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Phase Relations in the System Cu-Eu-O and Thermodynamic Properties of $CuEu_2O_4$ and $CuEuO_2$

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Phase relations in the system Cu-Eu-O have been determined by equilibrating samples of different average composition at 1200 K and by phase analysis after quenching using optical microscopy (OM), x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive x-ray (EDX). The equilibration experiments were conducted in evacuated ampoules and under flowing inert gas and pure oxygen. The Cu-Eu alloys were found to be in equilibrium with EuO. The higher oxides of europium, Eu_3O_4 and Eu_2O_3, coexist with metallic copper. Two ternary oxides $CuEu_2O_4$ and $CuEuO_2$ were found to be stable. The ternary oxide $CuEuO_2$, with copper in the monovalent state, can coexist with Cu, Cu_2O, Eu_2O_3 and $CuEu_2O_4$ in different phase fields. The compound $CuEu_2O_4$ can be in equilibrium with Cu_2O, CuO, $CuEuO_2$, Eu_2O_3, and O_2 gas under different conditions at 1200 K. Thermodynamic properties of the ternary oxides were determined using three solid-state cells based on yttria-stabilized zirconia as the electrolyte in the temperature range from 875 to 1250 K. The cells essentially measure the oxygen chemical potential in the three-phase fields: $Cu+Eu_2O_3+CuEuO_2$, $Cu_2O+CuEuO_2+CuEu_2O_4$, and $Eu_2O_3+CuEuO_2+CuEu_2O_4$. The thermodynamic properties of the ternary oxides can be represented by the equations:

$$\tfrac{1}{2}\,Cu_2O + \tfrac{1}{2}\,Eu_2O_3\ (\text{C-rare earth}) \rightarrow CuEuO_2$$

$$\Delta_{f,ox}G°/\text{J mol}^{-1} = -570 - 0.463\ T/\text{K}\ (\pm 20)$$

$$CuO + Eu_2O_3\ (\text{C-rare earth}) \rightarrow CuEu_2O_4$$

$$\Delta_{f,ox}G°/\text{J mol}^{-1} = -3530 - 5.96\ T/\text{K}\ (\pm 110)$$

Thermogravimetric analysis (TGA) studies in Ar + O_2 mixtures confirmed the results from emf measurements. An oxygen potential diagram for the system Cu-Eu-O at 1200 K was evaluated from the results of this study and information available in the literature on the binary phases.

1. Introduction

Potential application of pure and doped lanthanide cuprates as electrodes, catalysts, and superconductors provides the motivation for the study of their stability domains in the temperature-composition-oxygen potential space. The ternaries Cu-*Ln*-O form one of the bounding surfaces of the quaternary systems *Ln*-Ba-Cu-O, which contain high-T_C superconducting oxides. Phase relations and accurate thermodynamic data on bounding ternary systems are fundamental inputs for the calculation of the properties of complex higher order systems. As a part of systematic investigations into the bounding ternaries of the multinary systems containing superconducting oxides, isothermal phase relations in the ternary Cu-Eu-O have been elucidated, and accurate thermodynamic data on two ternary oxides $CuEu_2O_4$ and $CuEuO_2$ determined using a solid-state electrochemical technique.

Tretyakov et al.[1] and Idemoto et al.[2] have tried to determine the Gibbs (*G*) energy of formation of $CuEu_2O_4$ by measuring the oxygen potential corresponding to the three-phase field $CuEu_2O_4 + Eu_2O_3 + Cu_2O$ using the solid-state electromotive force (emf) technique. As demonstrated in this study, the three-phase mixture supposedly used by these authors is not stable under equilibrium conditions. Tretyakov et al.[1] and Idemoto et al.[2] ignored the presence of the ternary oxide $CuEuO_2$ containing a cuprous ion. Hence, their results are not very reliable. Petrov et al.[3] and Fitzner[4] attempted to measure the *G* energies of formation of $CuEu_2O_4$ and $CuEuO_2$ using similar electrochemical cells incorporating oxide solid electrolytes. As demonstrated later in the discussion, the results of Petrov et al.[3] are not internally consistent. Results of Fitzner[4] are compatible with the phase diagram. The enthalpy of formation of $CuEu_2O_4$ from its component binary oxides deduced from the measurements of Fitzner[4] is 885 J mol^{-1}. Muromachi and Navrotsky[5] obtained a value of −1900 (±3500) J mol^{-1} for enthalpy of formation from binary oxides at 977 K using high-temperature solution calorimetry with molten $Pb_2B_2O_5$ as the solvent. Using a twin type microcalorimeter and aqueous $HClO_4$ solution as the solvent, Idemoto et al.[6]

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obtained a positive value of 10 100 (±3600) J mol^{-1} for the enthalpy of formation of $CuEu_2O_4$ from component oxides at room temperature. In view of the discrepancies in thermodynamic data reported in the literature, additional measurements were conducted using improved techniques.

All previous electrochemical measurements were conducted using the conventional two-electrode cell design with air as the reference electrode. When there is a large difference in the chemical potential of oxygen between the reference and working electrodes, there is always a small electrochemical flux of oxygen through the solid electrolyte, from the electrode with higher oxygen potential to the electrode with lower oxygen potential. The trace electronic conduction, as well as the consequent coupled migration of oxygen ions and electronic defects in the oxygen potential gradient, causes the flux.[7,8] The oxygen flux can polarize multiphase solid electrodes and cause errors in the measured thermodynamic data. Introduction of a buffer electrode between the reference and measuring electrodes to absorb the flux has been recently shown to minimize polarization and generate high-quality data.[9-11] In this study, oxygen chemical potentials corresponding to two three-phase mixtures were measured using the three-electrode cell design with pure oxygen gas at a pressure of 0.1 MPa as the reference electrode. The data were confirmed by measurements on a third cell and TGA under controlled Ar + O_2 mixtures.

2. Experimental Procedure

2.1 Materials

The ternary oxides $CuEu_2O_4$ and $CuEuO_2$ were prepared from component binary oxides CuO, Cu_2O, and Eu_2O_3, each of purity greater than 99.9%. Eu_2O_3 used in this study had the cubic (C-rare earth oxide, Mn_2O_3-type) structure with lattice parameter a = 1.086 nm. When heated above 1350 K, it transforms to a monoclinic form. For the synthesis of $CuEu_2O_4$, equimolar amounts of CuO and Eu_2O_3 were mixed, pelletized and heated at 1273 K in flowing dry oxygen for ~100 ks with intermittent grinding. The compound was black in color and had the T'-type structure (space group $I4/mmm$, $Z = 2$), which is closely related to the T-type (K_2NiF_4-type) structure. The metal positions are essentially the same in these structures, but the oxygen positions are different. Copper has square planar coordination and europium is 8-coordinated in $CuEu_2O_4$. The ternary oxide $CuEuO_2$ exhibiting yellow color was synthesized by heating pellets containing well-mixed stoichiometric amounts of Cu_2O and Eu_2O_3 in a zirconia crucible at 1223 K for 300 ks. The zirconia crucible was sealed in an evacuated quartz ampoule to prevent oxidation of Cu_2O. After heat treatment, pellets were quenched in liquid nitrogen or chilled mercury. Characterization using x-ray diffraction (XRD) showed the formation of single-phase compounds $CuEu_2O_4$ and $CuEuO_2$. The lattice parameters characterizing the tetragonal unit cell of $CuEu_2O_4$ were $a = b$ = 0.3901 and c = 1.189 nm. The unit cell parameters of rhombohedral ($R3m$, $Z = 3$) $CuEuO_2$ were $a = b$ = 0.36310 and c = 1.7066 nm. The lattice parameters obtained in this study are in good agreement with those published in the ICDD/JCPDS compilation.

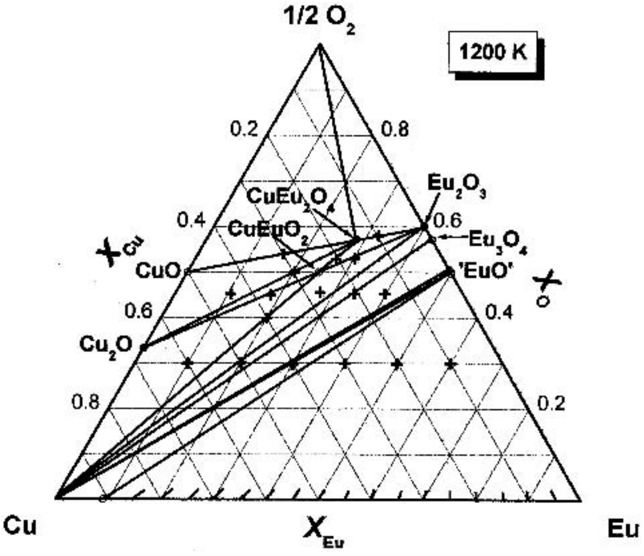

Fig. 1 Phase relations in the system Cu-Eu-O at 1200 K. The average composition of the analyzed samples is shown by the symbol (+).

Ultrahigh-purity argon gas used to provide an inert atmosphere was first dried by passing through silica gel, anhydrous $Mg(ClO_4)_2$ and P_2O_5, and then deoxidized by passing through copper wool at 723 K and titanium granules at 1100 K. High-purity oxygen was purified by passing over CuO at 800 K to convert residual CO to CO_2 and H_2 to H_2O. Pass over NaOH pellets then removed the CO_2 from oxygen. The oxygen was further dried using the same chemicals as described above for argon gas.

2.2 Phase Relations in the System Cu-Eu-O

Phase relations at 1200 K were established by equilibrating different mixtures of metals, alloys and oxides for ~450 ks. Preliminary experiments indicated that ~300 ks was sufficient to attain equilibrium. Samples representing 17 compositions inside the ternary triangle were investigated. The average compositions of the samples are shown in Fig. 1 by the plus sign. The samples containing metallic phases were equilibrated in closed molybdenum containers kept under pre-purified argon gas flowing at a rate of 3 ml s^{-1}. Oxide mixtures, containing either copper or europium in lower valent states, were equilibrated in closed zirconia crucibles, which were placed in evacuated quartz ampoules at a pressure of ~0.1 Pa. Oxide mixtures containing copper in divalent and europium in trivalent states were equilibrated in pure oxygen at a pressure of 0.1 MPa. After equilibration samples were quenched in liquid nitrogen or chilled mercury. Phase compositions of the quenched samples were determined using XRD, scanning electron microscopy (SEM), and energy-dispersive x-ray (EDX). To check for equilibrium, samples of the same overall composition were prepared using different starting materials. The approach to equilibrium from different directions was thus verified.

2.3 Electromotive Force Measurements

The reversible emf of the following cells were measured as a function of temperature in the range from 875 to 1250 K:

$$\text{Pt, Cu} + \text{CuEuO}_2 + \text{Eu}_2\text{O}_3 \parallel (\text{Y}_2\text{O}_3)\ \text{ZrO}_2 \parallel \text{Cu} + \text{Cu}_2\text{O, Pt} \qquad \text{(I)}$$

$$\text{Pt, Eu}_2\text{O}_3 + \text{CuEuO}_2 + \text{CuEu}_2\text{O}_4 \parallel (\text{Y}_2\text{O}_3)\ \text{ZrO}_2 \parallel \text{O}_2\ (0.1\ \text{MPa}), \text{Pt} \qquad \text{(II)}$$

$$\text{Pt, Cu}_2\text{O} + \text{CuEuO}_2 + \text{CuEu}_2\text{O}_4 \parallel (\text{Y}_2\text{O}_3)\ \text{ZrO}_2 \parallel \text{O}_2\ (0.1\ \text{MPa}), \text{Pt} \qquad \text{(III)}$$

The cells are written such that the right-hand electrodes are positive. They were designed based on phase relations established in this study. Cell I was fashioned such that the emf is directly related to the standard *G* energy of formation of $CuEuO_2$ from its component oxides Cu_2O and Eu_2O_3. The nature of phase relations in the system Cu-Eu-O does not permit the creation of a cell that will directly yield the *G* energy of formation of $CuEu_2O_4$ from CuO and Eu_2O_3. This information can be obtained indirectly by combining the emf of cell I with the emf of either cell II or cell III and the standard *G* energy change for the oxidation of Cu_2O to CuO. Alternatively, emfs of cells II and III can be combined with the *G* energy change for the oxidation of Cu_2O to CuO to generate the *G* energies of formation of the two ternary oxides. Thus, measurements on three cells provide for a check of internal consistency.

The solid-state cell I had a two-electrode design similar to that described by Jacob et al.[12] The simpler two-electrode design was adequate for measurements on cell I since the emf, and consequently the oxygen potential gradient across the electrolyte, was relatively small. The electrodes were prepared by mixing fine powders of metal and oxides. The compacted electrode pellets were presintered in a vacuum at 1050 K. The measuring and reference electrode compartments were physically separated by the electrolyte tube. Separate streams of pure, dry Ar gas were passed over each electrode. The temperature of the cell was monitored by a Pt / Pt-13% Rh thermocouple, and the emf was measured using a high impedance digital voltmeter. The reversibility of the emf was checked by microcoulometric titration in both directions. In each case, the emf returned to the original value. Temperature cycling confirmed the attainment of equilibrium during emf measurements. The emf was also independent of the flow rate of argon gas over the electrodes in the range 1.5-4 ml s^{-1}. After the attainment of thermal equilibrium, ~40 ks were required to attain steady emf at 873 K and ~8 ks at 1250 K. Slow establishment of equilibrium oxygen partial pressure over the three-phase electrode is probably responsible for the sluggish response of the cell. Often the cell was left overnight to check the stability of the emf.

For measurements on cells II and III, a three-electrode configuration[9-11] was used since the emfs were relatively large. A schematic of the three-electrode cell assembly is given below:

Measuring		Buffer		Reference
Electrode	$(Y_2O_3)ZrO_2$	Electrode	$(Y_2O_3)ZrO_2$	Electrode
$O_2(P''_{O_2})$, Pt	No flux	$O_2(P''_{O_2})$, Pt	$\leftarrow$	O_2(0.1 MPa), Pt
		$P'_{O_2} \approx P''_{O_2}$	O^{2-}	

It consisted of three distinct compartments, separated by two impervious yttria-stabilized zirconia tubes each closed at one end. The measuring and reference electrodes were contained inside separate zirconia tubes. When the difference in the chemical potential of oxygen between these electrodes is substantial, there is always a small flux of oxygen through the zirconia electrolyte separating them, even in the absence of physical porosity.[7,8] The electrochemical permeability is caused by the coupled transport of oxygen ions and electrons (or holes) in the solid electrolyte under the oxygen potential gradient. Only opposing it with an external direct current (dc) voltage, exactly equivalent to the oxygen chemical potential difference, can stop this flow of oxygen.[13]

The electrochemical flux of oxygen would have caused polarization of multiphase solid electrodes. The chemical potential of oxygen in the micro-system near the solid electrode/electrolyte interface would have been altered due to the semi-permeability of the electrolyte to oxygen. The buffer electrode, introduced between reference and measuring electrodes was designed to act as a sink for the oxygen flux and prevent the flux from reaching the measuring electrode. The buffer electrode was maintained at an oxygen chemical potential close to that of the measuring electrode. Since there was no significant difference between the chemical potentials of buffer and measuring electrodes, driving force for transport of oxygen through the zirconia tube separating these electrodes did not exist. The measuring electrode therefore remained non-polarized. Pure oxygen gas at a pressure of 0.1 MPa flowing over a platinized surface of zirconia constituted the primary reference standard for oxygen potential and formed a non-polarizable electrode. Thus, the three-electrode design of the cell prevented error in emf caused by polarization of the measuring electrode. Measuring the emf between the buffer and measuring electrodes assessed the magnitude of the polarization effect. In this study the polarization effect varied from 7-9 mV for cells II and III. The details of the cell assembly were the same as those reported earlier.[9-11]

The measuring electrodes were chosen based on the phase relations established at 1200 K for the ternary Cu-Eu-O. The measuring and buffer electrodes of cells II and III were kept under static vacuum during measurements since their equilibrium oxygen partial pressures are relatively high. When an inert gas flow was maintained over these electrodes at high temperature, oxygen was removed by entrainment in the gas. The static vacuum arrangement was found to be better than the inert gas flow system. Excess of the ternary oxide $CuEu_2O_4$ was used in the preparation of each electrode, since a small amount of this phase had to decompose initially to establish the equilibrium oxygen pressure in the apparatus. The electrode mixture was rammed against the closed end of a stabilized zirconia tube with a Pt lead embedded in the mixture.

2.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) studies on $CuEu_2O_4$ were conducted under Ar + 0.1% O_2 gas mixtures using a commercial apparatus (STA POLYMER 1500). The premixed gas mixture from a cylinder was dried using silica gel before use. Different flow rates of the gas mixture were used, up to maximum value of 90 ml s^{-1}. Initially trial runs were carried out to identify roughly the decomposition temperature of $CuEu_2O_4$. Subsequently, close to the decomposition temperature, between 1173 and 1273 K, heating was carried out at a slow rate of 0.0083 K s^{-1}. The slow heating rate was used to facilitate equilibration of the sample with the gas, and decomposition at the equilibrium temperature. At the slow heating rate, there was no sharp differential thermal analysis (DTA) signal. The residue after decomposition was cooled to room temperature under pure Ar gas and subjected to XRD for phase identification.

3. Results and Discussion

3.1 Phase Diagram

Phase relations in the system Cu-Eu-O at 1200 K composed from the results of this study are shown in Fig. 1. Along the binary Eu-O, three oxides were identified; nonstoichiometric $EuO_{1\pm x}$, Eu_3O_4 and Eu_2O_3. EuO had a cubic structure (*Fm*3*m*) with a = 0.5142 nm, black-colored Eu_3O_4 crystallized in the space group *Pnam* with a = 1.007, b = 1.204 and c = 0.3499 nm, and Eu_2O_3 had the Mn_2O_3-type structure with a = 1.087 nm. Two oxides, Cu_2O and CuO with cuprite and tenorite structures respectively, were present in the binary system Cu-O. A liquid alloy phase field and a two-phase region [Cu + $Cu_{1-x}Eu_x$ (*l*)], characterize the binary Cu-Eu at 1200 K. Two ternary oxides, $CuEuO_2$ and $CuEu_2O_4$, were identified inside the ternary triangle. Copper is monovalent in $CuEuO_2$ and divalent in $CuEu_2O_4$: europium is in the trivalent state in both compounds. All the alloy compositions were in equilibrium with EuO_{1-x}, which had a brownish-black color. The monoxide in equilibrium with pure liquid Eu had the composition $EuO_{0.988}$, and that in equilibrium with Eu_3O_4 had the composition $EuO_{1.02}$ at 1200 K. Pure copper metal coexisted with all three europium oxides under different conditions. Eight three-phase fields involving condensed phases were identified. They are

(i) Cu + $Cu_{0.91}Eu_{0.09}$ (*l*) + EuO_{1-x},
(ii) Cu + EuO_{1+x} + Eu_3O_4,
(iii) Cu + Eu_3O_4 + Eu_2O_3,
(iv) Cu + Eu_2O_3 + $CuEuO_2$,
(v) Cu + Cu_2O + $CuEuO_2$,
(vi) $CuEuO_2$ + $CuEu_2O_4$ + Eu_2O_3,
(vii) Cu_2O + $CuEuO_2$ + $CuEu_2O_4$, and
(viii) Cu_2O + CuO + $CuEu_2O_4$.

The phases $CuEu_2O_4$ and Cu can not coexist at equilibrium. Similarly, there is no tie line connecting $CuEuO_2$ and CuO. Solid solubility between the oxides was negligible (<0.2 mol %) at 1200 K. According to the phase rule, each three-phase field is associated with zero degree of freedom at constant temperature. Hence, each of these phase fields is characterized by a unique oxygen partial pressure. The oxygen potential associated with four of the three-phase fields, (ii, iii, v, and viii), can be computed from thermodynamic data on the binary oxides available in the literature. The activity of Eu in the liquid alloy and the standard *G* energy of formation of EuO determine the oxygen potential corresponding to the first three-phase field. The oxygen potentials corresponding to the three remaining phase fields (iv, vi and vii) were measured in this study. Thermodynamic considerations require oxygen potential to increase in the phase fields traversed when one proceeds in a straight line from any point on the binary Cu-Eu toward the oxygen apex in Fig. 1.

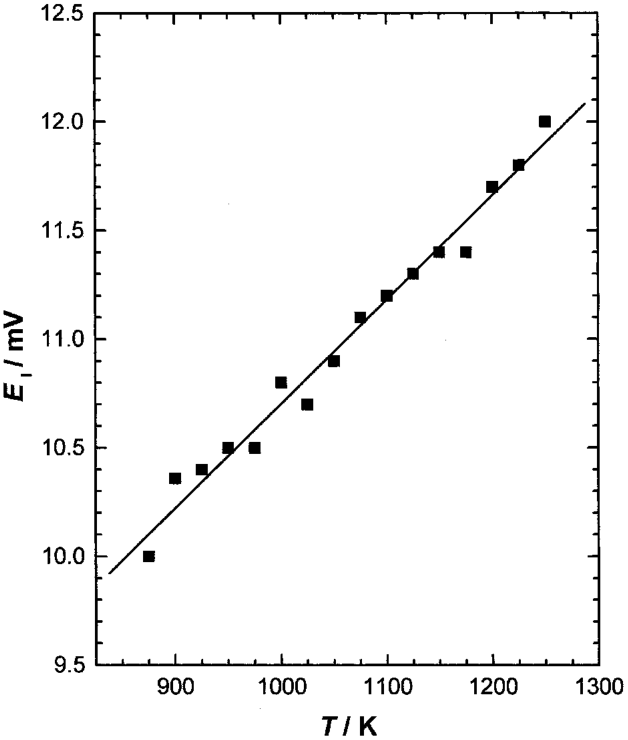

Fig. 2 Reversible emf of cell I as a function of temperature

3.2 Thermodynamic Properties

The reversible emf of cell I is displayed in Fig.2 as a function of temperature. The least-squares regression analysis gives the expression:

$$E_I/\text{mV} = 5.9 + 0.0048\ T/\text{K}\ (\pm 0.17) \qquad \text{(Eq 1)}$$

The electrochemical reaction at the right-hand electrode of cell I is

$$Cu_2O + 2e^- \rightarrow 2\ Cu + O^{2-} \qquad \text{(Eq 2)}$$

At the left-hand electrode, the electrochemical reaction is,

$$2\ \mathrm{Cu} + \mathrm{O}^{2-} + \mathrm{Eu_2O_3}\ (\text{C-rare earth}) \rightarrow 2\ \mathrm{CuEuO_2} + 2\ e^- \qquad \text{(Eq 3)}$$

The virtual cell reaction, obtained by combining the two half-cell reactions, is

$$\mathrm{Cu_2O} + \mathrm{Eu_2O_3}\ (\text{C-rare earth}) \rightarrow 2\ \mathrm{CuEuO_2} \qquad \text{(Eq 4)}$$

Because Eu_2O_3 is polymorphic, the structure of the compound used in this study is specified to avoid ambiguity.: The emf of cell I is directly related to the standard *G* energy change for reaction 4:

$$\Delta_{r(4)}G^{o}/\mathrm{J\ mol^{-1}} = -2\mathrm{F}E_{\mathrm{I}} = -1140 - 0.926\ T/\mathrm{K}\ (\pm 35) \qquad \text{(Eq 5)}$$

where F = 96 485 J V^{-1} mol^{-1} is the Faraday constant. The standard *G* energy of formation of $CuEuO_2$ from its component oxides Cu_2O (cuprite) and Eu_2O_3 (cubic) is exactly half the *G* energy change given by Eq 5:

$$\tfrac{1}{2}\ \mathrm{Cu_2O} + \tfrac{1}{2}\ \mathrm{Eu_2O_3}\ (\text{C-rare earth}) \rightarrow \mathrm{CuEuO_2} \qquad \text{(Eq 6)}$$

$$\Delta_{f,ox}G^{o}/\mathrm{J\ mol^{-1}} = -570 - 0.463\ T/\mathrm{K}\ (\pm 18) \qquad \text{(Eq 7)}$$

The temperature-independent term gives the enthalpy of formation, and the temperature-dependent term is related to the entropy of formation. The ternary oxide is only marginally stable relative to its component binary oxides. The standard *G* energy of formation of $CuEuO_2$ from its component oxides obtained in this study is compared with the results of Fitzner[4] as a function of temperature in Fig. 3. Although the values from the two studies are in reasonable agreement at a temperature of 1120 K, the temperature coefficients of the *G* energy have opposite signs. Calorimetric data on either the enthalpy of formation or entropy of $CuEuO_2$ will be useful to resolve the discrepancy.

The oxygen potential corresponding to the equilibrium between the three phases Cu, Eu_2O_3, and $CuEuO_2$ can be computed from the emf of cell I and the oxygen potential for the Cu + Cu_2O reference.[14] The oxygen potential is defined by

$$4\ \mathrm{Cu} + \mathrm{O_2} + 2\ \mathrm{Eu_2O_3}\ (\text{C-rare earth}) \rightarrow 4\ \mathrm{CuEuO_2} \qquad \text{(Eq 8)}$$

$$\Delta\mu_{\mathrm{O_2}}/\mathrm{J\ mol^{-1}} = -337\,660 + 141.35T\ (\pm 845) \qquad \text{(Eq 9)}$$

The major source of uncertainty in Eq (9) comes form thermodynamic data for pure Cu_2O [$\Delta_f G^o/\mathrm{J\ mol^{-1}} = -167\,690 + 71.60\ T/\mathrm{K}\ (\pm 420)$].[14]

The temperature dependence of the reversible emfs of cells II and III are shown in Fig. 4. The least-squares regression analysis gives

$$E_{\mathrm{II}}/\mathrm{mV} = 706.7 - 0.4297\ T/\mathrm{K}\ (\pm 0.40) \qquad \text{(Eq 10)}$$

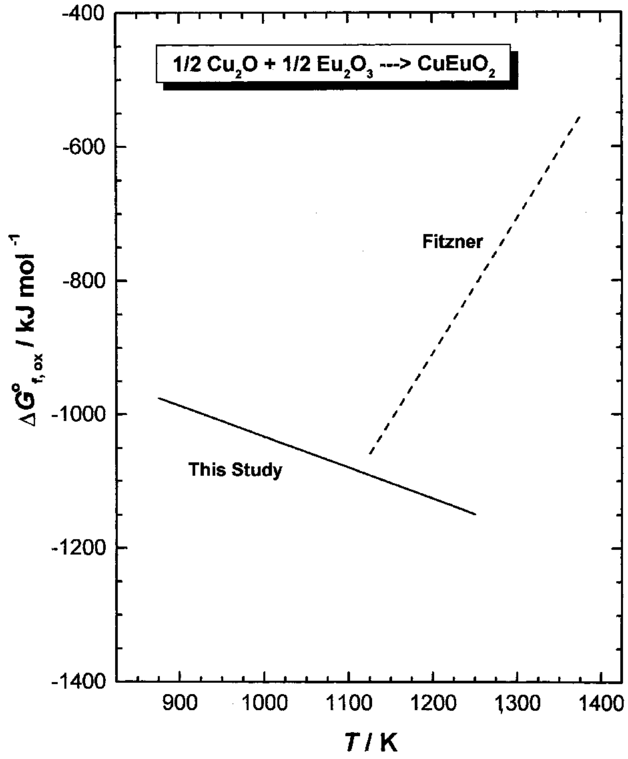

Fig. 3 Temperature dependence of the standard *G* energy of formation of $CuEuO_2$ from its component binary oxides with comparison of the results obtained in this study and data in the literature[4]

$$E_{\mathrm{III}}/\mathrm{mV} = 700.8 - 0.4345\ T/\mathrm{K}\ (\pm 0.44) \qquad \text{(Eq 11)}$$

The emf of cell II gives directly the oxygen potential for three-phase equilibrium defined by the reaction:

$$4\ \mathrm{CuEuO_2} + 2\ \mathrm{Eu_2O_3}\ (\text{C-rare earth}) + \mathrm{O_2} \rightarrow 4\ \mathrm{CuEu_2O_4} \qquad \text{(Eq 12)}$$

The oxygen chemical potential corresponding to the three-phase field $CuEuO_2$ + $CuEu_2O_4$ + Eu_2O_3 is given by

$$\Delta\mu_{\mathrm{O_2}}/\mathrm{J\ mol^{-1}} = -4\mathrm{F}E_{\mathrm{II}} = -272\,744 + 165.84\ T/\mathrm{K}\ (\pm 155) \qquad \text{(Eq 13)}$$

The oxygen potential measured in this study is compared with those reported by Petrov et al.[3] and Fitzner[4] in Fig. 5. In the common temperature range, the results of this study are about 5 kJ mol^{-1} more negative than that reported by Fitzner.[4] The data of Petrov et al.[3] are internally inconsistent as discussed below.

The emf of cell III directly gives the oxygen potential for three-phase equilibrium defined by the reaction:

$$8\ \mathrm{CuEuO_2} + \mathrm{O_2} \rightarrow 4\ \mathrm{CuEu_2O_4} + 2\ \mathrm{Cu_2O} \qquad \text{(Eq 14)}$$

$$\Delta\mu_{\mathrm{O_2}}/\mathrm{J\ mol^{-1}} = -4\mathrm{F}E_{\mathrm{III}} = -270\,466 + 167.69\ T/\mathrm{K}\ (\pm 170) \qquad \text{(Eq 15)}$$

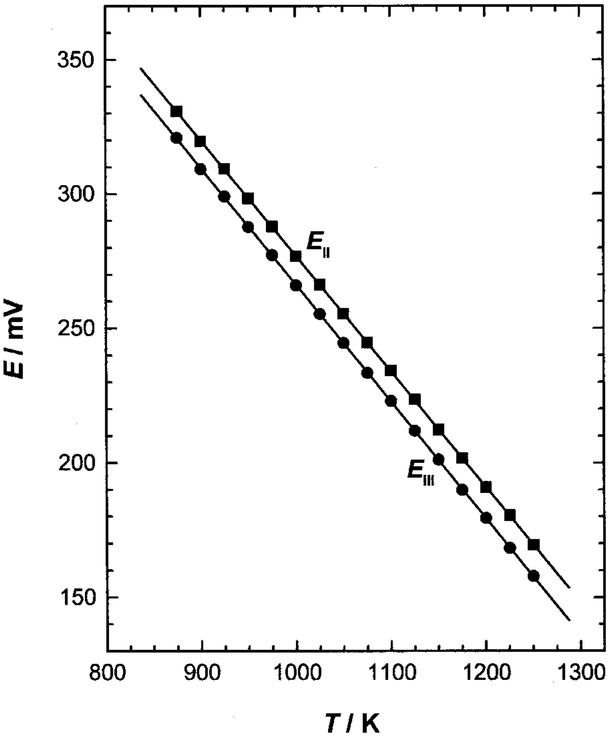

Fig. 4 The reversible emfs of cells II and III as a function of temperature

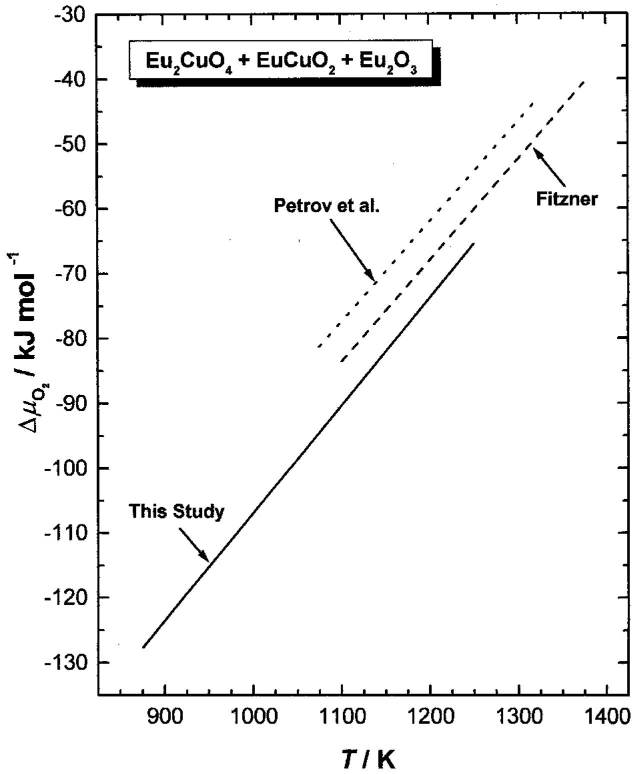

Fig. 5 Comparison of the oxygen chemical potential measured in this study for the three-phase field $CuEu_2O_4$+ $CuEuO_2$ + Eu_2O_3 with information in the literature[3,4]

Figure 6 compares the values obtained in this study with those of Petrov et al.[3] and Fitzner.[4] The results of this study are in excellent agreement with the measurements of Petrov et al.[3] for the $CuEu_2O_4$+$CuEuO_2$+Cu_2O equilibrium; they are again approximately 5 kJ mol^{-1} more negative than that reported by Fitzner.[4] It is quite likely that this error is caused by polarization of their three-phase electrodes as a result of the electrochemical flux of oxygen through the solid electrolyte from the reference side. The oxygen potentials measured in this study using the new cell design with buffer electrodes are more reliable.

The oxygen potential corresponding to Cu_2O + CuO has been reported in an earlier publication[14] as

$$\Delta\mu_{O_2}/\text{J mol}^{-1} = -260\,889 + 187.82\ T/\text{K}\ (\pm 420) \qquad \text{(Eq 16)}$$

Combining Eq 16 with Eq 5 and 13, standard Gibbs energy of formation of $CuEu_2O_4$ from component binary oxides CuO and Eu_2O_3 is obtained:

$$CuO + Eu_2O_3\ (\text{C-rare earth}) \rightarrow CuEu_2O_4 \qquad \text{(Eq 17)}$$

$$\Delta_{f,ox}G^o/\text{J mol}^{-1} = -3530 - 5.96\ T/\text{K}\ (\pm 110) \qquad \text{(Eq 18)}$$

Almost identical values for $CuEu_2O_4$ are obtained by combining Eq 16, 5, and 15, thus demonstrating internal consistency between emfs of the three cells. The data obtained in this study are compared in Fig. 7 with other values reported in the literature. There is fair agreement with the data of Fitzner.[4] The results of Tretyakov et al.[1] and Idemoto et al.[2] are significantly more positive. They measured the oxygen potential corresponding to the three-phase mixture $CuEu_2O_4$ + Eu_2O_3 + Cu_2O. Figure 1 indicates that the three phases at their electrodes are not in equilibrium. Tretyakov et al.[1] and Idemoto et al.[2] ignored the presence of the ternary oxide $CuEuO_2$. Hence, their results are not reliable. The "second-law" enthalpy of formation of $CuEu_2O_4$ from its component oxides obtained from emf measurement at a mean temperature of 1060 K is −3.53 (±0.5) kJ mol^{-1}. It is in fair agreement with the value of −1.9 (±3.5) kJ mol^{-1} reported by Muromachi and Navrotsky[5] at 977 K, but strongly disagrees with the positive value of 10.1 (±3.6) kJ mol^{-1} at room temperature recorded by Idemoto et al.[6]

TGA studies on $CuEu_2O_4$ in Ar + 0.1% O_2 gas mixture showed the decomposition at 1221 (±2) K with a mass loss of 1.82%, which is in close agreement with theoretical value of 1.8%. A moderate change in the flow rate of the gas did not significantly affect the result. The phases present in the residue after decomposition were identified as $CuEuO_2$ and Eu_2O_3 by XRD. The decomposition reaction can therefore be written as

$$CuEu_2O_4 \rightarrow CuEuO_2 + \tfrac{1}{2} Eu_2O_3\ (\text{C-rare earth}) + \tfrac{1}{4} O_2 \qquad \text{(Eq 19)}$$

The decomposition temperature calculated from the measured oxygen potential corresponding to the three-phase

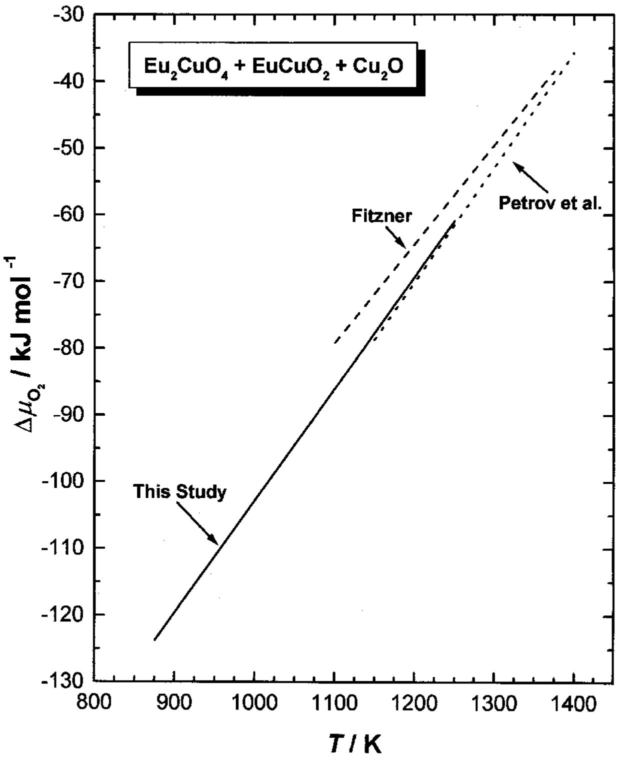

Fig. 6 Comparison of the oxygen chemical potential measured in this study for the three-phase field Cu_2O + $CuEuO_2$ + $CuEu_2O_4$ with data in the literature[3,4]

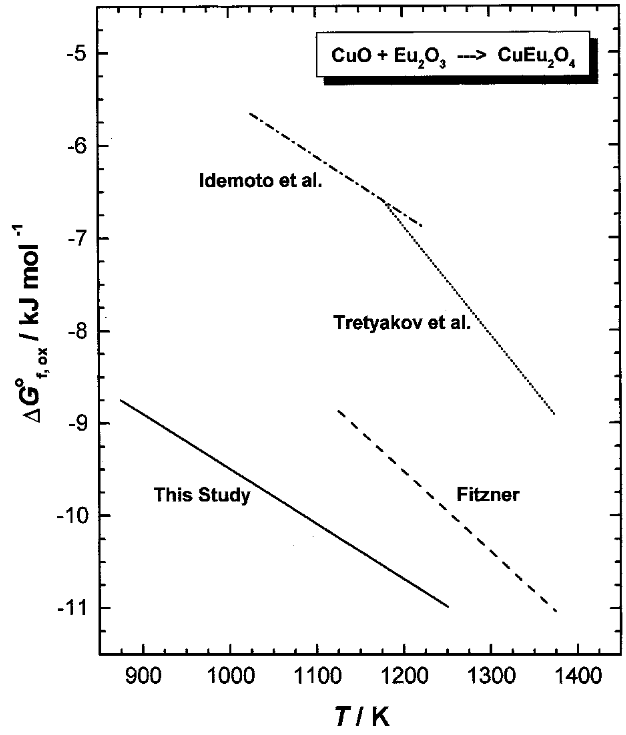

Fig. 7 Temperature dependence of the standard *G* energy of formation of $CuEu_2O_4$ from its component binary oxides and comparison of the data obtained in this study with those given in the literature[1,2,4]

field $CuEuO_2$ + $CuEu_2O_4$ + Eu_2O_3 using cell II is 1221.5 K. Thus, TGA studies confirm the results obtained from electrochemical measurements.

Petrov et al.[3] measured the emf's of two solid-state cells:

Pt, $CuEu_2O_4$ + $CuEuO_2$ + Eu_2O_3 | | Oxide Electrolyte | | O_2 ($P_{O_2}/P^o = 0.21$), Pt (IV)

in the temperature range from 1073 to1330 K, and

Pt, $CuEu_2O_4$ + $CuEuO_2$ + Cu_2O | | Oxide Electrolyte | | O_2 ($P_{O_2}/P^o = 0.21$), Pt (V)

in the range 1157-1415 K. Since the oxygen potential corresponding to three-phase field $CuEu_2O_4$ + $CuEuO_2$ + Cu_2O should be higher than that for the field $CuEu_2O_4$ + $CuEuO_2$ + Eu_2O_3 according to the phase diagram, the emf of the cells (IV) should be higher than that of cell (V). The data reported by Petrov et al.[3] show the reverse:

$$E_{IV}/\text{mV} = 640 - 0.433\ T/\text{K}\ (\pm 0.4) \qquad \text{(Eq 20)}$$

$$E_{V}/\text{mV} = 716 - 0.479\ T/\text{K}\ (\pm 0.5) \qquad \text{(Eq 21)}$$

Thus, the emf results of Petrov et al.[3] are inconsistent with the phase diagram. The inconsistency can be demonstrated in many ways. For example, by combining the emf of the two cells reported by Petrov et al.,[3] the standard *G* energy of formation of $CuEuO_2$ from component oxides Cu_2O and Eu_2O_3 according to reaction 6 can be derived as

$$\Delta_{f,ox}G^o/\text{J mol}^{-1} = 14\,670 - 8.88\ T/\text{K} \qquad \text{(Eq 22)}$$

which suggests that $CuEuO_2$ is unstable below 1652 K. Not only are the measured emf data inconsistent, but the derived standard *G* energy changes for decomposition reactions are also inconsistent with emf. Therefore, reliable thermodynamic properties of $CuEu_2O_4$ and $CuEuO_2$ cannot be obtained from Petrov et al.[3] By comparison with the results of this study, the error in the measurements of Petrov et al.[3] can be located at one of their cells, identified as cell IV above. The other cell used by them (cell-V above) appears to have functioned well. Fitzner[4] also used emf cells similar to those of Petrov et al.[3] to measure oxygen chemical potentials and also *G* energies in the system Cu-Eu-O. The oxygen potentials reported by Fitzner[4] for two three-phase fields are in the correct sequence.

3.3 Oxygen Potential Diagram

The oxygen potential diagram for the system Cu-Eu-O at 1200 K, composed from the results of this study and data from the literature on binary oxides[14-18] and alloys,[19] is shown in Fig. 8. The composition of a component is nor-

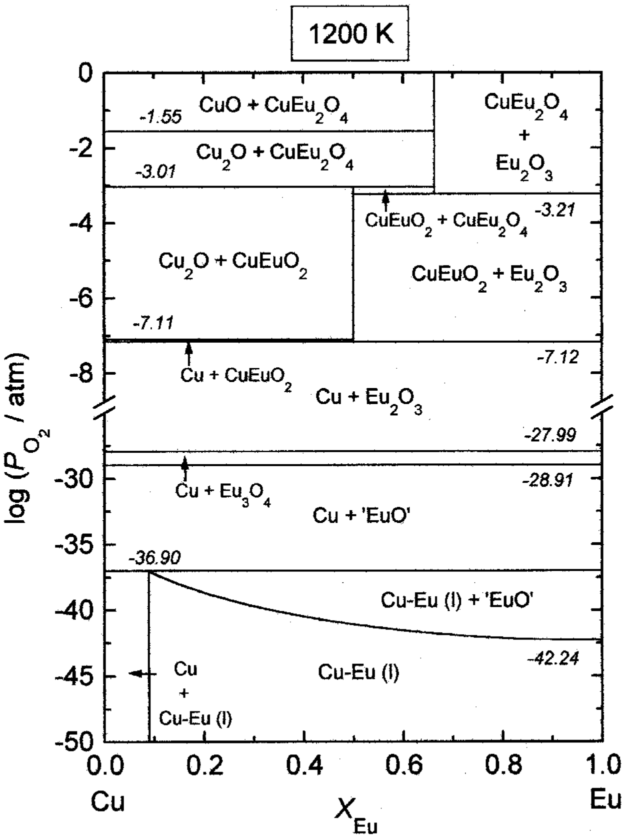

Fig. 8 Oxygen chemical potential diagram for the system Cu-Eu-O at 1200 K composed from the results obtained in this study

mally designated by its mole fraction, which is obtained by dividing the number of moles of the component by the sum of moles of all components. The normalized mole fraction, used as the composition variable in the chemical potential diagram, is obtained by removing the component (in the present case, oxygen), the chemical potential of which is being plotted, from the summation. The normalized mole fraction on the X-axis is identical to the cationic fraction of Eu ($\eta_{Eu}/\eta_{Eu} + \eta_{Cu}$) in oxides, where η_i represent moles of component i. With this choice of composition variable, the chemical potential of oxygen becomes an independent variable. However, since oxygen is not included in the composition parameter, information on oxygen nonstoichiometry cannot be displayed on the diagram. Nevertheless, the diagram provides useful information on the oxygen potential range for the stability of various phases. The diagram is complimentary to the conventional *G* triangle representation of phase relations in the ternary Cu-Eu-O (Fig. 1). When three condensed phases and a gas phase coexist at equilibrium in the ternary Cu-Eu-O, the system is mono-variant; at a fixed temperature, three condensed phases coexist only at a unique partial pressure of oxygen. Horizontal lines on the diagram therefore represent equilibria involving three condensed phases.

Chemical potential of oxygen corresponding to the equilibria Cu+Cu_2O, Cu_2O+CuO, Eu + EuO, EuO + Eu_3O_4, and Eu_3O_4 + Eu_2O_3 were calculated from the available thermodynamic data on binary europium oxides. For the alloy Cu-Eu, *G* energy of mixing (ΔG^m) at 1200 K was represented by a sub-regular solution model,[19]

$$\Delta G^m/\text{J mol}^{-1} = X_{Cu}X_{Eu}[-48\,406 + 18\,100\,X_{Eu}] + RT\{X_{Cu}\ln X_{Cu} + X_{Eu}\ln X_{Eu}\} \quad \text{(Eq 23)}$$

The activity of Eu in the liquid alloy Cu-Eu (*L*) was calculated using the expression for the *G* energy of mixing. From the standard *G* energy of formation of EuO and activity of Eu in the liquid alloy Cu-Eu, partial pressure of oxygen for the two-phase field Cu-Eu (*L*) + EuO was obtained at 1200 K:

$$\log(P_{O_2}/\text{atm}) = \{[2\Delta_f G^o(\text{EuO})/2.303\,RT] - 2\log a_{Eu}\} \quad \text{(Eq 24)}$$

Experimental measurement of the chemical potential of oxygen for the equilibrium involving Cu-Eu (*L*) and 'EuO' is difficult since the partial pressures of oxygen range from log (P_{O_2}/atm) = −42.24 to −36.90 at 1200 K, well below the domain of application of current techniques. The values of P_{O_2} for the three-phase fields starting from Cu + $CuEuO_2$ + Eu_2O_3 to Cu_2O + $CuEuO_2$ + $CuEu_2O_4$ are based on electrochemical measurements reported in this article.

4. Conclusions

The phase diagram for the ternary system Cu-Eu-O has been experimentally determined at 1200 K by phase analysis of quenched samples using XRD, SEM, and EDX. There are two stable ternary oxides in the system $CuEuO_2$ and $CuEu_2O_4$. Based on the isothermal phase relations, solid-state cells were designed for the measurement of thermodynamic properties of the ternary oxides. Although measurements on two solid-state cells were sufficient to generate the data, three cells were actually used to provide a crosscheck on derived data. A novel three-electrode design, with a buffer electrode placed between the reference and measuring electrodes, minimized errors due to polarization during measurement of oxygen potential in the three-phase fields relative to pure diatomic oxygen gas as the reference. TGA studies on $CuEu_2O_4$ under controlled partial pressure of oxygen (Ar + 0.1% O_2) confirmed the results obtained from emf measurements. The standard *G* energies of formation for the ternary oxides $CuEuO_2$ and $CuEu_2O_4$ obtained in the current study are compared with values reported in the literature. An oxygen chemical potential diagram is constructed for the ternary system Cu-Eu-O at 1200 K from the results obtained in the current study and data available in the literature. The stability domain of alloys and oxides are clearly shown on the diagram as a function of oxygen potential.

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