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# GIBBS FREE ENERGY OF FORMATION OF SOLID PHASE $CuEu_2O_4$ AND $CuEuO_2$

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## ABSTRACT

Employing electrochemical cells with the solid electrolyte

$Cu_2O, CuEu_2O_4, CuEuO_2 | O^{2-} | \text{air} \left(p_{O_2} = 0.21 \text{ atm}\right)$

$CuEu_2O_4, CuEuO_2, Eu_2O_3 | O^{2-} | \text{air} \left(p_{O_2} = 0.21 \text{ atm}\right)$

the Gibbs free energy of formation of the solid $CuEu_2O_4$ and $CuEuO_2$ phases was determined over the temperature range 1123–1373 K. The results obtained were used to derive the Gibbs free energy change of the reaction of formation of the $CuEu_2O_4$ and $CuEuO_2$ phases from the respective oxides

$Cu_2O + Eu_2O_3 \rightarrow 2CuEuO_2$

$\Delta G_f^0 = -6640 + 4.02\ T$ (J)

$CuO + Eu_2O_3 \rightarrow CuEu_2O_4$

$\Delta G_f^0 = 885 - 8.67\ T$ (J)

Finally, the results presented were applied to determine phase relationships in the Cu–Eu–O system at 1273 K.

## INTRODUCTION

Since the pioneering work of Bednorz and Muller [1] was published, a virtual flood of papers concerned with the properties of superconducting ceramic phases has appeared in the literature worldwide. Most efforts were concentrated on the Y–Ba–Cu–O system, in which Chu and coworkers [2] discovered a new phase having a transition temperature above 90 K. It was soon discovered that this phase belongs to the perovskite family, and that substitution of yttrium by other rare earth elements does not actually change the critical temperature $T_c$ (ca. 90 K).

Although (rare earth)–Ba–Cu–O systems show almost no difference in superconducting property of the "1–2–3" phase, there is no reason to believe that their phase diagrams are identical. For example, if Y–Ba–Cu–O

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and Eu–Ba–Cu–O quaternary systems are compared it is seen that in the respective ternary Y–Cu–O and Eu–Cu–O systems different phases appear. The ternary Y–Cu–O system exhibits the presence of $Cu_2Y_2O_5$ [3], and under certain conditions of temperature and oxygen partial pressure $CuYO_2$ may be formed [4]. In turn, in the ternary Eu–Cu–O system, $CuEu_2O_4$ and $CuEuO_2$ phases exist (5].

Consequently, one may ask if this difference can influence phase relations in the respective quaternary systems. Phase relationships for the quaternary Y–Ba–Cu–O system have been investigated so far mainly for high oxygen potential [6–8]. Therefore it seems interesting to gather experimental information about phase relationships and thermodynamic properties of phases in Eu–Ba–Cu–O systems if such a comparison is to be made. As the first part of this study, the thermodynamic stability of $CuEu_2O_4$ and $CuEuO_2$ phases in the ternary Eu–Cu–O system was investigated using a solid oxide galvanic cell with a solid electrolyte.

## EXPERIMENTAL

### *Materials*

Copper oxide (99.99%) was obtained from Alfa Products (U.S.A.). Europium(III) oxide and cuprous oxide were 99.9% and 99.99% pure, respectively, and were both obtained from Aldrich Chemical Co. (U.S.A.). $CuEu_2O_4$ (black) was synthesized by heating pressed pellets containing an equimolar mixture of CuO and $Eu_2O_3$, prepared in a dry-box, for 6 h in oxygen at 1223 K. Formation of the compound was confirmed by X-ray diffraction analysis. $CuEuO_2$ (yellow) was prepared by heating pressed pellets containing an equimolar mixture of $Cu_2O$ and $Eu_2O_3$, prepared in a dry-box and sealed in evacuated silica capsules, overnight at 1123 K. The capsules were then quenched, the pellets were reground, and the whole procedure was repeated. Formation of the required compound was confirmed by an X-ray analysis. Fully stabilized zirconia tubes closed at one end (diameter 10 mm) were supplied by the Yamari Trading Co. (Japan).

### *Oxygen potential measurements*

At first, an EMF cell of the type

$$Cu_2O + Eu_2O_3 + CuEu_2O_4 \,|\, ZrO_2 + CaO \,|\, \text{air} \qquad \text{I}$$

was used for oxygen potential measurements in a way analogous to that reported earlier [9]. A schematic diagram of the cell assembly is shown in Fig. 1. The investigated electrode contained a large excess of $Cu_2O$. After about 24 h the cell produced stable EMF values, as shown in Fig. 2, and it

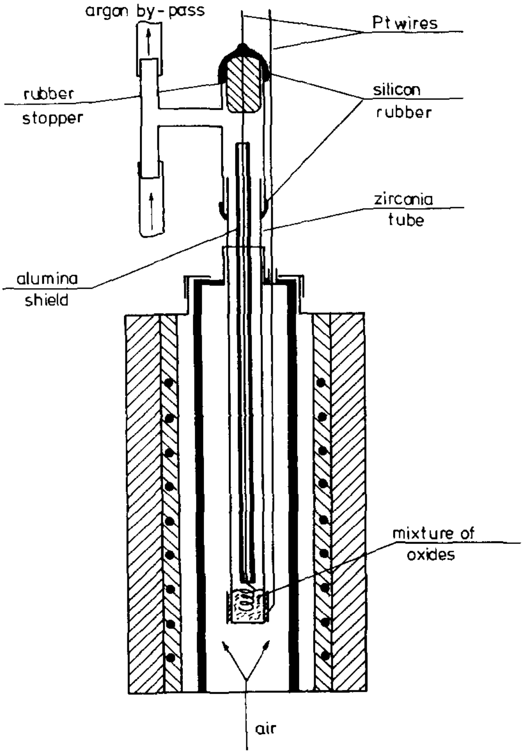

Fig. 1. Schematic diagram of the cell assembly.

then worked reproducibly for about 1 week in the temperature range 1100–1373 K. However, when after experiments an X-ray analysis of the investigated electrode was performed, it showed that $Eu_2O_3$ had disappeared

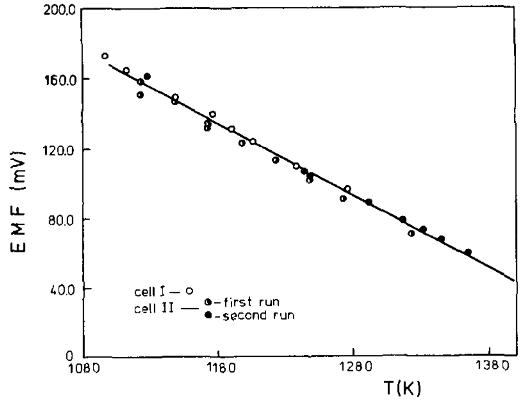

Fig. 2. Temperature dependence of the EMF of cell II.

from the mixture and the final equilibrium of the sample correspond to the $Cu_2O + CuEu_2O_4 + CuEuO_2$ field

Consequently, two EMF cells of the types

$$Cu_2O + CuEuO_2 + CuEu_2O_4 \,|\, ZrO_2 + CaO \,|\, \text{air} \qquad \text{II}$$

$$Eu_2O_3 + CuEuO_2 + CuEu_2O_4 \,|\, ZrO_2 + CaO \,|\, \text{air} \qquad \text{III}$$

were used for oxygen potential measurements over the $Cu_2O + CuEuO_2 + CuEu_2O_4$ and $Eu_2O_3 + CuEuO_2 + CuEu_2O_4$ equilibrium fields. Oxygen potential over the three-phase field is related to the measured EMF by the relationship

$$E = -\frac{RT}{4F} \ln\left(\frac{p_{O_2}}{0.21}\right) \qquad (1)$$

where $F = 96\,580$ J $V^{-1}mol^{-1}$, $E$ is the EMF (V), $R$ is the gas constant, $T$ is the absolute temperature (K), and $p_{O_2}$ is the oxygen partial pressure exerted by the working electrode (a mixture of the oxide phases under investigation). In most of the experiments, yttria–stabilized zirconia was used as the electrolyte, but in some cases magnesia–stabilized zirconia was also used. Air was used as the reference electrode with platinum as the lead wire. A sample consisting of mixed oxide powders was kept at the bottom of the electrolyte tube. Electrical contact was made using a platinum lead wire; contact was assured by pressing an alumina shield with a flat base onto the sample. An inert atmosphere was maintained inside the cell by passing purified argon gas through the system.

Experiments were performed in a resistance furnace produced by Metals Research Ltd. (U.K.). The cell was kept in the mullite tube of the furnace within the constant temperature zone (ca. 100 mm long), and the sample at the bottom of the electrolyte tube was always placed in this zone. After a constant temperature was reached, the cell was left overnight to attain an equilibrium state, and then the EMF was recorded with a V 544 digital voltmeter (Elwro, Poland).

The temperature was cycled in the range 1100–1380 K, and the full run was completed after about one week.

## RESULTS

Electromotive force values obtained for cells II and III are shown in Figs. 2 and 3. They were treated by the least-squares method, and are represented by the following equations

$$E_{II}(\pm 1.0) = 627.2 - 0.4175T \text{ (mV)} \qquad (2)$$

$$E_{III}(\pm 2.3) = 661.6 - 0.4383T \text{ (mV)} \qquad (3)$$

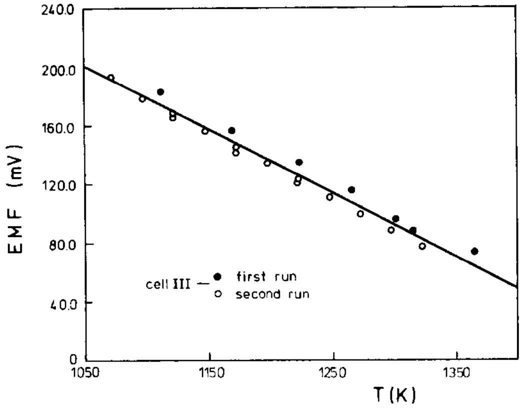

Fig. 3. Temperature dependence of the EMF of cell III.

The equilibrium oxygen pressure for the three-phase fields described by the reactions

$$2CuEu_2O_4 + Cu_2O \rightarrow 4CuEuO_2 + \tfrac{1}{2}O_2 \qquad (4)$$

and

$$2CuEu_2O_4 \rightarrow 2CuEuO_2 + Eu_2O_3 + \tfrac{1}{2}O_2 \qquad (5)$$

was determined from the relationship

$$\log p_{O_2} = \log 0.21 - (4FE/4.575T) \qquad (6)$$

Using eqns. (2), (3) and (6), the Gibbs free energy change of reactions (4) and (5) was calculated from their equilibrium constants, and is given in the following form

$$\Delta G^0_{T(4)} = 121\ 120 - 74.13T \text{ (J)} \qquad (7)$$

and

$$\Delta G^0_{T(5)} = 127\ 760 - 78.15T \text{ (J)} \qquad (8)$$

Combining reactions (4) and (5), one can derive the Gibbs free energy of formation of solid $CuEuO_2$ from the respective oxides

$$Cu_2O + Eu_2O_3 \rightarrow 2CuEuO_2 \qquad (9)$$

which is equal to

$$\Delta G^0_{f,\text{oxides}} = -6640 + 4.02T \text{ (J)} \qquad (10)$$

Next, combining reactions (4) and (9) with the reaction

$$Cu_2O + \tfrac{1}{2}O_2 \rightarrow 2CuO \qquad (11)$$

the reaction of formation of solid $CuEu_2O_4$ from respective oxides was derived

$$CuO + Eu_2O_3 \rightarrow CuEu_2O_4 \qquad (12)$$

The resulting Gibbs free energy change of reaction (12) is equal to

$$\Delta G^0_{f,\text{oxides}} = 885 - 8.67T \text{ (J)} \tag{13}$$

while the Gibbs free energy change of reaction (11) used for calculations was that given by Turkdogan [10].

## DISCUSSION

Thermodynamic properties of double oxides formed from CuO and rare earth oxides were investigated by Tretyakov et al., [11], who used solid oxide galvanic cells with zirconia electrolyte in the temperature range 1223–1423 K. Their results were derived under the general assumption that an equilibrium of the type $Cu_2O$–(rare earth)$_2O_3$–Cu(rare earth)$_2O_4$ took place in the cell.

However, Petrov et al. [12,13] demonstrated for the La–Cu–O, Pr–Cu–O and Nd–Cu–O systems that the nature of the phase relationship in this type of system is more complicated. Apparently, in the considered temperature range the existence of a (rare earth)$CuO_2$-type compound must be taken into account. Recently, Petrov et al. [14] measured the Gibbs free energy of formation of a series of solid phases formed between CuO, $Cu_2O$ and rare earth oxides. In the case of the Cu–Eu–O system, $\Delta G^0_T$ values obtained in this study from eqns. (10) and (13) agree within 1 kJ with those calculated in Petrov's paper (at 1073 K, $-2.33$ and $-8.41$ kJ, in comparison with $-2.94$ and $-9.72$ kJ [14]; at 1273 K, $-1.52$ and $-10.14$ kJ, in comparison with $-1.16$ and $-10.19$ kJ [14], respectively). It should be mentioned, however, that eqns. (10) and (13) of this paper differ from those in ref. 14 as far as the split into enthalpy and entropy terms is concerned. Enthalpy terms obtained in this paper ($-6.64$ and 0.89 kJ, respectively) and those derived from ref. 14 ($-12.51$ and $-7.25$ kJ, respectively) differ considerably.

Similarly, the entropy terms ($-4.02$ and 8.67 J/K) are different from those derived from ref. 14 ($-8.92$ and 2.3 J/K, respectively). As these discrepancies are connected with the slope of the obtained relationships, only experiments conducted over a wider temperature range (preferably above 1400 K) could resolve this problem. Alternatively, calorimetric measurements of the enthalpy of formation can give more reliable answers.

Using the obtained information as well as literature data, Gibbs triangle representation of phase equilibria and the representation of a phase relationship as a function of oxygen partial pressure at the chosen temperature of 1273 K are suggested. The estimation oxygen partial pressure for the $Eu_3O_4$–$Eu_2O_3$ equilibrium at 1273 K, based on the data of McCarthy and White [15] and of Kulikov [16], yields a value of $p_{O_2}$ of the order of $10^{-25}$–$10^{-26}$ atm. It is hardly possible that any compound based on copper oxides can exist at this pressure. Thus, one can safely assume that only

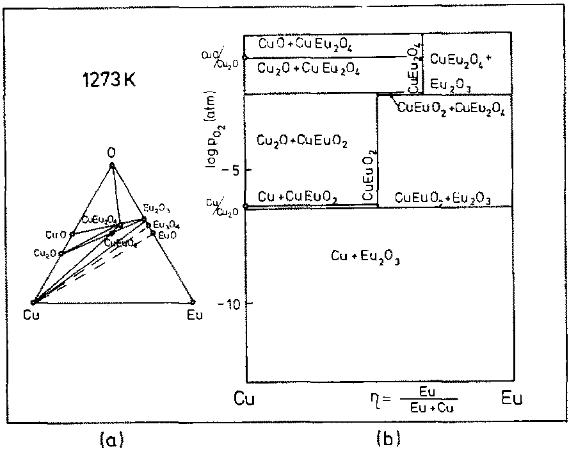

Fig. 4. Stability diagram of the Cu–Eu–O system at $T = 1273$ K.

$Eu_2O_3$ can take part in all reactions with copper oxides. Combining reaction (9) with that of the formation of cuprous oxide one can obtain

$$2Cu + Eu_2O_3 + \tfrac{1}{2}O_2 \Rightarrow 2CuEuO_2 \qquad (14)$$

and the respective Gibbs free energy change is

$$\Delta G^0_{14} = -175\,130 + 75.31T \text{ (J)} \qquad (15)$$

The calculated equilibrium oxygen partial pressure for reaction (14) indicates that, at 1273 K, $CuEuO_2$ will be formed under the pressure determined by $\log p_{O_2} = -6.502$, i.e. lower than that characteristic for Cu–$Cu_2O$ equilibrium ($\log p_{O_2} = -6.38$, see ref. 10). Equilibrium lines shown in Fig. 4 for higher oxygen pressure were derived from eqns. (7) and (8) and from ref. 10.

Finally, two more conclusions can be drawn from the measured quantities. The $CuEuO_2$ phase tends to decompose at high temperature into $Cu_2O$ and $Eu_2O_3$ [eqn. (10)]. Thus, the $Cu_2O$–$Eu_2O_3$–$CuEu_2O_4$ equilibrium field might exist only in the vicinity of the $Cu_2O$ melting point. In turn, $CuEu_2O_4$ is an entropy stabilized compound and becomes less stable at low temperature [eqn. (13)]. Thus, an exchange reaction

$$CuEu_2O_4 + Cu_2O \rightarrow 2CuEuO_2 + CuO \qquad (16)$$

can be anticipated at low temperature.

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