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Umbrella stoichiometry: a guide to the solid state chemistry of copper-rich oxides

D.A. Vander Griend, K.R. Poeppelmeier*
Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, USA

Abstract

Umbrella stoichiometries are relatively unstable compositions that can be leveraged to promote the formation of unconventional solid state structures. La^{III} and Cu^{II} in a one to one ratio is such a stoichiometry. The addition of a third metal such as Mo^{VI}, V^{V}, or Ru^{V} generates a complex set of potential products. Nonetheless, $La_4Cu_3MoO_{12}$ forms a single phase because no low energy multiphase alternatives exist for a stoichiometry so close to an umbrella stoichiometry. The cations in the structure are severely under-coordinated, yet oxygen can be removed from the structure by substituting Cu^{II} for Mo^{VI}. $La_4Cu_{3+x}Mo_{1-x}O_{12-2x}$ forms a single phase for $0.0 \leq x \leq 0.12$ before $La_2Cu_2O_5$ appears. This structurally unfavorable substitution is tolerated because it moves the composition even closer to the umbrella stoichiometry.

Keywords: Umbrella stoichiometry; $La_4Cu_3MoO_{12}$

1. Introduction

Solid state chemistry relies heavily on exploratory synthesis, and it is well recognized that the complexity of the possibilities often defies predictability [1]. High temperature solid state reactions of metal oxides and carbonates always render the most thermodynamically stable result. If a single phase forms, then it is more stable than all conceivable multiphase results of equivalent stoichiometry. If multiple products form then the free energy of those phases is less than any possible structure that incorporates all the reactant ions. The latter occurs much more frequently than the former owing to inherently low energy phases that act as thermodynamic sinks and frustrate the formation of new materials.

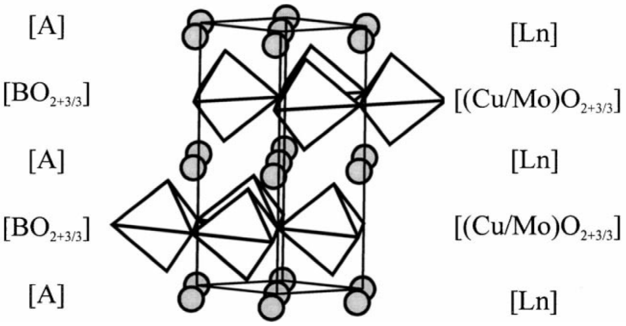

Fig. 1. Rare-earth hexagonal structure type for ABO_3 compounds.

1.1. The $Ln_4Cu_3MoO_{12}$ and $Ln'_2Ln''_2Cu_3MoO_{12}$ families

The study of the $Ln_4Cu_3MoO_{12}$ system reveals the importance of umbrella stoichiometries as counterbalances to thermodynamic sinks [2]. Just as a compound can act as a thermodynamic sink and frustrate attempts to make compounds of comparable stoichiometries, so a thermodynamic umbrella stoichiometry increases the likelihood of finding new compounds nearby in phase space by creating a pocket of stability. Both single and multiphase examples exist within the set of $Ln'_2Ln''_2Cu_3MoO_{12}$ and $Ln_4Cu_3MoO_{12}$ stoichiometries. The single-phase members share a common structure, and the multiphase members share common phase analogues. The bifurcation points to systematic thermodynamic trends in phase stability.

$La_4Cu_3MoO_{12}$ is an exceptional $(ABO_3)_{n=4}$ phase [3]. The perovskite structure would seem favorable based on cation size arguments, but the thermodynamically stable result is the rare-earth (RE) hexagonal structure which commonly accommodates mid-sized RE cations along with transition metal (TM) cations (Fig. 1) [4,5]. The La^{III} is only 6+2 coordinate and the Cu^{II} and Mo^{VI} both adopt trigonal bipyramidal coordination. Previously, no lantha-

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*Corresponding author. Tel.: +1-847-491-3505.
E-mail address: krp@northwestern.edu (K.R. Poeppelmeier).

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nide cation larger than europium has been incorporated. Truly, the discovery of the lanthanum compound is anomalous, but that of the smaller lanthanide analogues can be anticipated. Substitution is often possible because of the similarity between the trivalent lanthanides, and the predicted isomorphic structures of $Ln_4Cu_3MoO_{12}$ for smaller Ln approach the expected hexagonal structure type based on ABO_3 radius ratio comparisons [4].

$Ln_4Cu_3MoO_{12}$ formed a single phase for all of the common trivalent lanthanides larger than ytterbium (Ln = La, Pr, Nd, Sm–Tm) and Fig. 2 shows which combinations of $Ln'_2Ln''_2Cu_3MoO_{12}$ formed a single phase [2]. The lattice parameters change linearly with average A-cation size and those of the $Ln'_2Ln''_2Cu_3MoO_{12}$ members correspond closely to the average of the two end members, $Ln_4Cu_3MoO_{12}$ and $Ln''_4Cu_3MoO_{12}$. This particular B-cation composition (75% copper and 25% molybdenum) increases the tolerable average A-cation size of the RE hexagonal structure type, but could not stabilize the smallest lanthanide analogues, Yb and Lu, which typically form a different structure for ABO_3 stoichiometries. No single phases with a 50/50% mixture of lanthanide A-cations form with Yb or Lu either. The nine white squares lie at the boundary between single and multiple phase samples and indicate samples that contained a mixture of phases one of which resembled the target phase in structure.

Attempts to make $La_2Ho_2Cu_3MoO_{12}$ did not result in a single phase. Surprisingly, they also did not result in the segregation of the two parent phases, $La_4Cu_3MoO_{12}$ and $Ho_4Cu_3MoO_{12}$, both of which form under identical conditions. Furthermore, no phase with the targeted rare-earth hexagonal structure formed. The result was an ordinary set of simple oxides: La_2MoO_6, CuO and $Ho_2Cu_2O_5$. The same result proved true for the other combinations of Ln′ and Ln″ where the size mismatch between the lanthanides was too large ($\Delta r > 14$ pm). Fig. 2 codes all the experimental results for the $Ln'_2Ln''_2Cu_3MoO_{12}$ family. Additional results (marked with an *) are anticipated based on the two requirements for the formation of the single phase: (1)

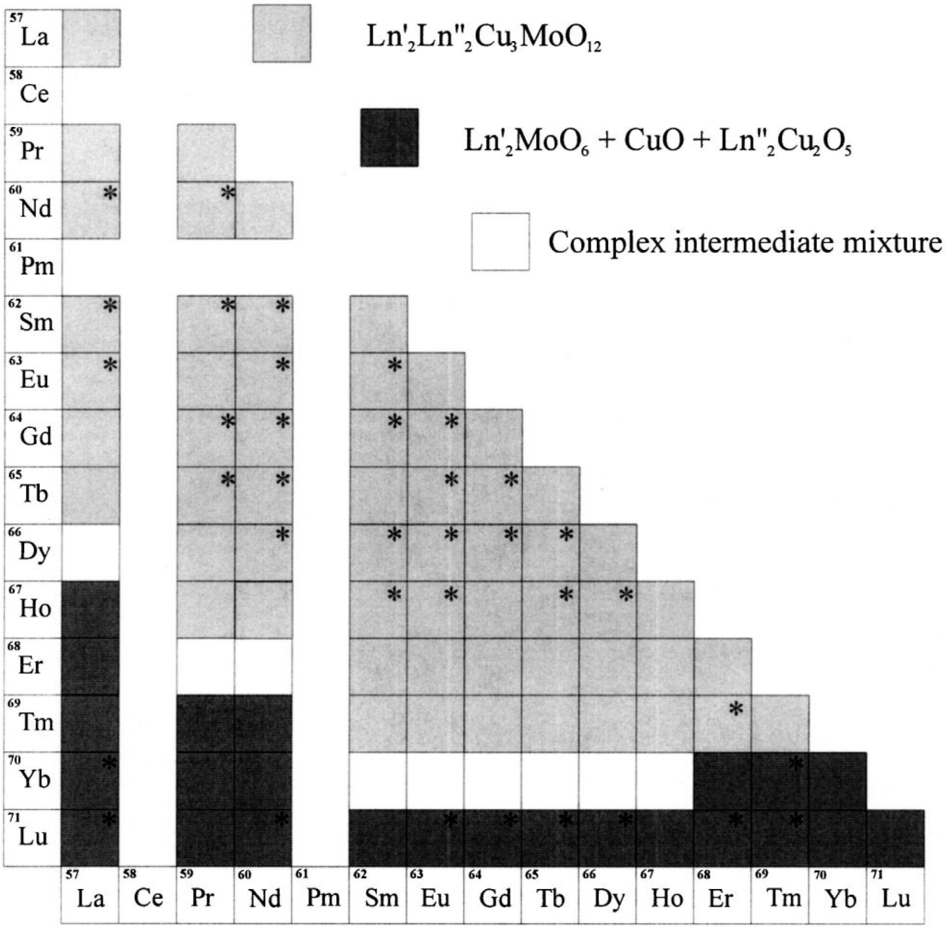

Fig. 2. Chart of $Ln_4Cu_3MoO_{12}$ and $Ln'_2Ln''_2Cu_3MoO_{12}$ synthesis attempts. Light gray squares indicate single-phase products. Dark gray squares indicate multiphase products comprised solely of metal and binary metal oxides. White squares indicate multiphase products where one of the phases has the targeted rare-earth hexagonal structure. Squares marked with an asterisk are anticipated results in accordance with experimental results ($\bar{r} \geq 105$ pm and $\Delta r \leq 14$ pm).

sufficiently large average lanthanide size ($\bar{r} \geq 105$ pm $= r(^{IX}Tm^{III})$), and (2) sufficiently small difference between the lanthanide cation sizes ($\Delta r \leq 14$ pm).

1.2. Substantiation of umbrella stoichiometry concept

The fact that an ordinary set of products forms when targeting $La_2Ho_2Cu_3MoO_{12}$ illustrates the peculiarity of single-phase compositions like $La_4Cu_3MoO_{12}$ and $Ho_4Cu_3MoO_{12}$. The explanation for this extraordinary result leads to the chemical principle of umbrella stoichiometries.

The specific oxide compositions that form as the thermodynamic products define a stability hierarchy. Since $La_4Cu_3MoO_{12}$ and $Ho_4Cu_3MoO_{12}$ form single phases, they are more stable than any set of multiphase alternatives.

$$\Delta G(La_4Cu_3MoO_{12}) < \Delta G(La_2Cu_2O_5 + La_2MoO_6 + CuO) \tag{1}$$

$$\Delta G(Ho_4Cu_3MoO_{12}) < \Delta G(Ho_2Cu_2O_5 + Ho_2MoO_6 + CuO) \tag{2}$$

Averaging Eqs. (1) and (2) yields an overall comparison.

$$\tfrac{1}{2}\Delta G(La_2Cu_2O_5 + La_2MoO_6 + Ho_2Cu_2O_5 + Ho_2MoO_6 + 2CuO) > \tfrac{1}{2}\Delta G(La_4Cu_3MoO_{12} + Ho_4Cu_3MoO_{12}) \tag{3}$$

Experiment reveals that

$$\Delta G(La_2MoO_6 + Ho_2Cu_2O_5 + CuO) < \Delta G(\tfrac{1}{2}La_4Cu_3MoO_{12} + \tfrac{1}{2}Ho_4Cu_3MoO_{12}) \tag{4}$$

The right sides of Eqs. (3) and (4) are equal, and so the transitive property of inequality demands that

$$\Delta G(La_2MoO_6 + Ho_2Cu_2O_5 + CuO) < \tfrac{1}{2}\Delta G(La_2Cu_2O_5 + La_2MoO_6 + Ho_2Cu_2O_5 + Ho_2MoO_6 + 2CuO) \tag{5}$$

or after subtracting common terms and multiplying by two to eliminate fractions,

$$\Delta G(La_2MoO_6 + Ho_2Cu_2O_5) < \Delta G(La_2Cu_2O_5 + Ho_2MoO_6) \tag{6}$$

Eq. (6) can be generalized for any pair of lanthanide cations in the copper molybdate system that differ in size by more than 14 pm. $Ln_2Cu_2O_5$ is more stable for smaller lanthanides (green phase), and likewise Ln_2MoO_6 is more stable for larger lanthanides. If this were not true, then the segregation of the two parent phases, $Ln'_4Cu_3MoO_{12}$ and $Ln'_4Cu_3MoO_{12}$, would be the most stable multiphase result. Conversely, $Ln_2Cu_2O_5$ is relatively unstable for larger lanthanides and Ln_2MoO_6 for smaller lanthanides. $Ln_4Cu_3MoO_{12}$ must represent a stoichiometry that is couched between the stability of $Ln_2Cu_2O_5$ and $Ln_2MoO_6 + CuO$. All three stoichiometries ($Ln_4Cu_3MoO_{12}$, $Ln_2Cu_2O_5$, and $Ln_2MoO_6 + CuO$) represent $Ln(Cu/Mo)O_3$ stoichiometries that differ only in the ratio of Cu^{II} to Mo^{VI}.

Fig. 3 depicts the qualitative stabilities for such stoichiometries for all the lanthanides. The stability of $Ln_2Cu_2O_5$ (100% of the TM cations are copper) is less than that for $Ln_4Cu_3MoO_{12}$ (75%) on the right side of the diagram and greater than it on the left side. The opposite is true for the stability of $Ln_2MoO_6 + CuO$ (50%). The specific 3 to 1 ratio of copper to molybdenum permits the formation of the single phase by rendering all alternative sets of products less stable than the single phase. Despite a possible oxide that is more stable than the single phase, the hypothetical leftover is too unstable. The multiphase line, which is the average of the $Ln_2Cu_2O_5$ stability line and the $Ln_2MoO_6 + CuO$ stability line, lies above the single-phase line except for Ln = Yb and Lu. For Ln = La–Tm, a single phase forms as the thermodynamic product; and for the larger lanthanides, this phase forms despite inappropriate cation sizes because the stoichiometry renders all other possibilities even less stable.

The drawing of Fig. 3 is qualitative in nature and intended to help explain the stability of the $Ln_4Cu_3MoO_{12}$ and $Ln'_2Ln''_2Cu_3MoO_{12}$ phases. The small lanthanides prefer to pair up with the copper, while the large ones prefer the molybdenum. We observe that there exists an intermediate ratio between 100% copper and 50% copper that allows for the formation of a new single phase if the two lanthanides are close enough in size. If either $Ln_2Cu_2O_5$ or Ln_2MoO_6 were to form, then the leftover stoichiometry is restrictively unstable. However, if the two lanthanides differ sufficiently in size, then both $Ln_2Cu_2O_5$ and Ln_2MoO_6 are stabilized. This is the case for La/Ho and the other stoichiometries represented in the lower left-hand corner of Fig. 2. Consistent with Eq. (6), the large lanthanide cation reacts to from a pure molybdate, while the smaller one reacts to form a pure cuprate.

An umbrella stoichiometry is a relatively unstable composition that promotes the formation of single phases by leveraging thermodynamic sinks. La_2MoO_6 is more stable than $La_4Cu_3MoO_{12}$, but $La_2Cu_2O_5$ is too unstable. The absence of low energy alternatives causes $La_4Cu_3MoO_{12}$ to crystallize in the rare earth hexagonal structure even though the lanthanum is only 6 + 2 coordinate and the copper and molybdenum are in fairly unusual trigonal bipyramidal coordination. The structural unconventionality of this phase is directly attributable to it proximity to the unstable composition $La_2Cu_2O_5$. The situation is reversed for $Ho_4Cu_3MoO_{12}$. $Ho_2Cu_2O_5$ is more stable than the single-phase composition while Ho_2MoO_6 is not.

The result is simple, but its application to other systems is powerful. The discovery of the $La_4Cu_3MoO_{12}$ could not be anticipated because of severely unstable features of the structure. However, the La/Cu umbrella stoichiometry

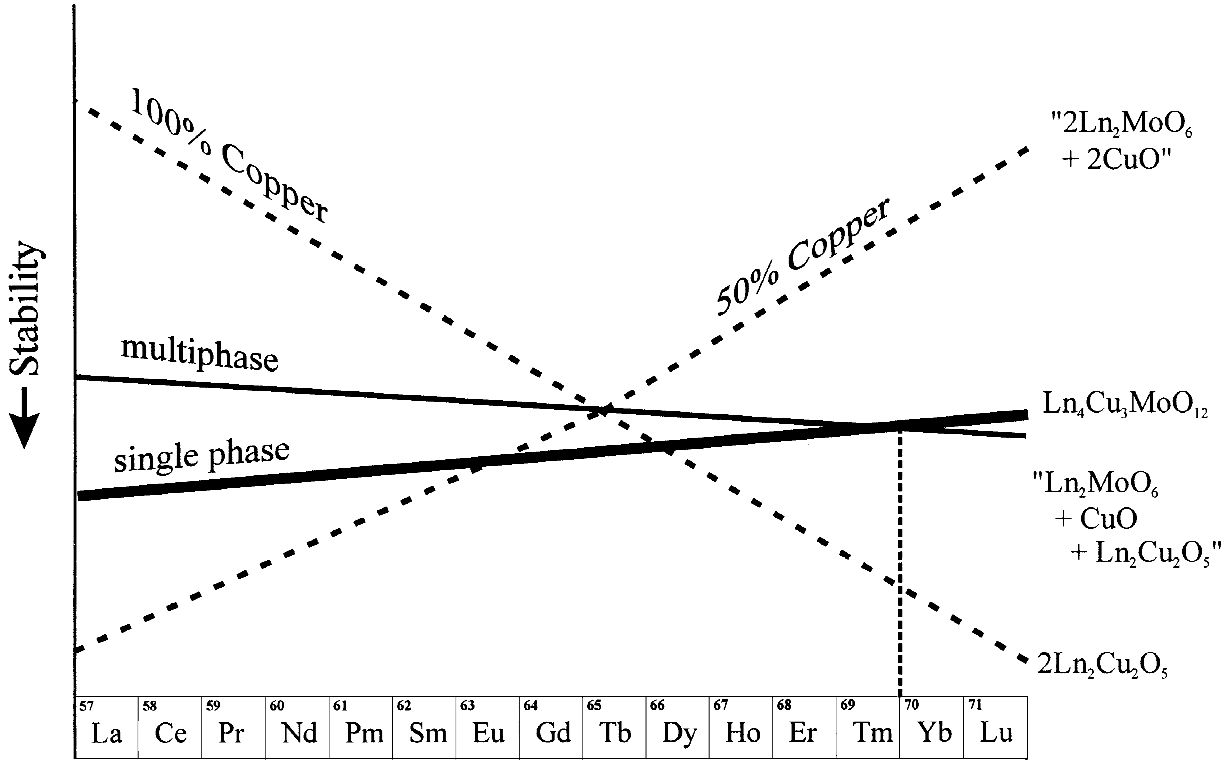

Fig. 3. Graph of qualitative stabilities for '$Ln_4(Cu/Mo)_4O_{12}$' stoichiometries. Single phase materials form for Cu/Mo = 3/1 even when either $Ln_2Cu_2O_5$ or Ln_2MoO_6 + CuO is more stable. The multiphase line is the average of the $Ln_2Cu_2O_5$ (100% copper) and the Ln_2MoO_6 + CuO (50% copper) line and lies above the single phase line except for Ln = Yb and Lu.

facilitates the formation of a single phase by destabilizing all multiphase alternatives. The usefulness of the concept is two-fold: known single-phase stoichiometries can be modified with substitutions that shift them towards umbrella stoichiometries, and the many phases that remain undiscovered are more likely to be found close to such stoichiometries.

2. Experimental results

To test the former concept, the molybdenum in $La_4Cu_{3-x}Mo_{1-x}O_{12-\delta}$ was substituted with copper. This shifts the overall stoichiometry of the phase towards the La/Cu umbrella stoichiometry. Eight samples corresponding to $x = 0.04$, 0.08, 0.12, 0.16, 0.20, 0.25, 0.33, and 0.50 were made by solid state reaction of stoichiometric amounts of La_2O_3, CuO, and MoO_3. Samples were intimately ground, heated at 1025°C for 4 days with two intermittent grindings. These conditions are identical to the synthesis conditions of $La_4Cu_3MoO_{12}$ ($x = 0.0$). The weight of the samples did not change during the reactions. Fig. 4 shows the PXD data along with that of the $x = 0.0$ phase. The dominant phase in each is the $La_4(Cu/Mo)_4O_{3-\delta}$ parent phase. $La_2Cu_2O_5$ ($C2/c$ with $a = 13.864(1)$ Å, $b = 3.747(3)$ Å, $c = 27.943(3)$ Å, and $\beta = 106.06(2)°$) [6], identified by the main peak at 33° 2θ, appears in the $x \geq 0.16$ samples. Rietveld refinements of $La_2Cu_2O_5$ and $La_4(Cu/Mo)_4O_{12-\delta}$ ($P2_1/m$, $\beta \approx 90°$)[3] led

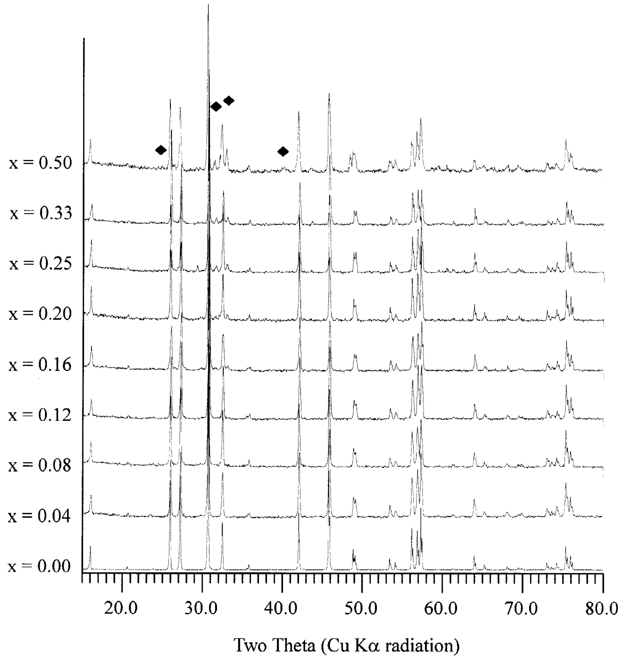

Fig. 4. PXD patterns for $La_4Cu_{3-x}Mo_{1-x}O_{12-2x}$. Diamonds mark the peaks of $La_2Cu_2O_5$.

Table 1
Phase results for substitution in $La_4Cu_{3+x}Mo_{1-x}O_{12-2x}$

x	a (Å)	b (Å)	c (Å)	β (°)	% $La_2Cu_2O_5$
0.00	7.903(1)	10.995(1)	6.844(1)	90.08(1)	0
0.04	7.913(4)	11.004(1)	6.849(1)	~90	0
0.08	7.906(2)	11.003(1)	6.844(1)	~90	0
0.12	7.906(1)	11.004(1)	6.848(4)	~90	0
0.16	7.905(1)	11.003(1)	6.849(1)	~90	0.6(1)
0.20	7.902(1)	11.004(1)	6.848(1)	~90	0.8(1)
0.25	7.905(2)	11.004(1)	6.847(2)	~90	1.5(1)
0.33	7.911(1)	11.007(1)	6.845(1)	~90	9.0(7)
0.50	7.907(1)	11.007(1)	6.834(1)	~90	14.4(7)

to the lattice parameters and phase proportions given in Table 1 [7]. Thermogravimetric analysis of the $x=0.12$ sample in H_2/N_2 further revealed that two oxygen vacancies were introduced along with each substitution of a Cu^{II} for a Mo^{VI} ($\delta=2x$).

3. Discussion

Cation substitutions in the solid state can only take place to the extent that the single phase is still the most thermodynamically stable. Substituting copper for molybdenum in $La_4Cu_3MoO_{12}$ so as to move towards the La/Cu umbrella stoichiometry resulted in a solid solution up to $x=0.12$ with concomitant oxygen loss. This is surprising since the cations are under-coordinated by oxygen already and probably the reason why further substitution is not tolerable. Since the La^{III} would be least likely to relinquish coordinated oxygen, the oxygen vacancies probably occur in the BO plane. At $x=0.12$, the density of vacancies would be 6% in that plane. This substitution is clearly structurally unfavorable, and the fact that it is tolerated establishes the veracity of umbrella stoichiometries.

The formation of many oxides with unpredictable structures can be attributed to a balance between stable and unstable compositions. Obviously, a single thermodynamic phase forms only if it is more stable than all possible mixtures of products for a given set of reaction conditions. What this means to the synthetic chemist is that undiscovered phases likely exist near umbrella stoichiometries. La^{3+} and Cu^{2+} in a 1 to 1 ratio is one such stoichiometry. Ho^{3+} and Mo^{6+} in a 2 to 1 ratio is another. The formation of $La_2Ba_2Cu_2Ti_2O_{11}$ can be attributed to such a stoichiometric balance [8]. $BaTiO_3$ is a very stable binary product that could result from that stoichiometry, but the instability of what would be left over, $La_2Cu_2O_5$, causes nature to find another alternative. Layered La_2CuSnO_6 is a third example [9]. The stable pyrochlore $La_2Sn_2O_7$ does not form so that $La_2Cu_2O_5$ does not have to.

La^{III} to Cu^{II} in a one to one ratio is a relatively unstable composition, and $La_2Cu_2O_5$ itself forms a highly unconventional structure at ambient pressure owing to the absence of stable alternatives. Cava et al. have observed that it forms in air for a narrow temperature range (999–1012°) as the $n=2$ member of the homologous series: $La_{2+2n}Cu_{4+n}O_{7+4n}$ [6]. The $n=3$ member ($La_8Cu_7O_{19}$) forms a single phase between 1019 and 1037°C, and higher members ($n>3$) have been observed by electron microscopy. No evidence for the $n=0$ and 1 members has been observed. Cava points out ‘it is remarkable that, given the simple ratio of the constituent elements, such complex structures form instead of the structurally simpler Ruddlesden–Popper series. The variety of energetically favorable Cu^{2+}–O coordination polyhedral geometries no doubt plays a significant role.’ Only under high pressure does $La_2Cu_2O_5$ form the oxygen-deficient perovskite structure [10]. Clearly all of the ambient pressure members of this homology are unconventional in structure, and given our understanding of the molybdate system, we can now conclude that it is the lack of energetically favorable alternatives that leads to their formation.

In general, the structure and properties of new oxides can be anticipated based on the choice of the constituent cations. However, the targeted structures are often so complex that there is no guarantee that a given set of cations will form a single phase. The stability of such complex structures is often less than that of multiphase alternatives. Simply stated, many hypothetical phases do not form, no matter how ideal their properties may be expected to be. This is true in all areas of materials research. To promote single-phase results, umbrella stoichiometries can be used to counterbalance thermodynamic sinks. The overall stoichiometry can be designed to facilitate the incorporation of all the desired cations into a single phase under the specific synthesis conditions. This is a powerful idea that predicted the substitution of copper for molybdenum in $La_4Cu_3MoO_{12}$, and has yet to be applied widely to the rational design of materials.

Acknowledgements

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