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Transforming $n = 1$ members of the Ruddlesden–Popper phases to a $n = 3$ member through metathesis: synthesis of a new layered perovskite, $Ca_2La_2CuTi_2O_{10}$

T. Sivakumar,[a] S.E. Lofland,[b] K.V. Ramanujachary,[b] K. Ramesha,[c] G.N. Subbanna,[a] and J. Gopalakrishnan[a,d,*]

[a] Solid State and Structural Chemistry Unit, Materials Research Centre, Indian Institute of Science, Bangalore-560 012, India
[b] Department of Chemistry and Biochemistry, Rowan University, Glassboro, NJ 08028, USA
[c] Materials Department, University of California, Santa Barbara, CA 93106, USA
[d] Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560 064, India

Abstract

We report the formation of a new $n = 3$ Ruddlesden–Popper (R–P) layered perovskite oxide, $Ca_2La_2CuTi_2O_{10}$ (**I**), in the metathesis reaction between $NaLaTiO_4$ and $Ca_2CuO_2Cl_2$ ($n = 1$ R–P phases) at 700°C in air. Rietveld refinement of powder XRD data shows that **I** is isostructural with $Sr_4Ti_3O_{10}$ (space group $I4/mmm$; $a = 3.8837(5)$, $c = 27.727(6)$ Å), consisting of triple perovskite $CuTi_2O_{10}$ sheets wherein Cu and Ti are ordered at the central and terminal octahedral sites, respectively. Magnetization data provide support for the presence of strong antiferromagnetically coupled CuO_2 sheets in the structure. **I** is metastable decomposing at higher temperatures (~ 950°C) to a mixture of perovskite-like $CaLa_2CuTi_2O_9$ and CaO. Interestingly, the reaction between $NaLaTiO_4$ and $Sr_2CuO_2Cl_2$ follows a different metathesis route, $2NaLaTiO_4 + Sr_2CuO_2Cl_2 \rightarrow La_2CuO_4 + 2SrTiO_3 + 2NaCl$, revealing multiplicity of reaction pathways for solid-state metathesis reactions.
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1. Introduction

Among several strategies that are available today for the synthesis/assembly of layered perovskite materials [1], metathesis [2,3] is a convenient route that enables to build new solids from already known ones in a predictable manner. We have employed this strategy to prepare several novel layered perovskites [2]: for example, reaction of the Ruddlesden–Popper phase $K_2La_2Ti_3O_{10}$ with BiOCl yielded a new Aurivillius phase $(Bi_2O_2)La_2Ti_3O_{10}$ in the metathesis reaction, Eq. (1)

$$K_2La_2Ti_3O_{10} + 2BiOCl \rightarrow (Bi_2O_2)La_2Ti_3O_{10} + 2KCl. \quad (1)$$
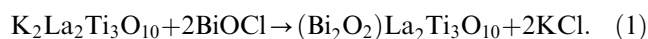
Extending this strategy, we have now prepared a new $n = 3$ R–P phase $Ca_2La_2CuTi_2O_{10}$ (**I**) in the metathesis reaction between $NaLaTiO_4$ and $Ca_2CuO_2Cl_2$. Considering that both the reactants are $n = 1$ members of the R–P family, $A_{n+1}B_nX_{3n+1}$, the formation of **I** from $NaLaTiO_4$ and $Ca_2CuO_2Cl_2$ could be regarded as transformation of lower ($n = 1$) members of the R–P family to a higher ($n = 3$) member through metathesis. We describe the synthesis, structure and electronic properties of the new phase **I** in this paper.

2. Experimental

$NaLaTiO_4$ was prepared, as reported in the literature [4], by reacting stoichiometric amounts of the starting materials, Na_2CO_3, La_2O_3, and TiO_2 with 20% molar excess of Na_2CO_3 at 900°C for 48 h with intermediate grindings. After the reaction, the product was washed

with distilled water and dried in air at 110°C. $Ca_2CuO_2Cl_2$ was obtained by mixing stoichiometric quantities of CaO and $CuCl_2 \cdot 2H_2O$ in *n*-hexane; the mixture was heated in air at 200°C for 3 h, then the temperature was slowly (2°C/min) raised to 750°C and kept at this temperature for 9 h. $Sr_2CuO_2Cl_2$ was prepared [5] by reacting stoichiometric quantities of $SrCl_2$, $SrCO_3$ and CuO at 800°C in N_2 for 18 h with one intermediate grinding. We investigated the reaction between the $n = 1$ R–P phases, $NaLaTiO_4$ and $Ca_2CuO_2Cl_2/Sr_2CuO_2Cl_2$ in the solid state, by heating a stoichiometric mixture of the reactants at various temperatures and duration in air.

The products were characterized at various stages of the reaction by powder XRD (Siemens D-5005 powder diffractometer, $CuK\alpha$ radiation). Unit cell parameters of single-phase material were determined by least-squares refinement of the powder XRD data using the PROSZ-KI [6] program. Structural refinements of the powder XRD data were carried out by the Rietveld method using the XND program [7]. For structure refinement, the data were collected in the 2θ range 3–100° with a step size of 0.02° and a step time of 7 s. DC Magnetization measurements were performed with a Physical Property Measuring System (PPMS) of Quantum Design Inc. (USA) featuring a 9 T magnet. The data were recorded at various temperatures between 10 and 300 K under the applied magnetic fields in the range 0.5–5 T. DC electrical resistivity measurements were carried out on sintered pellets by a four-probe technique using a closed cycle helium cryostat that goes down to 15 K.

3. Results and discussion

Examination of the products of the reaction between $NaLaTiO_4$ and $Ca_2CuO_2Cl_2$ by powder XRD revealed that a new $n = 3$ R–P phase was formed at 700°C/12 h in air according to the following metathesis reaction, Eq. (2):

$$2NaLaTiO_4 + Ca_2CuO_2Cl_2 \rightarrow Ca_2La_2CuTi_2O_{10} + 2NaCl.$$

(2)
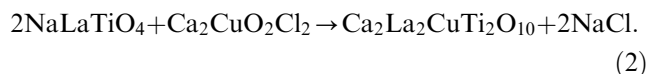
Major reflections in the powder XRD pattern of the washed product, $Ca_2La_2CuTi_2O_{10}$ (**I**), could be indexed on a tetragonal cell with the lattice parameters $a = 3.88(1)$, $c = 27.70(1)$ Å. Weak reflections around 3.05, 2.87, 2.26 and 2.07 Å suggest the presence of an impurity phase, most likely $La(OH)_3$ (JCPDS 36-1481), which could have formed during washing of the product.

We have determined the structure of $Ca_2La_2CuTi_2O_{10}$ (**I**) by Rietveld refinement of the powder XRD data, using $K_2La_2Ti_3O_{10}$ as the model compound [8] where the central titanium (Ti1) in the perovskite slab and K in the interlayer region are replaced by Cu and Ca, respectively. Refinement was carried out by fixing the

isotropic atomic displacement parameter (B_{iso}) for oxygen at 1.2 Å^2. This procedure is commonly used in the literature to obtain stable refinement of powder XRD data [9,10]. Experimental, calculated and difference profiles for **I** are shown in Fig. 1. The atomic coordinates and selected bond lengths are listed in Table 1. The bond valence sums calculated from bond length data for Ti (4.193) and Cu (2.226) are in reasonable agreement with the expected valences. In Fig. 2, we show schematically the metathesis conversion of $NaLaTiO_4$ and $Ca_2CuO_2Cl_2$ to **I**. The structure of **I** drawn from the atomic coordinates (Table 1) is shown in Figs. 2c and d.

From Fig. 2 and Table 1, we see that the structure of **I** is quite similar to that of the well-known $n = 3$ R–P phases such as $Sr_4Ti_3O_{10}$ [11] and $A_2La_2Ti_3O_{10}$ ($A = K$, Na) [8,12], consisting of triple perovskite $CuTi_2O_{10}$ sheets. Unlike with the structure of $A_2La_2Ti_3O_{10}$ ($A = K$, Na) where K/Na and La are perfectly ordered in the interlayer (4e) and intralayer (4e) sites in the layered perovskite structure, Ca and La are disordered in the inter and intralayer sites, rendering the structure of $Ca_2La_2CuTi_2O_{10}$ (**I**) more similar to $Sr_4Ti_3O_{10}$. But what is remarkable is that there is no Cu/Ti disorder in the structure, the central octahedral (2a) sites in the triple perovskite sheets being exclusively occupied by copper atoms, while the terminal octahedral sites (4e), by titanium atoms. This is borne out not only by the Cu–O and Ti–O bond lengths but also by magnetic susceptibility data (see later). The terminal Ti–O bond lengths are similar to the corresponding bond lengths in $NaLaTiO_4$ [4], while the Cu–O bond lengths of the central CuO_6 octahedron are similar to the corresponding bond lengths in La_2CuO_4 [13]. Thus the second-order Jahn–Teller distortion of the TiO_6 octahedra in the $NaLaTiO_4$ structure and the first-order Jahn–Teller
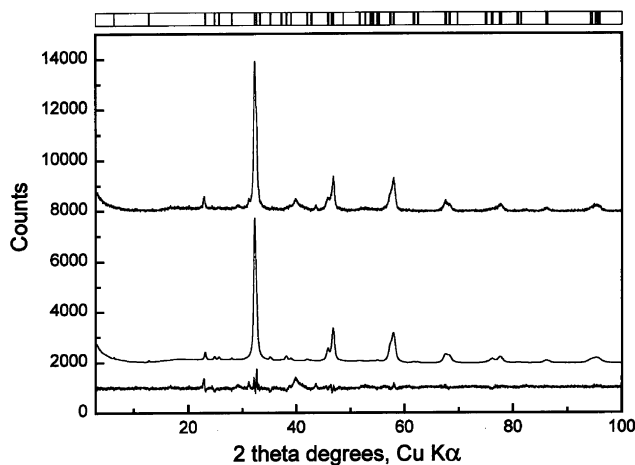

Fig. 1. Experimental (top), Rietveld refined (middle) and difference (bottom) XRD profiles of $Ca_2La_2CuTi_2O_{10}$. The vertical lines on the top panel are the expected peak positions for the space group $I4/mmm$.

distortion of the CuO_6 octahedra in $Ca_2CuO_2Cl_2$ are, by and large, retained in the product oxide, $Ca_2La_2CuTi_2O_{10}$. Indeed, the metathesis conversion [Eq. (2)] has been possible because of the special ordering of Na/La in the alternate interlayer sites of $NaLaTiO_4$ structure (Fig. 2a).

$Ca_2La_2CuTi_2O_{10}$ (**I**) shows a small magnetization (Fig. 3) (ordered moment ~ 0.003 B.M. in the 300–20 K range that is nearly independent of temperature). The small magnetization values and characteristic jump around 215 K could arise from antiferromagnetically coupled CuO_2 sheets and the Dzyaloshinsky–Moriya interaction [14,15]. The magnetic data of

$Ca_2La_2CuTi_2O_{10}$ (**I**) is therefore consistent with the structure (Fig. 2c) containing $CuO_{6/3}$ sheets without Cu/Ti disorder. DC electrical resistivity of $\sim 10^5\,\Omega\,cm$ at room temperature and the apparent activation energy $E_a \sim 0.14\,eV$ in the 150–300 K suggests insulating behavior for **I**. Further work is essential to characterize the magnetic and electrical transport properties of **I**.

$Ca_2La_2CuTi_2O_{10}$ (**I**) is metastable decomposing at higher temperatures ($\sim 950^\circ C$) to a mixture of perovskite-like $CaLa_2CuTi_2O_9$ and CaO. Interestingly, the reaction between $NaLaTiO_4$ and $Sr_2CuO_2Cl_2$ did not yield the expected $Sr_2La_2CuTi_2O_{10}$ or $SrLa_2CuTi_2O_9$. Instead, the reaction follows a different route at

Table 1
Final atomic coordinates, isotropic atomic displacement parameters (B_{iso}) (Å), occupancy and bond distances[b] (Å) for $Ca_2La_2CuTi_2O_{10}$[a]

Atom	Wyckoff position	x	y	z	B_{iso} (Å^2)	Occupancy
Ca1/La1	4e	0	0	0.2906(3)	2.7(3)	0.55/0.45
Ca2/La2	4e	0	0	0.4267(3)	3.7(2)	0.45/0.55
Cu	2a	0	0	0	1.1(4)	1.0
Ti	4e	0	0	0.1454(5)	0.6(1)	1.0
O1	4c	0	0.5	0	1.2	1.0
O2	4e	0	0	0.087(1)	1.2	1.0
O3	8g	0	0.5	0.1630(7)	1.2	1.0
O4	4e	0	0	0.228(1)	1.2	1.0

[a] Lattice parameters: $a = 3.8837(5)$ Å, $c = 27.727(6)$ Å; Space group: $I4/mmm$; $Z = 2$; $R_p = 5.52$, $R_{wp} = 7.96$, $R_{Bragg} = 12.71$, $R_f = 11.32$. B_{iso} for oxygen atoms were fixed at 1.2 Å^2.
[b] Cu–O1 ($\times 4$) = 1.94(1); Cu–O2 ($\times 2$) = 2.41(3); Ti–O3 ($\times 4$) = 2.00(1); Ti–O4 = 2.29(3); Ti–O2 = 1.62(3).
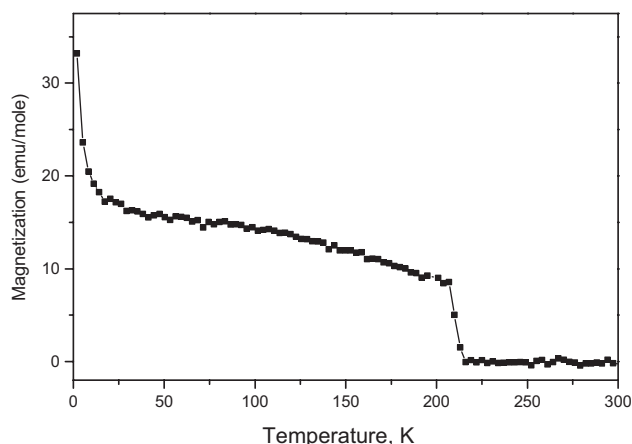

Fig. 3. Magnetization vs. temperature plot for $Ca_2La_2CuTi_2O_{10}$ ($H = 500\,G$).

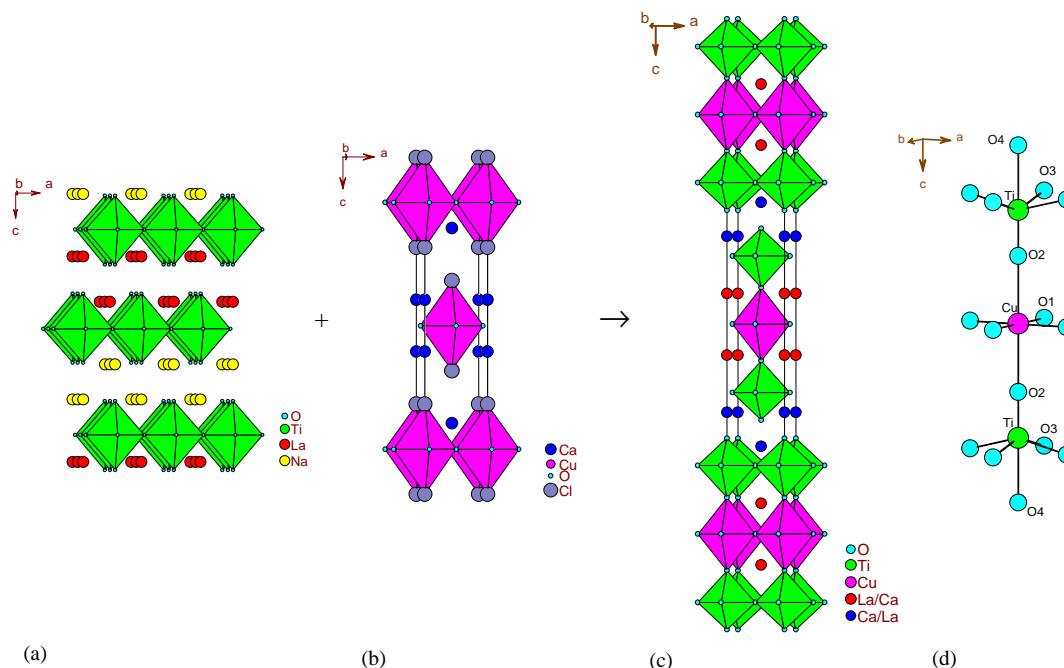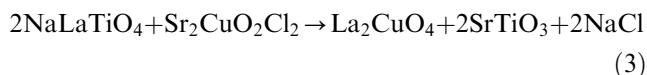Fig. 2. Schematic representation of the metathesis reaction between $NaLaTiO_4$ (a) and $Ca_2CuO_2Cl_2$ (b). Structure of $Ca_2La_2CuTi_2O_{10}$ is shown in (c) and (d).

1000°C [Eq. (3)]

$$2NaLaTiO_4 + Sr_2CuO_2Cl_2 \rightarrow La_2CuO_4 + 2SrTiO_3 + 2NaCl \quad (3)$$

yielding a mixture of products. The powder XRD pattern of the washed product clearly shows the formation of La_2CuO_4 and $SrTiO_3$. The difference in the reactivity of $Ca_2CuO_2Cl_2$ and $Sr_2CuO_2Cl_2$ with $NaLaTiO_4$ [Eqs. (2) and (3)] reveals that metathesis reactions between similar layered perovskites could follow multiple reaction pathways.

In summary, we have synthesized a new ($n = 3$) R–P phase, $Ca_2La_2CuTi_2O_{10}$, by a metathesis reaction between $NaLaTiO_4$ and $Ca_2CuO_2Cl_2$ ($n = 1$ R–P phases). $Ca_2La_2CuTi_2O_{10}$ is related to $Sr_4Ti_3O_{10}$, consisting of triple perovskite $CuTi_2O_{10}$ sheets where the central octahedral layer is occupied by copper and the terminal octahedral layers by titanium. Magnetic behavior of the new cuprate suggests the presence of strong antiferromagnetically coupled CuO_2 sheets. The reaction of $NaLaTiO_4$ with $Sr_2CuO_2Cl_2$ follows a different route yielding a mixture of La_2CuO_4, $SrTiO_3$ and $NaCl$ as final products.

Acknowledgments

References

[1] R.E. Schaak, T.E. Mallouk, Chem. Mater. 14 (2002) 1455–1471.
[2] J. Gopalakrishnan, T. Sivakumar, K. Ramesha, V. Thangadurai, G.N. Subbanna, J. Am. Chem. Soc. 122 (2000) 6237–6241.
[3] T. Sivakumar, R. Seshadri, J. Gopalakrishnan, J. Am. Chem. Soc. 123 (2001) 11496–11497.
[4] S.-H. Byeon, K. Park, M. Itoh, J. Solid State Chem. 121 (1996) 430–436.
[5] V.B. Grande, Hk. Müller-Buschbaum, Z. Anorg. Allg. Chem. 417 (1975) 68–74.
[6] W. Losocha, K. Lewinski, J. Appl. Crystallogr. 27 (1994) 437–438.
[7] J.-F. Bérar, ESRF, Grenoble, France. More information under: http://www.ccp14.ac.uk; J.-F. Bérar, Proceedings of the IUCr satellite Meeting on Powder Diffractometry, Toulouse, France, July 1990;
J.-F. Bérar, P. Garnier, II APD conference, NIST (USA), Gaithersburg, Maryland, May 1992;
J.-F. Bérar, P. Garnier, NIST Special Publication, 846 (1992) 212.
[8] K. Toda, J. Watanabe, M. Sato, Mater. Res. Bull. 31 (1996) 1427–1435.
[9] M.-W. Chu, M.-T. Caldes, L. Brohan, M. Ganne, A.-M. Marie, O. Joubert, Y. Piffard, Chem. Mater. 16 (2004) 31–42.
[10] F. Le Berre, M.-P. Crosnier-Lopez, J.-L. Fourquet, Solid State Sciences 6 (2004) 53–59.
[11] S.N. Ruddlesden, P. Popper, Acta Crystallogr. 11 (1958) 54–55.
[12] A.J. Wright, C. Greaves, J. Mater. Chem. 6 (1996) 1823–1825.
[13] K. Yamada, E. Kudo, Y. Endoh, K. Tsuda, M. Tanaka, K. Kokusho, H. Asano, F. Izumi, M. Oda, Y. Hikada, M. Suzuki, T. Murakami, Jpn. J. Appl. Phys. 27 (1988) 1132–1137.
[14] I. Dzyaloshinsky, J. Phys. Chem. Solids. 4 (1958) 241–255.
[15] T. Moriya, Phys. Rev. 120 (1960) 91–98.