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A novel metathesis route for the synthesis of La_2CuO_4 and its superconducting analogues: synthesis of a new lithium-substituted derivative of La_2CuO_4

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The metathesis reaction, $Li_2CuO_2 + 2\ LnOCl \rightarrow Ln_2CuO_4 + 2\ LiCl$, (Ln = La, Nd), provides a convenient route for the synthesis of La_2CuO_4 and Nd_2CuO_4 at relatively low temperatures (700–800 °C). Use of Sr/Ba-substituted LaOCl in the above reaction enables synthesis of superconducting analogues, $La_{1.85}A_{0.15}CuO_4$ (A = Sr, Ba), as well. A new lithium-substituted derivative of nominal composition $La_{1.8}Li_{0.2}CuO_4$ has also been synthesized in the metathesis reaction between Li_2CuO_2 and $La(OH)_3$.

1 Introduction

There is continuing interest in La_2CuO_4 and its derivatives, not only because of superconductivity[1] in $La_{2-x}A_xCuO_4$ (A = Ca, Sr, Ba), but also because of many other properties. For instance, La_2CuO_4 and its derivatives are known to catalyze several chemical reactions,[2–5] including CO oxidation, NO reduction and CH_4 oxidation, besides functioning as three-way automobile exhaust catalysts.[3] La_2CuO_4 also exhibits unusual low temperature oxygen intercalation[6] that renders it a superconductor as well as a mixed electronic oxide ion conductor. Accordingly, there is parallel interest in developing new routes for the synthesis of La_2CuO_4 and its derivatives. For example, Galkin *et al.*[7] have recently reported a new route for the synthesis of La_2CuO_4 by simultaneous hydrolysis of La(III) and Cu(II) acetates in supercritical water followed by annealing the product at 600 °C for 5 h.

As a part of our interest in developing metathesis routes for the synthesis of oxide materials,[8] we have investigated metathesis reactions in the solid state between Li_2CuO_2 and LnOCl/$La(OH)_3$ (Ln = La, Nd). Our investigations have not only provided a convenient route for the synthesis of La_2CuO_4 and its superconducting analogues, but also yielded a new lithium-substituted derivative of La_2CuO_4 in the reaction between Li_2CuO_2 and $La(OH)_3$. The details are reported in this paper.

2 Experimental

The starting materials, Li_2CuO_2, LaOCl, NdOCl, Sr/Ba-doped LaOCl and $La(OH)_3$, were prepared as reported in the literature.[9–11] Li_2CuO_2 was prepared by reacting stoichiometric quantities of Li_2CO_3 and CuO at 600 °C for 24 h and 650 °C for 48 h in air with intermediate grindings.[9] LnOCl (Ln = La, Nd) was prepared by reacting Ln_2O_3 (Ln = La, Nd; pre-dried at 900 °C) with an equal quantity of NH_4Cl at 300, 500 and 900 °C for 2–4 h each.[10] Sr/Ba-substituted LaOCl was synthesized similarly from stoichiometric quantities of La_2O_3 (pre-dried at 900 °C), $SrCO_3$/$BaCO_3$ and NH_4Cl at 300 and 500 °C for 3 h each. $La(OH)_3$ was prepared hydrothermally by reacting 2 g of La(III) nitrate in 2 ml of H_2O and 7 g of NaOH in 7 ml of H_2O in a sealed Teflon bomb at 200 °C for 1 day.[11]

The metathesis reaction,

$$Li_2CuO_2 + 2\ LaOCl \rightarrow La_2CuO_4 + 2\ LiCl \qquad (1)$$

was investigated by heating stoichiometric mixtures of the reactants at various temperatures for a range of times air. The products were examined by powder X-ray diffraction. Single-phase La_2CuO_4 was formed in reaction (1) at 800 °C for 24 h. Nd_2CuO_4 was formed in a similar reaction at 700 °C for 24 h. The superconducting derivatives $La_{1.85}A_{0.15}CuO_4$ (A = Sr, Ba) were obtained by similar metathesis reactions between Li_2CuO_2 and $La_{1-x}A_xO_{1-x/2}\square_{x/2}Cl$ ($x = 0.075$; $\square$ indicates vacancy). For this purpose, an intimate mixture of stoichiometric quantities of the reactants was heated at 800 °C for 24 h in air with one grinding in between, and the resulting product, after washing with water and drying in air, was pelletized and oxygen-annealed at 800 °C for 12 h.

In our efforts to synthesize a perovskite oxide, '$LiLaCuO_3$', we obtained a new lithium-substituted derivative of La_2CuO_4 in the reaction between Li_2CuO_2 and $La(OH)_3$. The new derivative of nominal composition $La_{1.8}Li_{0.2}CuO_4$ was obtained in the reaction between 1 mol of Li_2CuO_2 and 2 mol of $La(OH)_3$ at 500 °C for 12 h, 600 °C for 12 h and finally at 800 °C for 12 h, with grindings between each stage.

The precursors as well as the product oxides were characterized by powder X-ray diffraction (XRD) using a JEOL JDX-8P X-ray powder diffractometer (Cu-Kα radiation). Lattice parameters of single-phase products were refined by least-squares refinement of the powder diffraction data using the PROSZKI program.[12] Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) studies were carried out using a JEOL JSM-840A scanning electron microscope. The oxidation state of copper in La_2CuO_4 derivatives was determined by iodometric titration[13] using KI. Electrical resistivity measurements were carried out on sintered pellets by the standard four-probe technique in the temperature range 25–300 K using a closed cycle helium cryostat. DC magnetic susceptibility for the lithium-substituted sample was measured in the temperature range 25–300 K using a Lewis coil magnetometer (George Associates, model 2000).

3 Results and discussion

We investigated metathesis reaction (1) between Li_2CuO_2 and LaOCl at temperatures from 500 °C increasing in increments of 50 °C for reaction times of 12 and 24 h. We found that single-phase La_2CuO_4 was formed at 800 °C after 24 h reaction with

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Table 1 Synthesis by the metathesis route and characterization of La_2CuO_4 and its derivatives

Composition	Reaction conditions	Lattice parameters/Å			Property
		a	*b*	*c*	
La_2CuO_4	800 °C/24 h	5.360(1)	5.404(1)	13.157(3)	Insulator
Nd_2CuO_4	700 °C/24 h	3.950(1)		12.179(3)	Insulator
$La_{1.85}Sr_{0.15}CuO_4$	800 °C/24 h in air; 800 °C/12 h in oxygen	3.791(1)		13.223(3)	Superconductor (onset $T_c = 36$ K)
$La_{1.85}Ba_{0.15}CuO_4$	800 °C/24 h in air; 800 °C/12 h in oxygen	3.806(1)		13.257(4)	Superconductor (onset $T_c = 38$ K)
$La_{1.8}Li_{0.2}CuO_4$	500 °C/6 h; 600 °C/6 h; 800 °C/12 h	3.750(1)		13.292(5)	Semiconductor

one intermediate grinding. The refined lattice parameters (Table 1) found for our sample are in good agreement with the values already reported in the literature.[14] The formation of La_2CuO_4 is further confirmed by the EDX analysis, which shows the expected 2 : 1 La : Cu ratio and the absence of any chlorine impurities. The SEM studies show that the particle sizes are in the range 2–4 μm.

The temperature of formation (800 °C) of La_2CuO_4 by the metathesis reaction is considerably lower than the temperatures (1000–1200 °C)[15] at which La_2CuO_4 is formed in the ceramic reaction between La_2O_3 and CuO; it is however higher than the formation temperature (600 °C) reported by Galkin[7] *et al.* using supercritical water as a medium. In a similar reaction between Li_2CuO_2 and NdOCl (1 : 2 molar ratio) at 700 °C for 24 h, we have synthesized Nd_2CuO_4. This temperature is considerably lower than the usual synthesis temperature[16] (1100 °C) of Nd_2CuO_4 by the direct reaction between Nd_2O_3 and CuO.

More importantly, we have synthesized superconducting $La_{1.85}A_{0.15}CuO_4$ (A = Sr, Ba) in the reaction between Li_2CuO_2 and $La_{1-x}A_xO_{1-x/2}\square_{x/2}Cl$ (A = Sr, Ba; $x = 0.075$).

$$Li_2CuO_2 + 2\ La_{0.925}A_{0.075}O_{0.962}\square_{0.038}Cl + 0.038\ O_2 \rightarrow La_{1.85}A_{0.15}CuO_4 + 2\ LiCl\ (A = Sr, Ba) \quad (2)$$

The superconducting phases formed in the metathesis reaction have been characterized by powder XRD. The lattice parameters and the superconducting transition temperatures (onset $T_c = 36$ and 38 K, respectively) (Table 1) determined by resistivity measurements (Fig. 1) are in agreement with the corresponding data reported in the literature.[1,14,17]

A comment about the possible mechanism of the metathesis reaction is in order. In the recently reported metathetical transformation[8] of Ruddlesden–Popper oxides [$K_2La_2Ti_3O_{10}$] to Aurivillius phases [(Bi_2O_2)$La_2Ti_3O_{10}$], the structural integrity of the perovskite sheet and (Bi_2O_2) sheet is preserved. In the metathesis reaction reported here, there seems to be no obvious retention of structural features in view of the differences between the structures of the parent Li_2CuO_2 and product La_2CuO_4 (Fig. 2). The metathesis reported here is probably more like the conventional metathesis[18,19] where the reaction is driven by the high lattice energy of LiCl and its low melting point (605 °C). Molten LiCl would act as a medium for the facile formation of La_2CuO_4 and its derivatives at relatively low temperatures.

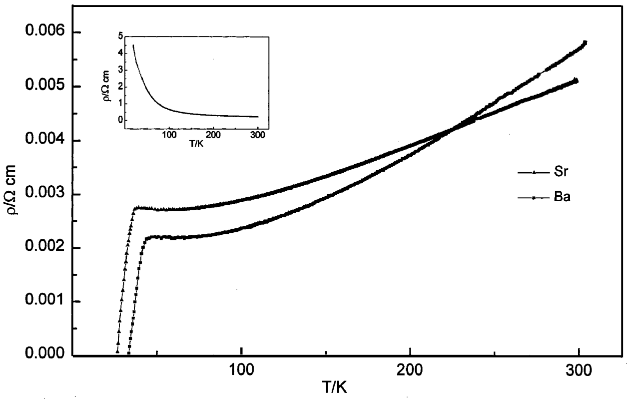

Fig. 1 Electrical resistivity data for (a) $La_{1.85}Sr_{0.15}CuO_4$ and (b) $La_{1.85}Ba_{0.15}CuO_4$. The inset shows the data for (c) $La_{1.8}Li_{0.2}CuO_4$.

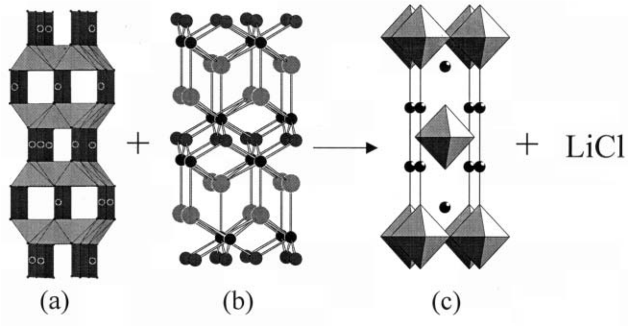

Fig. 2 Structures of (a) Li_2CuO_2, (b) LaOCl and (c) La_2CuO_4.

Having synthesized La_2CuO_4 and its derivatives, we explored the possibility of synthesizing other cuprates by the metathesis route. One of the long-standing challenges in copper oxide chemistry is to synthesize three-dimensional perovskites containing Cu^{II}. We envisaged that a perovskite-related oxide of the formula '$LiLaCuO_3$' would exist when additional Li^+ ions are inserted into the $LaCuO_3$ framework, in a manner similar to that in $(LiLa)TiO_3$.[20] To realize this possibility, we explored the following metathesis reaction

$$Li_2CuO_2 + La(OH)_3 \rightarrow LiLaCuO_3 + LiOH + H_2O \quad (3)$$

at various temperatures (300–800 °C) and durations (6–24 h). The reaction product, however, was a mixture of a tetragonal $La_{2-x}A_xCuO_4$-like phase along with CuO. Accordingly, we believed that a new Li-substituted La_2CuO_4 derivative was obtained in reaction (3), instead of '$LiLaCuO_3$'. To prepare a single-phase Li-substituted La_2CuO_4, we carried out the reaction between Li_2CuO_2 and $La(OH)_3$ in a 1 : 2 molar ratio. We obtained a tetragonal K_2NiF_4-like phase of nominal composition, $La_{1.8}Li_{0.2}CuO_4$, in reaction (4) (Table 1).

$$Li_2CuO_2 + 1.8\ La(OH)_3 + 0.1\ O_2 \rightarrow La_{1.8}Li_{0.2}CuO_4 + 1.8\ LiOH + 1.8\ H_2O \quad (4)$$

Iodometric titration[13] showed that the oxidation state of copper in the product is 2.4 ± 0.02, consistent with the formulation $La_{1.8}Li_{0.2}CuO_4$. Formation of $La_{1.8}Li_{0.2}CuO_4$ instead of La_2CuO_4 in the reaction between Li_2CuO_2 and $La(OH)_3$ is most likely due to the presence of LiOH formed *in situ* in the reaction, which would act as an oxidizing flux. Molten NaOH/KOH is known to act as an oxidizing flux in the formation of superconducting $La_{2-x}Na_xCuO_4$ and $La_{2-x}K_xCuO_4$.[21]

The powder XRD pattern of $La_{1.8}Li_{0.2}CuO_4$ could be indexed on a tetragonal (*I*4/*mmm*) structure similar to that of $La_{1.85}Sr_{0.15}CuO_4$ (Table 2). Significantly, Na/K-substituted La_2CuO_4 crystallizes in a primitive tetragonal structure,[22]

Table 2 X-Ray powder diffraction data for $La_{1.8}Li_{0.2}CuO_4$

$h\ k\ l$	d_{obs}/Å	$d_{calc}{}^a$/Å	I_{obs}	$I_{calc}{}^b$
1 0 1	3.623	3.609	25	15
0 0 4	3.334	3.323	14	10
1 0 3	2.866	2.862	100	100
1 1 0	2.652	2.652	64	65
1 1 2	2.486	2.463	1	1
0 0 6	2.217	2.215	11	13
1 0 5	2.171	2.169	18	24
1 1 4	2.074	2.073	32	25
2 0 0	1.875	1.875	28	33
1 1 6	1.700	1.700	10	12
1 0 7	1.692	1.694	11	11
2 1 1	1.664	1.664	8	5
0 0 8	1.663	1.662	6	4
2 0 4	1.633	1.633	7	6
2 1 3	1.568	1.568	32	35
2 0 6	1.430	1.431	11	12
2 1 5	1.417	1.418	10	11
1 1 8	1.407	1.408	8	8

^{a}a = 3.750(1); c = 13.292(5) Å. ^{b}Intensities have been calculated by LAZY PULVERIX[12] using the atomic coordinates of $La_{1.85}Sr_{0.15}CuO_4$ (ref. 13) where the Sr is replaced by Li and the occupancy factors adjusted according to the composition $La_{1.8}Li_{0.2}CuO_4$.

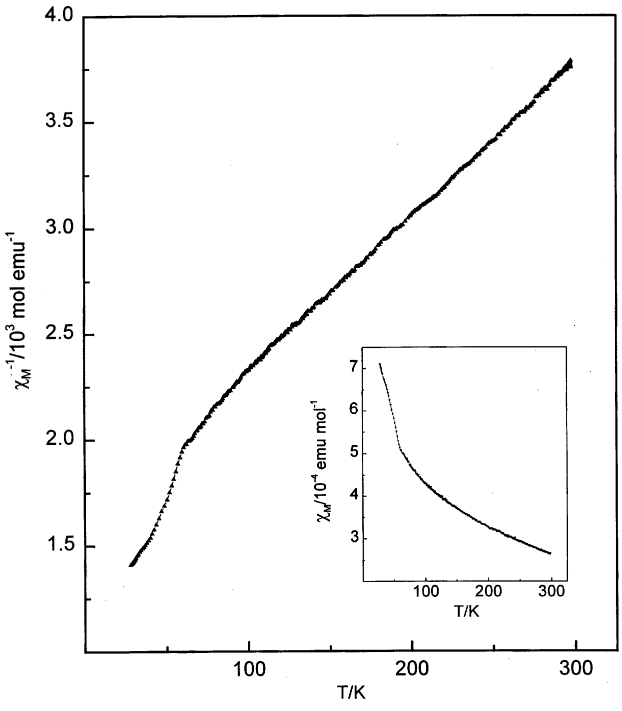

Fig. 3 Magnetic susceptibility data for $La_{1.8}Li_{0.2}CuO_4$.

space group *P*4/*nmm*. Careful examination of the powder XRD pattern of $La_{1.8}Li_{0.2}CuO_4$, however, did not show reflections characteristic of *P*4/*nmm* symmetry. Moreover, measurement of the electrical resistivity (Fig. 1) and magnetic susceptibility (Fig. 3) revealed the absence of a superconducting transition above 10 K. The material is a semiconductor, showing Curie–Weiss paramagnetism above 60 K with a $\mu_{eff} = 1.04\ \mu_B$; $\theta = -220$ K. The $\chi_M{}^{-1}$–T plot (Fig. 3) shows a magnetic transition around 60 K, with an enhancement of susceptibility below this temperature. A similar susceptibility enhancement occurs in non-superconducting $La_{2-x}Sr_xCuO_{4-\delta}$ samples[23] for $x \geqslant 0.5$. The enhancement in susceptibility could signal a ferromagnetic interaction[24] $Cu^{II}(d_{x^2-y^2})^1$–O–$Cu^{III}(d_{x^2-y^2})^0$ (localized holes) in overdoped La_2CuO_4-derived oxides.

The absence of superconductivity and the difference in the space group of $La_{1.8}Li_{0.2}CuO_4$ as compared to that of $La_{1-x}Na_xCuO_4$ and $La_{1-x}K_xCuO_4$ suggests that Li atoms are likely distributed over both La and Cu sites. We believe that the $La_{1.8}Li_{0.2}CuO_4$ prepared by us is not exactly the same as the $La_2Cu_{1-x}Li_xO_4$ reported in the literature,[25,26] in view of the differences in electrical and magnetic properties. Further work is required to characterize the Li-substituted La_2CuO_4 obtained in the metathesis reaction between Li_2CuO_2 and $La(OH)_3$.

4 Conclusions

We have described a novel metathesis reaction between Li_2CuO_2 and LnOCl (Ln = La, Nd) in the solid state which provides a convenient route for the synthesis of La_2CuO_4 and Nd_2CuO_4 at relatively low temperatures (700–800 °C). More importantly, the route enables synthesis of superconducting $La_{1.85}A_{0.15}CuO_4$ (A = Sr, Ba) by using Sr/Ba-substituted LaOCl in the reaction. We have also synthesized a new lithium-substituted La_2CuO_4 of nominal composition, $La_{1.8}Li_{0.2}CuO_4$, in the reaction between Li_2CuO_2 and 2 $La(OH)_3$.

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