Reaction of La$_2$CuO$_4$ with Binary Metal Oxides in the Solid State: Metathesis, Addition, and Redox Metathesis Pathways

T. Sivakumar and J. Gopalakrishnan*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

Investigation of the reaction of La$_2$CuO$_4$ with several binary metal oxides in the solid state at elevated temperatures has revealed three different reaction pathways. Reaction of La$_2$CuO$_4$ with strongly acidic oxides such as Re$_2$O$_7$, MoO$_3$, and V$_2$O$_5$ follows a *metathesis* route, yielding a mixture of products: La$_3$ReO$_8$/La$_2$MoO$_6$/LaVO$_4$ and CuO. Oxides such as TiO$_2$, MnO$_2$, and RuO$_2$ which are not so acidic yield *addition* products: La$_2$CuMO$_6$ (M = Ti, Mn, Ru). SnO$_2$ is a special case which appears to follow a metathesis route, giving La$_2$Sn$_2$O$_7$ pyrochlore and CuO, which on prolonged reaction transform to the layered perovskite La$_2$CuSnO$_6$. The reaction of La$_2$CuO$_4$ with lower valence oxides VO$_2$ and MoO$_2$, on the other hand, follows a novel *redox metathesis* route, yielding a mixture of LaVO$_4$/LaCuO$_2$ and La$_2$MoO$_6$/Cu, respectively. This result indicates that it is the redox reactivity involving V^{IV} + Cu^{II} → V^{V} + Cu^{I} and Mo^{IV} + Cu^{II} → Mo^{VI} + Cu^{0}, and not the acidity of the binary oxide, that controls the nature of the products formed in these cases. The general significance of these results toward the synthesis of complex metal oxides containing several metal atoms is discussed.

Introduction

Many metal oxides of current interest contain several elements: for example, superconducting and nonsuperconducting cuprates[1] (HgBa$_2$Ca$_2$Cu$_3$O$_8$, Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$, Ln$_2$Ba$_2$Cu$_2$M$_2$O$_{11}$; M = Sn, Ti; Ln = rare-earth metals), ferromagnetic metals[2] (La$_{1-x}$Ca$_x$MnO$_3$, Ba$_2$FeReO$_6$), fast ion conductors[3] (Na$_3$Zr$_2$Si$_2$PO$_{12}$, LiSr$_{1.65}$□$_{0.35}$B$_{1.3}$B'$_{1.7}$O$_9$; B = Ti, Zr; B' = Nb, Ta), and so on. The synthesis of such materials is not a trivial task. In the absence of phase diagrams and phase relations obtained in such multicomponent systems, a common synthetic approach[4] toward such complex oxide materials is the *ceramic method* involving reaction of binary oxides/compounds of the constituent elements at elevated temperatures. There are two ways to carry out synthesis by this approach. One is a single-step method where all the components in the appropriate stoichiometry are reacted in one step. The other is a multistep process involving sequential reaction of the components in two or more steps. For example, the synthesis of supercon-

ducting mercury cuprates[5] such as HgBa$_2$CuO$_4$ and HgBa$_2$Ca$_2$Cu$_3$O$_8$ involves preparation of the precursors Ba$_2$CuO$_3$ and Ba$_2$Ca$_2$Cu$_3$O$_7$, respectively, from the constituent binary compounds in the first step. In the next step, this precursor oxide is reacted with the required quantity of HgO in an evacuated sealed container. Similarly, the ferromagnetic double perovskites Ba$_2$FeReO$_6$ and Ca$_2$FeReO$_6$ are synthesized in two steps:[6] First, a precursor oxide of composition Ba$_2$ReO$_{5.5}$/Ca$_2$ReO$_{5.5}$ is prepared by reacting stoichiometric quantities of BaCO$_3$/CaCO$_3$ and Re$_2$O$_7$ and is then reacted with the required quantities of Fe$_2$O$_3$ and Fe powder in an evacuated sealed silica tube. Such multistep procedures are commonly adopted when one of the constituents is volatile (e.g., HgO and Tl$_2$O$_3$) or when precise control of oxygen stoichiometry is required in the final product (e.g., Ba$_2$FeReO$_6$ and Ca$_2$FeReO$_6$).

An assumption implicit in this approach is that the multistep reactions always yield addition products: A + B → AB; AB + C → ABC. During the course of our investigations on the synthesis of oxide materials in Sr–Mo–Cu–O, La–Mo–Cu–O, and La–V–Cu–O systems, we found this is not always true. For instance, our attempts to synthesize complex ABO$_3$ oxides such as Sr$_2$CuMoO$_6$, Sr$_3$CuV$_2$O$_9$, La$_2$CuVO$_6$, and La$_3$Cu$_2$VO$_9$, starting from Sr$_2$CuO$_3$/La$_2$CuO$_4$ as precursors, have

* To whom correspondence should be addressed.

(1) (a) Sleight, A. W. *Science* **1988,** *242,* 1519–1527. (b) Cava, R. J. *Science* **1990,** *247,* 656–662. (c) Raveau, B.; Michel, C.; Hervieu, M.; Maignan, A. *J. Mater. Chem.* **1995,** *5,* 803–815. (d) Anderson, M. T.; Poeppelmeier, K. R.; Zhang, J.-P.; Fan, H.-J.; Marks, L. D. *Chem. Mater.* **1992,** *4,* 1305–1313. (e) Weller, M. T.; Knee, C. S. *J. Mater. Chem.* **2001,** *11,* 701–712.

(2) (a) Jin, S.; Tiefel, T. H.; McCormack, M.; Fastnacht, R. A.; Ramesh, R.; Chen, L. H. *Science* **1994,** *264,* 413–415. (b) Sleight, A. W.; Weiher, J. F. *J. Phys. Chem. Solids* **1972,** *33,* 679–687.

(3) (a) Goodenough, J. B.; Hong, H. Y.-P.; Kafalas, J. A. *Mater. Res. Bull.* **1976,** *11,* 203–220. (b) Thangadurai, V.; Shukla, A. K.; Gopalakrishnan, J. *Chem. Mater.* **1999,** *11,* 835–839.

(4) (a) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* **1993,** *259,* 1558–1564. (b) Gopalakrishnan, J. *Chem. Mater.* **1995,** *7,* 1265–1275. (c) Gillan, E. G.; Kaner, R. B. *Chem. Mater.* **1996,** *8,* 333–343.

(5) (a) Putilin, S. N.; Antipov, E. V.; Chmaissem, O.; Marezio, M. *Nature* **1993,** *362,* 226–228. (b) Chmaissem, O.; Huang, Q.; Antipov, E. V.; Putilin, S. N.; Marezio, M.; Loureiro, S. M.; Capponi, J. J.; Tholence, J. L.; Santoro, A. *Physica C* **1993,** *217,* 265–272. (c) Schilling, A.; Cantoni, M.; Guo, J. D.; Ott, H. R. *Nature* **1993,** *363,* 56–58.

(6) Gopalakrishnan, J.; Chattopadhyay, A.; Ogale, S. B.; Venkatesan, T.; Greene, R. L.; Millis, A. J.; Ramesha, K.; Hannoyer, B.; Marest, G. *Phys. Rev. B* **2000,** *62,* 9538–9542.

yielded multiphasic mixtures ($SrMoO_4$ + SrO + CuO; $Sr_3V_2O_8$ + CuO; $LaVO_4$ + $LaCuO_2$; $LaVO_4$ + La_2O_3 + 2CuO), instead of the expected single-phase addition products. Similarly, the reaction of La_2CuO_4 with MoO_3 yielded a mixture of La_2MoO_6 and CuO, instead of the expected La_2CuMoO_7. Clearly, these instances indicate the complexity of the reaction pathways in the solid state.

Considering the importance of such ceramic reactions in the exploratory synthesis and discovery of new oxide materials[7] containing copper, we investigated the reaction of La_2CuO_4 with a wide variety of binary oxides (Re_2O_7, MoO_3, V_2O_5, TiO_2, VO_2, MnO_2, MoO_2, RuO_2, and SnO_2) in the solid state. Our investigations, which are reported here, reveal certain novel reactivity patterns where the final products obtained seem to crucially depend on the "acidity" and/or the redox reactivity of the binary oxide vis-à-vis those of CuO.

Experimental Section

Materials. All starting materials, except La_2CuO_4, VO_2, and MoO_2, were high-purity (≥99%) samples obtained from Alfa or Fluka. La_2CuO_4 was prepared[8] by reacting La_2O_3 (predried at 900 °C) and CuO in stoichiometric proportion at 1100 °C in the air for 48 h with one grinding midway through the reaction period. VO_2 was prepared[9] by reacting V_2O_5 and V_2O_3 in equal proportion in an evacuated sealed silica tube at 750 °C for 60 h. MoO_2 was prepared[9] similarly, by reacting MoO_3 and Mo (2:1 mole ratio) at 700 °C for 72 h.

Reaction Studies. Reactions of La_2CuO_4 with Re_2O_7, MoO_3, V_2O_5, TiO_2, MnO_2, or SnO_2 in the solid state were investigated by heating intimate mixtures of stoichiometric quantities of the oxides at various temperatures and durations in the air, and the products were examined by powder X-ray diffraction (XRD). Re_2O_7 (predried in an air oven and stored over anhydrous $CaCl_2$) was weighed quickly and mixed with La_2CuO_4 in a drybox. In view of the volatility and low melting point (~295 °C) of this oxide, the reaction mixture was preheated at 200 °C for several hours, before the temperature was slowly (1 °C/min) raised to 900 °C. Reactions of La_2CuO_4 with VO_2, MoO_2, and RuO_2 (which are oxidizable to higher oxidation states in the air at elevated temperatures) were carried out in evacuated sealed silica tubes. Appropriate conditions for the completion of each reaction were ascertained by trial and error and are given in Table 1.

Characterization. The solid products were characterized by powder XRD (Siemens D-5005 powder diffractometer using Cu Kα radiation), scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) analysis (JEOL-JSM-5600 LV scanning electron microscope at a 20 kV accelerating voltage fitted with an Oxford Instruments Be window detector). Prior to imaging, the samples were fixed to double sticky carbon tabs and sputter-coated with ~150 nm of Au. Single-phase materials were identified by comparison with standard powder XRD patterns (JCPDS files) and, in selected cases, by least-squares refinement of the powder XRD data using the PROSZKI[10] program.

Results and Discussion

La_2CuO_4 readily reacts with several common binary oxides at elevated temperatures, giving different prod-

(7) Vander Griend, D. A.; Malo, S.; Wang, T. K.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2000**, *122*, 1308−1311.

(8) Longo, J. M.; Raccah, P. M. *J. Solid State Chem.* **1973**, *6*, 526−531.

(9) Brauer, G., Ed. *Handbook of Preparative Inorganic Chemistry*; Academic Press: New York, 1965; Vol. 2, pp 1267 and 1409.

(10) Losocha, W.; Lewinski, K. *J. Appl. Crystallogr.* **1994**, *27*, 437−438.

Table 1. Reaction of La₂CuO₄ with Binary Oxides

binary oxide	stoichiometry	conditions[a]	nature of the reaction	structural characterization of the product(s)	acidity[b] param, a
Re₂O₇	$3La_2CuO_4$ + Re_2O_7 → $2La_3ReO_8$ + 3CuO	200 °C/24 h/900 °C/48 h/air	metathesis	La₃ReO₈:[c] orthorhombic, a = 12.759(5) Å, b = 17.499(6) Å, c = 11.879(5) Å	9.0
MoO₃	La_2CuO_4 + MoO_3 → La_2MoO_6 + CuO	1000 °C/24 h/air	metathesis	La₂MoO₆:[d] tetragonal, a = 4.098(1) Å, c = 15.998(5) Å	5.2
V₂O₅	La_2CuO_4 + V_2O_5 → $2LaVO_4$ + CuO	800 °C/12 h/air	metathesis	LaVO₄:[e] monoclinic, a = 7.042(1) Å, b = 7.273(1) Å, c = 6.720(1) Å, β = 104.90(2)°	3.0
TiO₂	La_2CuO_4 + TiO_2 → La_2CuTiO_6	980 °C/36 h/air	addition	La₂CuTiO₆:[f] orthorhombic, a = 5.604(2) Å, b = 7.856(4) Å, c = 5.570(2) Å	0.7
VO₂	La_2CuO_4 + VO_2 → $LaVO_4$ + $LaCuO_2$	900 °C/72 h/evacuated sealed silica tube	redox metathesis	LaVO₄:[e] monoclinic, a = 7.017(3) Å, b = 7.258(2) Å, c = 6.697(4) Å, β = 104.74(4)° LaCuO₂:[g] hexagonal, a = 3.835(2) Å, c = 17.04(1) Å	
MnO₂	La_2CuO_4 + MnO_2 → La_2CuMnO_6	1100 °C/48 h/air	addition	La₂CuMnO₆:[h] cubic, a = 7.783(2) Å	
MoO₂	La_2CuO_4 + MoO_2 → La_2MoO_6 + Cu	900 °C/48 h/evacuated sealed silica tube	redox metathesis	La₂MoO₆:[d] tetragonal, a = 4.098(1) Å, c = 15.998(5) Å	
RuO₂	La_2CuO_4 + RuO_2 → La_2CuRuO_6	900 °C/24 h/960 °C/24 h/ 1000 °C/24 h/evacuated sealed silica tube	addition	La₂CuRuO₆:[i] monoclinic, a = 5.581(2) Å, b = 5.748(1) Å, c = 7.760(2) Å, β = 90.04(2)°	
SnO₂	La_2CuO_4 + SnO_2 → La_2CuSnO_6	980 °C/600 h/air	addition	La₂CuSnO₆:[j] monoclinic, a = 8.471(4) Å, b = 7.785(5) Å, c = 7.781(3) Å, β = 91.13(4)°	2.2

a With several intermediate grindings. b Data taken from ref 11. a = −6.1 and a = −2.5 for La₂O₃ and CuO, respectively. c JCPDS 27-1181. d JCPDS 24-0550. e JCPDS 23-0324. f JCPDS 45-0635. g JCPDS 35-1403. h Reference 14. i Reference 15. j Reference 16.
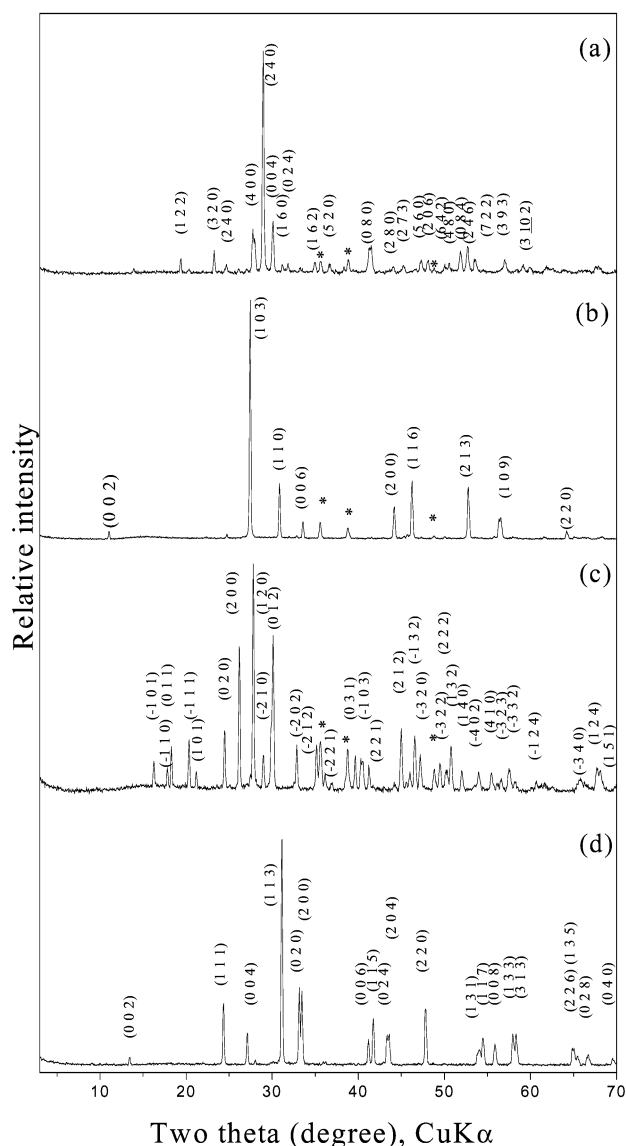
Figure 1. Powder XRD patterns of the products obtained from the reactions of La$_2$CuO$_4$ with (a) Re$_2$O$_7$, (b) MoO$_3$, and (c) V$_2$O$_5$. In (d) the powder XRD pattern of La$_2$CuO$_4$ is given for comparison. Reflections due to CuO are marked by asterisks.

Figure 2. (Top) SEM image of the product of the La$_2$CuO$_4$ + MoO$_3$ reaction, showing La$_2$MoO$_6$ (small particles) and CuO (large spheres). The corresponding EDX spectra for La$_2$MoO$_6$ and CuO are shown in the middle and bottom panels.

ucts. To establish the reactivity pattern, we have systematically investigated the reaction of La$_2$CuO$_4$ with the following binary transition-metal oxides: Re$_2$O$_7$, MoO$_3$, V$_2$O$_5$, TiO$_2$, VO$_2$, MoO$_2$, MnO$_2$, and RuO$_2$ as well as SnO$_2$. The reaction stoichiometry and the experimental conditions for the formation of single-phase products were identified by several trial and error experiments and are given in Table 1. From the data given in Table 1, we identify three different kinds of pathways in the reaction between La$_2$CuO$_4$ and binary metal oxides: viz., *metathesis*, *addition*, and *redox metathesis*. Highly acidic oxides such as Re$_2$O$_7$, MoO$_3$, and V$_2$O$_5$ (possessing a d^0 electronic configuration of the transition metal) undergo metathesis reaction with La$_2$CuO$_4$, where Cu^{II} and Re^{VII}/Mo^{VI}/V^V are exchanged. The product in each case is a mixture of CuO and the most stable ternary oxide of lanthanum with Re^{VII}/Mo^{VI}/V^V: La$_3$ReO$_8$, La$_2$MoO$_6$, LaVO$_4$. Powder XRD (Figure 1) and SEM pictures together with EDX data (Figure 2) clearly establish the identity of the products in each case. As such, the metathesis reactions involving dis-
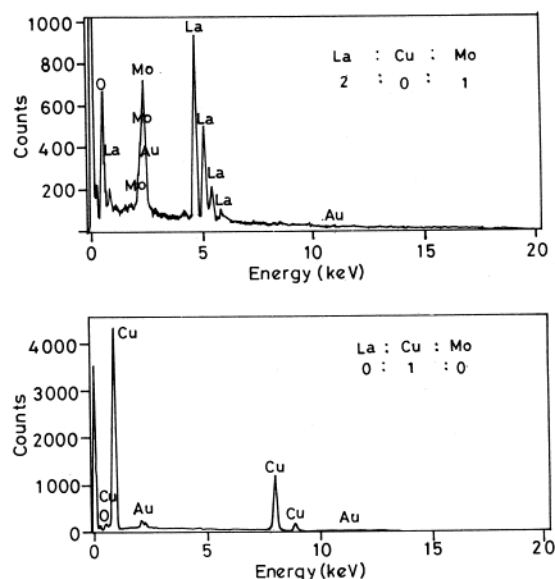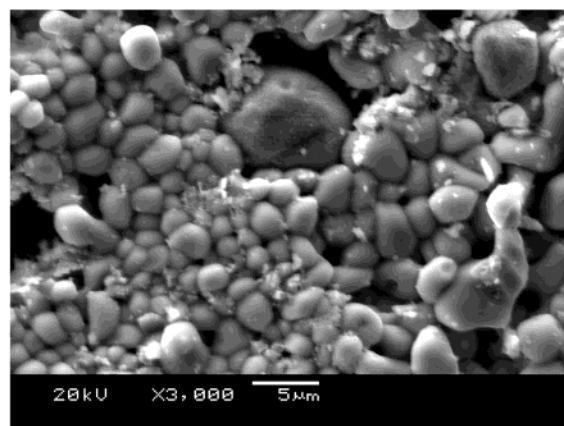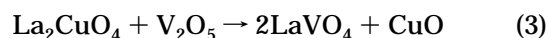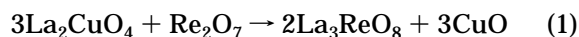
placement of Cu^{II} by Re^{VII}/Mo^{VI}/V^V could be formulated as

$$3La_2CuO_4 + Re_2O_7 \rightarrow 2La_3ReO_8 + 3CuO \quad (1)$$

$$La_2CuO_4 + MoO_3 \rightarrow La_2MoO_6 + CuO \quad (2)$$

$$La_2CuO_4 + V_2O_5 \rightarrow 2LaVO_4 + CuO \quad (3)$$

The formation of metathesis products instead of addition products in reactions 1–3 could be understood in terms of the relative acidity/basicity of the binary oxides involved. On the Smith acidity scale for binary oxides,[11] La$_2$O$_3$ is highly basic (acidity parameter $a = -6.1$) and Re$_2$O$_7$ ($a = 9.0$), MoO$_3$ ($a = 5.2$), and V$_2$O$_5$ ($a = 3$) are acidic; CuO ($a = -2.5$) falling between is neither strongly acidic nor strongly basic. This classification of the oxides in terms of Smith's acidity parameter[11] is also in agreement with the common perception of the acidity/basicity of binary oxides in inorganic chemistry.[12] Accordingly, the reaction of La$_2$CuO$_4$ with a strongly acidic

(11) Smith, D. W. *J. Chem. Educ.* **1987**, *64*, 480–481.
(12) Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; Oxford University Press: Oxford, 1991; pp 161–162 and 642–663.
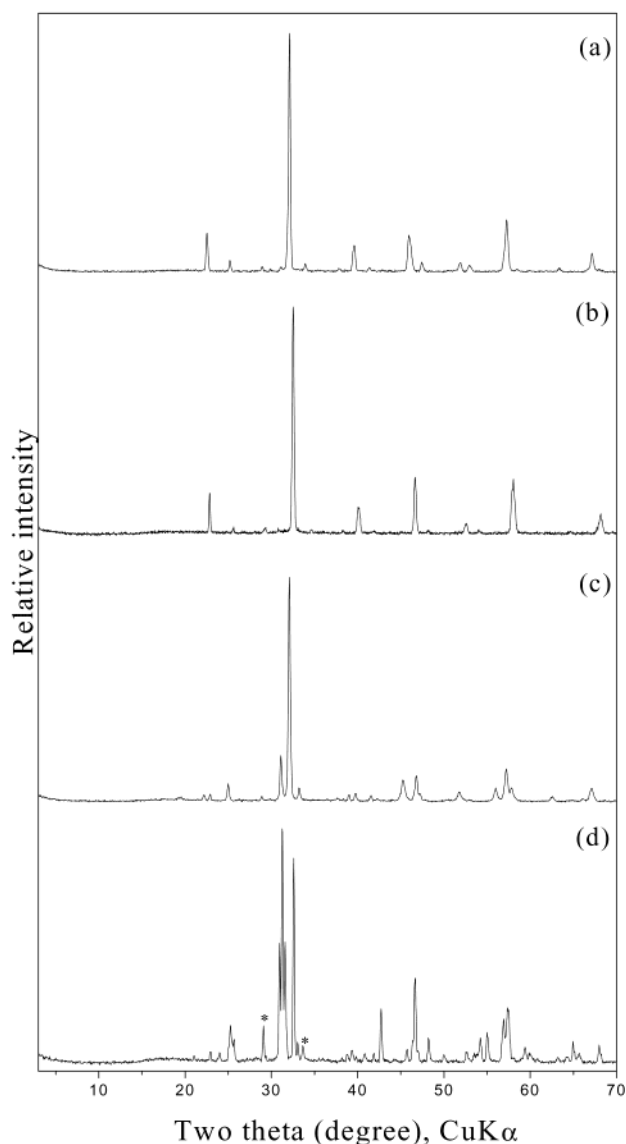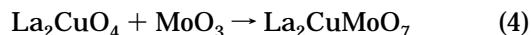
Figure 3. Powder XRD patterns of the products obtained from the reactions of La_2CuO_4 with (a) TiO_2, (b) MnO_2, (c) RuO_2, and (d) SnO_2. Reflections due to a $La_2Sn_2O_7$ impurity are marked by asterisks in (d).

oxide such as MoO_3 follows eq 2, instead of eq 4. The reactions of La_2CuO_4 with Re_2O_7 (eq 1) and V_2O_5 (eq 3) follow the same pattern.

$$La_2CuO_4 + MoO_3 \rightarrow La_2CuMoO_7 \qquad (4)$$

The reactions of La_2CuO_4 with TiO_2, MnO_2, and RuO_2 exhibit the second type of reactivity, giving addition products. The products, viz., La_2CuTiO_6, having a disordered double perovskite structure,[13] and La_2CuMnO_6 and La_2CuRuO_6, possessing an ordered double perovskite structure,[14,15] have already been reported. Powder XRD patterns (Figure 3) together with least-squares

(13) (a) Ramadass, N.: Gopalakrishnan, J.; Sastri, M. V. C. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1453−1454. (b) Palacin, M. R.; Bassas, J.; Rodriguez-Carvajal, J.; Gomez-Romero, P. *J. Mater. Chem.* **1993**, *3*, 1171−1177. (c) Anderson, M. T.; Balbarin, V. E.; Groenke, D. A.; Bain, G. A.; Poeppelmeier, K. R. *J. Solid State Chem.* **1993**, *103*, 216−227.

(14) Anderson, M. T.; Greenwood, K. B.; Taylor, G. A.; Poeppelmeier, K. R. *Prog. Solid State Chem.* **1993**, *22*, 197−233.

(15) Battle, P. D.; Frost, J. R.; Kim, S.-H. *J. Mater. Chem.* **1995**, *5*, 1003−1006.

refinement of the data reveal formation of single-phase products in each case. SEM pictures and EDX data (Figure 4) also support this conclusion. Formation of single-phase addition products instead of metathesis products in these cases is consistent with the lower acidity of these oxides. The Smith acidity parameter a for TiO_2 is 0.7, which is much less than those of V_2O_5, MoO_3, and Re_2O_7; the acidity parameters for MnO_2 and RuO_2 are not known. However, considering that these oxides are not the highest oxidation state compounds for these metals (the highest oxidation state for Mn is VII, represented by Mn_2O_7, and that for Ru is VIII, represented by RuO_4) and that the acidity of oxides decreases generally with decreasing oxidation state,[12] it is reasonable to expect that MnO_2 and RuO_2 possess an acidity equal to or less than that of TiO_2. Accordingly, formation of addition products La_2CuMO_6 (M = Ti, Mn, Ru) is favored in preference to metathesis products for the reaction of La_2CuO_4 with TiO_2, MnO_2, or RuO_2.

The reaction of La_2CuO_4 with SnO_2 deserves special mention. The acidity of SnO_2 ($a = 2.2$) lies between that of TiO_2 and V_2O_5 on the Smith scale.[11] Therefore, it is of interest to find out whether this oxide gives an addition or a metathesis product with La_2CuO_4. Our investigations show that, although we obtain the addition product, viz., La_2CuSnO_6 (Figure 3), on prolonged reaction of La_2CuO_4 with SnO_2 (as reported in the literature[16]), we do see the formation of $La_2Sn_2O_7$ pyrochlore in the initial stages of the reaction, which persists as an impurity phase even after prolonged reaction for 600 h. Accordingly, SnO_2 seems to be a borderline case, giving both metathesis and addition products, depending on the reaction conditions. We believe an acidity parameter $a \approx 2.0$ on the Smith scale for the binary oxide seems to demarcate whether an addition product or metathesis product is formed in the reaction with La_2CuO_4: binary oxides having $a > 2.0$ give metathesis products, and those having $a < 2.0$ give addition products.

The third and the last kind of reactivity is exemplified by VO_2 and MoO_2, which give a mixture of products, where the oxidation state of V/Mo as well as that of Cu is changed. Thus, in the reaction between La_2CuO_4 and VO_2, the products are $LaVO_4$ and $LaCuO_2$ (delafossite structure) (Figure 5), clearly indicating that the reaction involves the redox process $Cu^{II} + V^{IV} \rightarrow Cu^I + V^V$. Similarly, the reaction between La_2CuO_4 and MoO_2, yielding La_2MoO_6 and Cu metal as products, also appears to be driven by the redox process $Cu^{II} + Mo^{IV} \rightarrow Cu^0 + Mo^{VI}$. In both these cases, it appears that the redox reactivity between V^{IV}/Mo^{IV} with Cu^{II} is more important than the acidity of VO_2/MoO_2 in determining the nature of the final products obtained. Significantly, both the redox reactions $Mo^{IV} + Cu^{II} \rightarrow Mo^{VI} + Cu^0$ and $V^{IV} + Cu^{II} \rightarrow V^V + Cu^I$ are not expected to proceed toward the right on the basis of solution reduction potential data[12] (Mo^{VI}/Mo^{IV}, 0.646 V; V^V/V^{IV}, 1.000 V; Cu^{II}/Cu^I, 0.159 V; Cu^{II}/Cu^0, 0.340). Presumably, these redox processes become favorable in the solid state at high temperatures. Reduction potentials of transition-metal ions in aqueous media are known to get modified in the solid state depending on the coordination geom-

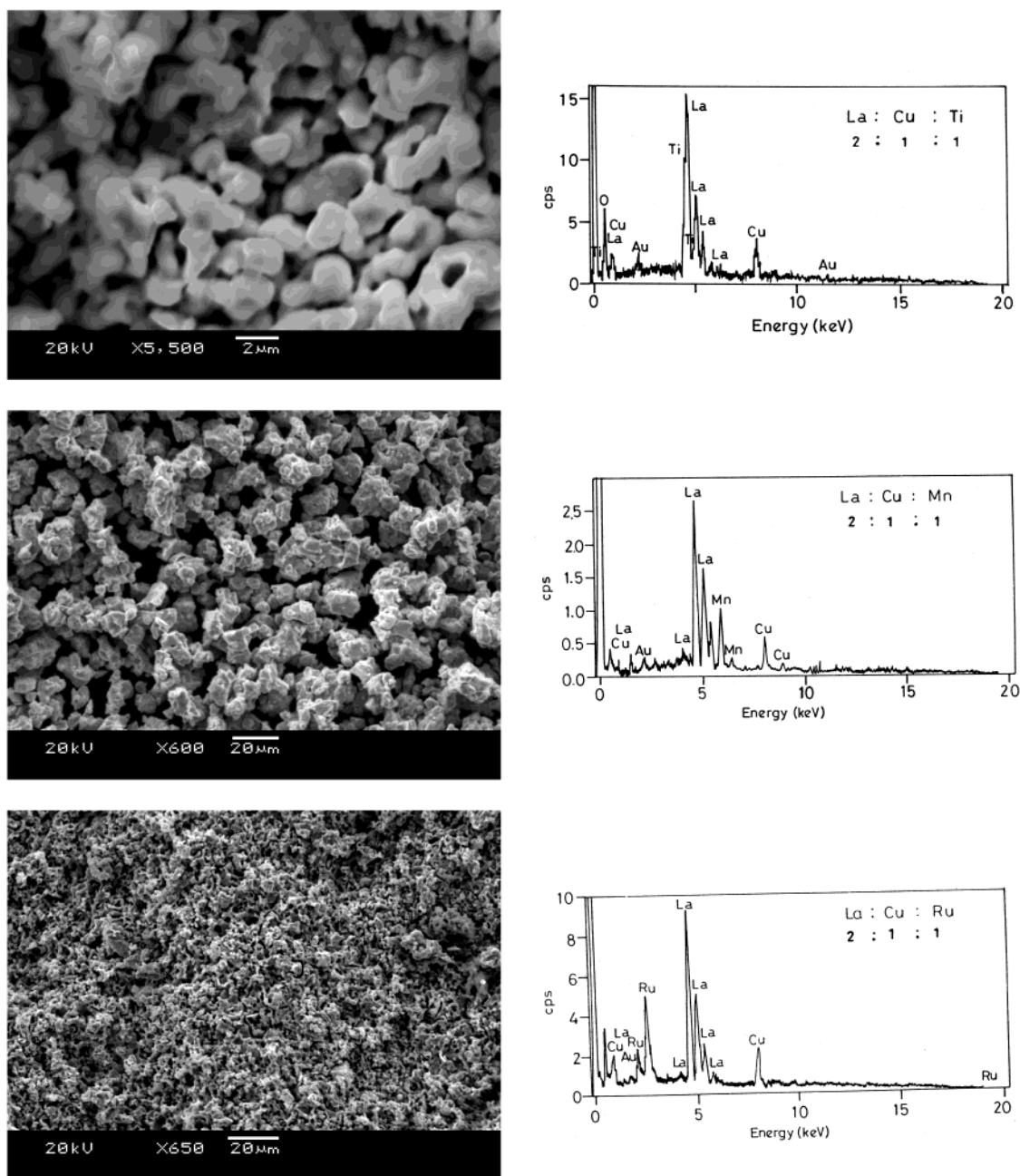(16) Anderson, M. T.; Poeppelmeier, K. R. *Chem. Mater.* **1991**, *3*, 476−482.

Figure 4. (Left) SEM image of the products of the reactions of La_2CuO_4 with TiO_2 (top), MnO_2 (middle), and RuO_2 (bottom). The corresponding EDX spectra of single-phase addition products La_2CuTiO_6, La_2CuMnO_6, and La_2CuRuO_6 are shown in the right-side panels.

etry, ligand atom, and nature of the metal–ligand bond.[17] In general, for a given redox couple, a higher metal–ligand covalency and a lower coordination number tend to stabilize the higher oxidation state and hence make the reduction potential more negative, as compared to the value in an aqueous medium. For example, the aqueous Fe^{III}/Fe^{II} reduction potential (0.77 V), which is close to that of the octahedral site Mo^{VI}/Mo^{V}, becomes 0.56 V in $Fe_2(SO_4)_3$ and -0.24 V in $Li_3Fe_2(PO_4)_3$, revealing the influence of the solid state.[18] The paucity of appropriate reduction potential data in

the solid state however makes quantitative prediction of redox processes involving solids difficult.

Our investigation of the $La_2CuO_4 + MoO_2/VO_2$ reactions was motivated by the interest to prepare ordered double perovskites $La_2Cu^{II}Mo^{IV}O_6$ and $La_2Cu^{II}V^{IV}O_6$, which could be half-metallic ferrimagnets, similar to Sr_2FeMoO_6.[19] In fact, it was predicted on the basis of density functional theory calculations[20] that La_2CuVO_6 would be a promising candidate for this property. But the experimental result showing that a mixture of $LaV^{V}O_4$ and $LaCu^{I}O_2$ is more stable than $La_2Cu^{II}V^{IV}O_6$ reveals the problems inherent in the solid-state synthesis of new materials of this kind.

(17) Goodenough, J. B. In *Chemistry and Uses of Molybdenum*; Barry, H. F., Mitchell, P. C. H., Eds.; Climax Molybdenum Co.: Ann Arbor, MI, 1982; pp 1–22.
(18) Nanjundaswamy, K. S.; Padhi, A. K.; Goodenough, J. B.; Okada, S.; Ohtsuka, H.; Arai, H.; Yamaki, J. *Solid State Ionics* **1996**, *92*, 1–10.

(19) Kobayashi, K.-I.; Kimura, T.; Sawada, H.; Terakura, K.; Tokura, Y. *Nature* **1998**, *395*, 677–680.
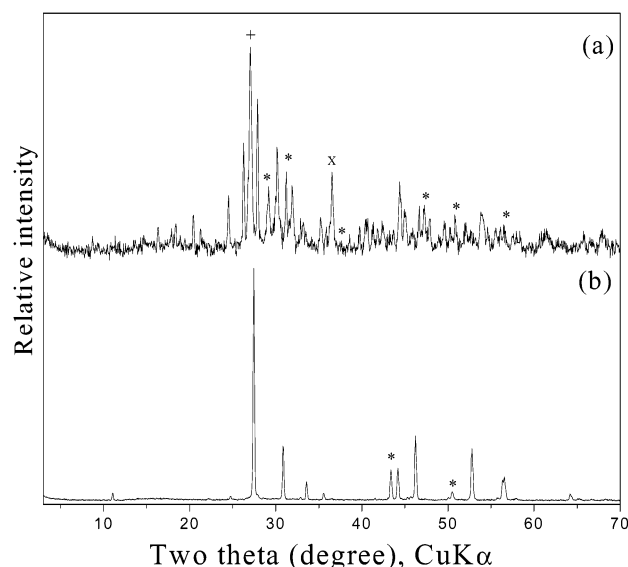(20) Pickett, W. E. *Phys. Rev. B* **1998**, *57*, 10613–10619.

Figure 5. Powder XRD patterns of the products obtained from the reactions of La_2CuO_4 with (a) VO_2 and (b) MoO_2. Reflections due to $LaCuO_2$ in (a) and Cu metal in (b) are marked by asterisks. Reflections due to La_2O_3 (+) and Cu_2O (x) are also marked in (a).

Conclusions

Investigation of the reaction of La_2CuO_4 with several binary transition-metal oxides in the solid state has revealed certain systematics that could be of significance for the synthesis of complex metal oxides in general. Strongly acidic oxides such as Re_2O_7, MoO_3, and V_2O_5 give metathesis products, while weakly acidic/amphoteric oxides, such as TiO_2, MnO_2, and RuO_2, having acidity comparable to that of CuO, yield addition products. SnO_2 appears to be a borderline case exhibiting both metathesis and addition types of reactivity with La_2CuO_4, the final product obtained being determined by the reaction duration. Lower valence transition-metal oxides such as VO_2 and MoO_2 having a strong tendency to get oxidized to the highest oxidation state, undergo

redox metathesis with La_2CuO_4, where the reactivity appears to be controlled by the redox process between these oxides and CuO rather than the inherent acidity.

The present work suggests that quaternary oxides containing (i) an alkali, alkaline-earth, or lanthanide metal, (ii) an early transition metal in its highest oxidation state, and (iii) a transition metal in a lower oxidation state may not be accessible through high-temperature solid-state reactions. However, the existence of several oxides such as $LiVMO_4$ (M = Co, Ni, Cu),[21] Ba_2TaCoO_6,[22] $Ba_3WFe_2O_9$,[23] $La_3Cu_2VO_9$,[24] and $La_4Cu_3MoO_{12}$[25] clearly indicates that factors other than acidity/basicity are involved in the formation and stability of complex oxide materials.

Supporting Information Available: Figure S1 showing the SEM image and EDAX spectra of the products $LaVO_4$ and CuO obtained from the reaction of La_2CuO_4 with V_2O_5 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM020601K

(21) González, C.; Gaitán, M.; López, M. L.; Veiga, M. L.; Saez-Puche, R. *J. Mater. Sci.* **1994**, *29*, 3458−3460.
(22) Padel, L.; Poix, P.; Bernier, J. C.; Michel, A. *Mater. Res. Bull.* **1972**, *7*, 443−448.
(23) Gagulin, V. V.; Fadeeva, N. V.; Belous, A. G.; Titov, A. V.; Mitrofanov, K. P.; Plotnikova, M. V.; Soloviev, S. P.; Venevtsev, N. *Phys. Status Solidi A* **1978**, *48*, 183−189.
(24) Vander Griend, D. A.; Malo, S.; Barry, S. J.; Dabbousch, N. M.; Poeppelmeier, K. R.; Dravid, V. P. *Solid State Sci.* **2001**, *3*, 569−579.
(25) Vander Griend, D. A.; Boudin, S.; Caignaert, V.; Poeppelmeier, K. R.; Wang, Y.; Dravid, V. P.; Azuma, M.; Takano, M.; Hu, Z.; Jorgensen, J. *J. Am. Chem. Soc.* **1999**, *121*, 4787−4792.