The Crystal Structure of RESrGaCuO$_5$ (RE: La, Pr, Nd), a Gallate–Cuprate with Strong Structural Similarities to Superconducting Cuprates

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The crystal structure and some basic properties of RESrGaCuO$_5$(RE: La, Pr, Nd, space group *Ima2*, $z = 4$, $a = 16.277(1)$ Å, $b = 5.5191(3)$ Å, $c = 5.3342(3)$ Å for RE = Nd) has been studied by powder and single-crystal X-ray methods, electrical resistivity and magnetic susceptibility measurements, DSC, TG, and optical microscopy. The structure consists of almost planar nets of distorted cornersharing Cu–O$_6$ octahedra connected along the longest axis via Ga–O$_4$ tetrahedral chains with RE and Sr ions filling the large voids between planes and chains. It is isotypic to the structure of the mineral Brownmillerite (Ca$_2$(Al,Fe)$_2$O$_5$). Together with its recently described double Cu–O$_n$ layer counterpart RESr$_2$GaCu$_2$O$_7$ it forms a homologous series of new gallate–cuprates which closely resemble the corresponding Ga-free superconducting cuprates with single and double Cu–O$_n$ layers. Stoichiometric RESrGaCuO$_5$ has a fixed oxygen content and is semiconducting with a strong anisotropy of the optical absorption, indicating a pronounced 2-dimensional character of the electronic properties. P-doping of these materials by partial substitution of RE by additional Sr has not been successful up to now. © 1992 Academic Press, Inc.

Introduction

Perovskite-related oxocuprates have been studied intensely during the last 2 decades (see, for instance, Refs. (*1–5*)) but they have attained their current enormous "popularity" only since the discovery of high-T_c superconductivity in this family of compounds by Bednorz and Müller in 1986 (*6*). A wealth of new Cu-containing compounds and structures has been found since then, among them a number of new superconducting cuprates with much higher su-

percondutivity transition temperature: than their "ancestor" (La,Ba)$_2$CuO$_4$ (see (*7* for a review). Common to all of these high-T structures are tetragonal or almost tetragonal planar or slightly buckled nets of cornersharing Cu–O$_n$ polyhedra (distorted octahedra ($n = 6$) as in (La,Ba)$_2$CuO$_4$ tetragonal pyramids ($n = 5$) as in YBa$_2$Cu$_3$O$_7$, or squares ($n = 4$) in (Nd,Ce)$_2$CuO (*7*)), which are supposed to be the key structural prerequisite for high-T_c superconductivity. These layers are then interleaved by some other structural units containing layers of RE, alkali earth, Pb, Bi, or Tl ions in oxygen coordinations reminiscent of some

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simple structure types like the rocksalt, fluorite, or red PbO structure. This very coarse description of the structure of superconducting cuprates as a stack of two different structural units implies that there are basically two different "crystal chemical degrees of freedom" which may be used (and have been used very successfully) to obtain new, hopefully superconducting compounds. The first class of changes is concerned with modifications of the Cu–O$_n$ layers themselves. There is little choice as to the principal nature of this structural motive because no cuprate superconductor has been found up to now which does not contain 2-dimensional layers of cornersharing Cu–O$_n$ polyhedra. What remains is either to change the nature of the Cu–O$_n$ polyhedra (as for instance in the sequence (La,Sr)$_2$CuO$_4$ (Cu–O$_6$ bipyramids) through (RE,Sr,Ce)$_2$CuO$_4$ (Cu–O$_5$ pyramids) to (Nd,Ce)$_2$CuO$_4$ (Cu–O$_4$ squares)) (7) or to vary the number of consecutive Cu–O$_n$ layers as in the homologous series of Tl compounds Tl$_2$Ba$_2$Ca$_{(1-n)}$Cu$_{(n)}$O$_{(4+2n)}$ with $n = 1$, 2, and 3 consecutive copper–oxygen layers (7).

The second class of crystal chemical changes aims at the "interlayer slabs," which appear to be potentially more variable because their exact composition and structure seems to be less important for the superconducting properties (or, rather, their influence is even less well understood than that of the Cu–O$_n$ layers). However, the mere fact that these interlayer blocks have to geometrically match with the quadratic Cu–O$_n$ nets apparently restricts the possible interlayer units to a very small number.

In a recent publication on the structure of *RE*Sr$_2$GaCu$_2$O$_7$ (1) we have described a novel such interlayer motive consisting of a stack of two "rocksalt-type" Sr–O layers with a Ga–O$_4$ tetrahedral zig-zag chain in between (see also (17)). The Ga–O$_4$ tetrahedra share two corners with each other and the two remaining oxygens are identical with the apical oxygen atoms (of the Cu–O$_n$

polyhedra) located in the rocksalt-type layers. The structure has been shown to be otherwise very similar to that of the superconductor YBa$_2$Cu$_3$O$_7$ in the sense that it contains double layers of Cu–O$_5$ pyramids with *RE*-ions in between. In continuation of this work we describe in this paper the preparation, structure, and some basic properties of the one Cu–O$_n$ layer equivalent of this structure with the general chemical formula *RE*SrGaCuO$_5$. It contains exactly the same interlayer block SrO–GaO–SrO as the compound mentioned above but has only one layer of cornersharing Cu–O$_6$ octahedra.

The structure type to which the new family of compounds *RE*SrGaCuO$_5$ belongs is the well known Brownmillerite type (general formula A$_2$BB'O$_5$). The mineral name Brownmillerite (first structure determination by Buessem (8)) stands for a solid solution series of composition Ca$_2$Al$_x$Fe$_{2-x}$O$_5$ with x between 0 and about 1.36 (9). The solid solution has, because of its technological importance (it is a constituent of Portland cement), been studied intensely (9, 10). The same is true for the pure Fe-end member for its interesting magnetic properties (11). Structurally Brownmillerite can be looked upon as an oxygen deficient, B-cation- and oxygen/vacancy-ordered variant of the perovskite structure (see also (12)). There are two crystallographically distinct sites for the small B cations, one with tetrahedral and one with octahedral oxygen coordination. The crystal chemistry of various cation substituted Brownmillerites (including Ga^{3+} but also Co^{3+}, Cr^{3+}, Sc^{3+}) is well established (9). Common to all of these substances is that they only contain trivalent B- and divalent A-cations. The family of compounds to be discussed here in contrast to that contains an ordered arrangement of di- and trivalent B-cations (Cu^{2+} and Ga^{3+}) and also di- and trivalent A-cations (Sr^{2+} and *RE*$^{3+}$), the latter however appear not to be (long range) ordered.

Recently the compound LaSrCuAlO$_5$ has been described in this journal (*13*). Its structure (with $a = 7.922$ Å, $b = 11.010$ Å, $c = 5.423$ Å, and space group *Pbcm*) is also closely related to the Brownmillerite type structure and contains chains of Al–O$_4$ tetrahedra between planes of Cu–O$_n$ polyhedra as well. The coordination of Cu by oxygen, however, is to a first approximation pyramidal rather than octahedral, and the La and Sr ions appear to be partially ordered (*13*).

Preparation

Almost single phase polycrystalline samples of *RE*SrGaCuO$_5$ may be obtained by using the following recipe: Stoichiometric proportions of *RE*$_2$O$_3$ (Pr$_6$O$_{11}$), SrCO$_3$, Ga$_2$O$_3$, and CuO are thoroughly mixed in a ball mill for 2 h, calcinated at 900°C in air for 16 h, reground, pressed into pellets and then fired at 1050°C in air for 16 h, followed by unregulated furnace cooling to room temperature. Exact stoichiometry (dry starting chemicals) and an extremely good homogenization of the mixture prior to the first heat treatment are essential to achieve a homogeneous product. Even with these provisions being taken, lines of at least one additional unidentified phase appear in the powder X-ray patterns (amounting to roughly 3% of the total integral intensity in the powder pattern). This phase (or phase assembly) does not dissolve even after prolonged heat treatment at elevated temperatures. Also, starting deliberately "off stoichiometry" did not improve the sample quality. The problems encountered here probably reflect the fact that the pseudo-quarternary phase diagram *RE*$_2$O$_3$–SrO–Ga$_2$O$_3$–CuO is an outstandingly complex one. Already for the pseudo-binary system SrO–Ga$_2$O$_3$ for instance, the JCPDS file lists at least five chemically and crystallographically distinct phases. The existence of several pseudoternary and pseudo-quarternary phases is established (among them the previously described *RE*Sr$_2$GaCu$_2$O$_7$) and there are presumably some others which are yet unidentified. It seems that in this part of the phase diagram the tie lines lie so close that even a small deviation from the desired stoichiometry can lead to substantial amounts of neighboring equilibrium phases. The resulting pellets are quite dense and contain only very small crystals hardly visible under the optical microscope. Grain growth seems to be negligible even after prolonged heat treatment close to but below the decomposition temperature (1080°C for NdSrGaCuO$_5$, see below). All efforts to find a suitable flux medium for growing larger crystals were unsuccessful. As in the case of *RE*Sr$_2$GaCu$_2$O$_7$ the most appropriate way of growing small crystals for single-crystal X-ray measurements is to rapidly heat a compact pellet (wrapped into platinum foil) to 1250°C (well above the decomposition temperature and in the region of partial melting) at a rate of 50°C/min and then immediately start cooling down with a rate of 1°C/min. This growth from "self flux" yields and assembly of different phases among them crystals of *RE* SrGaCuO$_5$ with varying shapes and linear dimensions of up to 40 μm which may be easily identified under the polarization microscope by the strong pleochroism (anisotropy of light absorption) they show in thin sections (colorless to light-brown if the polarization vector is perpendicular to the Cu–O$_6$ octahedral planes and opaque (black) for polarization parallel to the planes).

Figure 1 shows a DSC/TG curve for NdSrGaCuO$_5$ taken both upon heating and subsequently upon cooling with 10°C/min in air. We ascribe the strongest thermal event at about 1080°C which has a characteristic sluggish onset to a decomposition reaction accompanied by partial melting of the sample and a pronounced loss of oxygen similar to what has been observed for *RE*Sr$_2$Ga Cu$_2$O$_7$ (*1*). A second peak at about 980°C (onset) corresponds to another endothermic event (upon heating) which might be due to a
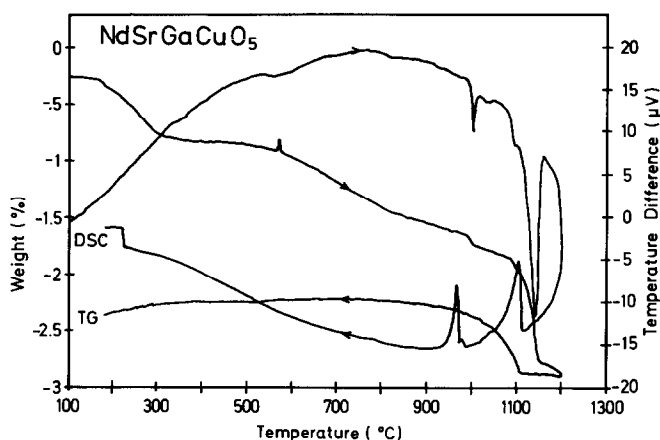
FIG. 1. DSC/TG-curve of NdSrGaCuO$_5$ upon heating and cooling. Rate: 10°C/min in air.

structural phase transformation in the solid state. A possible structural realization of this presumed transition is discussed below. As would be expected for a partial decomposition, the thermal effect at 1080°C is not strictly reversible. The other peak at lower temperatures, however, is reversible in magnitude provided the maximum temperature has not exceeded 1080°C and it shows a hysteresis of about 10 to 20°C. Due to the fact that the powder samples were not strictly single phase, it cannot be excluded that the thermal effect at about 980°C is due to a second phase. The magnitude of this peak together with the small percentage of spurious lines in the powder pattern, however, renders this possibility quite unlikely.

Structure Determination and Refinement

The structure was initially determined and its close similarity to the Brownmillerite type established by means of powder X-ray diffraction data of the Nd-compound using the trial and error method. Starting point was a structural model in space group $Ima2$ which had been derived from the two Cu-O$_n$ layer compound NdSr$_2$GaCu$_2$O$_7$. This struc-

ture was later confirmed and refined by single-crystal X-ray methods. Table I summarizes the experimental details relevant to these measurements.

The matter of space group symmetry of Al-Fe-Brownmillerites has been somewhat controversial and has been discussed in detail by several authors (see for instance (9)). Within the solid solution series Ca$_2$Al$_x$Fe$_{2-x}$O$_5$ there appears to be a transition from a body centered orthorhombic cell (s.g. $Imam$ referred to a cell of 14.5 Å × 5.5 Å × 5.4 Å) for $x \geq 0.6$ to a primitive cell (presumably $Pmcn$ (9)) for $x < 0.6$. With a B- to B'-cation ratio of 1 : 1, RESrGaCuO$_5$ would correspond to $x = 1$. Indeed for our "Ga-Cu Brownmillerites" we could not find any evidence for a violation of the body centering neither from powder X-ray nor from long exposed rotating crystal photographs or 4-circle diffractometer measurements (all done at ambient temperature). The diffraction symbol is I^*a^*. This leaves as possible space groups $Imam$ (centric) or $Ima2$ (acentric). $Imam$ was later ruled out on the basis of unphysically large z-components of the anisotropic temperature factors of atoms O(3) and Ga (situated

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TABLE I

DIFFRACTION MEASUREMENTS, EXPERIMENTAL DETAILS

	Powder X-ray diffraction	Single-crystal X-ray diffraction
Samples	RESrGaCuO$_5$ RE: La, Pr, Nd	LaSrGaCuO$_5$/NdSrGaCuO$_5$
Space group	$Ima2$	$Ima2$
Sample mounting	Li–borate glass capillary, 0.1 mm diameter, coated on the outside with sample powder ($\approx$0.5 mg) (+ silicone grease). Absorption coefficient of the material: $\mu \approx$ 400–1000 cm^{-1}, depending on RE	Single crystals 30 μm/40 μm diameter
Conditions	Room temperature, air	Room temperature, air
Equipment	STOE-powder diffractometer Debye–Scherrer geometry Monochromator: Ge(111) λ = 1.54056 Å (CuKα_1) 2Θ = 10°–130°, step 0.02° sin $\Theta/\lambda \leq 0.59$ Position sensitive detector	STOE-4-circle diffractometer Monochromator: Graphite λ = 0.71073 Å (MoKα) $2\Theta \leq 80°$, sin $\Theta/\lambda \leq 0.9$ $+h$, $\pm k$, $\pm l$ 282/329 independent reflections with $I > 3\sigma$ Internal R-value 0.098/0.093
Data evaluation	Rietveld line profile refinement Profile function: Pearson VII	Numerical absorption correction. Absorption coefficient $\mu \approx$ 300 cm^{-1} Isotropic extinction correction Full-matrix least-squares Scattering factors for RE^{3+}, Sr^{2+}, Cu^{2+}, Ga^{3+}, O$^-$

on the mirror plane perpendicular to c in *Imam*) which could be removed by choosing the lower symmetry. The most probable space group of RESrGaCuO$_5$ is thus neither that of natural Brownmillerite (*Imam*) nor one of its primitive subgroups (like *Pmcn*) but instead *Ima2*, yet another subgroup of *Imam* and occasionally the same as for the two Cu–O$_n$ layer compound RESr$_2$GaCu$_2$O$_7$ (*1*).

No split reflections or broadening within the experimental resolution was observed in single crystal diffractometer scans (in omega and theta) showing that twinning or other major inhomogeneities are absent in these crystals. Table II gives the results of structural refinements (both powder and single-crystal X-ray) in terms of cell parameters, atom coordinates, thermal parameters, and, where applicable, site occupancies.

The results of powder and single-crystal refinements agree nicely (within one standard deviation of the for principal reasons less accurate powder data). This is also taken as evidence that the different treatment during sample preparation (solid-state reaction vs partial melting) has no fundamental effect on the structural identity of this phase.

Description of the Structure

Figure 2 shows the structure of RESrGa CuO$_5$ in a perspective view approximately along the [011] direction. The oxygen positions are idealized for clarity (see below). Close crystal chemical relations exist between RESrGaCuO$_5$ and the previously described RESr$_2$GaCu$_2$O$_7$ (see (*1*)). The common feature is the novel interlayer slab of two consecutive Sr–O rocksalt-type layers

TABLE II

STRUCTURAL PARAMETERS

Sample; method		LaSrGaCuO$_5$; Single-crystal X-ray	LaSrGaCuO$_5$, Powder X-ray	PrSrGaCuO$_5$, Powder X-ray	NdSrGaCuO$_5$, Single-crystal X-ray	NdSrGaCuO$_5$, Powder X-ray
	a [Å]	16.51(1)	16.5070(14)	16.3358(11)	16.27(1)	16.2766(9)
	b	5.510(3)	5.5090(5)	5.5002(4)	5.518(3)	5.5191(3)
	c	5.369(3)	5.3729(4)	5.3534(3)	5.338(3)	5.3342(3)
RE/Sr:	x	0.1068(2)	0.1073(6)	0.1073(4)	0.1068(3)	0.1060(4)
	y	0.0164(10)	0.011(3)	0.014(3)	0.0180(10)	0.014(2)
	z	0.5	0.5	0.5	0.5	0.5
	N	0.82(1)	0.85(3)	0.82(2)	0.83(3)	0.81(2)
	B [Å^2]	0.84(15)	0.8	0.8	1.1(9)	0.8
Cu:	x	0.0	0.0	0.0	0.0	0.0
	y	0.0	0.0	0.0	0.0	0.0
	z	0.001(4)	0.01(2)	0.01(1)	0.002(3)	0.01(1)
	N	1.0	1.0	1.0	1.0	1.0
	B	0.6(3)	0.8	0.8	0.6(3)	0.8
Ga:	x	0.25	0.25	0.25	0.25	0.25
	y	−0.065(1)	−0.064(5)	−0.061(5)	−0.068(2)	−0.061(3)
	z	−0.038(2)	−0.035(9)	−0.028(9)	−0.030(6)	−0.026(7)
	N	1.0	1.0	1.0	1.0	1.0
	B	0.5(3)	0.8	0.8	0.9(5)	0.8
O$_1$:	x	0.01(2)	0.00(2)	0.006(6)	0.003(5)	0.01(1)
	y	0.25(1)	0.25(9)	0.23(4)	0.25(1)	0.26(7)
	z	0.25(1)	0.24(4)	0.23(3)	0.25(1)	0.25(3)
	N	1.0	1.0	1.0	1.0	1.0
	B	0.6(4)	0.8	0.8	1.0(6)	0.8
O$_2$:	x	0.146(3)	0.147(4)	0.151(3)	0.146(4)	0.146(3)
	y	0.063(5)	0.063(15)	0.064(12)	0.07(1)	0.065(9)
	z	0.01(1)	0.04(2)	0.03(2)	0.01(1)	0.04(2)
	N	1.0	1.0	1.0	1.0	1.0
	B	1.6(8)	0.8	0.8	1.9(9)	0.8
O$_3$:	x	0.25	0.25	0.25	0.25	0.25
	y	0.641(9)	0.64(2)	0.63(2)	0.637(14)	0.63(2)
	z	0.119(15)	0.09(3)	0.11(2)	0.13(2)	0.11(2)
	N	1.0	1.0	1.0	1.0	1.0
	B	1.9(8)	0.8	0.8	1.6(8)	0.8
Rw (F^2)		0.077			0.055	
R (F^2)		0.085			0.083	
GOF		2.4			1.8	
R_p			0.071	0.052		0.027
Rwp			0.127	0.088		0.037
GOF			14.0	11.9		11.9
R_I			0.126	0.103		0.105

with Ga–O$_4$ tetrahedral chains in between. The new compound *RE*SrGaCuO$_5$, however, contains single layers of distorted Cu–O$_6$ octahedra instead of the double layers of Cu–O$_5$ pyramids (plus an intervening *RE* layer) in *RE*Sr$_2$GaCu$_2$O$_7$. Nearest neigh-

bor cation–oxygen distances (from single-crystal data, except for PrSrGaCuO$_5$ where only powder data is available) are summarized in Table III together with the corresponding results for the two Cu–O$_n$ layer compound (atoms relabelled) and comple-
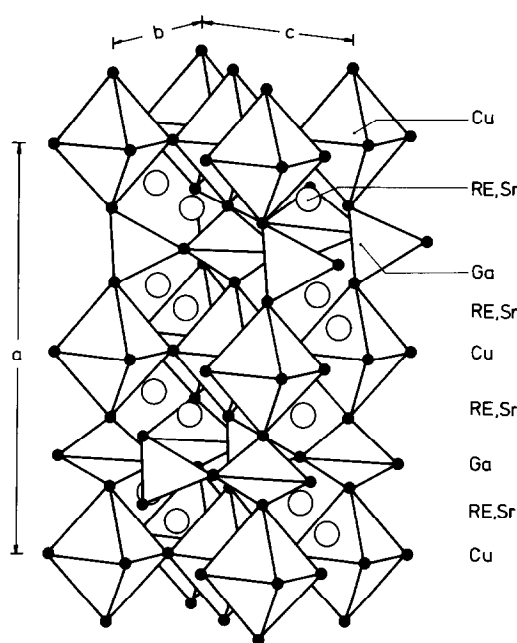
FIG. 2. Structure of RESrGaCuO$_5$ projected approximately along [011].

mented by some selected data for $Ca_2Fe_2O_5$ from Ref. (*10*). Before calculating distances, coordinates closer than 1 e.s.d. to 0.0 or 0.25 (see Table II) had been set to these "special"

values. α denotes the angle (in the a–b-plane) between the a-axis and "apical" Cu–O(2) bond; β is the angle from Ga to the two apical oxygen atoms O(2) (see also Fig. 3).

The similarity of the local coordination of the cations by oxygen in the one and two Cu–O$_n$ layer compound (compare 3rd and 4th columns in Table III) is obvious. For Gallium there are two symmetrically equivalent distances (1.862(5) Å) to the apical oxygen atom O(2), two other bond lengths (1.838(9) and 1.854(9) Å) to the chain oxygen O(3), five almost ideal O–Ga–O tetrahedral angles and one much larger one (132°(1)) from Ga to the two oxygens at the apices of the two neighbouring Cu–O$_6$ octahedra (numbers given in the text refer to the single-crystal data for NdSrGaCuO$_5$, column 3 in Table III). As the comparison with Ca$_2$ Fe$_2$O$_5$ clearly shows, this angular distortion of the tetrahedron is a specific property of this structure type and results presumably from the combination of two hardly compatible structural motives, namely square nets of octahedra and zig-zag chains of tetrahedra (see also paragraph on Cu–O polyhedral distortion).

The coordination of the RE/Sr-site by oxy-

TABLE III

DISTANCES (Å) AND ANGLES

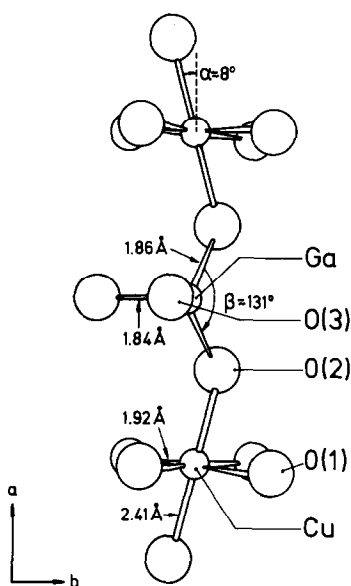|		LaSrGaCuO$_5$; Single-crystal X-ray	PrSrGaCuO$_5$; Powder X-ray	NdSrGaCuO$_5$; Single-crystal X-ray	NdSr$_2$GaCu$_2$O$_7$, Powder neutron (*1*)	Ca$_2$Fe$_2$O$_5$; Single-crystal X-ray (*10*)	
Cu–O(1)	4×	1.923(3)	1.92(6)	1.919(3)	1.952(3)	Fe(1)–O	1.965(4)
Cu–O(2)	2×	2.435(9)	2.49(7)	2.407(15)	2.321(3)		2.118(4)
Ga–O(2)	2×	1.867(5)	1.76(6)	1.862(5)	1.819(5)	Fe(2)–O	1.837(4)
–O(3)	1×	1.826(9)	1.85(9)	1.838(9)	1.907(5)		1.915(5)
–O(3)	1×	1.889(9)	1.97(9)	1.854(9)	1.910(5)		1.921(5)
Average	4×	1.862	1.84	1.854	1.864		1.877
RE/Sr–O(1)	2×	2.563(6)	2.56(7)	2.538(8)			
–O(1)	2×	2.658(7)	2.64(8)	2.643(8)			
–O(2)	2×	2.773(6)	2.78(7)	2.759(7)			
–O(2)	1×	2.406(7)	2.43(7)	2.361(6)			
–O(2)	1×	3.257(8)	3.26(8)	3.307(8)			
–O(3)	1×	2.598(6)	2.53(7)	2.577(7)			
Average	9×	2.694	2.69	2.681			
α (see text and		8.2(4)°	8.1(9)°	9.2(6)°	5.6(8)°		
β Fig. 3)		134(1)°	134(1)°	131(1)°	134(1)°		123.2(2)

Note. Estimated standard deviations in parentheses.

FIG. 3. Linkage of GaO₄ tetrahedron and CuO₆ octahedron along the longest axis (a); distances and angles are for NdSrGaCuO₅ (single-crystal X-ray results at r.t.).

gen also closely resembles that of the Sr-site in $RESr_2GaCu_2O_7$, while the separate rare earth site is, of course, missing in $RESrGaCuO_5$. Instead, RE and Sr occupy the same site statistically (as far as Bragg diffraction data can tell). The occupancy of this site (see Table II) (as refined from the single-crystal X-ray data) of 0.83 (3) (in units of the scattering power of Nd) agrees well with the expected value of 0.82 for Nd : Sr = 1 : 1. Furthermore, the arithmetic mean of the RE/Sr–O distance (2.68 Å) lies close to the "expected" one for 9-fold coordination (2.63 Å) calculated from the effective crystal radii given in Ref. (14). Finally, application of the bond length–bond strength formalism (15) which just takes an exponentially weighted average over different bonds, gives 2.6 as the "bond strength sum" which may, with some caution, be interpreted as an effective charge on the "mixed" atom, again close to the expected charge of +2.5.

Of particular interest are the Cu–O nearest-neighbor distances. For $RESrGaCuO_5$ the space group symmetry that has been chosen would permit two pairs of different bondlengths in the basal plane of the distorted octahedra. The two pairs are, however, equal within the accuracy of the experiment, if one considers the small deviations (less than 1 e.s.d.) of $z(Cu)$ and x,y,z (O(1)) from their special values as being insignificant. These 4 identical in-plane distances (1.919(3) Å for RE = Nd) together with two larger distances (2.407(5) Å) to the apical oxygen atoms complete a distorted octahedron around the Cu-atom. The in plane Cu–O distance lies in between those for $RESr_2GaCu_2O_7$ (1) and $(La,Sr)_2CuO_4$ (see (7)) while the apical distance is significantly larger than in $RESr_2GaCu_2O_7$, reflecting of course the increased coordination number (6 instead of 5) and compares nicely with the apical Cu–O distance in the Cu–O₆ octahedra of $(La,Sr)_2CuO_4$. The extreme elongation of the Cu–O₆ octahedra, which is typical for Cu-containing K_2NiF_4-type compounds and may at least in part be attributed to the Jahn–Teller distortion around d^9–Cu^{2+}, is less pronounced in $RESrGaCuO_5$ but clearly still present if one compares $RESrGaCuO_5$ with the isostructural $Ca_2Fe_2O_5$ (last column Table III). The abovementioned similarity between $RESrGaCuO_5$ and $(La,Sr)_2CuO_4$ in terms of Cu–O distances, however, does not hold for the O–Cu–O bond angles. Just as in $RESr_2GaCu_2O_7$ $RESrGaCuO_5$ shows a characteristic pattern of angular distortions of the Cu–O$_n$ polyhedra which had, for clarity, been omitted in Fig. 2. We believe that this structural deformation is worth being discussed in some detail because it could very well affect severely the electronic structure and thereby also macroscopic properties like electrical conductivity or magnetic susceptibility. Figure 3 shows the linkage of the Cu–O₆ octahedra with the Ga–O₄ tetrahedra along the longest axis (a). As in $RESr_2Ga Cu_2O_7$ the Ga-atom is displaced (mainly along b) from its symmetrical position between the two apical oxygens (O(2)) of the Cu–O₆ octahedra, while these apical oxy-

gens are displaced into the opposite direction. This permits the Ga-atom to acquire an acceptable O–Ga–O angle of about 132°. In the double Cu–O_n layer compound $RESr_2GaCu_2O_7$ the resulting structural deformation could to a first approximation be described as a rotation of the complete Cu–O_n polyhedron (two adjacent Cu–O_5 pyramids in that case). For $RESrGaCuO_5$ the situation is different: Although symmetry does not require this (at least, all three coordinates of O(1) are free), the oxygen atom in the Cu–O plane stays within the basal (b–c) plane within the accuracy of the experiment. The abovementioned deformation would therefore correspond to an angular distortion of the Cu–O_6 octahedron in the sense that the apical bond is inclined with respect to the longest axis (a) by an angle of about 8° toward c (or $-c$). The direction of this inclination changes from one Cu–O_6 layer to the next one along a (see Fig. 3). The Cu–O_2 planes are basically flat and not, like in $RESr_2GaCu_2O_7$ and also in the Al–Fe-Brownmillerites (10), buckled along c. It should be noted, however, that the x-component of the anisotropic temperature factor of O(1) (which, for reasons of the limited accuracy of the data available, have generally not been included in Table II) is about three times larger than the corresponding y- and z-components. This could be taken as an indication of yet a small buckling of the Cu–O_6 octahedral net which would either have to be disordered (spatially or dynamically) or only locally ordered (in the form of microdomains).

Another open question which we feel should be mentioned is the significance of the small z-component of the position of the Ga atom. While being significantly different from zero (by about 5 standard deviations in the case of the single crystal refinement of $NdSrGaCuO_5$, compare Table II), the R-value is amazingly insensitive to a change of the sign of this component. Putting the atom onto $z = 0$ or introducing a split position with 50% occupancy on either side of

this position on the other hand increases the R-factor significantly. In fact at present we are not able, on the basis of this data, to decide which position is the correct one. Of course this also leads to an ambiguity with respect to the Ga–O(3) distances (in the Ga–O_4 tetrahedral chains). Crystal chemically, however, choosing one or the other position does not make too much difference because it leads to just an exchange of two bond lengths (the short and the long Ga–O(3) distance in Table III). It seems that the Ga–O tetrahedral chain exhibits some kind of disorder which does not affect the direction of the chain but only the Ga–O(3) bond lengths within the chain. Larger y- and z-components of the thermal parameters of the chain oxygen O(3) seem to support this view. The observation that a split Ga-position does not describe the data properly seems to suggest that it is not really a local disorder but more probably an effect of an undetected twinning (presumably meroedric or pseudomeroedric because no split single-crystal reflections have been observed). In case the size of the twin domains were considerably larger than the coherence length of the diffraction experiment, such problems should not occur with powder X-ray data. Unfortunately, the significance of a nonzero z-coordinate for Ga in the X-ray powder data is not very clear and, with respect to this point, the powder diffraction experiment is therefore inconclusive. The two structural pathologies mentioned above could both be related to the presumed structural phase transition the existence of which had been deduced from the DSC/TG curves. The clarification of these questions by diffraction methods has to be set aside until larger single crystals prepared under equilibrium conditions or more homogeneous powder samples for powder neutron experiments will be available.

Crystal Chemical Considerations

The similarity of the Cu–O_6 octahedral net of $RESrGaCuO_5$ with the corresponding

motive in the La_2CuO_4 family of 40-K super-conductors has already been pointed out above. Even closer relations exist between the previously described double $Cu-O_n$ layer compounds $RESr_2GaCu_2O_7$ (1) and the 90-K superconductor $YBa_2Cu_3O_7$. $RESr_2GaCu_2O_7$ could formally be derived from $YBa_2Cu_3O_7$ by replacing the interlayer slab BaO–CuO–BaO containing the CuO-chains by blocks with the sequence SrO–GaO–SrO. Such a direct relation does not exist between $RESrGaCuO_5$ and any of the superconducting cuprates with single $Cu-O_n$ layers known at present. The reason is that in the Ga-free superconductors with single octahedral layers (like for instance $(La,Sr)_2CuO_4$) there is a characteristic shift of $(\frac{1}{2}, \frac{1}{2}, 0)$ (referring to a (pseudo)tetragonal cell of approx. 3.8 Å × 3.8 Å × 13.1 Å) between the two consecutive La–O layers forming the La_2O_2-interlayer slab. The Cu-positions of adjacent $Cu-O_6$ layers therefore do not project onto the same position (if seen along the longest axis). In $RESrGaCuO_5$, however Cu and Ga lie approximately above each other (along the longest axis a). The title compound would therefore have to be derived from a hypothetical Ga-free ancestor of composition $RE_2Cu_2O_5$ consisting of alternating $Cu-O_6$ octahedral nets and $Cu-O_4$ square planar chains (sharing the apical oxygen with each other) with RE ions filling the large voids. Such a phase has, to our knowledge, not been prepared up to now. For the smaller RE ions a compound with the abovementioned chemical formula actually exists, but with a completely different structure (16). For the larger rare earths the compounds of the type RE_2CuO_4 with the so-called T or T' structure (a derivative of the K_2NiF_4 structure type) are formed instead (plus CuO).

The variability of $RESrGaCuO_5$ with respect to the RE-ion radius is much more limited than in the case of the two $Cu-O_n$ layer counterpart $RESr_2GaCu_2O_7$, where almost all RE-ions between La and Er (and Y) fit into the structure while the Brownmill-erite-type structure only forms with RE = La, Pr, Nd. The basic difference is, of course, that $RESr_2GaCu_2O_7$ provides a separate site for the RE-ions while in $RESrGaCuO_5$ the RE- and Sr-ions have to share the same site. We have no evidence for any (long range) ordering of RE and Sr so that it seems that a disordered RE/Sr distribution is necessary and large differences in the radii of Sr and RE are unfavourable for the formation of this structure type. Furthermore, due to mainly ionic bonding across the RE-layer in $RESr_2GaCu_2O_7$ the distance between two consecutive $Cu-O_5$ pyramidal layers can almost freely expand to match the space requirement of the different RE-ions. In fact, metric changes upon RE-substitution in the two layer compound mainly occur in the length of the longest axis a that is perpendicular to the $Cu-O_n$ planes, changes of the lattice parameters within the relatively stiff $Cu-O_n$ planes are small (see (1, 17)). The RE/Sr-site in $RESrGaCuO_5$ on the other hand (just like the very similar Sr site in the two layer compound) is much less variable in size because any contraction or expansion of the oxygen environment around this site would require predominantly covalent Cu–O bonds to change their length. Still, the strongest effect upon RE substitution is along a, the largest cell parameter (see Table II), as this is the direction of the longest (and presumably weakest, least covalent) Cu–O bond to the apical oxygen. We believe that similar arguments could apply to understand, why it appears to be quite difficult to p-dope $RESrGaCuO_5$ by simply replacing part of the RE-ions by divalent Sr. In fact experiments of this kind (performed under conditions similar to those which were used to synthesize the undoped compounds) have always yielded massively multiphase samples and we therefore do not feel ready to make any sound statement about solubilities in the solid state for these compounds. In $RESr_2GaCu_2O_7$, again, we have found (1) quite similarly that those members of this family of compounds which contain large

RE-ions (predominantly for La but also for Pr and Nd) show a tendency toward an *RE*/Sr-disorder accompanied by structural distortions and the occurrence of spurious lines in the powder patterns.

Of particular interest is also the comparison to the closely related compound LaSr CuAlO$_5$ (*13*). The basic difference between the structure of LaSrCuAlO$_5$ and the Brownmillerite type lies in the arrangement of the oxygen vacancy situated approximately in the Al–O plane. In LaSrCuAlO$_5$ the vacancies in adjacent Al–O planes are aligned while in Brownmillerite (and in the title compound *RE*SrGaCuO$_5$) they are staggered (see Figs. 4b and 4c in Ref. (*13*)). As a result the unit cell has a different size and symmetry. Also, there are two different sites for the large cations permitting a (partial) ordering of these cations in LaSrCu AlO$_5$ (*13*). Just like in the two Cu–O$_n$ layer compounds such details of the structures depend sensitively on the nature (size) of the tetrahedral cation.

The matter of a possible partial Cu/Ga disorder in *RE*SrGaCuO$_5$ is also a very important one if one aims at possible superconductivity in this type of compounds, knowning that even small amounts of foreign cations on the Cu-site reduce superconductivity transition temperatures drastically in the known superconducting cuprates. Again, as stated for *RE*Sr$_2$GaCu$_2$O$_7$ (*1*), conventional diffraction methods (X-ray as well as neutron) can contribute very little to the solution of this problem, because Cu and Ga are hardly discernable on grounds of their scattering power. Atom type specific local probes like NMR, NQR, EXAFS, or Möβ-bauer spectroscopy would be very useful for this purpose.

Crystal chemically it is reasonable to assume that Cu^{2+} is not very likely to be found in a tetrahedral oxygen environment (although there are some counter examples, among the spinels for instance). Ga^{3+} on the other hand is known to occupy tetrahedral as well as octahedral sites. It is therefore

hardly credible that the Ga atoms should strictly be confined to the tetrahedral site in *RE*SrGaCuO$_5$. A partial Ga-occupation of the octahedral Cu-site could occur either isochemically (Cu would then have to appear in the Ga–O chains, possibly in a distorted square planar coordination) or accompanied by a shift of the total composition of the phase off stoichiometry. In this case the modified Ga/Cu-ratio would have to be compensated by either a corresponding shift of the *RE*/Sr-ratio or by changes of the oxygen content or cation vacancies. The above-mentioned problems in preparing single phase samples and the spurious lines observed in the X-ray powder patterns could point towards this possibility. We wish to emphasize, however, that we have no indication for a pronounced disorder on any of the small cation sites from our diffraction experiments. This statement, of course, has to be seen in the light of the limited sensitivity of conventional X-ray diffraction experiments (performed on rather small crystals in our case, see again Table I) to Ga/Cu disorder as well as to oxygen nonstoichiometry. It is worth nothing that the situation with respect to a possibly unavoidable partial Ga/Cu-disorder might be different (more advantageous if one is interested in new superconducting compounds) in the two Cu–O$_n$ layer member (*RE*Sr$_2$Ga Cu$_2$O$_7$) of the homologous series of compounds because here Cu^{2+} is in a pyramidal oxygen coordination which, to our knowledge, has not been observed for Ga^{3+}.

Conclusion

We have described in this paper preparation, crystal structure, and some basic properties of a new family of gallate–cuprates with the general formula *RE*SrGaCuO$_5$ constituting the one Cu–O$_n$ layer member of a homologous series of compounds (the two Cu–O$_n$ layer member of which has been found about a year ago (*1*, *17*)). They closely resemble the structures of high-T_c cuprates

and, in particular, contain exactly those structural motives (here: quadratic nets of cornersharing, distorted $Cu-O_6$ octahedra) which are assumed to be crucial to superconductivity in high-T_c cuprates. They differ from these by the chemical composition and crystallographic arrangement of the structural unit between these $Cu-O_n$ layers. The second prerequisite for metallic conductivity (and hopefully also superconductivity) in such compounds, the introduction of additional charge carriers by doping has, in the case of the title compound, not been achieved up to now. Yet, despite the various problems occurring during the preparation and characterization of such samples, it would be highly desirable to find some way of also doping these compounds.

Very recently reports have appeared which claim superconductivity at 30 K in doped $RESr_2GaCu_2O_7$, the two layer counterpart of the title compound, after a high temperature/high oxygen pressure treatment (17, 18). With all necessary caution this could at least give some hope that, provided the suitable amount of doping is achieved and the various disorder penomena are kept under control, $RESrGaCuO_5$ could very well be another potential superconductor.

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