**Sr\textsubscript{2}GaScO\textsubscript{5}, Sr\textsubscript{10}Ga\textsubscript{6}Sc\textsubscript{4}O\textsubscript{25} and SrGa\textsubscript{0.75}Sc\textsubscript{0.25}O\textsubscript{2.5}: a play in octahedra to tetrahedra ratio in oxygen-deficient perovskites.**

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**KEYWORDS:** oxygen deficient perovskite, crystal structure, proton conductors, oxide-ion conductors.

Supporting Information Placeholder

**ABSTRACT:** Three different perovskite-related phases were isolated in the SrGaScO\textsubscript{x} system: SrGaScO\textsubscript{5}, Sr\textsubscript{10}Ga\textsubscript{6}Sc\textsubscript{4}O\textsubscript{25}, and SrGa\textsubscript{0.75}Sc\textsubscript{0.25}O\textsubscript{2.5}, which crystallizes in a brownmillerite-type structure (S.G. I\textsubscript{4}2/mmm, \(a = 5.9104(5)\) Å, \(b = 15.1594(1)\) Å and \(c = 5.70926(4)\) Å) with complete ordering of Sc and Ga over octahedral and tetrahedral positions, respectively. The crystal structure of SrGaScO\textsubscript{0.4} was determined by the Monte Carlo method and refined using a combination of X-ray, neutron, and electron diffraction data (S.G. I\textsubscript{4}2/m, \(a = 17.517(1)\) 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 SrGaScO\textsubscript{5} can be described as a stacking of eight perovskite layers along the \(c\)-axis, ..., [ScGa\textsubscript{5}O\textsubscript{10} - SrO\textsubscript{2} - [ScGa\textsubscript{5}O\textsubscript{10} - SrO\textsubscript{2} - ...]. Similar to SrGaScO\textsubscript{5}, this structure features a complete ordering of the Sc and Ga cations over octahedral and tetrahedral positions, respectively, within each layer. A specific feature of the crystal structure of SrGaScO\textsubscript{5} is that 1/3 of the tetrahedra have one vertex not connected with other Sc/Ga cations. Further partial replacement of Sc\textsuperscript{3+} by Ga leads to the formation of the cubic perovskite phase SrGa\textsubscript{0.75}Sc\textsubscript{0.25}O\textsubscript{2.5} with \(a = 3.9817(4)\) Å. This compound incorporates water molecules in the structure forming SrGaScO\textsubscript{2.5}H\textsubscript{2}O hydrate, which exhibits proton conductivity \(\sim 2.0 \times 10^{-4} \text{ S/cm at 673K.}\)

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 ABO\textsubscript{x}, A = Sr, Ba; B = Ce; Zr, or oxygen-deficient perovskite-related niobium...
and tantalum oxides like $\text{A}_2\text{B}_5\text{O}_{12}; \text{A} = \text{alkaline-earth}; \text{B} = \text{Nb, Ta}$ (see, for example, a recent review ). The latter includes various oxygen-deficient compounds, e.g. $\text{Zr}_x\text{Y}_y\text{O}_z$, $\text{YSZ}$, and $\text{LaSrGa}_{1-x}\text{Mg}_x\text{O}_{3+y}$ [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 Ga and In cations. Thus the oxide-ion conductivity of LSGM outperforms traditional SOFC materials like YSZ 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 gellant at high temperatures and its high reactivity towards metallic Ni, often used as a component of anodes in SOFC. Another example is $\text{BaInO}_3$ with the brownmillerite structure which transforms at ~930°C to the disordered perovskite with high oxide-ion conductivity . The cubic perovskite phase can be stabilized by appropriate doping, and $\text{BaSrLa}_2\text{In}_3\text{O}_x$ is known to exhibit oxide-ion conductivity up to 0.1 S/cm at 800°C.

Perovskite-like oxides $\text{A}_2\text{B}_x\text{O}_{2x+1}; \text{A} = \text{Sr, Ba and B} = \text{group 13 element}; \text{B}^\text{II} = \text{other trivalent cation with invariable oxidation state like Se or small rare-earth cations},$ 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. $\text{BaAlSeO}_5$ and $\text{BaGaSeO}_5$ have ordered structures with the hexagonal closed packing of the $\text{BaO}$ layers (so called anion-deficient hexagonal perovskites). In the $\text{SrSeO}_2$ system several compounds have been reported. $\text{SrAlSeO}_5$ has a cubic structure ($a = 7.9078(4)$ Å) with oxygen vacancies randomly distributed around two B-cation sites . Y. Takeda et al. have reported the formation of the cubic $\text{SrAlSeO}_5$ perovskite with $a = 3.9554(6)$ Å and the perovskite related phases in the compositional range $\text{SrAlSeO}_x, 0 \leq x \leq 0.15$. $\text{SrAlSeO}_5$ exhibits low oxide-ion conductivity of ~10 S/cm at 1000°C.

In the present paper we report on the investigation of the $\text{SrGaSeO}_x$ system, where three novel oxygen-deficient perovskites have been isolated: $\text{SrGa}_{2-x}\text{O}_y$ with the cubic perovskite structure, brownmillerite type $\text{SrGaSeO}_5$, and $\text{SrGa}_2\text{SeO}_6$ with a novel type of ordering of the B-cations and oxygen vacancies. The high-temperature conductivity of $\text{SrGaSeO}_5$ in various atmospheres including wet gases was also studied.

2. EXPERIMENTAL

Samples of $\text{SrGaSeO}_5, 0.05 \leq x \leq 0.75$ were prepared by the polycrystalline gel synthesis . Stoichiometric mixtures of $\text{SeO}_2$, $\text{GaO}$, $\text{SrCO}_3$ were dissolved in a minimal amount of concentrated $\text{HNO}_3$. Thereafter an aqueous solution of ammonium citrate (NH$_4$)Cit was added. The amount of citrate was calculated according to the chemical formula ML$_x$, 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$_4$OH. Acrylamide and N,N'-methyleneacrylamide 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.-Azoisobutyronitrile (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 $\text{SrGaSeZr}_xO_{5-x}, x = 0.01-0.12; x = 0.01$ stoichiometric mixtures of $\text{SeO}_2$ and $\text{GaO}$ were dissolved in minimal quantity of concentrated nitric acid. The obtained solution together with stoichiometric amounts of $\text{SrCO}_3$ and $\text{ZrO(NO)}_3, 5.3\text{H}_2\text{O}$ 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 radiation, image foil detector). High-temperature X-ray powder diffraction (HT XRPD) data for $\text{SrGaSeO}_5$ and room-temperature data for the Rietveld refinement of $\text{SrGaSeO}_5$ crystal structure were collected in air using a Bruker D8-Advance diffractometer (CuK radiation, Yanacant PSD) in reflection mode equipped with a high-temperature camera XRS-900 (Anton Paar). XRPD pattern for the structural refinement of $\text{SrGaSeO}_5$ crystal structure was collected with a PANalytical X'Pert PRO MPD diffractometer using CuK radiation, variable slits with a constant area of 4 cm 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 package .

Electron diffraction (ED) patterns were recorded with JEOL JEM2000FX and Philips CM20 TEMs with a LaB
of the tetrahedral and octahedral structures having space groups between the relative orientation of the tetrahedral unit cell. It is well known that depending on the relative orientation of the tetrahedral chains between the octahedral layers in brownmillerite two high order structures having space groups \( \text{iibm2} \) (no. 46) and \( \text{Pcmn} \) (no. 62) can be obtained. A random ordering of the tetrahedral layers leads to space group \( \text{Icmm} \) (no. 74).

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 \( \text{SrGaScO}_5 \). For the electrical conductivity measurements pellets of \( \text{SrGaScO}_5 \) \((d = 12.4 \text{ mm}, h = 1.5 \text{ mm})\) were coated by Pt-paste (Heraeus CL 11-5100) and heated at 1273 K for 1 h.

Netzsch 402C dilatometer operated in air \((298-1173 K, 10 \text{K/min})\) was used for the thermal expansion coefficient measurements of the \( \text{SrGaScO}_5 \) 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 \((\text{Linde Gas}, 99.997\%), 5 \text{ ppm \ H}_2\) or nitrogen \((\text{AGA}, 5 \text{ ppm \ H}_2\) 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 \( \text{SrGaScO}_5 \) system. The formation of single-phase samples was observed for the compositions \( \text{SrGaScO}_5,x=0.25, 0.375, \) 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 \( \text{SrGaO}_3 \), while for \( 0.25 < x < 0.35 \) unidentified admixture phase(s) was observed as well. The 0.375–0.5 samples contained a mixture of the two phases with \( x = 0.375 \) and 0.5. Also the samples with \( 0.5 < x < 0.75 \) were not single-phase and contained unknown admixture phase(s), together with the \( x=0.5 \) phase.

3.1. \( \text{SrGaScO}_5 \) with the brownmillerite structure.

Single phase samples of \( \text{SrGaScO}_5 \) were obtained by annealing at 1473 K for 15 hours followed by cooling down to room temperature with a rate of \( \sim 150 \text{ K/h} \). The XRPD pattern of \( \text{SrGaScO}_5 \) was indexed with an orthorhombic unit cell with \( a = 5.91048(5) \text{ Å}, b = 15.1394(1) \text{ Å}, \) and \( c = 5.70926(4) \text{ Å} \). Suggesting the formation of the brownmillerite type structure, hereinafter referred to as \( \text{SrGaScO}_5 \). 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 \( \text{iibm2} \) (no. 46) and \( \text{Pcmn} \) (no. 62) can be obtained. A random ordering of the tetrahedral layers leads to space group \( \text{Icmm} \) (no. 74).

Reflection conditions do not allow distinguishing between \( \text{iibm2} \) and \( \text{Icmm} \) space groups. The \( \text{SrGaScO}_5 \) 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 \( \text{Icmm} \) led to slightly better R-values \((R = 0.0796, R = 0.0618, \sim 2.23)\) compared to \( \text{iibm2} \) \((R = 0.0804, R = 0.0623, \sim 2.28)\). Moreover, some interatomic distances between B-cations and oxygen atoms in \( \text{iibm2} \) were unreasonably short. For example, two distances between scandium and equatorial oxygen atoms were \( 1.92(1) \text{ Å} \) in comparison with a typical Sc-O distance of \( \sim 2.1 \text{ Å} \). This indicates that the correct space group for \( \text{SrGaScO}_5 \) is \( \text{Icmm} \). 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 \( \text{SrGaScO}_5 \) 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 \((2.250(4) \text{ Å})\) in comparison with equatorial ones \((2.0647(4) \text{ Å})\). This together with disorder in the tetrahedral layers leads to distortion of the gallium tetrahedron with the Ga-O bond length varying between \( 1.799(4)-1.877(8) \text{ Å} \).

The DSC experiment on \( \text{SrGaScO}_5 \) shows a strong exothermal effect at \( \sim 1663 \text{K} \), which can be most likely interpreted as melting. XRPD pattern of the \( \text{SrGaScO}_5 \) sample quenched from 1723 K (Figure 2) can be indexed in a cubic perovskite cell with \( a = 3.90382(1) \text{ Å} \), 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.
without indications of disorder. A number of tilt series investigation revealed the material to be well crystallized. The SAED indicated the supercell. The SAED indicated numerous weak superstructure reflections. The formation of a perovskite structure was observed. A solid solution with the perovskite supercell was found. The composition of the supercell in addition to the perovskite subcell is shown in Figure 4. SAED indicates the reflection conditions \( hkl \), \( h+k+l = 2m \), \( h,k \neq 2n \), \( l = 4n \), 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 \( \text{SrGaScO}_x \), which differs only slightly from the composition of the sample \( \text{SrGaSeO}_x \). Therefore the composition of the phase will hereinafter be referred to as \( \text{SrGaSeO}_x \).

3.2.1. Refinement of the crystal structure of \( \text{SrGaSeO}_x \). The XRPD pattern of \( \text{SrGaSeO}_x \) was fully indexed with the unit cell parameters and space group obtained from the SAED study \( (a = 17.517(1) \text{ Å}; c = 32.830(3) \text{ Å}) \). 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 \( \text{SrGaSeO}_x \). The solution of the structure was simplified by the fact that it contains B-cations with different crystal chemistry. Large Sc cations are known to possess octahedral oxygen coordination. A localization of all 4 ScO tetrahedra 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 SeO 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 SeO 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 $R_w = 3.56$; $R = 0.023$ for the XRPD data (4475 reflections) and $R = 0.0339$ for the NPD data (154,435 reflections at 1.77-2.28 Å) (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 Å (average distance 2.105 Å) for the SeO octahedra and 1.76 – 1.93 Å (average distance 1.831 Å) for the GaO 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 SrGaSeO.

Figure 6. The crystal structure of SrGaSeO. Red spheres are Sr cations; Sc cations are located in octahedra (blue) and Ga cations in tetrahedra (yellow and green).

The crystal structure of SrGaSeO. 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/GaO 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 $K/a$ space group. As in the structure of brownmillerite SrGaSeO, gallium and scandium cations are fully ordered in the structure with Ga and Sc 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 tetrahedra and 8 SeO 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 SeO octahedra, while in the layer 2 only pairs of corner sharing SeO octahedra are present. These units are connected through the GaO 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 SeO 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 Ga2O in the layer 1 and Ga5O in the layer 2, one of the tetrahedral vertexes (O6 and O15, respectively) is not connected to other Ga/Se polyhedra. In the layer 1 the remaining oxygens of the Ga2O tetrahedra are connected with both tetrahedral and octa-
hedral units, while in the layer 2 the Ga5O tetrahedra are connected with the octahedral units only. This leads to different orientation of the Ga2O and Ga5O tetrahedra (O15 belongs to the (Sc/Ga)O layer, while O6 belongs to the SrO layer). As a result, the oxygen content of the layer 1 is (Sc/Ga)O, while it is (Sc/Ga)O for the layer 2. Therefore the sequence of layers along to c-axis can be written as ...[(Sc/Ga)O - SrO - (Sc/Ga)O - SrO -]......

Figure 7. Two unique (Sr/Ga)O layers in the crystal structure of SrGaScO, with different oxygen content: (Sc/Ga)O, layer 1 [a] and (Sc/Ga)O, layer 2 [b]. GaO 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. SrGaScO with cubic perovskite structure. The XRPD pattern of the sample with the nominal composition SrGaScO (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 SrGaO 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 SrGaScO 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 SrGaScO (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 7. Two unique (Sr/Ga)O layers in the crystal structure of SrGaScO, with different oxygen content: (Sc/Ga)O, layer 1 [a] and (Sc/Ga)O, layer 2 [b]. GaO 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 sample.

Figure 9. a) SAED patterns of the cubic perovskite SrGaScO 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 SrGaScO, 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 (208-498K) the TEC value is 16.1 ppm K while it decreases sharply down to 11.8 ppm K in the high-temperature region (698-1098K). The latter value is close to 11.2 ppm K obtained from dilatometry data for the SrGaScO brownmillerite.
that starting from ~500K it exhibits significant mass loss due to the release of water molecules from the crystal structure. The weight of the sample stabilizes at ~1150K. The composition of the prehydrated sample was calculated from TG data as SrGa$_{0.75}$Sc$_{0.25}$O$_{2.5}$•0.043H$_2$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 423 K in dry Ar; 3. finally the samples were heated up to 1273 K in wet Ar and the conductivity was measured in the cooling cycle.

Complex impedance plots for prehydrated SrGa$_{0.75}$Sc$_{0.25}$O$_{2.5}$ 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=773K. 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=773K 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 $\sigma_p$ can be calculated as the difference between the conductivity in HO-saturated Ar, $\sigma_{\text{HO}}$, and the conductivity of water-free sample obtained during the cooling cycle in dry Ar, $\sigma_{\text{dry}}$:

$$\sigma_p = \sigma_{\text{HO}} - \sigma_{\text{dry}}$$

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 \( \text{SrGa}_{0.75}\text{Sc}_{0.25}\text{O}_{2.5} \) 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 \( (\) \( \text{H} \)) for \( \text{SrGa}_{0.75}\text{Sc}_{0.25}\text{O}_{2.5} \) calculated as the difference between the conductivity in \( \text{H}_2\text{O} \)-saturated Ar (wet) and the conductivity of water-free sample (dry).

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

\[ t_H = \frac{\sigma_H}{\sigma_{\text{tot}}} \]

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.

4. DISCUSSION

The \( \text{A}^{2+}\text{B}^{2+}\text{O}_5 \) 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 \( \text{CaMnO}_5 \), \( \text{SrMnO}_5 \), and \( \text{LaCuO}_5 \). In their crystal structures BO square pyramids are connected by vertexes forming a 3D framework (Figure 14a). In the crystal structure of \( \text{LaNiO}_5 \) Ni (3d) cations are distributed over an equal amount of corner shared squares and octahedra (Figure 14b). Brownmillerite structure type \( \text{(Ca,Fe,Al)}_6\text{O}_{10} \) is the most widely spread among the \( \text{A}^{2+}\text{B}^{2+}\text{O}_5 \) 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 SrFeO₃, CaFeO₃, BaInO₃ or SrInO₃. 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 LaSrCuGaO₅ and MgAlON₃, M = Ca, Sr, Ba. Partial ordering of B-cations can be found in CaGa₃(AlFeO₅)₂ or Sr(Co,Ga)₅O₇ where the 3d-metal cations preferentially occupy octahedral positions. In the above-listed structures all corners of the BO₆ polyhedra are connected with each other. To our knowledge, however, there is at least one example of the anion-deficient perovskite Ba₅MO₆ (or Ba₅M₃O₁₄, R = rare-earth elements, M = Al, Ga) in which structures are tetrahedral units with some vertexes not connected to other B-cations.

The studied SrGaSeO₅ 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 Se and Ga, r(Se) = 0.73Å; r(Ga) = 0.62Å for CN = 6 and r(Ga) = 0.47Å for CN = 4 and a strong preference of Sc for an octahedral environment. As a consequence, the variation of the Se/Ga ratio in SrGaSeO₅ is equivalent to the variation of the octahedra/tetrahedra ratio. In SrGaSeO₅ (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 BaInO₃ with the brownmillerite structure which reversibly transforms to a disordered perovskite phase at T ≈ 930°C due to a disorder in the O-sublattice. The ordering of Ga and Se in SrGaSeO₅ brownmillerite prevents a disorder of oxygen vacancies without a disorder in the B-cation sublattice. A complete 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 SrGaSeO₅ by partial replacement of Se by Zr according to the formula SrGaSeZrO₄. For SrGaSeO₅, a third way to transform to the cubic phase is the partial replacement of octahedral Sc by Ga as achieved in the cubic perovskite SrGaSe₃O₅. The substitution introduces disorder in the octahedral layers of the brownmillerite structure due to the substantial size difference between Ga and Sc cations and also allows the disorder in the oxygen sublattice since Ga, in comparison with Se, has a rather high flexibility of its coordination environment.

The transformation of the SrGaSeO₅ brownmillerite to a cubic perovskite by substitution of Sc by Ga does not occur continuously and at intermediate composition the novel SrGaSeO₅ 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 = 2√3|a and c = 8|a; S.G. I4/a; to some elpasolites type-compounds like - badly, the crystal structure is different. In elpasolites, ABB’F, 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 CN = 7, 8 like e.g. in - badly. In the crystal structure of SrGaSeO₅ there is a complete ordering of B-cations over the octahedral (Se) and tetrahedral (Ga) sites. In comparison with brownmillerite SrGaSeO₅ the number of tetrahedra in SrGaSeO₅ exceeds the number of octahedra by 50%. The oxygen stoichiometry O₅ is maintained by that 1/3 of the tetrahedra in the SrGaSeO₅ crystal structure have one vertex not connected with other Sc/Ga cations. A similar effect is also observed in the already mentioned Ba₅MO₆ (or Ba₅M₃O₁₄, R = rare-earth elements, M = Al, Ga) anion-deficient perovskites . In Ba₅MO₆, the R and M cations, substantially different in size, are fully ordered over octahedral and tetrahedral sites. However, the arrangement of these polyhedra in Ba₅MO₆ is completely different in comparison with SrGaSeO₅.

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:

\[ H_2O + V^+_O + O_2^- \rightarrow 2OH^- \]

Thus LaBaSeO₄ exhibits high proton conductivity ~1.5×10⁻⁶ S/cm at 673 K . We have shown that
SrGaScO is capable to conduct protons. However, its proton conductivity is much lower (~2.0·10⁻⁷ S/cm at 673K) in comparison with that of the doped LaScO. One can explain it by a high concentration of the remaining oxygen vacancies in the studied SrGaScO samples, which are not filled by OH groups.

5. CONCLUSIONS

The SrGaScO 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 SrGaSeO, 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 SrGaScO having a perovskite-like structure with a large unit cell \(a = b \approx 2\sqrt{5}a, c \approx 8a\). A perovskite subcell 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 SrGaScO 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 SrGaSeO with the cubic perovskite structure. This compound is capable, as other scandium-contained perovskites, of being a proton conductor with ~2.0·10⁻⁷ S/cm at 673K.

FIGURES

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

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

Figure 3. The compositional dependence of the unit cell parameters for SrGaSeO.

Figure 4. SAED patterns of SrGaScO. 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 \(a = b \approx 2\sqrt{5}a, c \approx 8a\).

TABLES.

Table 1. Summary of the results of the least-square fits, final atomic coordinates and displacement parameters for SrGaSeO.

<table>
<thead>
<tr>
<th>Space group</th>
<th>Icmm</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, Å</td>
<td>5.91159(7)</td>
</tr>
<tr>
<td>b, Å</td>
<td>15.1526(2)</td>
</tr>
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</table>
Table 2. Selected interatomic distances (Å) for SrGaSeO$_5$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U$_{eq}$/Å$^2$</th>
<th>Occ.</th>
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<tbody>
<tr>
<td>Sr</td>
<td>8h</td>
<td>0.0200(1)</td>
<td>0.11199(4)</td>
<td>0.5</td>
<td>1.09(9)</td>
<td>1</td>
</tr>
<tr>
<td>Sc</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.9(1)</td>
<td>1</td>
</tr>
<tr>
<td>Ga</td>
<td>8i</td>
<td>-0.0718(2)</td>
<td>0.25</td>
<td>-0.0268(7)</td>
<td>1.3(1)</td>
<td>0.5</td>
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<tr>
<td>O1</td>
<td>8g</td>
<td>0.25</td>
<td>-0.0140(2)</td>
<td>0.25</td>
<td>0.4(1)</td>
<td>1</td>
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<td>O2</td>
<td>8h</td>
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<td>0.1458(3)</td>
<td>0</td>
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<tr>
<td>O3</td>
<td>8i</td>
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<td>0.25</td>
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<td>2.0</td>
<td>0.5</td>
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Table 3. Summary of the results of the least-square fits to the XRPD (NPD) data collected for SrGaSeO$_5$.

<table>
<thead>
<tr>
<th>Space group</th>
<th>a, Å</th>
<th>c, Å</th>
<th>Z</th>
<th>cell volume, Å$^3$</th>
<th>calcd density, g/cm$^3$</th>
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<tbody>
<tr>
<td>I4$_1$/c</td>
<td>17.52963(4)</td>
<td>32.85749(9)</td>
<td>16</td>
<td>10096.7(1)</td>
<td>4.932</td>
</tr>
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</table>

Table 4. Selected bond lengths for the crystal structure of Sr$_{10}$Ga$_6$Sc$_4$O$_{25}$.

<table>
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<tr>
<th>Sc1</th>
<th>08</th>
<th>2.19(1)</th>
<th>Sc2</th>
<th>09</th>
<th>2.28(1)</th>
<th>Sc3</th>
<th>01</th>
<th>2.22(1)</th>
<th>Sc4</th>
<th>04</th>
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<tr>
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<td>O12</td>
<td>2.07(1)</td>
<td>O5</td>
<td>2.16(1)</td>
<td>O17</td>
<td>2.04(1)</td>
<td>O16</td>
<td>2.02(1)</td>
<td>O13</td>
<td>2.13(1)</td>
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<tr>
<td>O18</td>
<td>2.04(1)</td>
<td>O19</td>
<td>2.17(1)</td>
<td>O22</td>
<td>1.97(1)</td>
<td>O21</td>
<td>2.12(1)</td>
<td>O20</td>
<td>2.12(1)</td>
<td>O22</td>
<td>2.13(1)</td>
</tr>
<tr>
<td>O21</td>
<td>2.04(1)</td>
<td>O22</td>
<td>2.13(1)</td>
<td>O24</td>
<td>2.07(1)</td>
<td>O25</td>
<td>2.11(1)</td>
<td>O21</td>
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<td>O22</td>
<td>2.13(1)</td>
<td>O22</td>
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<table>
<thead>
<tr>
<th>Ga1</th>
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<th>Ga2</th>
<th>05</th>
<th>1.81(1)</th>
<th>Ga3</th>
<th>02</th>
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<tbody>
<tr>
<td>O2</td>
<td>1.79(1)</td>
<td>O6</td>
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<td>1.85(1)</td>
<td>O12</td>
<td>1.89(1)</td>
<td>O11</td>
<td>1.87(1)</td>
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</table>
ASSOCIATED CONTENT

Supporting Information. Table with final atomic coordinates and displacement parameters for SrGaSeO$_4$; 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.

ACKNOWLEDGMENT

This work was partially supported by RFBR (11-03-01225) and by the Swedish Research Council and Swedish Institute (Visbyprogram). Authors are grateful to Prof. A.V. Shevelkov for valuable discussions.
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Table of Contents (TOC) summary

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