Preparation and Stoichiometry of EuTe–SrTe Solid Solution*

J. HAUCK[†], F.-J. BÖRGERMANN** and D. WILLMANN

Institut für Festkörperforschung, KFA Jülich, D-5170 Jülich, F.R.G.

The antiferromagnetic EuTe can be diluted with diamagnetic SrTe in a solid solution of NaCl structure with spin glass properties below $T = 3$ K at 15–50% EuTe [1]. Neutron scattering data for determination of the short-range order of magnetic moments can only be obtained from solids containing the isotope ^{153}Eu because of the large absorption of natural ^{151}Eu. The ^{153}Eu isotope is only available as $^{153}Eu_2O_3$ (Hempel, Düsseldorf). Therefore we started the present investigation to find a procedure to prepare EuTe–SrTe solid solutions with Eu_2O_3 as a starting material.

Usually EuTe, SrTe and the solid solution of both are prepared by melting the elements in sealed tungsten crucibles to prevent the volatilization of tellurium [2]. Another method for the preparation of EuTe is the reaction of Eu(II)-oxalate with H_2Te at elevated temperatures [3]. SrTe with oxide impurities can be obtained by reduction of $SrTeO_3$ in H_2 [4]. The latter experiments suggest that EuTe–SrTe solid solutions can be obtained from oxides in a Te_2 atmosphere at low $p(O_2)$ of H_2 to reduce the oxygen content and reduce Eu^{3+} to Eu^{2+}. The Te-rich tellurites(IV) $Eu_2Te_4O_{11}$ and $SrTe_2O_5$, which can be obtained from TeO_2, Eu_2O_3 or $SrCO_3$, respectively in N_2 [5, 6], were reduced to EuTe and SrTe above the melting point of the excess Te at 450 °C, so that the $p(Te_2)$ partial pressure was high enough for telluride formation. The samples prepared at ~450–800 °C, however, contained Eu_2O_2Te and SrO or $SrCO_3$ impurities because of the sluggish reaction and the relatively fast volatilization of Te at increased temperatures. The loss of Te had to be compensated by a Te melt at ~600 °C which yields $p(Te_2) = 8$ mbar [7]. With this $p(Te_2)$ partial pressure, homogeneous EuTe–SrTe solid solutions could also be obtained from $Eu_2O_3/SrCO_3/Te$ mixtures within 1–3 h above ~900 °C. At temperatures above ~1150 °C the $p(Te_2)$ partial pressure of EuTe is too high, leading to decomposition. Therefore, 1050 °C was chosen as the proper temperature for the experiments in 1 bar of H_2. These samples can contain Eu^{3+} besides Eu^{2+}, an excess of Te [8], and oxygen impurities within the general formula $Eu_xSr_{1-x}Te_yO_z$. Therefore, we determined the deviation of stoichiometry to obtain well characterized samples for investigation of spin glass properties.

Experimental

Preparation and Analysis of $Eu_xSr_{1-x}Te_yO_z$ Solid Solutions

Eu_2O_3 (99.99%, Auer-Remy, Hamburg) and $SrCO_3$ (pure, Merck, Darmstadt) were mixed carefully in different ratios and 0.5–1 g of the mixtures were reacted in corundum crucibles for 2 h at 1050 °C in a flow of 308 ml/min H_2 (99.999%) from a $FeTiH_x$ tank [9]. The Eu_2O_3 which was dried at 110 °C lost about 6% of its initial weight on heating for 2 h at 1050 °C, which might be due to a stable hydrate [10] and this had to be considered for the determination of the Eu/Sr ratio. A crucible with ~5 g Te (99.9999%, Preussag Metall, Goslar) was placed in the silica tube in the 600 °C hot zone of the furnace, to supply a constant tellurium partial pressure of 8 mbar [7]. The oxygen partial pressure could be varied by mixing CO_2 with H_2 at a constant flow rate with a gas mixing pump (Wösthoff, Bochum). The influence of $p(Te_2)$ was neglected for the determination of oxygen partial pressure from the H_2/CO_2 ratio [11]. After the reaction the horizontal furnace could be opened to take out the quartz tube for rapid cooling on a cold steel platform. The samples were analysed immediately afterwards in air or stored in an argon box, because of the increase in Eu^{3+} content after keeping the samples several hours in air. The following methods were applied for characterization:

(a) The phases were analysed by X-ray diffraction (Bragg–Brentano and Guinier geometry) with a least-squares refinement of lattice constant after correction of diffraction angle by the Au standard with $a = 407.86$ pm as reference.

(b) The Eu^{3+}/Eu^{2+} ratio of natural ^{151}Eu was determined by Mössbauer spectroscopy with $^{151}Sm_2O_3$ as source.

(c) The Te content relative to Eu and Sr was determined by atom emission spectroscopy.

(d) The oxygen content could be determined from the change of weight during preparation when oxygen of europium and strontium oxide is replaced by the heavy Te and combination of these data with the Eu^{3+} content and the Te/(Eu + Sr) ratio. The change

---

*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

[†]Author to whom correspondence should be addressed.

**Present address: Vakuumschmelze GmbH, Rhenaniastr. 9/17, 1000 Berlin 20.

0020-1693/87/$3.50

of mass $\Delta m/m$ is related to the mass m of Eu_2O_3 + SrO (= 100%).

Results

Figure 1 exhibits the phase relations of the $Eu_xSr_{1-x}Te_yO_z$ system at 1050 °C, $p = 1$ bar, $p(Te_2) = 8$ mbar and varied oxygen partial pressures. A complete $Eu_xSr_{1-x}Te_yO_z$ solid solution with NaCl structure is formed below $p(O_2) = 10^{-16.5}$ bar (4% CO_2). EuTe is successively oxidized to tetragonal Eu_2O_2Te ($a = 397.9$, $c = 1258.1$ pm, isomorphous with Nd_2O_2Te [12]) and at $p(O_2) = 10^{-16}$ bar (7% CO_2) to monoclinic Eu_2O_3. The occurrence of cubic Eu_2O_3 at slightly increased $p(O_2)$ might be due to a different Sr or Te content in comparison to the monoclinic modification, which was not investigated in detail. SrTe is oxidized to SrO or $SrCO_3$, respectively, at $p(O_2) = 10^{-12}$ bar of a 80% CO_2/20% H_2 mixture.

Samples prepared in pure H_2 with $p(O_2) \leqslant 10^{-22}$ bar still exhibit ~10% Eu^{3+} out of the total Eu content, which scatters somewhat depending on oxygen impurities and $p(Te_2)$ partial pressure (Fig. 2). The oxygen partial pressure decreases about 10 times stronger than the decrease of O_2, H_2O or CO_2 impurities in H_2, so that $p(O_2)$ of very pure H_2 is not well defined. The ratio $y = Te/(Eu + Sr)$ increases from 1.030 ± 0.003 at high Eu content to 1.100 ± 0.005 at high Sr content. It can be concluded from these data that the Eu^{3+} charge of Eu-rich samples is partially compensated by the excess of Te^{2-} and to a fraction $z = 0.02$ by O^{2-}, which is also in reasonable agreement with the change of weight, as discussed later in Fig. 6. At high Sr content, e.g. at $x = 0.1$, the negative charge $q^- = 2.20$ of $Te_{1.10}{}^{2-}$ would be larger than the total positive charge $q^+ = 2.01$ of $Eu_{0.09}{}^{2+}$-$Eu_{0.01}{}^{3+}Sr_{0.9}{}^{2+}$. For the compensation of charge, at least 9.5% Te should be in oxidation state Te^0 and a larger fraction if the solid solution contains O^{2-}.

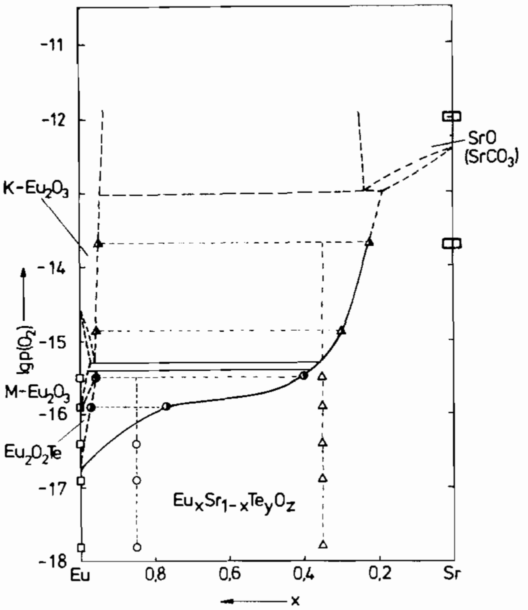

Fig. 1. Phase relations of the $Eu_xSr_{1-x}Te_yO_z$ system at 1050 °C and $p(Te_2) = 8$ mbar depending on the oxygen partial pressures of H_2/CO_2 mixtures at $p = 1$ bar.

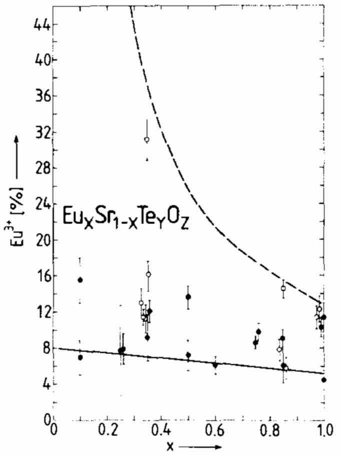

Fig. 2. Eu^{3+} relative to total Eu content for $Eu_xSr_{1-x}Te_yO_z$ samples prepared in H_2 (closed circles, lower limit, full line) or in H_2/CO_2 mixtures at increased $p(O_2)$ (open circles, upper limit, dashed line).

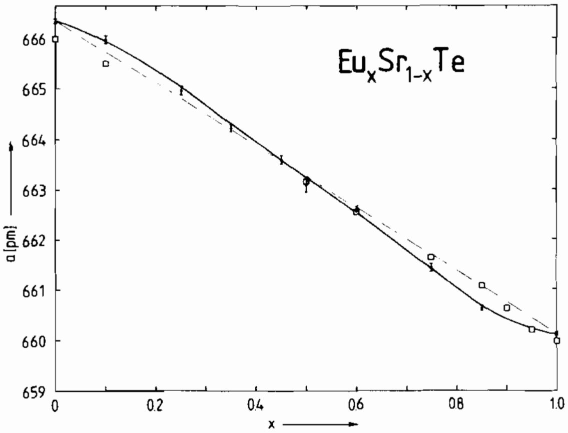

Fig. 3. Lattice constants of $Eu_xSr_{1-x}Te_yO_z$ solid solution prepared in H_2 (♦) compared to single crystal data (□) [13].

The lattice constants of the solid solution prepared in H_2 can be compared to lattice parameters of $Eu_xSr_{1-x}Te$ single crystals [13] prepared by melting the elements (Fig. 3). The single crystals contain less than 1% Eu^{3+}, very little oxygen [2] and the Te content $y = 0.99$ is close to stoichiometry. The smaller lattice constant of powder samples with high Eu content compared to single crystals might be due to the partial replacement of Eu^{2+} by the smaller Eu^{3+}, of Te^{2-} by the smaller O^{2-} and by ~5% vacancies in the metal sublattice at an excess of Te^{2-} and O^{2-}. At high Sr content the lattice constants of powder samples prepared in H_2 are increased compared to single crystal data. This may be due to an excess of the smaller Te^0 and O^{2-} at interstitial sites. The different behaviour of lattice constants at low and high Eu content suggests that both factors influence the intermediate solid solution, where lattice parameters are very close to single crystal data.

At increased $p(O_2)$ in H_2/CO_2 mixtures, the Eu^{3+} content of the single phase material increases to about 13% at the Eu-rich side and to larger values at increased Sr content, so that the Eu^{3+} content relative to Eu + Sr content amounts to ~13% (Figs. 2, 4). The mass change $\Delta m/m$ (Fig. 5) exhibits behaviour similar to the Eu^{3+} content. The values increase continuously in the single phase or two phase region and exhibit steps for the coexistence of two or three solid phases, as shown in Fig. 1. The Eu^{3+} content, $\Delta m/m$ values and y = Te/Eu values for $EuTe_yO_z$ can be compared to values calculated for the system EuTe–EuO–'Eu_2Te_3'–Eu_2O_3 (Fig. 6). The combination of Eu^{3+} content and y = Te/Eu ratio (closed circles) or the combination of Eu^{3+} content and $\Delta m/m$ values (open circles) yield somewhat different values for the composition. The plot shows that the sample prepared in H_2 exhibits 2% oxygen which increases at increased oxygen partial pressure by ~5% before the sample is oxidized to Eu_2O_2Te and Eu_2O_3.

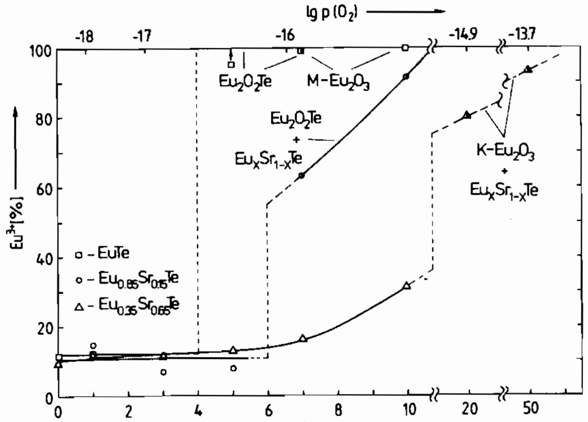

Fig. 4. Eu^{3+} content of $Eu_xSr_{1-x}Te_yO_z$ samples (x = 1, 0.85, 0.35) at different $p(O_2)$ of H_2/CO_2 mixtures.

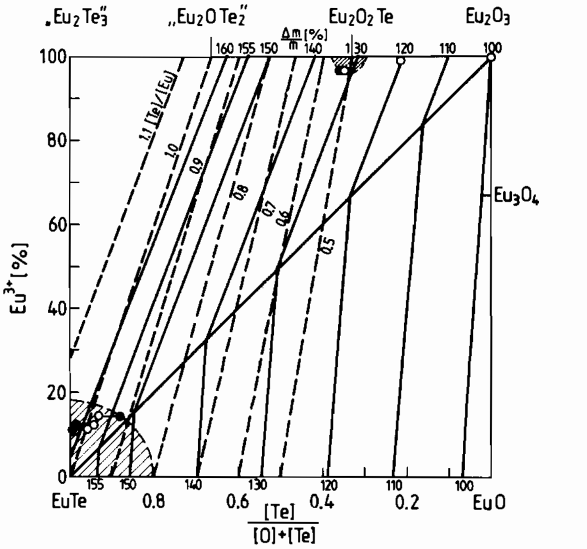

Fig. 6. Eu^{3+} content, ratio y = Te/Eu (dashed lines) and mass change $\Delta m/m$ relative to m of Eu_2O_3 (100%) for $EuTe_yO_z$ samples in EuTe–EuO–'Eu_2Te_3'–Eu_2O_3 system at different $p(O_2)$. The composition of phases can be determined from Eu^{3+} content and y (closed circles) or Eu^{3+} content and $\Delta m/m$ values (open circles).

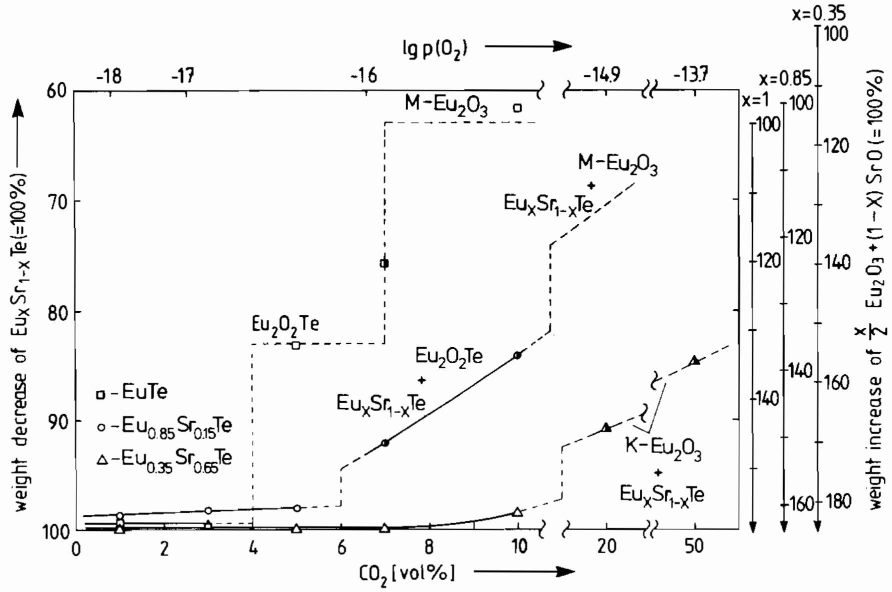

Fig. 5. Mass change $\Delta m/m$ of $Eu_xSr_{1-x}Te_yO_z$ samples (x = 1, 0.85, 0.35) at different $p(O_2)$ of H_2/CO_2 mixtures relative to the mass m of Eu_2O_3 + SrO (= 100%) at right scale or the mass of $Eu_xSr_{1-x}Te$ (= 100%) at left scale.

The present investigation shows that EuTe–SrTe solid solution can be prepared from Eu_2O_3, $SrCO_3$ and Te mixtures at 1050 °C in 1 bar H_2 and 8 mbar Te_2. The solid solution exhibits a wide range of non-stoichiometry. The samples obtained by the present procedure contain ~10% Eu^{3+}, ~2% oxygen impurities and an excess of 3–10% Te. The influence of non-stoichiometry on spin glass properties is not known. Therefore we are trying to reduce the Eu^{3+}, oxygen and excess Te content by annealing the powder samples in evacuated sealed quartz tubes with a second crucible containing a getter material, e.g. Th or Eu metal.

References

1 F. J. Börgermann, H. Maletta and W. Zinn, *J. Magn. Magn. Mater., 54–57,* 71 (1986).

2 E. Kaldis, *J. Cryst. Growth, 9,* 281 (1971).

3 H. Pink, *Z. Anorg. Allg. Chem., 364,* 248 (1969).

4 M. Haase, *Z. Kristallogr., 65,* 509 (1927).

5 'Gmelin Handbook of Inorganic Chemistry', Vol. 11 (Te), Suppl. B1, 1976.

6 M. Trömel and H. Ziethen-Reichnach, *Z. Anorg. Allg. Chem., 378,* 232 (1970).

7 R. E. Honig and D. A. Kramer, *RCA Rev., 30,* 285 (1969).

8 O. A. Sadovskaya and E. I. Yarembash, *Inorg. Mater. (U.S.S.R.), 6,* 1097 (1970).

9 K. H. Klatt, S. Pietz and H. Wenzl, *Z. Metallk., 69,* 170 (1978).

10 V. S. Rudenko and A. G. Boganov, *Inorg. Mater. (U.S.S.R.), 6,* 1893 (1970).

11 P. Deines, R. H. Nafziger, G. C. Ulmer and E. Woermann, *Pennsylvania State Univ., Coll. Earth Mineral Sci. Bull.,* (1971).

12 P. M. Raccah, J. M. Longo and H. A. Eick, *Inorg. Chem., 6,* 1471 (1967).

13 K. Bickmann, P. Ehrhart, K. Fischer and U. Köbler, unpublished data.