Stability of $Cu_2Ln_2O_5$ Compounds – Comparison, Assessment and Systematics

K. P. Jayadevan and K. T. Jacob*

Materials Research Center and Department of Metallurgy,
Indian Institute of Science, Bangalore 560 012, India.

(Received March 31, 2000)

ABSTRACT

Phase diagram studies show that at ambient pressure only one ternary oxide, $Cu_2Ln_2O_5$, is stable in the ternary systems Cu-*Ln*-O (*Ln* = Tb, Dy, Ho, Er, Tm, Yb, Lu) at high temperatures. The crystal structure of $Cu_2Ln_2O_5$ can be described as a zig-zag arrangement of one-dimensional Cu_2O_5 chains parallel to the *a*-axis with *Ln* atoms occupying distorted octahedral sites between these chains. Four sets of emf measurements on Gibbs energy of formation of $Cu_2Ln_2O_5$ (*Ln* = Tb, Dy, Ho, Er, Tm, Yb, Lu; Y) from component binary oxides and one set of high-temperature solution calorimetric data on enthalpy of formation have been reported in the literature. Except for $Cu_2Y_2O_5$, the measured values for the Gibbs energies of formation of all other $Cu_2Ln_2O_5$ compounds fall in a narrow band (±1 kJ mol^{-1}) and indicate a regular increase in stability with decreasing ionic radius of the lanthanide ion. The values for the second law enthalpy of formation, derived from the temperature dependence of emf obtained in different studies, show larger differences, as high as 25 kJ mol^{-1} for $Cu_2Tm_2O_5$. Though associated with an uncertainty of ±4 kJ mol^{-1}, the calorimetric measurements help to identify the best set of emf data. The trends in thermodynamic data correlate well with the global instability index (*GII*) based on the overall deviation from the valence sum rule. Low values for the index calculated from crystallographic information indicate higher stability. Higher values are indicative of the larger stress in the structure.

1. INTRODUCTION

The ternary Cu-*Ln*-O forms one of the bounding surfaces of the quaternary system *Ln*-Ba-Cu-O which contains superconducting oxides. Phase relations and accurate thermodynamic data on bounding ternary systems are fundamental inputs for calculation of the properties of complex higher order systems. From this point of view, experimental determination of thermodynamic properties of ternary oxides has special significance. Apart from forming a portion of the quaternary *Ln*-Ba-Cu-O, the systems belonging to the family Cu-*Ln*-O (*Ln* = La-Lu, Y) have compounds with interesting crystal structures and transport properties /1, 2/. Although Y is not a lanthanide element, its ionic radius in the trivalent state falls in the range of the other lanthanides. The chemical behavior of Y is often similar to that of the lanthanides. The known compounds in the Cu-*Ln*-O family of systems are $CuLn_2O_4$, $CuLnO_2$ and $Cu_2Ln_2O_5$. The type of ternary oxide formed depends on the radius of the trivalent lanthanide cation (Ln^{3+}). There is a decrease in coordination number of Ln^{3+} ion as one moves from La to Lu /1/. The lanthanides, La to Gd, form ternary oxides $CuLn_2O_4$, which can crystallize in three forms (T, T' and T^*) /1/. T-type structure, shown

---

* Author for correspondence

by the largest lanthanide La, has *Ln* in nine-fold coordination and Cu in six-fold coordination with oxygen. With decrease in size of the lanthanide cation, T'-phase, having *Ln* in eight-fold and Cu in four-fold coordination, becomes stable. A typical example for T' structure is Nd_2CuO_4. Further reduction in size of *Ln* to Gd leads to the stabilization of T^*-type crystal structure with *Ln* in octahedral and Cu in square pyramidal coordination /1/. However, high-pressure can stabilize cuprates with T'-type structure for lanthanides smaller than Gd (*Ln* = Y, Dy, Ho, Er, Tm) /3/. $CuLnO_2$-type oxides are found to be unstable for systems having lanthanides smaller than Eu /4/. However, $CuYO_2$ is stable /5/ despite unfavorable ionic radius. For elements from Tb to Lu and Y, a series of ternary oxides of general formula $Cu_2Ln_2O_5$ have been identified /6/.

Using different techniques such as solution calorimetry /7/ and electromotive force (emf) measurements /8-16/, high-temperature thermodynamic properties of interoxide compounds in the ternaries Cu-*Ln*-O have been determined. Presented in this article is a critical discussion of the published values of standard Gibbs energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) of formation of $Cu_2Ln_2O_5$ from its component binary oxides Ln_2O_3 and CuO. The trend in structural stability of the series of oxides with the stoichiometry $Cu_2Ln_2O_5$ is also examined using crystallographic information to see how well it correlates with thermodynamic data.

2. PHASE DIAGRAM

Isothermal phase relations at 1273 K for the ternary system Cu-*Ln*-O (*Ln* = Tb-Lu) is shown in Figure 1 based on the investigations by Jacob and coworkers /8, 9,10/. There is only one stable ternary oxide, $Cu_2Ln_2O_5$, at ambient pressure. The compound $Cu_2Ln_2O_5$ coexists with CuO and Ln_2O_3. At lower partial pressures of O_2, the compound is in equilibrium with Cu_2O. However, the compound does not coexist with metallic copper. Phase relations in the binary Cu-*Ln* change with the lanthanide element. Hence, fine details on the binary Cu-*Ln* are not presented in Figure 1. In general, alloys in the binary Cu-*Ln* are in equilibrium with Ln_2O_3. In the ternary system Cu-Y-O, phase relations are different. Two ternary oxides, $Cu_2Y_2O_5$ and $CuYO_2$, are found to be stable at 1273 K /11/.

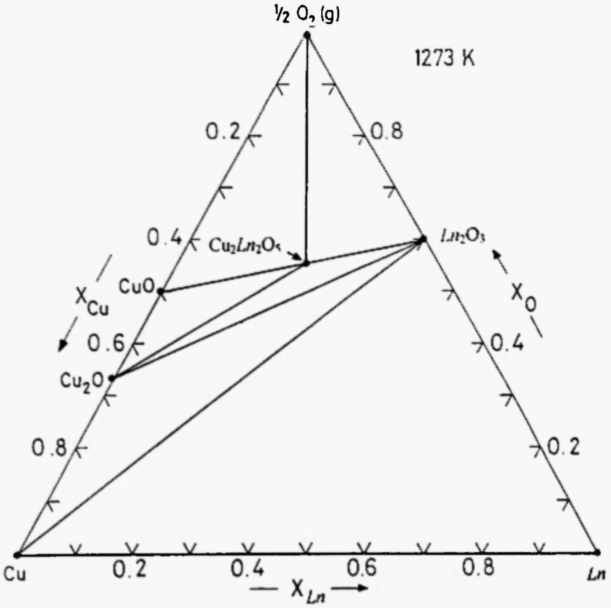

Fig. 1: Isothermal section of the phase diagram for the ternary system Cu-*Ln*-O (*Ln* = Tb-Lu) at 1273 K /8, 9, 10/.

3. CRYSTAL STRUCTURE

X-ray diffraction studies on $Cu_2Ln_2O_5$-type compounds have been reported as early as 1968 by Bergerhoff and Kasper /17/. The compounds are termed 'blue phases' because of their color. A recent study by Munoz and Carvajal /18/ using high-resolution neutron powder diffraction assigns a noncentrosymmetric orthorhombic space group $Pna2_1$ for $Cu_2Ln_2O_5$. A projection of the crystal structure along the *ac* plane is presented in Figure 2. Close examination of the projection reveals a zig-zag arrangement of one-dimensional Cu_2O_5 chains parallel to the *a*-axis with *Ln* atoms occupying distorted octahedral sites between these chains. In a unit cell of $Cu_2Ln_2O_5$, the copper atoms are in square pyramidal coordination with distorted quadrilateral as the base. There is a gradual expansion of LnO_6 octahedra and systematic elongation of the apical Cu-O distance in the CuO_5 polyhedra as the size of the rare earth ion is increased. Lattice parameters as well as cell volume show a systematic

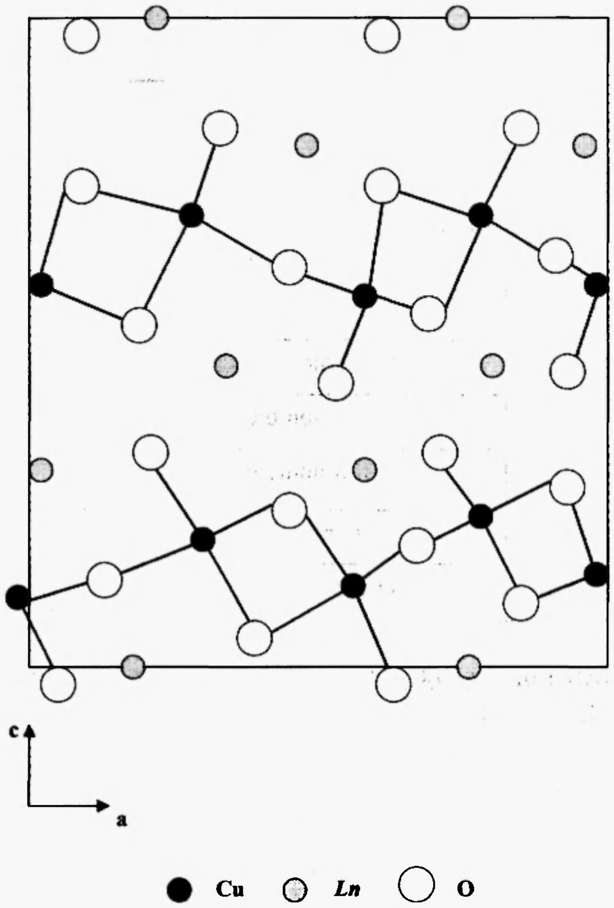

Fig. 2: Schematic projection of the crystal structure of $Cu_2Ln_2O_5$ on the *ac* plane.

increase with increase in rare earth ionic radius (Figures 3 and 4). Table I summarizes crystallographic data for the compounds $Cu_2Ln_2O_5$ (*Ln* = Tb-Lu). In the temperature range of thermodynamic investigations /7-16/, from 900 to1300 K, Ln_2O_3 (*Ln* = Tb-Lu and Y) exhibit C-type cubic crystal structure belonging to the space group $Ia\bar{3}$ /19/. The structure is the same as that of mineral bixbyite $(Fe,Al)_2O_3$. When eight anion deficient unit cells of CaF_2 structure are placed together in the appropriate manner, a unit cell of C-rare earth oxide structure results. The metal atoms have a distorted f.c.c lattice and only 3/4 of the tetrahedral sites are occupied by the anions. All metal atoms have an octahedral anion coordination. CuO has a monoclinic tenorite structure with space group $C2/c$ /20/.

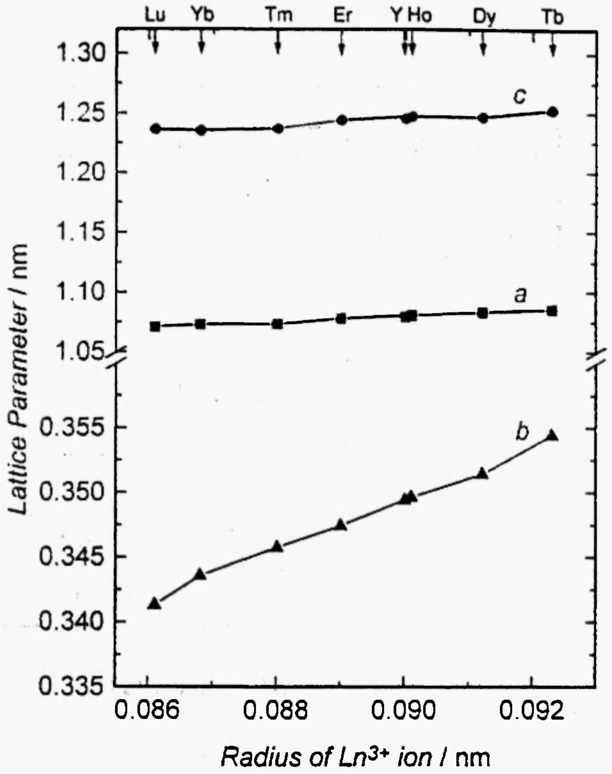

Fig. 3: Variation of cell parameters of $Cu_2Ln_2O_5$ as a function of the radius of Ln^{3+} ion.

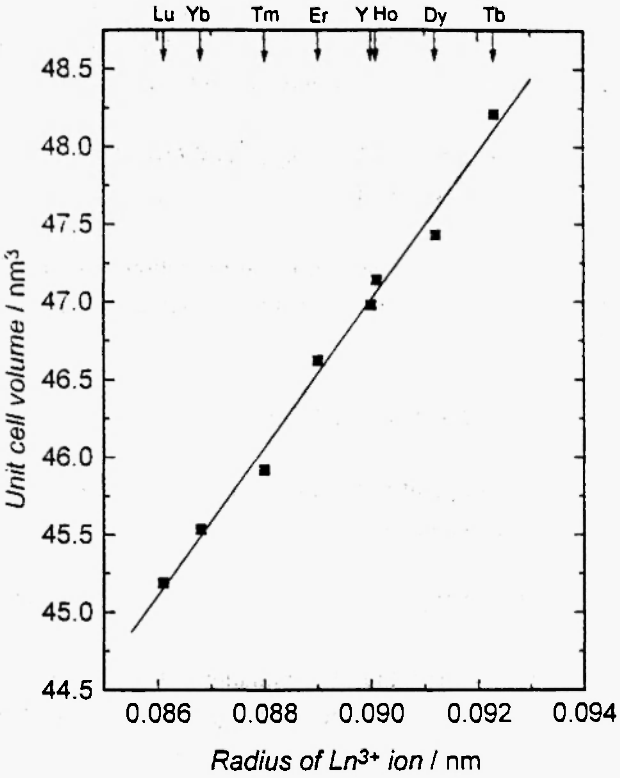

Fig. 4: Variation of unit cell volume of $Cu_2Ln_2O_5$ as a function of the radius of Ln^{3+} ion.

Table 1

Crystallographic Data for $Cu_2Ln_2O_5$ (Ln = Tb-Lu, Y) /18/

Ternary oxide	Lattice parameters			Structure / Space group
	a (nm)	b (nm)	c (nm)	
$Cu_2Tb_2O_5$	1.0856	0.3544	1.2530	Orthorhombic / $Pna2_1$
$Cu_2Dy_2O_5$	1.0830	0.3514	1.2465	Orthorhombic / $Pna2_1$
$Cu_2Ho_2O_5$	1.0810	0.3496	1.2473	Orthorhombic / $Pna2_1$
$Cu_2Y_2O_5$	1.0796	0.3494	1.2455	Orthorhombic / $Pna2_1$
$Cu_2Er_2O_5$	1.0784	0.3474	1.2443	Orthorhombic / $Pna2_1$
$Cu_2Tm_2O_5$	1.0735	0.3457	1.2370	Orthorhombic / $Pna2_1$
$Cu_2Yb_2O_5$	1.0729	0.3435	1.2353	Orthorhombic / $Pna2_1$
$Cu_2Lu_2O_5$	1.0709	0.3413	1.2363	Orthorhombic / $Pna2_1$

4. THERMODYNAMIC PROPERTIES

Experimental results on the standard Gibbs energies of formation (ΔG^o) of $Cu_2Ln_2O_5$ at 1273 K, obtained by four groups /8-16/, are compared in Figure 5. All the four groups used solid-state emf technique to determine the Gibbs energy of formation. The cell used by Jacob and coworkers /8, 9, 10/ can be represented as:

$$\text{Pt}, Cu_2O + Cu_2Ln_2O_5 + Ln_2O_3 \,||\, (Y_2O_3)ZrO_2 \,||\, Cu_2O + CuO, \text{Pt} \qquad (1)$$

The virtual cell reaction is the formation reaction of $Cu_2Ln_2O_5$ from component binary oxides, CuO and Ln_2O_3.

$$2\,CuO + Ln_2O_3 \rightarrow Cu_2Ln_2O_5 \qquad (1)$$

The emf of cell I (E_I) is related to ΔG^o for $Cu_2Ln_2O_5$ by the Nernst equation:

$$\Delta G_1^0 = -2FE_I \qquad (2)$$

However, for the determination of ΔG^o for the compound $Cu_2Y_2O_5$, the working electrode of the solid-state cell was a mixture of Y_2O_3, $CuYO_2$ and $Cu_2Y_2O_5$ based on the phase relations for the ternary Cu-Y-O /11/. Standard Gibbs energies of formation (ΔG^o) of $Cu_2Ln_2O_5$ (Ln = Tb-Lu, Y) from component binary oxides at 1273 K, obtained from the experimental results reported in literature by various groups of investigators /8-16/, are plotted as a function of the radius of Ln^{3+} ion /21/ in Figure 5. For all the lanthanide compounds considered, the formation reaction is isostructural, i.e, reactants and products have the identical structures for each lanthanide. Barring the results for $Cu_2Y_2O_5$, the measured data for all other compounds fall in a narrow band (±1 kJ mol^{-1}). Gibbs energy gradually becomes more negative with decrease in the size of the Ln^{3+} ion. Jacob and coworkers /8-11/ have reported ΔG^o for all eight compounds in the series. Apart from $Y_2Cu_2O_5$ /11/, which shows a slightly more negative value, ΔG^o of other seven members exhibit a smooth trend with radius of Ln^{3+} ion /8, 9, 10/. Data of Kale and coworkers /12,13/ for $Cu_2Ln_2O_5$ (Ln = Tb-Lu) also show a similar trend. The standard Gibbs energies of $Cu_2Yb_2O_5$, $Cu_2Er_2O_5$, $Cu_2Dy_2O_5$ and $Cu_2Tb_2O_5$, reported by Tretyakov *et al.* /14/, further confirm the general trend. The stability of ionic compounds increase with decreasing ionic radius of the Ln^{3+} ion.

Second-law enthalpies of formation (ΔH^o) of $Cu_2Ln_2O_5$ (Ln = Tb-Lu, Y) from component binary oxides obtained from the temperature dependence of emf by the four groups /8-16/ are compared with the high-temperature solution calorimetric data of Muromachy and Navrotsky /7/ in Figure 6. All the

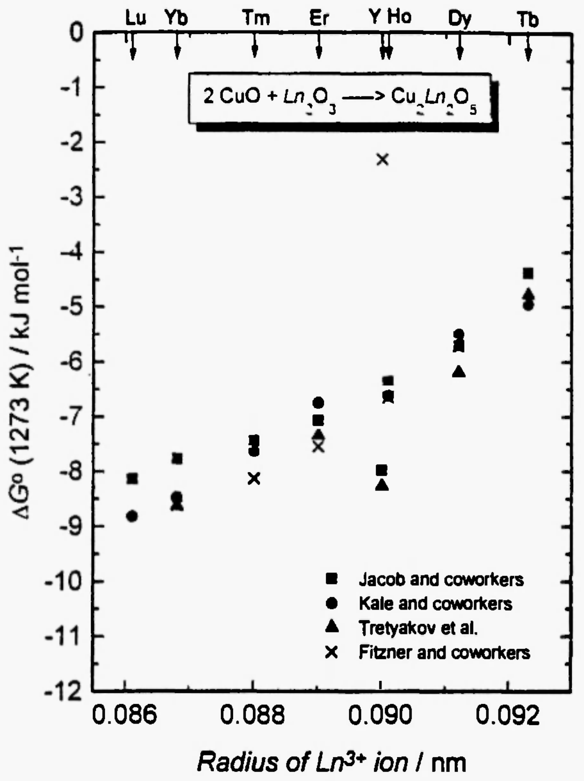

Fig. 5: Comparison of standard Gibbs energies of formation of $Cu_2Ln_2O_5$ from their component oxides /8-16/ as a function of the radius of Ln^{3+} ion.

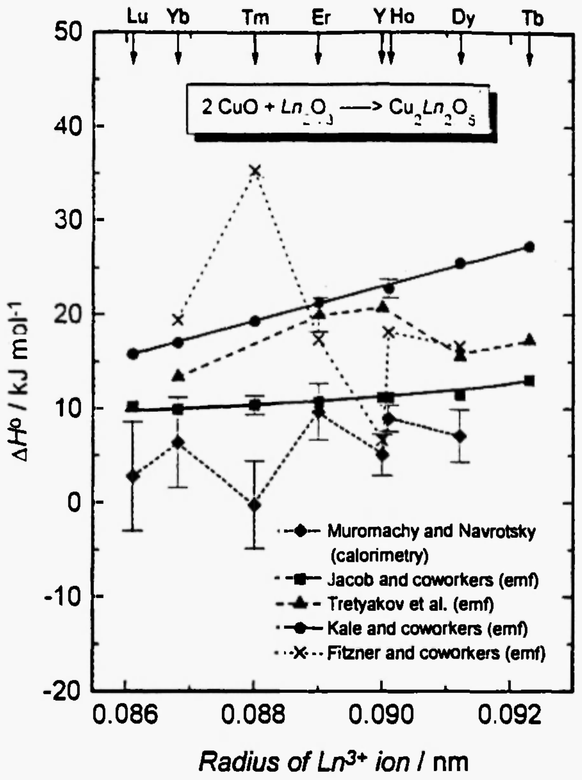

Fig. 6: Comparison of standard enthalpies of formation of $Cu_2Ln_2O_5$ from their component oxides /7-16/ as a function of the radius of Ln^{3+} ion.

$Cu_2Ln_2O_5$ (Ln = Tb-Lu, Y) compounds have positive enthalpies of formation except for $Cu_2Tm_2O_5$ which according to Muromachy and Navrotsky /7/ has a small negative value of -0.2 (± 5) kJ mol^{-1}. Though the enthalpy values obtained by high-temperature solution calorimetry are associated with relatively large error limits (±4 kJ mol^{-1}), they help in identifying the best set of emf data. For example, the large positive value of ~34 kJ mol^{-1}, reported by Kopyto and Fitzner for $Cu_2Tm_2O_5$ /15/, appears to be erroneous. The enthalpy values from emf studies of Fitzner and coworkers /15,16/, and Tretyakov *et al.* /14/ do not display any regular trend whereas the data reported by Jacob and coworkers /8-11/ and Kale and coworkers /12,13/ show a steady increase in the enthalpy of formation with radius of Ln^{3+} ion. The enthalpy of formation obtained from high-precision emf measurements by Jacob and coworkers /8-11/ is more consistent with calorimetric data than that obtained from other electrochemical measurements. In view of the approximate calorimetric confirmation, the data reported by Jacob and coworkers /8-11/ probably represent the best available information on $Cu_2Ln_2O_5$ compounds. The positive values for the enthalpies of formation may be associated with a change in coordination of Cu^{2+} ions from square planar in CuO to square pyramidal in $Cu_2Ln_2O_5$. More strain is also introduced into the structure with increasing size of the lanthanide ion. This results in more positive values of enthalpies of formation for larger Ln^{3+} ions.

Standard entropies of formation ($\Delta S°$) of $Cu_2Ln_2O_5$ compounds from component oxides, obtained from emf measurements /8-16/, are compared in Figure 7. The positive values indicate that these oxides are 'entropy-stabilized' at high temperature. The values of $\Delta S°$, obtained by Jacob and coworkers /8-11/ for eight members in the series, exhibit a small decrease with increasing ionic radius. Kale and coworkers /12,13/ report a regular increase in the value towards Tb. They

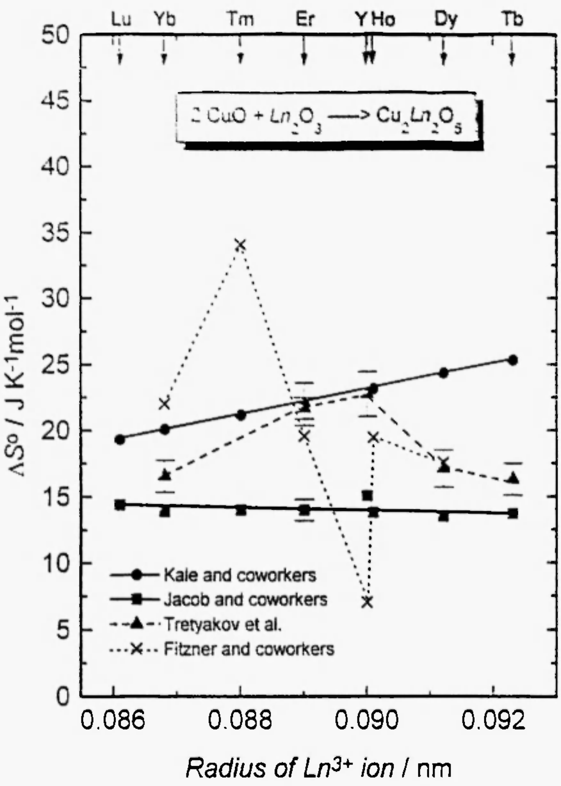

Fig. 7: Comparison of standard entropies of formation of $Cu_2Ln_2O_5$ from their component oxides /8-16/ as a function of the radius of Ln^{3+} ion.

have suggested that the positive values of ΔS^o might indicate cation mixing in the crystallographically nonequivalent sites of the structure and randomization of the Jahn-Teller distortions around the Cu^{2+} ion. However, there is no crystallographic evidence for either site disorder or symmetry around Cu^{2+} ion. The change in molar volume (ΔV^o) associated with the formation of $Cu_2Ln_2O_5$ from component binary oxides CuO and Ln_2O_3 is positive. The average value of ΔV^o is 1.5×10^{-6} m^3 mol^{-1}. The decrease in vibration frequency in the ternary oxide relative to the binary oxides is probably responsible for the positive value of entropy of formation.

5. DECOMPOSITION AND DISSOCIATION TEMPERATURES

The formation of $Cu_2Ln_2O_5$-type oxides from their component binary oxides, CuO and Ln_2O_3, is endothermic. The compounds are metastable relative to starting materials at low temperature. The calculated critical temperatures below which $Cu_2Ln_2O_5$ compounds are thermodynamically unstable are listed in Table 2. It is found that the highest critical temperature is obtained for the least stable ternary oxide, $Cu_2Tb_2O_5$, in the series. The solid-state decomposition of $Cu_2Ln_2O_5$ to its component binary oxides is slow. Hence, experimental confirmation of the decomposition temperatures may be difficult.

Mathews and Jacob have systematically studied the dissociation of $Cu_2Ln_2O_5$ (*Ln* = Tb, Dy, Ho, Er, Tm, Yb, Lu) to Cu_2O, Ln_2O_3 and O_2 at a controlled partial pressure of oxygen ($P_{O_2} = 5.0 \times 10^3$ Pa) using thermal

Table 2

Standard Gibbs Energies of Formation and the Lower Critical Temperatures for Stability of $Cu_2Ln_2O_5$ (*Ln* = Tb-Lu, Y) Formation Reaction: $2 CuO + Ln_2O_3 \rightarrow Cu_2Ln_2O_5$ /8-11/

Compound	ΔG^o / J mol^{-1}	Critical Temperature / K
$Cu_2Tb_2O_5$	13,080 - 13.70 T / K (+80)	955
$Cu_2Dy_2O_5$	11,480 - 13.51 T / K (±60)	850
$Cu_2Y_2O_5$	11,210 - 15.07 T / K (±85)	744
$Cu_2Ho_2O_5$	11,190 - 13.80 T / K (±120)	811
$Cu_2Er_2O_5$	10,750 - 13.99 T / K (±60)	768
$Cu_2Tm_2O_5$	10,400 -14.00 T / K (±100)	743
$Cu_2Yb_2O_5$	9,920 - 13.90 T / K (±60)	714
$Cu_2Lu_2O_5$	10,210 - 14.410 T / K(±100)	709

analysis (TG/DTA) /22/. The dissociation reaction can be written as:

$$Cu_2Ln_2O_5 \rightarrow Cu_2O + Ln_2O_3 + 1/2\ O_2 \qquad (3)$$

$$\Delta G^\circ_3 = -RT \ln P_{O_2}{}^{1/2} \qquad (4)$$

when the oxides are present at unit activity. The decomposition temperature for the above reaction can be calculated from the standard Gibbs energy change for reaction (3), which is obtained by combining data for reaction (1) in Table 2 with the Gibbs energy change for the decomposition of CuO to Cu_2O and O_2 /23/. For the reaction,

$$2\ CuO \rightarrow Cu_2O + 1/2\ O_2 \qquad (5)$$

$$\Delta G^\circ_5 / \mathrm{J\ mol^{-1}} = 130{,}320 - 93.82\ T / \mathrm{K}\ (\pm 210) \qquad (6)$$

The calculated decomposition temperatures at $P_{O_2} = 5.0 \times 10^3$ Pa are given in Table 3 for all the eight members in the series. The more stable members in the series have higher decomposition temperatures. The calculated values are found to be in good agreement (±2 K) with the experimental data reported by Mathews and Jacob /22/. At high partial pressures of diatomic oxygen gas, decomposition involves a liquid phase. The dissociation reaction of the ternary oxide $Cu_2Y_2O_5$ is different. The products are $CuYO_2$ and O_2 /11/.

6. INSTABILITY INDEX

A method for examining the stability of the crystal structures of inorganic compounds based on valence sum rule was introduced by Brown /24/. The method involves determination of a statistical quantity termed as "instability index". The first step in the procedure is to obtain the sum of the bond valence (s_{ij}) around an ion i. The value of s_{ij} is determined using an empirical expression which relates s_{ij} and the bond length R_{ij} in Angström units between the ions i and j.

$$s_{ij} = \exp\left[(R_0 - R_{ij}) / 0.37\right] \qquad (7)$$

where R_0 is a constant characteristic of the bond type. The second step is to compare the sum of the empirically obtained s_{ij} with formal valence state (V_i) of the ion under consideration. For an ideal crystal, the following relation holds good.

$$V_i = \sum_j s_{ij} \qquad (8)$$

This equation is known as the valence sum rule, which states that the sum of valence bonds around each ion must be equal to its formal valence. The root-mean square deviation between V_i and s_{ij}, for a nonideal crystal structure, is a measure of the instability of that structure /24/.

Table 3

Calculated Dissociation Temperatures for $Cu_2Ln_2O_5$ (Ln = Tb-Lu) at $P_{O_2} / P^\circ = 0.05$.

Dissociation Reaction: $Cu_2Ln_2O_5 \rightarrow Cu_2O + Ln_2O_3 + 1/2\ O_2$

Compound	ΔG° / J mol^{-1}	Dissociation Temperature / K
$Cu_2Tb_2O_5$	117,240 - 92.66 T / K (±230)	1265
$Cu_2Dy_2O_5$	118,840 - 92.85 T / K (±230)	1280
$Cu_2Ho_2O_5$	119,130 - 92.56 T / K (±250)	1287
$Cu_2Er_2O_5$	119,570 - 92.37 T / K (±230)	1294
$Cu_2Tm_2O_5$	119, 920 - 92.36 T / K (±240)	1298
$Cu_2Yb_2O_5$	120,400 - 92.46 T / K (±230)	1302
$Cu_2Lu_2O_5$	120,110 - 91.95 T / K (±240)	1306

The coordination environments of both Ln^{3+} and Cu^{2+} in $Cu_2Ln_2O_5$ are highly distorted. This leads to violation of valence sum rule (Eq. 8). Munoz and Carvajal /18/, based on the sum of bond valence, report large deviation (5-8 %) in formal valence of Cu^{2+} in $Cu_2Ln_2O_5$. Valence bond sums for Cu^{2+} give a value of ~1.8 valence units, lower than the theoretical value of 2. This is probably related to the Jahn-Teller effect of Cu^{2+} ions. Valence bond sums remain almost constant, very close to 3, for lanthanides. Munoz and Carvajal /18/ have defined a term called "Global Instability Index" (*GII*) and calculated values of *GII* for all eight $Cu_2Ln_2O_5$-type oxides (*Ln* = Tb-Lu, Y) to quantify the extent of instability in the structure based on the valence sum rule.

$$GII = \sqrt{\sum_{i=1}^{N}\left\{\left(\sum_{j} s_{ij} - V_i\right)^2\right\} \Big/ N} \qquad (9)$$

where *N* is the number of ions of a given type in the structure whose formal valence needs to be verified. The *GII* is essentially a root-mean square of bond valence sum deviation from the valence sum rule for all ions. It is a measure of the stress present in the crystal caused by the presence of different structural units.

In order to compare the trend in structural and thermodynamic stability, *GII* is shown as a function of the ionic radius of Ln^{3+} ion in Figure 8. The high value of instability index implies a strained crystal structure with large deviation from valence sum rule. In this series of $Cu_2Ln_2O_5$ compounds, $Cu_2Tb_2O_5$ has the highest value of *GII* and $Cu_2Lu_2O_5$ has the lowest value. Thus, as the size of the Ln^{3+} ion decreases, a steady increase in stability of the crystal structure with less strain is anticipated. The stability trend predicted from structural considerations is almost identical to that shown by thermodynamic data (compare Figures 5 and 8). Such correlations are useful for the estimation of thermodynamic properties of ternary oxides from structural data.

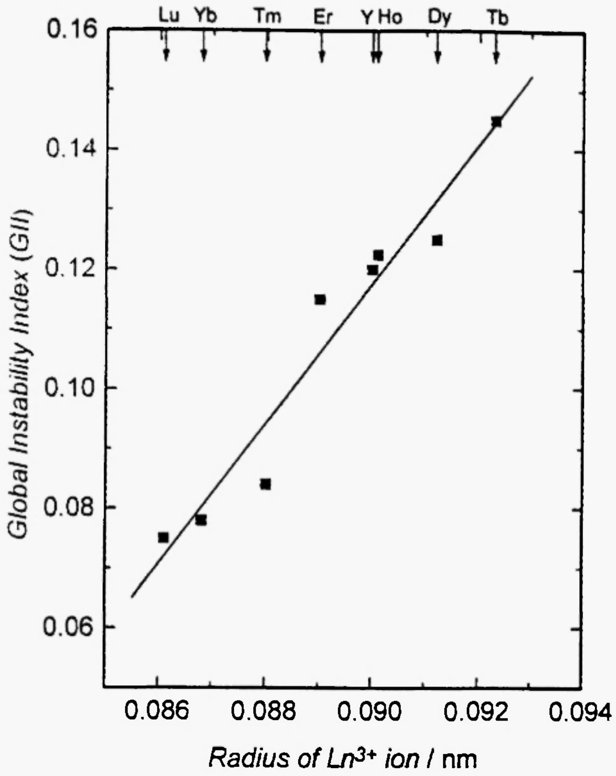

Fig. 8: Variation of Global Instability Index (*GII*) /18/ as a function of the radius of Ln^{3+} ion.

7. CONCLUSIONS

A comparative study of thermodynamic properties of $Cu_2Ln_2O_5$ compounds (*Ln* = Tb-Lu, Y) reported in the literature indicate a systematic increase in stability with decreasing radius of the lanthanide ion. $Cu_2Tb_2O_5$ is the least stable and $Cu_2Lu_2O_5$ is the most stable in the series. All the eight $Cu_2Ln_2O_5$-type oxides in this series are metastable at low temperatures. The critical temperature below which these compounds are thermodynamically unstable with respect to their component binary oxides are calculated from the experimental results of Jacob and coworkers /8-11/. The least stable $Cu_2Tb_2O_5$ has the highest critical temperature. The temperature for the dissociation of each $Cu_2Ln_2O_5$ to Cu_2O, Ln_2O_3 and O_2, calculated at $P_{O_2} / P^{\circ} = 0.05$, show a monotonic increase with atomic number of the lanthanide element. The least stable $Cu_2Tb_2O_5$ has the lowest dissociation temperature. Global instability indices (*GII*), reported in literature for $Cu_2Ln_2O_5$-type oxides, are presented as a function of ionic radius of the trivalent lanthanide cation. The trend in structural instability is a mirror image of thermodynamic properties.

ACKNOWLEDGEMENT

One of the authors, K.P.J., wishes to thank Council of Scientific and Industrial Research (CSIR), India, for a Senior Research Fellowship (SRF).

REFERENCES

1. J.F. Bringely, S.S. Trail and B.A. Scott, *J. Solid State Chem.*, **86**, 310-322 (1990).
2. A. Lappas and K. Prassides, *J. Solid State Chem.*, **115**, 332-346 (1995).
3. H. Okada, M. Takano and Y. Takeda, *Physica C*, **166**, 111- 114 (1990).
4. H. Haas and E. Kordes, *Z. Kristallogr.*, **129**, 259-270 (1969).
5. T. Ishiguro, N. Ishizawa, N. Mizutani and M. Kato, *J. Solid State Chem.*, **49**, 232-236 (1983).
6. O. Schmitz-Du Mont **and** H. Kasper, *Mon. für Chem.*, **96**, 506-515 (1965).
7. E. Takayama-Muromachy and A. Navrotsky, *J. Solid State Chem.*, **106,** 349-356 (1993).
8. K.T. Jacob, T. Mathews and J.P. Hajra, *High Temp. Mater. Process.*, **12**, 251-258 (1993).
9. T. Mathews and K.T. Jacob, *J. Mater. Chem.*, **3**, 1025-1029 (1993).
10. T. Mathews and K.T. Jacob, *J. Am. Ceram. Soc.*, 77, 131-136 (1994).
11. G.M. Kale and K.T. Jacob, *Chem. Mater.*, **1**, 515-519 (1989).
12. G.M. Kale, R.V. Kumar and D.J. Fray, *Solid State Ionics*, **86-88**, 1421-1425 (1996).
13. G.M. Kale, *J. Solid State Chem.*, **125**, 13-18 (1996).
14. Yu.D. Tretyakov, A.R. Kaul and N.V. Makukhin, *J. Solid State Chem.*, **17**, 183-189 (1976).
15. M. Kopyto and K. Fitzner, *J. Mater. Sci.*, **31**, 2797-2800 (1996).
16. W. Przybylo and K. Fitzner, *Thermochim. Acta*, 113-123 (1995).
17. G. Bergerhoff and H. Kasper, *Acta Crystallogr.*, **24 B**, 388-391 (1968).
18. J.L. Garcia-Munoz and J. Rodriguez-Carvajal, *J. Solid State Chem.*, **115**, 324-331 (1995).
19. R.G. Haire and L. Eyring, *Handbook on the Physics and Chemistry of Rare Earths*: Ed. K.A. Gscneidner, Jr., L. Eyring, G.R. Choppin and G.R. Lander, Elsevier Science, **18**, 413-505 (1994).
20. *Joint Committee for Powder Diffraction Standards (JCPDS)*: International Centre for Diffraction Data, Swarthmore, PA, Card No: **5-0661**, (1990).
21. R.D. Shannon, *Acta Crystallogr.*, **A32**, 751-767 (1976).
22. T. Mathews and K.T. Jacob, *J. Mater. Res.*, **8**, 3015-3018 (1993).
23. K.T. Jacob and C.B. Alcock, *J. Am. Ceram. Soc.*, **8**, 192-198 (1975).
24. I.D. Brown, *Phys. Chem. Minerals*, **15**, 30-34 (1987).