

Cation Disorder in Ga1212

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Substitution of calcium for strontium in $\text{LnSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ ($\text{Ln} = \text{La, Pr, Nd, Gd, Ho, Er, Tm, and Yb}$) materials at ambient pressure and 975 °C results in complete substitution of calcium for strontium in the lanthanum and praseodymium systems and partial substitution in the other lanthanide systems. The calcium saturation level depends on the size of the Ln cation, and in all cases, a decrease in the lattice parameters with calcium concentration was observed until a common, lower bound, average A-cation size is reached. Site occupancies from X-ray and neutron diffraction experiments for $\text{LnSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ ($x = 0$ and $x = 2$) confirm that the A-cations distribute between the two blocking-layer sites and the active-layer site based on size. A quantitative link between cation distribution and relative site-specific cation enthalpy for calcium, strontium, and lanthanum within the gallate structure is derived. The cation distribution in other similar materials can potentially be modeled.

Introduction

Almost all layered cuprates based on oxygen-deficient perovskite structures ($\text{ABO}_{3-\delta}$) contain multiple cations on the A-sites. Copper–oxygen planes, which can support superconductivity up to relatively high temperatures, are the common structural motif in these layered materials. The coordination preferences of the different A-cations stabilize two-dimensional cuprate planes. The site between the planes is 8-coordinate, while those in the blocking layer are variable, often 9-coordinate or higher.¹

The substitution chemistry of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) has been intensely investigated. Strontium substitutes for barium in $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$ only partially up to $x = 1$ under ambient pressure, but fully up to $x = 2$ under 7 GPa of pressure.^{2,3} The solubility of calcium on the barium site is limited even more, reaching only $x = 0.25$ at ambient pressure. T_c decreases linearly with both Sr^{2+} and Ca^{2+} substitution.^{2–4}

A novel family of layered cuprates was developed by Vaughey et al.⁵ and Roth et al.⁶ by replacing the blocking-layer copper of YBCO with tetrahedrally coordinated Ga^{3+} . All the strontium analogues, $\text{LnSr}_2\text{Cu}_2\text{GaO}_7$ ($\text{Ln} = \text{La–Nd, Sm–Yb, and Y}$), can be synthesized at ambient pressure. While the substitution of Sr^{2+} by Ba^{2+} causes the framework of $\text{LaSr}_2\text{Cu}_2\text{GaO}_7$ to expand,⁷ the effects of Ca^{2+} substitution for Sr^{2+} have not been investigated. Compared to Sr^{2+} , Ca^{2+} is smaller and prefers A-sites in layered cuprates such as the 8-coordinate site between cuprate planes, as in $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ ⁸ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$.⁹ However, the situation is not so simple. Mixing of the A-cations can thwart superconductivity when it occurs in sufficient degree. Attfield et al. have demonstrated that T_c varies inversely with the variance in A-cation size for constant mean A-cation radius in A_2CuO_4 materials.¹⁰ In order to understand cation disorder in the Ga1212 phases, the A-cation distributions in $\text{LaSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ for $x = 0$ and $x = 2$ have been analyzed on the basis of neutron diffraction. The results can be used to generate a predictive model for cation distribution in the Ga1212 structure type.

Experimental Section

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Sample Preparation. Many compositions of $\text{LnSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$, $\text{Ln} = \text{La, Pr, Nd, Gd, Ho, Er, Tm, Yb, and Lu}$, $0 \leq x \leq 2$, were prepared by solid-state reaction of the appropriate ratio of lanthanide oxide, yttrium oxide, strontium carbonate, calcium carbonate, copper oxide, and gallium oxide. More specifically, for $\text{Ln} = \text{La}$, samples with $x = 0.20, 0.40, 0.75, 1.00, 1.25, 1.50,$ and 2.00 were prepared. For each of the Ln cations smaller than lanthanum, usually three or more samples were prepared using a consecutive step size of 0.1 in x near the expected saturation point. The reagents were ground in acetone, pressed into pellets, and fired at 975 °C in an alumina boat for 10 days with three intermediate regrindings.

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X-ray Diffraction. A Rigaku diffractometer with nickel-filtered Cu K α radiation was used to collect X-ray diffraction data on the polycrystalline samples. These data were used to determine the lattice parameters and ascertain the extent of calcium substitution for strontium in $\text{LnSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ ($\text{Ln} = \text{La, Pr, Nd, Gd, Ho, Er, Tm, and Yb}$). Lattice parameters were calculated by a least-squares technique using the programs XRAYFIT¹¹ and POLSQ¹² or refined Rietveld analysis.¹³ X-ray data for $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$, which were refined by the Rietveld method, were obtained by counting 10 s every 0.02° from 15° to 90° 2θ . Silicon was used as an internal standard. Forty-one parameters were refined including scale factor, zero-point shift, eight background parameters, six peak shape parameters, unit cell, atomic coordinates, and site occupancies. The mean atomic scattering factors at $\sin \theta/\lambda = 0$ used for La, Ca, Cu, Gd, and O were 57.00, 20.0, 29.00, 31.00, and 8.00, respectively.

Neutron Diffraction. The intense pulsed neutron source (IPNS) at Argonne National Laboratory was used to collect time-of-flight data on 10 g of a polycrystalline sample of $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$. Data were obtained for 6 h at room temperature and ambient pressure. The data set from $d = 0.5$ to 4.0 \AA was analyzed by Rietveld methods.¹⁴ Fifty parameters were refined, including scale factor, diffractometer constant, zero-point error, five background parameters, six peak shape parameters, unit cell, atomic positions, site occupancies, isotropic thermal factors, and absorption and extinction parameters. The coherent scattering lengths used for La, Ca, Cu, Ga, and O were 8.27, 4.90, 7.72, 7.29, and 5.81 fm, respectively.

Thermogravimetric Analysis. A DuPont Instruments 891 thermogravimetric analyzer was used to measure the oxygen content of $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$. Powdered samples were heated at 650°C in a flowing mixture of 8.5% hydrogen and 91.5% helium gas until all of the copper species present in the sample had been reduced to copper metal.

Results

The X-ray diffraction data sets for $\text{LnSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ ($\text{Ln} = \text{lanthanide, Y}$) could all be indexed on a body-centered $\sqrt{2}a_p \times \sqrt{2}a_p \times 6a_p$ (a_p is the lattice parameter of a simple cubic perovskite, i.e., $\sim 4 \text{ \AA}$) orthorhombic unit cell, similar to the parent compound $\text{LaSr}_2\text{Cu}_2\text{GaO}_7$ (see Figure 1).⁶ Each diffraction pattern showed the presence of impurity phases on the order of a few percent. The calcium saturation point was therefore defined as the highest calcium concentration at which the fraction of impurity phases did not exceed a few percent. Based on this criterion, calcium substituted for strontium in $\text{LaSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ and $\text{PrSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ over the entire range and resulted in a linear contraction of each lattice parameter as a function of increasing x (see Figure 2). For the rest of the lanthanides, calcium substitutes progressively less with decreasing lanthanide size through $\text{YbSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$, in which it saturates at $x = 0.60$ (see Figure 3). $\text{LuSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ did not form under the experimental conditions employed for any value of x , consistent with prior attempts to synthesize $\text{LuSr}_2\text{Cu}_2\text{GaO}_7$ at ambient pressure.⁵ Lattice parameters at the limit of calcium solubility for $\text{LnSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$, $\text{Ln} = \text{La, Pr, Nd, Gd, Ho, Er, Tm, and Yb}$, are given in Table 1.

The structure of $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$ was refined from both X-ray and neutron diffraction data, and the observed and calculated patterns for each are given in the Supporting Information. The structural parameters of $\text{LaSr}_2\text{Cu}_2\text{GaO}_7$ ($\text{Ima}2$; $a = 22.8014(5) \text{ \AA}$, $b = 5.4819(1) \text{ \AA}$, $c = 5.3936(1) \text{ \AA}$)⁶ were used as a starting

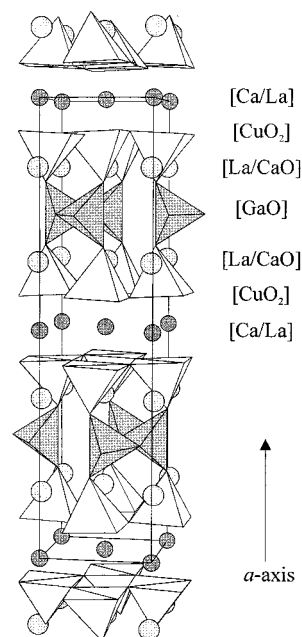


Figure 1. Structure of $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$, which is isomorphic with $\text{LaSr}_2\text{Cu}_2\text{GaO}_7$.

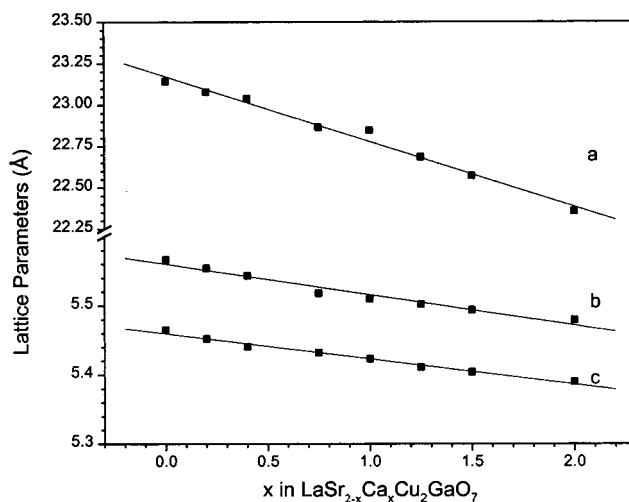


Figure 2. Orthorhombic lattice parameters for $\text{LaSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ as a function of x .

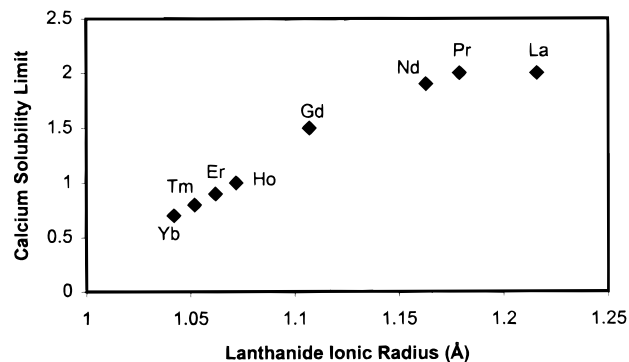


Figure 3. Calcium saturation points in $\text{LnSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ materials versus the 9-coordinate ionic radii of the Ln^{3+} cations.

model for the analysis of the X-ray data. The structure refined from the X-ray data was then used as a starting model for the analysis of the neutron data. The reflections for both sets of data exhibit conditions consistent with the non-centrosymmetric space group $\text{Ima}2$ (No. 46) and the centrosymmetric space group

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Table 1. Orthorhombic Unit Cell Parameters and Average 9-Coordinate A-Cation Size for $\text{LnSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ (Ln = La, Pr, Nd, Gd, Ho, Er, Tm, and Yb) at the Calcium Saturation Levels^a

Ln	x at the Ca satn level	a (Å)	b (Å)	c (Å)	cell vol (Å ³)	av A-cation size (Å)
La	2.0	22.359(1)	5.4795(2)	5.3902(2)	660.39(5)	1.19
Pr	2.0	22.396(1)	5.4709(3)	5.3691(3)	657.86(6)	1.18
Nd	1.9	22.161(1)	5.4855(1)	5.3752(1)	653.44(2)	1.18
Gd	1.5	22.118(2)	5.4906(5)	5.3794(4)	653.29(9)	1.18
Ho	1.0	22.323(1)	5.4751(3)	5.3691(3)	656.21(6)	1.19
Er	0.9	22.158(2)	5.4798(5)	5.3741(5)	652.53(10)	1.19
Tm	0.8	22.377(2)	5.4649(3)	5.3661(3)	656.21(8)	1.19
Yb	0.7	22.401(2)	5.4599(4)	5.3655(4)	656.24(9)	1.19

^a The lattice parameters of all the samples decrease with calcium substitution of the pure strontium analogues similar to the lanthanum case (Figure 2). While subtle trends in the individual parameters with changing lanthanide hint at structure-distribution interactions, all the unit cell volumes converge to within 1% of a constant value at the solubility limit.

Table 2. Refined Structural Parameters of $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$ in *Ima2* (No. 46)^a

atom	site	x	y	z	100U _{iso} ^b (Å ²)	occupancy
A1	4a	0	0	0		0.125(4) La/0.875(4) Ca
		0	0	0	0.54(16)	0.208(14) La/0.792(14) Ca
A2	8c	0.148(1)	0.984(1)	0.999(5)		0.438(2) La/0.562(2) Ca
		0.1490(1)	0.9835(7)	0.9828(21)	0.12(10)	0.396(7) La/0.604(7) Ca
Cu	8c	0.074(1)	0.498(1)	0.997(4)		1
		0.0736(1)	0.4993(5)	0.9960(22)	0.13(7)	1
Ga	4b	0.25	0.434(1)	0.029(5)		1
		0.25	0.4333(8)	0.0242(25)	1.05(16)	1
O1	8c	0.076(1)	0.263(8)	0.255(18)		1
		0.0760(1)	0.2508(14)	0.2452(23)	0.16(9)	1
O2	8c	0.069(1)	0.753(9)	0.748(21)		1
		0.0673(1)	0.7479(15)	0.7485(25)	0.12(11)	1
O3	8c	0.181(1)	0.558(3)	0.962(7)		1
		0.1770(2)	0.5600(6)	0.9585(23)	0.96(13)	1
O4	4b	0.25	0.379(5)	0.403(7)		1
		0.25	0.3860(11)	0.3891(23)	1.40(15)	1

^a The first line of data for each atom is from the X-ray refinement ($a = 22.359(1)$ Å, $b = 5.480(1)$ Å, and $c = 5.390(1)$ Å), and the second is from the neutron ($a = 22.366(1)$ Å, $b = 5.482(1)$ Å, and $c = 5.391(1)$ Å). For refinement of X-ray data: $R_p = 3.47$, and $R_{wp} = 4.57$. For refinement of neutron data: $R_p = 5.26$, $R_{wp} = 7.39$, $R(F^2) = 5.89$, and $\chi^2 = 9.415$ where $R_p = 100(\sum|Y_{obs} - Y_{calc}|/\sum Y_{obs})$; and $R_{wp} = 100\sqrt{(\sum W(Y_{obs} - Y_{calc})^2/\sum W Y_{obs}^2)}$ with $W = 1/Y_{obs}$; $R(F^2) = 100(\sum|I_{Kobs} - I_{Kcalc}|/\sum I_{Kobs})$. ^b For refinement of X-ray data: $\beta_{overall} = 0.24(5)$ Å².

Imam (No. 74). In the latter, two oxygen sites are disordered and half-occupied because the two possible orientations of the gallate tetrahedra are averaged together. Krekels et al. discuss how the subtle distinctions have been experimentally differentiated.¹⁵ The A-cation sites are the same in either case. Since the non-centrosymmetric space group was used for the refinement of $\text{LaSr}_2\text{Cu}_2\text{GaO}_7$, it was also used for $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$.

Refinement of the X-ray data accounted for two phases: $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$ and the internal standard silicon. A small amount of $\text{LaCaGa}_3\text{O}_7$ (<5%) was detected, but not included in the refinement. Three phases were refined for the neutron diffraction data: $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$, $\text{La}_{2-x}\text{Ca}_{1+x}\text{Cu}_2\text{O}_{6+\delta}$,¹⁶ and $\text{LaCaGa}_3\text{O}_7$. Only the powder diffraction pattern of $\text{LaCaGa}_3\text{O}_7$ has been reported in the literature,¹⁷ so the structure of $\text{LaCaGa}_2.34\text{Al}_{0.66}\text{O}_7$ was used to model it.¹⁸ Both $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$ refinements allowed lanthanum and calcium to occupy either of the two different A-cation sites while the ratio of lanthanum to calcium was confined to 1:2. The oxygen sites were fully occupied in the refinement in accordance with the TGA result in which the oxygen content was 7.02 ± 0.04 based on four individual measurements. In the final neutron refinement cycle,

parameters were allowed to refine undamped and the best R_p factor was 5.26 ($R_{wp} = 7.39$, $R(F^2) = 5.89$, and $\chi^2 = 9.415$). The weight percentages of the three phases refined to 93(3)% $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$, 4(1)% $\text{La}_{1.94}\text{Ca}_{1.06}\text{Cu}_2\text{O}_{6.03}$, and 3(1)% $\text{LaCaGa}_3\text{O}_7$. The A-cation distribution for lanthanum was 21% between the copper–oxygen planes: $(\text{La}_{0.21}\text{Ca}_{0.79})(\text{La}_{0.79}\text{Ca}_{1.21})\text{Cu}_2\text{GaO}_7$. Although the X-ray and neutron refinements were conducted on independent samples, the atomic parameters are comparable within experimental error. Table 2 lists the results of the refinements of both sets of data including positional parameters, thermal factors, and site occupancies. Selected bond lengths and angles are provided in the Supporting Information. Preliminary electron microscopy work reveals the presence of superstructure reflections, indicating that the structure of $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$ is more detailed than reported here.

Discussion

The linear relationship between the size of the lanthanide cation and the calcium solubility limit in $\text{LnSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ (Ln = Pr–Yb) materials suggests that the structure requires a minimum average A-cation size of around 1.19 Å (see Table 1). Both the lattice parameters and cell volumes of the calcium-saturated materials also remain relatively constant regardless of the fact that the specific cations in this study range in size from Yb^{3+} (1.075 Å) to Sr^{2+} (1.31 Å). (All cationic radii mentioned in this paper refer to 9-coordinate ionic radii.)¹⁹ In general, the smaller cations prefer the 8-coordinate site in the

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active layer to the 9-coordinate site in the blocking layer, but some mixing occurs owing to entropy. Even if we assume that there is no Sr²⁺ in the active layer, the result is that, for every calcium cation in the active layer, a lanthanide cation is relegated to the blocking layer. It is not surprising then that calcium is completely soluble in the La³⁺ (1.216 Å) and Pr³⁺ (1.18 Å) systems because these are the two lanthanide cations which are not smaller than Ca²⁺ (1.18 Å) and readily occupy blocking-layer sites. As the size of the lanthanide cation decreases, the average A-cation size of the strontium analogue decreases (LnSr₂Cu₂GaO₇), and consequently, the amount of calcium required to bring the average A-cation size down to the lower limit is less. The tendency for the lanthanide to occupy the 9-coordinate blocking-layer site over the 8-coordinate active layer one also decreases with size. This confines the calcium to the blocking layer and negates a portion of the entropic stability.

While the formation of the structure depends significantly on the overall average A-cation size, the A-cation distribution depends largely on the specific cations involved. The experimental cation distribution for LaCa₂Cu₂GaO₇ and LaSr₂Cu₂GaO₇ from neutron data refinement allow us to quantify the site-specific energetics involved with cation substitution. In the former, the 8-coordinate site between the cuprate planes is 79% Ca²⁺ according to the neutron refinement, i.e., (La_{1-d}Ca_d)-(La_dCa_{2-d})Cu₂GaO₇ with a distributional parameter, **d** = 0.79. This differs from the purely statistical distribution of **d** = 0.67 revealing that there is a nonzero enthalpy term for the exchange of calcium and lanthanum between the active layer and the blocking layer. A mathematical relationship between **d** and the exchange enthalpy can be derived because the entropy change of switching the cations between the two sites must balance the enthalpy change for a system at equilibrium at the synthesis temperature, i.e., 1248 K. The chemical reaction for switching lanthanide and alkaline earth cations between the 8-coordinate active-layer site and the 9-coordinate blocking-layer site is



This switching reaction relates a completely ordered state of the system (**d** = 0) to the equilibrium state. ΔG_{system} must be at a minimum as a function of **d**, which is also the switching reaction coordinate. Statistical thermodynamics for mixing allows us to calculate ΔS_{system} directly. The sum of four entropy terms, one for each cation type on each site of (Ln_{1-d}AE_d)-(Ln_dAE_{2-d})Cu₂GaO₇, gives the total entropy of the system relative to a completely ordered state as a function of **d**:

$$\Delta S_{\text{system}}(\mathbf{d}) = -R[(1 - \mathbf{d})\ln(1 - \mathbf{d}) + \mathbf{d} \ln(\mathbf{d}) + \mathbf{d} \ln(\mathbf{d}/2) + (2 - \mathbf{d})\ln((2 - \mathbf{d})/2)] \quad (2)$$

The enthalpy of the system, relative to the **d** = 0 state, is simply the total enthalpy of switching the cations between sites:

$$\Delta H_{\text{system}}(\mathbf{d}) = \mathbf{d}\Delta H_{\text{switch}} \quad (3)$$

If ΔH_{switch} is constant, then its magnitude can be calculated by minimizing $\Delta G_{\text{system}}(\mathbf{d})$.

$$\frac{\delta}{\delta \mathbf{d}} \Delta G_{\text{system}}(\mathbf{d}) = \frac{\delta}{\delta \mathbf{d}} [\mathbf{d}\Delta H_{\text{switch}} - T\Delta S_{\text{system}}(\mathbf{d})] = 0$$

$$\Delta H_{\text{switch}} = -RT \ln[\mathbf{d}^2/(1 - \mathbf{d})(2 - \mathbf{d})] = -RT \ln K_{\text{switch}} \quad (4)$$

Notice that $\Delta H_{\text{switch}} = 0$ for **d** = 0.67 as required. It is now clear that the inherent entropy of a switching reaction is zero:

$$T\Delta S_{\text{switch}} = \Delta H_{\text{switch}} - \Delta G_{\text{switch}} = \Delta H_{\text{switch}} + RT \ln K_{\text{switch}} = 0$$

Several graphs of $\Delta G_{\text{system}}(\mathbf{d})$, $\Delta H_{\text{system}}(\mathbf{d})$, and $-T\Delta S_{\text{system}}(\mathbf{d})$ for specific systems are given in the Supporting Information.

The enthalpy for the specific switching reaction between calcium and lanthanum in (La_{0.21}Ca_{0.79})(La_{0.79}Ca_{1.21})Cu₂GaO₇ can now be calculated from the experimentally observed distribution:



$$\Delta H_{\text{switch}}(\mathbf{d} = 0.79) = -9 \text{ kJ/mol}$$

Clearly Ca²⁺ prefers the 8-coordinate pseudo-square-prismatic site between copper planes while La³⁺ prefers the 9-coordinate site. The switching reaction is exothermic, and so mixing takes place beyond the statistical value.

An analogous calculation can be done for (La_{0.7}Sr_{0.3})(La_{0.3}Sr_{1.7})Cu₂GaO₇ in which the distributional parameter, **d**, was measured via neutron diffraction to be 0.30.⁵ This is much lower than the statistical limit, and the switching reaction between strontium and lanthanum,



$$\Delta H_{\text{switch}}(\mathbf{d} = 0.30) = 27 \text{ kJ/mol}$$

is endothermic. In this case the situation is reversed as La³⁺ (1.216 Å) preferentially occupies the site between copper planes while Sr²⁺ (1.31 Å) preferentially occupies the blocking-layer site.

The enthalpies for these exchange reactions are calculated on the basis of two observed distributions. However, they can be applied to other related systems when the distribution is not known because the reactions are symmetric with respect to both cations and cation sites. The structures of LaCa₂Cu₂GaO₇ and LaSr₂Cu₂GaO₇ are isomorphic, but differ in the volume of the unit cell. Indeed, both A-cation sites in the latter are larger, so the effect on the switching energy is offsetting. In the case of LaSr₂Cu₂GaO₇, if the size of the unit cell changes, the switching enthalpy between La³⁺ and Sr²⁺ would still be about 27 kJ/mol because the absolute enthalpy of all four species of eq 6, IXSr²⁺, VIII La³⁺, VIII Sr²⁺, and IX La³⁺, would increase comparably, preserving the overall reaction energy. This is true as long as the different A-cation sites are not differentiated. Switching enthalpies would not be transferable to different structures such as YBCO. In general, the energy of switching the position of two cations in a structure does not depend on the volume of the unit cell, but rather on the type of structure.

If the enthalpy required to switch two cations between two sites is independent of the unit cell volume size, then the switching reactions 5 and 6 for the gallate structure can be combined to estimate the switching enthalpy between calcium and strontium between the active and blocking layers:



$$\Delta H_{\text{switch}} = 36 \text{ kJ/mol}$$

The relationship between cation distribution and switching enthalpies can be used to model cation distribution. The entropy of distributional states can be calculated directly so only the enthalpy is required. The independence of the switching enthalpy from the lattice parameters allows us to apply the above enthalpy

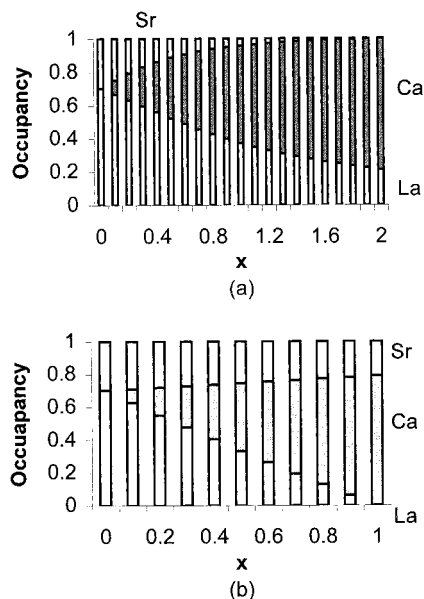


Figure 4. Cation distribution on the 8-coordinate active-layer site for (a) $\text{LaCa}_x\text{Sr}_{2-x}\text{Cu}_2\text{GaO}_7$ and (b) $\text{La}_{1-x}\text{Ca}_x\text{Sr}_2\text{Cu}_2\text{GaO}_7$ as a function of x .

terms to any hypothetical stoichiometry involving lanthanum, calcium, and strontium on the A-sites of the gallate structure, $(\text{La}/\text{Ca}/\text{Sr})_3\text{Cu}_2\text{GaO}_7$. In general, enthalpies can be calculated easily from distributional parameters as described above. However, the reverse calculation is more difficult, especially for systems involving three or more cations. Unknown site distributions can be calculated from known enthalpy values indirectly though since only one distribution will lead to the correct switching enthalpies for the system. Figure 4a shows the anticipated distribution for the A-site between the copper planes in $\text{LaSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ as a function of x . This is the distribution model for the solid solution between $\text{LaSr}_2\text{Cu}_2\text{GaO}_7$ and $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$. Note that the calcium displaces the strontium between the planes in a nonlinear fashion. This is not unexpected since Ca^{2+} is smaller than both La^{3+} and Sr^{2+} . A second model mimics a doping situation where calcium replaces lanthanum, $\text{La}_{1-x}\text{Ca}_x\text{Sr}_2\text{Cu}_2\text{GaO}_7$. Figure 4b shows the distribution for this hypothetical case. The strontium occupation of the 8-coordinate site decreases slightly because Ca^{2+} does not mix with Sr^{2+} as well as La^{3+} . The model is a physical-structural one and does not take the introduction of charge carriers into account in any way. Experiments must be conducted to determine whether or not such phases form. If they do, then this model projects three-cation (La/Ca/Sr) distributions based on the experimental two-cation distributions (La/Ca and La/Sr). The result can facilitate structural refinements as well by differentiating between cation distributions.

To extend the method to the other rare earth gallates $(\text{Ln}/\text{Ca}/\text{Sr})_3\text{Cu}_2\text{GaO}_7$, the enthalpy of one additional switching reaction involving another lanthanide is needed. In contrast to lanthanum, holmium is considerably smaller than both calcium and strontium. No cation distribution data for any gallate containing Ca^{2+} and Ho^{3+} could be found in the literature, so we will approximate the switching enthalpy, ΔH_{switch} , for



at 25 kJ/mol based on a linear extrapolation of cation size. The estimated value is used to demonstrate how hypothetical A-cation distributions of $(\text{Ho}/\text{Ca}/\text{Sr})_3\text{Cu}_2\text{GaO}_7$ compare to the lanthanum case. Figure 5 shows the anticipated occupancies for

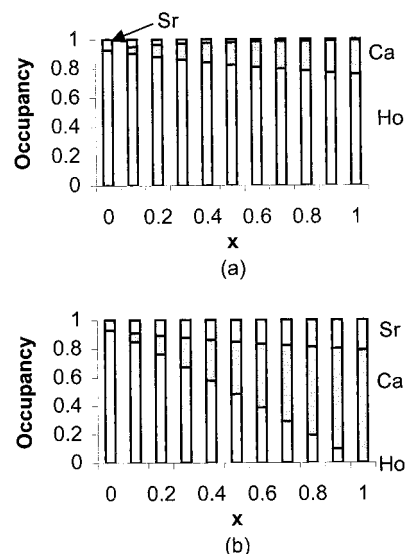


Figure 5. Cation distribution on the 8-coordinate active-layer site for (a) $\text{HoCa}_x\text{Sr}_{2-x}\text{Cu}_2\text{GaO}_7$ and (b) $\text{Ho}_{1-x}\text{Ca}_x\text{Sr}_2\text{Cu}_2\text{GaO}_7$ as a function of x .

$\text{HoSr}_{2-x}\text{Ca}_x\text{Cu}_2\text{GaO}_7$ and $\text{Ho}_{1-x}\text{Ca}_x\text{Sr}_2\text{Cu}_2\text{GaO}_7$, both as a function of x . Notice that the percentage of strontium between the planes decreases from 7% to 1% in the first case as it is displaced by calcium, and increases in the second case from 7% to 21% as calcium facilitates disorder between the sites. These models suggest that a stoichiometry such as $\text{Ho}_{0.7}\text{Ca}_{1.3}\text{SrCu}_2\text{O}_7$ should limit the presence of strontium between the planes to around 1%, i.e., $(\text{Ho}_{0.58}\text{Ca}_{0.41}\text{Sr}_{0.01})(\text{Ho}_{0.12}\text{Ca}_{0.89}\text{Sr}_{0.99})\text{Cu}_2\text{GaO}_7$.

Cation size governs the ambient pressure A-cation substitutions in the gallate perovskite structure. Indeed, the architecture of each family of layered cuprates creates various A-cation sites, and only certain combinations of cations stabilize a structure at ambient pressure. The ability of a particular combination to stabilize a structure is largely a function of average cation size. For example, the average allowable A-cation size in the gallate of 1.19 Å is smaller than that for $\text{Y}(\text{Ca}/\text{Sr}/\text{Ba})_2\text{Cu}_3\text{O}_7$ systems, which is closer to 1.30 Å.^{2,3} The difference is likely structural in nature, originating in the blocking layer owing to the different coordination requirements of Ga^{3+} and $\text{Cu}^{2+,3+}$.

Within a particular structure type, the distributions of the A-cations are largely a function of individual cation size. The closer two cations are in size, the more they will mix. In the gallate system, the size difference of -0.036 Å between Ca^{2+} and La^{3+} results in a switching energy of -9 kJ/mol. The 0.094 Å size difference between Sr^{2+} and La^{3+} results in a switching energy of 27 kJ/mol. Extensive A-cation mixing does not occur in YBCO owing to the size difference between Ba^{2+} and Y^{3+} of 0.395 Å. Substituting the barium with strontium or calcium facilitates cation mixing since the intermediate size cation exchanges more readily with both yttrium and barium. As long as the structures are the same type, regardless of size, a common set of switching energies can be used to model the cation distribution. However, different structure types selectively change the coordination environments and therefore require a set of switching energies specific for that structure type.

Cation order is an important factor in regard to many different properties in solid materials. The distribution of A-cation size for a specific site, a key factor for superconducting materials,¹⁰ increases with mixing. $\text{LaBa}_2\text{Cu}_3\text{O}_7$ superconducts when synthesized in such a way as to mitigate site mixing between

lanthanum and barium.²⁰ While mixing can never be eliminated completely, sufficiently large energetic barriers exist. If all cation mixing is detrimental to superconductivity, then strongly differentiated cations are optimal. However, there is evidence to suggest that calcium between the copper planes may even be beneficial for the energetics of the superconducting state.²¹ Then compounds such as $\text{Ln}_{0.7}\text{Ca}_{1.3}\text{SrCu}_2\text{GaO}_7$ for smaller lanthanides should prove to be good candidates for superconductivity because the strontium occupancy between the planes is less than a few percent.

We have demonstrated and modeled here how cations of various sizes contribute to site disorder. Size is the primary factor controlling the mixing of cations. The number of solid-state materials that involve multiple cations is increasing rapidly as more complex systems are explored. The degree of order of the cations is a critical factor for many properties, and controlling the distribution of the cations is paramount to developing useful materials. Some order can be promoted by slow-cooling, but only a limited amount since cation rearrangement occurs above approximately 900 °C. Material design considerations should include relative cation sizes and site-specific energetics to control cation order and optimize properties.

Summary

Calcium completely substitutes for strontium in $\text{LaSr}_2\text{Cu}_2\text{GaO}_7$ and $\text{PrSr}_2\text{Cu}_2\text{GaO}_7$ to form the new materials $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$ and $\text{PrCa}_2\text{Cu}_2\text{GaO}_7$. A minimum threshold for average A-cation size in the gallate structure limits the calcium solubility in the phases formed with the smaller lanthanides ($\text{LnCa}_x\text{Sr}_{2-x}\text{Cu}_2\text{GaO}_7$). Each of these materials was indexed on a body-

centered $\sqrt{2a_p} \times \sqrt{2a_p} \times 6a_p$ orthorhombic unit cell with lattice parameters that decreased with increasing calcium concentration. The A-cation site occupancies of two systems were refined to quantify the tendencies of cation pairs to switch positions within the gallate architecture. While average cation size dictates the formation of a particular structure, relative cation size is the dominant factor that determines the extent of disorder within that structure and the related properties. In general, experimentally measured distributions from two-cation systems can be used to predict the distributions of more complex cation systems.

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Supporting Information Available: Neutron and X-ray powder diffraction patterns for $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$ along with tables listing detailed crystallographic data, selected bond lengths and angles based on the independent Rietveld refinement of each data set. Table of indices for $\text{LaCa}_2\text{Cu}_2\text{GaO}_7$ X-ray powder diffraction pattern, and graphs of thermodynamic calculations [$\Delta G_{\text{system}}(\mathbf{d})$, $\Delta H_{\text{system}}(\mathbf{d})$, and $-T\Delta S_{\text{system}}(\mathbf{d})$]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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