Journal of Alloys and Compounds, 207/208 (1994) 436–439
JALCOM 3092

Valence fluctuation and its effect on the synthesis, structure and properties of compounds

Hongjian Liu, Liping Li and Yifeng Wang
Group of Rare Earth Solid State Physics, Jilin University, Changchun 130023 (China)

Weina Liu
Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021 (China)

Wenhui Su
Group of Rare Earth Solid State Physics, Jilin University, Changchun 130023, International Center for Material Physics, Chinese Academy of Sciences, Shenyang 110015 and CCAST (World Laboratory), PO Box 8730, Beijing 100080 (China)

Abstract

The valence fluctuations of terbium and europium were studied using *in situ* electrical resistance measurement under high pressure and high temperature, X-ray diffraction, X-ray photoelectron spectra and Eu emission spectra. The synthesis process of $CeTbO_3$ under high pressure can be marked by the valence fluctuation of $Tb^{4+} \rightarrow Tb^{3+}$. The relationship between the intensity ratio, I, of the higher binding energy peak to the lower one and the content ratio, Z, of Tb^{4+}/Tb in Tb_{4d} photoelectron spectra can be described by the equation $I = -0.98Z^2 + 2.15Z$ $(0 \leq Z \leq 1)$. Using this equation the valence state of terbium and its effect on the superconductivity in $Eu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ were investigated. In addition, the phenomenon of pressure-induced valence fluctuation was also observed in the SrB_2O_4:Eu system.

1. Introduction

As a result of the special properties of their electron shells, research on lanthanides has become an important issue. Much of work has been done on the synthesis of lanthanide compounds [1,2] and their properties [3–5]. These studies have shown many interesting results. It is known that the lanthanide has the $[Xe]4f^{0-14}5d^{0-1}6s^2$ electron shell, containing unfilled 4f and almost empty 5d shells. After the valence electrons are lost, they form the common Ln^{3+} ions. According to Hund's rules the La^{3+}, Gd^{3+} and Lu^{3+} are the most stable in these Ln^{3+} ions because they have empty, half-filled and fully filled 4f shells, respectively. The elements near the three elements, for example, Tb, Eu, will tend to lose or gain electrons to reach or get close to the stable state, which results in the valence fluctuation phenomenon. The valence fluctuation of rare earth ions may directly affect the functional properties of materials, so the study of the synthesis of rare earth compounds and the valence fluctuation process and its effect on the physical and chemical properties may reveal some novel properties of valence changed lanthanide, which is important for predicting and designing new materials. In this paper, some compounds containing terbium or europium were selected for study, with the aim of obtaining some information about the valence fluctuation and its influence on the synthesis, structure and properties of lanthanide compounds.

2. Experimental details

The rare earth oxides CeO_2, Tb_4O_7, Eu_2O_3 with 99.95% purity were used as starting materials. According to some appropriate proportion in the present study, they were weighed and mixed. The common high temperature solid state reaction was employed for the preparation of a sintered sample, and the high pressure and high temperature synthesis was performed using a 4.9 MN (500 T) Bridgman press [2]; the *in situ* electrical resistance was measured on a 1.96 MN (200 T) Bridgman press [6].

After the high pressure experiment, the above samples were tested using X-ray diffraction, X-ray photoelectron and Eu emission spectra methods.

0925-8388/94/$07.00 © 1994 Elsevier Science S.A. All rights reserved
SSDI 0925-8388(93)03092-W

3. Results and discussion

3.1. CeO_2-Tb_4O_7 system

For studying the high pressure synthesis process of the compound $CeTbO_3$, the resistances of CeO_2, Tb_4O_7, a mixture ($4CeO_2+Tb_4O_7$) and compound $CeTbO_3$ prepared previously were measured *in situ* at a pressure of 0.5 GPa and at temperatures ranging from room temperature to 800 °C. The experimental results of resistance–temperature variation showed that under a pressure of 0.5 GPa, CeO_2 has a semiconducting character and exhibits a higher stability of the perfect fluorite structure; however, for the Tb_4O_7 and the mixture, there appear fluctuating changes in resistance above 600 °C, indicating a change in inner electronic state. The resistance–temperature curves for the mixture of ($CeO_2+Tb_4O_7$) in a 4:1 mole ratio are shown in Fig. 1. The resistance–temperature variation with decreasing temperature were also measured for comparison.

The experimental results suggest that the irregular resistance change in the system of the mixture above 600 °C may be considered to come from Tb_4O_7. The Tb_4O_7 has a defect fluorite structure in which Tb^{3+} and Tb^{4+} ions are about 50%, respectively, causing some oxygen deficiencies. Therefore the carrier should consist of intrinsic carriers and anion deficiencies, but the latter may be the predominant conductivity mechanism at a high temperature. It can be estimated that the innate oxygen deficiencies are 12.5% in total oxygen sites in Tb_4O_7. When one Tb^{4+} transits to Tb^{3+}, 0.5 oxygen deficiencies occur due to the electrical neutrality. If small amounts of oxygen deficiencies caused by the pressing are ignored, the contribution to conductivity of the sample comes from the intrinsic carriers and the innate oxygen deficiencies at the initial stage of increasing temperature. With increase in temperature, a certain amount of new oxygen deficiencies will take part in conducting, but they are not large. It is only close to the transition temperature that a large number of deficiencies are produced and they influence the conductivity seriously. The present experimental results, the resistance in the mixture and Tb_4O_7 showing irregular change above 600 °C, may be considered as the beginning of $Tb^{4+} \rightarrow Tb^{3+}$; the transition temperature is about 600 °C. At this temperature, a great deal of Tb^{4+} transforms to Tb^{3+}, resulting in an abrupt increase in oxygen deficiency. If the temperature is maintained, the oxygen deficiencies will increase to the saturated value with time. The new deficiencies produced are in a disordered state because of the constant temperature and pressure, hence no contribution to the conductivity but increasing the scattering defect on the intrinsic carriers (point defect scattering). At the same time, the production of deficiencies also decreases the concentration of intrinsic carriers. Therefore the conductivity will be lower than it was previously, *i.e.* the resistance increases at a constant temperature with time. With further increase in temperature, the deficiencies produced before become more active and partly take part in conducting, which makes the resistance decrease again with increasing temperature. In conclusion, this may explain the irregular change in the resistance–temperature curves with increasing temperature in Fig. 1 and similarly for the process of decreasing temperature.

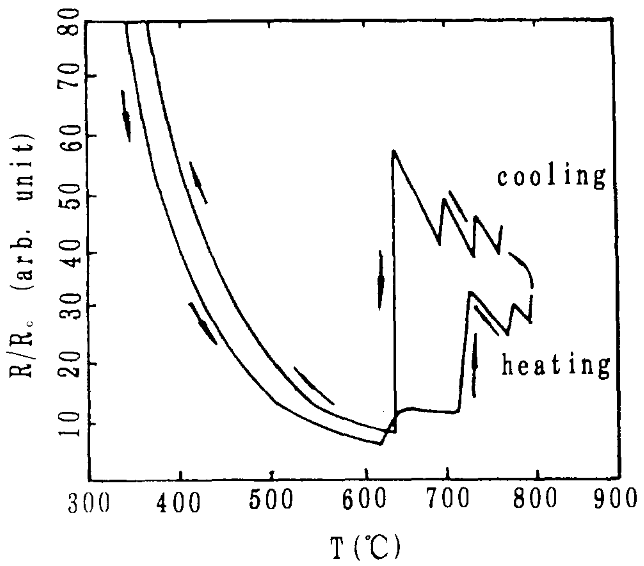

Fig. 1. Resistance–temperature curve for the ($4CeO_2+Tb_4O_7$) mixture under 0.5 GPa (the interval of up-and-down change is related to the maintaining temperature time).

The X-ray diffraction spectra for this mixture under 0.5 GPa and at different temperatures are shown in Fig. 2. It can be seen that there are changes in the diffraction patterns with increase in temperature. At room temperature, it is the simple combination of CeO_2 and Tb_4O_7 diffraction peaks, and at 400 °C no obvious change can be observed. But at 650 °C, the split of the peaks corresponding to Tb_4O_7 take place, forming a fluorite phase (F), a cubic phase (C) and only a small monoclinic phase (B). Here phase C is $TbO_{1.5+x}$, phase B is Tb_2O_3, all resulting from the transition of $Tb^{4+} \rightarrow Tb^{3+}$ [5]. At 1000 °C, there is a single phase of fluorite structure. The X-ray diffraction spectra are in good agreement with the measured resistances. Thus it may be suggested that the compound $CeTbO_3$ was formed by the $Tb^{4+} \rightarrow Tb^{3+}$ transition in the mixture, which makes the fluorite Tb_4O_7 gradually disintegrate and the Tb^{3+} ions enter the perfect fluorite structure of CeO_2, finally the $CeTbO_3$ compound forms with the fluorite structure.

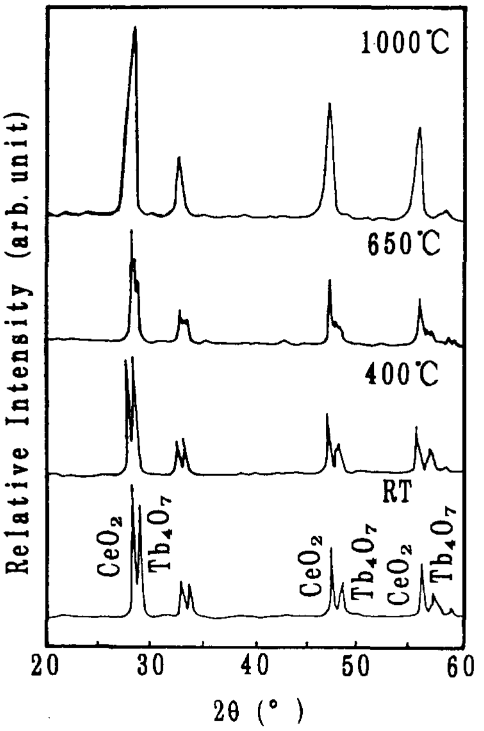

Fig. 2. X-Ray diffraction spectra of ($4CeO_2+Tb_4O_7$) mixture prepared at different temperatures ($P=0.5$ GPa).

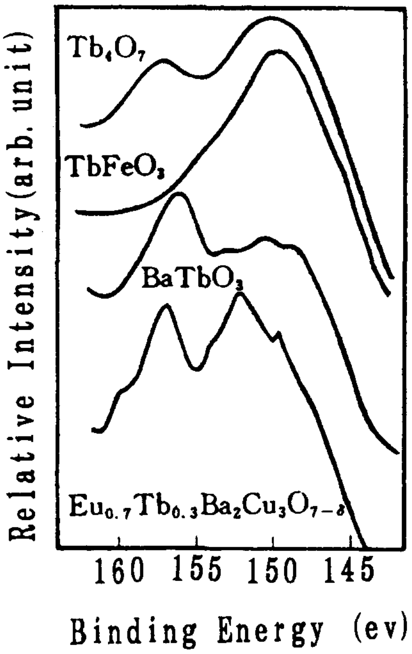

Fig. 3. Tb_{4d} X-ray photoelectron spectra in some compounds containing terbium.

3.2. $Eu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ system

The yttrium in $YBa_2Cu_3O_{7-\delta}$ can be substituted by lanthanides, with the exception of praseodymium, cerium and terbium, to form a single phase of 123 structure, high T_c superconductors [7]; the three elements commonly exhibit the Ln^{4+} ions state. But the reason why Ln^{4+} influences the superconductivity is not clear.

$Eu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ ($x=0$–0.30) was sintered in the atmosphere [8]. In order to determine the valence state of Tb ions in $Eu_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$, the Tb_{4d} X-ray photoelectron spectra in these compounds of $BaTbO_3$, $TbFeO_3$ and Tb_4O_7 were measured, as shown in Fig. 3. It is noticed that $BaTbO_3$ is a perovskite structure in which Tb is quadrivalent with six coordination, and Tb is trivalent with twelve coordination in $TbFeO_3$. The Tb ions are quadrivalent and trivalent in the defect fluorite Tb_4O_7 and $Tb^{3+}/Tb^{4+}=1$. Therefore from the photoelectron spectra, the characteristic peaks of Tb^{3+} and Tb^{4+} can be determined to be 149.45 and 156.20 eV, respectively. If the intensity ratio of higher to lower binding energy peak is taken as I and the content of Tb^{4+}/Tb is Z, the approximate relationship between I and Z is obtained first by fitting the experimental data. That is $I=-0.98Z^2+2.15Z$ ($0\leqslant Z\leqslant 1$), which can be used to determine the valence state of Tb ions in the compounds. By fitting the photoelectron spectrum of $Eu_{0.7}Tb_{0.3}Ba_2Cu_3O_{7-\delta}$ in Fig. 3, I is 0.95, and then the corresponding Z may be estimated, $Tb^{4+}/Tb\approx 0.61$, which means that terbium is in mixed valence states in this compound, Tb^{3+}, Tb^{4+} being about 0.12, 0.18, respectively.

The divalent copper (Cu^{2+}) is six coordinate in the 123 phase, the corresponding ionic radius being 0.073 nm. The radii of six-coordination, eight-coordination for Tb^{3+} and Tb^{4+} are 0.092 and 0.076 nm, 0.104 and 0.088 nm, respectively. Thus Tb^{3+} should be in Eu^{3+} sites and Tb^{4+} in Eu^{3+} or Cu^{2+} sites if Tb enters into the lattice. The X-ray diffraction data showed that the lattice volume is enlarged with increasing Tb doping content x [8], which suggests that some Tb^{4+} must be in the 123 lattice because the radius of Tb^{4+} (0.076 nm) is more than that of Cu^{2+} (0.073 nm) and Tb^{3+} (0.104) less than Eu^{3+} (0.107). The existence of Tb^{4+} in the 123 phase will result in the oxygen content increasing near the Eu layer and the oxygen deficiency decreasing in the rare earth element layer because of the electrical neutrality. The decrease in oxygen deficiency results in the decrease of $Cu^{>2+}$ ions and O_{2p} holes, and therefore in the decrease in charge transfer of $Cu^{>2+}\rightarrow O^{2-}$, the weakening of the Cu(2)–O(2) bond and the lowering of the Cu_{2p} binding energy. The decrease in O_{2p} hole number in the Cu(2)–O(2) plane may be one of the reasons for the loss of superconductivity after doping terbium.

3.3. $Sr_{1-x}Eu_xB_2O_4$ system

SrB_2O_4:Eu^{2+} with a high pressure cubic structure is an efficient Eu^{2+} activated luminescence material [3]; some studies on this subject have been done by the present authors [4,9], and as additional work, the valence

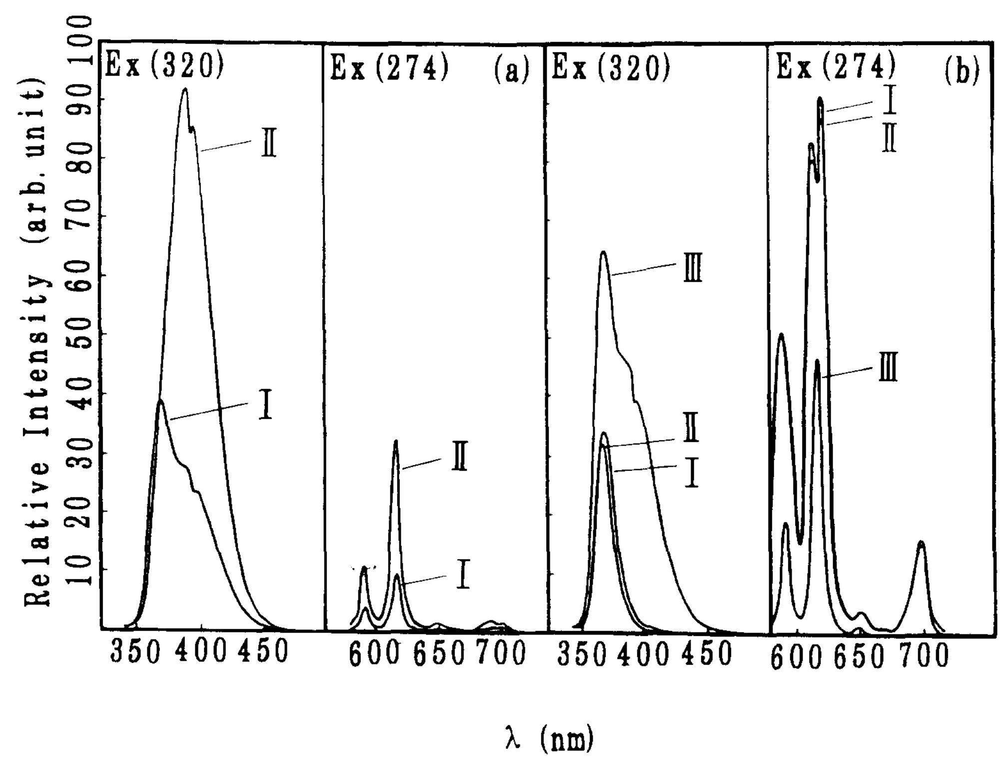

Fig. 4. Eu emission spectra of $Sr_{1-x}Eu_xB_2O_4$ samples prepared under different pressures and at different temperatures. (a) $x=0.02$; $P=2.75$ GPa; I, 600 °C; II, 800 °C; (b) $x=0.1$; $T=800$ °C; I, 2.55 GPa; II, 2.75 GPa; II, 2.95 GPa. $E_x(320)$, 320 nm exciting wavelength; $E_x(274)$, 274 nm exciting wavelength.

change of europium was investigated using Eu emission spectrum. The SrB_2O_4:Eu^{2+} samples were commonly prepared by means of reducing atmosphere which makes Eu^{3+} reduce to Eu^{2+}. Here, the Eu_2O_3 (Eu ions are trivalent) with 99.95% purity was used as the starting material and weighed to form a mixture of $Sr_{1-x}Eu_xB_2O_4$ ($x=0.02$, $x=0.1$) for high pressure experiments. The europium emission spectra of $Sr_{1-x}Eu_xB_2O_4$ prepared under different pressures and at different temperatures are shown in Fig. 4. This shows the different emissions of Eu^{2+} and Eu^{3+}, meaning that the high pressure indeed makes some Eu^{3+} reduce to Eu^{2+}.

For the $x=0.02$ samples prepared under the same pressure of 2.75 GPa (Fig. 4(a)), at 800 °C and 600 °C, for the emissions of Eu^{2+} and Eu^{3+}, the former are all stronger than the latter; the reason may be related to a better crystal at the high temperature. For the $x=0.1$ samples (Fig. 4(b)), the emissions of Eu^{2+} and Eu^{3+} for samples I and II are very close to each other. But the emission of Eu^{2+} for sample III is twice that of samples I or II, and the corresponding Eu^{3+} emission is half that of samples I or II. The above temperature and pressure are suitable for the formation of cubic phase SrB_2O_4 [3], so the intensity of Eu^{2+} emission is mainly dependent on the concentration of Eu^{2+} in the cubic phase if it is smaller than the quenching concentration of Eu^{2+}; that is at the temperature of 800 °C, increasing pressure is beneficial in the reduction of Eu^{3+}, especially under 2.95 GPa, the reduction of Eu^{3+} is obviously increased and the intensity of Eu^{2+} strengthened.

Acknowledgments

This work has been supported by the National Natural Science Foundation of China and the Science Foundation of the National Education Commission of China.

References

1 S.J .Schneider and R.S. Roth, *J. Res. Natl. Bur. Std., 64A* (1960) 317.
2 W.H. Su, D.M. Wu, X.Y. Li and X.F. Ma, *Physica B, 139&140* (1986) 658.
3 K. Machida, G. Adachi, J. Shiokawa, M. Shimada and M. Koizumi, *J. Lumin., 21* (1980) 233.
4 H.J. Liu, Y.F. Wang, J.H. Yang, L.P. Li and W.H. Su, *J. Alloys Comp., 191* (1993) 1.
5 J.S. Zhou and W.H. Su, *J. Chin. Rare Earth Soc., 6* (1988) 57.
6 H.J. Liu, W.H. Su, Z.N. Qian, Y.F. Wang, D.M. Wu and S.J. Cui, *Chin. J. High Pressure Phys., 2* (1988) 146.
7 C.Y. Sun, W.H. Su, H.J. Liu, J.S. Zhou, F.T. Wang and Y.P. Zhang, *Phys. Status Solidi (a), 108* (1988) 337.
8 L.P. Li, Q. Wei, Y.F. Wang, H.J. Liu and W.H. Su, *Chem. J. Chin. Univ., 13* (1992) 217.
9 W. Xu, W.H. Su, S.J. Cui and D.M. Wu, *Chin. J. High Pressure Phys., 2* (1988) 237.