0.5}\text{Ga}_{0.5}\text{Sc}_{0.5}\text{O}_{1.5}$ is capable to conduct protons. However, its proton conductivity is much lower ($\sim 2.0 \cdot 10^{-4}$ S/cm at 673K) in comparison with that of the doped LaScO_3 . One can explain it by a high concentration of the remaining oxygen vacancies in the studied $\text{Sr}_{0.5}\text{Ga}_{0.5}\text{Sc}_{0.5}\text{O}_{1.5}$ samples, which are not filled by OH groups.

5. CONCLUSIONS

The $\text{Sr}_{0.5}\text{Ga}_{0.5}\text{Sc}_{0.5}\text{O}_{1.5}$ system provides a unique example of the substantial difference in crystal chemistry of Sc and Ga cations, for which the variation of the Sc/Ga ratio leading to three different perovskite-related phases with fixed oxygen content. In brownmillerite-like $\text{Sr}_2\text{GaScO}_7$, Sc and Ga cations are fully ordered over an equal amount of the octahedral and tetrahedral positions of the crystal structure. Partial substitution of scandium by gallium leads to the formation of $\text{Sr}_2\text{Ga}_2\text{Sc}_2\text{O}_{12}$ having a perovskite-like structure with a large unit cell ($a = b \approx 2\sqrt{5}a_p$, $c \approx 8a_p$, a_p - perovskite sub-cell parameter). Like in the case of brownmillerite, in its structure a full ordering of Ga and Sc over tetrahedral and octahedral positions takes place. However, the number of tetrahedral positions in $\text{Sr}_2\text{Ga}_2\text{Sc}_2\text{O}_{12}$ is by 50% higher in comparison with the number of octahedral ones. This leads to the fact that 1/3 of the tetrahedra have one vertex not connected with other Sc/Ga cations. Further substitution of Sc by Ga leads to the complete disorder of the B-cations and oxygen vacancies and to the formation of SrGaScO_3 with the cubic perovskite structure. This compound is capable, as other scandium-contained perovskites, of being a proton conductor with $\sigma_p = 2.0 \cdot 10^{-4}$ S/cm at 673K.

FIGURES

Figure 1. Observed, calculated and difference between them XRPD profiles for $\text{Sr}_2\text{GaScO}_7$.

Figure 2. XRPD pattern of the $\text{Sr}_2\text{GaScO}_7$ sample quenched from 1723K.

Figure 3. The compositional dependence of the unit cell parameters for $\text{Sr}_{1-x}\text{Ga}_x\text{Sc}_{1-x}\text{ZrO}_{3-0.5x}$.

Figure 4. SAED patterns of $\text{Sr}_2\text{Ga}_2\text{Sc}_2\text{O}_{12}$. Selected low index zone axes patterns in the perovskite subcell are shown as well in the supercell. The relation between the perovskite subcell and supercell is $a = b \approx 2\sqrt{5}a_p$, $c \approx 8a_p$.

TABLES.

Table 1. Summary of the results of the least-square fits, final atomic coordinates and displacement parameters for $\text{Sr}_2\text{GaScO}_7$.

Space group	Icmm
a, Å	5.91159(7)
b, Å	15.1526(2)

Figure 5. Observed, calculated and difference between them XRPD (a) and NPD (b) profiles for $\text{Sr}_{0.5}\text{Ga}_{0.5}\text{Sc}_{0.5}\text{O}_{1.5}$.

Figure 6. The crystal structure of $\text{Sr}_{0.5}\text{Ga}_{0.5}\text{Sc}_{0.5}\text{O}_{1.5}$. Red spheres are Sr cations, Sc cations are located in octahedra (blue) and Ga cations in tetrahedra (yellow and green).

Figure 7. Two unique (Sr/Ga)O layers in the crystal structure of $\text{Sr}_{0.5}\text{Ga}_{0.5}\text{Sc}_{0.5}\text{O}_{1.5}$ with different oxygen content: (Sc/Ga)O_{0.5}, layer 1 (a) and (Sc/Ga)O_{1.5}, layer 2 (b). GaO₄ tetrahedra belong to two groups with all vertexes shared with other Sc/Ga polyhedra (marked green) or with some oxygen atoms not connected to other Sc/Ga polyhedra (marked yellow).

Figure 8. XRPD pattern of the SrGaScO_3 sample.

Figure 9. a) SAED patterns of the cubic perovskite SrGaScO_3 viewed along [001], [11-1], [110] and [1-30]. b) Dark field image from the diffuse intensities in the [001] SAED pattern.

Figure 10. Temperature variation of the unit cell parameter of SrGaScO_3 determined from high-temperature XRPD data. Thermal expansion coefficients (TEC) for different temperature ranges are given.

Figure 11. Temperature dependences (Arrhenius plots) of the total conductivities of the prehydrated $\text{Sr}_{0.5}\text{Ga}_{0.5}\text{Sc}_{0.5}\text{O}_{1.5}$ samples in heating and cooling cycles in dry Ar. Curve 1 corresponds to the heating of the prehydrated sample in dry Ar; curve 2 corresponds to the cooling of the water-free sample in dry Ar; curve 3 corresponds to the heating of the water-free sample in wet Ar.

Figure 12. Temperature dependence (Arrhenius plot) of the proton conductivity (σ_p) for $\text{Sr}_{0.5}\text{Ga}_{0.5}\text{Sc}_{0.5}\text{O}_{1.5}$ calculated as the difference between the conductivity in H₂O-saturated Ar (σ_{wet}) and the conductivity of water-free sample (σ_{dry}).

Figure 13. Proton transfer number (t_p) in wet Ar for $\text{Sr}_{0.5}\text{Ga}_{0.5}\text{Sc}_{0.5}\text{O}_{1.5}$.

Figure 14. Crystal structures of different oxygen-deficient perovskites AB_2O_5 : a) $\text{Sr}_2\text{Mn}_2\text{O}_7$; b) $\text{La}_2\text{Ni}_2\text{O}_7$; c) brownmillerite $\text{Ca}_2(\text{Fe,Al})_2\text{O}_7$.

c, Å	5.70458(7)
Z	8
cell volume, Å ³	510.99(2)
calcd density, g/cm ³	4.808
Radiation	CuK ₁ , λ=1.54060 Å
2Θ range; step, deg	5 ≤ 2Θ ≤ 100, 0.0081
params. refined	37
² , R _F ² , R _{wp} , R _p	2.23; 0.0406, 0.0796, 0.0618

Atom	Site	x	y	z	U _{iso} *100/Å ²	Occ.
Sr	8h	0.0200(1)	0.11199(4)	0.5	1.09(9)	1
Sc	4a	0	0	0	0.9(1)	1
Ga	8i	-0.0718(2)	0.25	-0.0268(7)	1.3(1)	0.5
O1	8g	0.25	-0.0140(2)	0.25	0.4(1)	1
O2	8h	0.0719 (6)	0.1458(3)	0	2.2(2)	1
O3	8i	0.833(1)	0.25	0.660(1)	2.0	0.5

Table 2. Selected interatomic distances (Å) for Sr₁₀Ga₆Sc₄O₂₅.

O1-Sc:	(x4)	2.0647(4)
O2-Sc:	(x2)	2.250(4)
O2-Ga:	(x2)	1.799(4)
O3-Ga:	(x2)	1.877(8)
Sr-O1:	(x2)	2.605(2)
	(x2)	2.743(3)
Sr-O2:		2.466(4)
	(x2)	2.9142(7)
Sr-O3:	(x2)	2.534(4)

Table 3. Summary of the results of the least-square fits to the XRPD (NPD) data collected for Sr₁₀Ga₆Sc₄O₂₅.

Space group	I4 ₁ /c
a, Å	17.52963(4)
c, Å	32.85749(9)
Z	16
cell volume, Å ³	10096.71(6)
calcd density, g/cm ³	4.932
XRPD data set:	
Radiation	CuK ₁ , λ=1.54060Å
2Θ range; step, deg	5 ≤ 2Θ ≤ 125, 0.0167
R _F ² , R _{wp} , R _p	0.023, 0.0374, 0.0294
NPD data set:	
d range, Å	0.75-14
R _F ² , R _{wp} , R _p	0.0339, 0.0273, 0.0231
params. refined	310
_{tot} ²	3.56

Table 4. Selected bond lengths for the crystal structure of Sr₁₀Ga₆Sc₄O₂₅.

Sc1	O8 2.19(1)	Sc2	O9 2.28(1)	Sc3	O1 2.22(1)	Sc4	O4 2.17(1)
	O10 2.14(1)		O12 2.07(1)		O5 2.16(1)		O17 2.04(1)
	O16 2.02(1)		O13 2.13(1)		O14 2.10(1)		O20 2.13(1)
	O18 2.04(1)		O19 2.17(1)		O22 1.97(1)		O21 2.12(1)
	O21 2.04(1)		O22 2.13(1)		O24 2.07(1)		O25 2.11(1)
	O23 2.05(1)		O23 2.10(1)		O24 2.01(1)		O25 2.08(1)
Ga1	O1 1.81(1)	Ga2	O5 1.81(1)	Ga3	O2 1.88(1)	Ga4	O11 1.87(1)
	O2 1.79(1)		O6 1.80(1)		O9 1.85(1)		O12 1.89(1)

	03 1.86(1)		07 1.93(1)		010 1.81(1)		013 1.81(1)
	04 1.77(1)		08 1.81(1)		011 1.84(1)		014 1.86(1)
Ga5	015 1.79(1)	Ga6	03 1.83(1)				
	016 1.85(1)		07 1.76(1)				
	017 1.83(1)		019 1.83(1)				
	018 1.84(1)		020 1.82(1)				
Sr1	017 2.95(1) (x2)	Sr2	01 2.773(7)	Sr3	04 2.49(1)	Sr4	02 2.767(9)
	018 2.799(9) (x2)		02 2.88(1)		08 2.62(1)		03 2.86(1)
	021 3.122(7) (x2)		05 2.833(9)		010 2.66(1)		05 2.81(1)
	025 2.82(1) (x2)		06 2.923(8)		015 3.07(1)		07 3.02(1)
	025 2.64(1) (x2)		011 2.551(9)		016 2.53(1)		08 3.15(1)
			013 3.10(1)		017 2.60(1)		09 2.837(9)
			014 2.57(1)		020 2.65(1)		015 2.51(1)
			022 2.507(8)				018 2.872(9)
			024 2.782(9)				022 2.81(1)
							023 2.60(1)
Sr5	07 2.51(1) (x2)	Sr6	01 2.479(7)	Sr7	06 2.640(9)	Sr8	01 2.883(8)
	08 2.74(1) (x2)		05 2.84(1)		07 3.13(1) (x2)		03 2.70(1)
	016 2.73(1) (x2)		08 2.76(1)		012 2.73(1) (x2)		05 2.64(1)
	018 2.554(9) (x2)		010 2.63(1)		013 2.995(9) (x2)		09 2.62(1)
			012 2.80(1)		019 2.65(1) (x2)		011 2.952(9)
			014 3.07(1)				013 2.428(9)
			022 2.937(8)				014 2.50(1)
			023 2.52(1)				019 2.79(1)
			024 2.51(1)				
Sr9	02 2.88(1)	Sr10	03 3.05(1)	Sr11	012 2.71(1) (x2)	Sr12	02 2.90(1)
	03 2.87(1)		04 2.85(1)		014 3.004(9) (x2)		06 2.412(8)
	04 3.15(1)		09 2.476(9)		022 2.98(1) (x2)		010 3.04(1)
	010 3.36(1)		017 2.84(1)		024 2.604(9) (x2)		011 2.803(9)
	015 2.35(1)		018 2.736(9)		024 2.89(1) (x2)		012 2.95(1)
	016 2.78(1)		019 2.91(1)				019 2.60(1)
	017 2.70(1)		021 2.812(8)				021 2.83(1)
	020 2.88(1)		025 2.61(1)				021 2.554(8)
	021 2.527(8)						023 2.87(1)
	025 2.70(1)						

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ASSOCIATED CONTENT

Supporting Information. Table with final atomic coordinates and displacement parameters for $\text{Sr}_2\text{GaScO}_5$; X-ray crystallographic files of the refined structures (CIF); Figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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All authors have given approval to the final version of the manuscript.

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Table of Contents (TOC) summary

The $\text{SrGa}_{1-x}\text{Sc}_x\text{O}_{2.5}$ system provides a unique example of the substantial difference in crystal chemistry of Sc^{3+} and Ga^{3+} cations, for which the variation of the Sc/Ga ratio leading to three different perovskite-related phases with fixed oxygen content.

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