Structural Characterisation of PrBCNO and Pr_{1.2}SCNO

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The crystal structures of Pr_{1.2}Sr_{1.8}Cu_{2.2}Nb_{0.8}O_{8-y} (Pr_{1.2}SCNO) and PrBa₂Cu₂NbO_{8-y} (PrBCNO) have been determined from X-ray powder diffraction spectra recorded in the pressure range up to 60 GPa. Both samples have a tetragonal structure at ambient pressure. PrBCNO was found to have an orthorhombic high-pressure phase, the transition pressure being 13 GPa. The bulk moduli evaluated at zero pressure are 212 GPa and 215 GPa for Pr_{1.2}SCNO and PrBCNO, respectively. [phase transformation, bulk modulus, equation of state, X-ray diffraction, synchrotron radiation]

1. Introduction

In parallel with the search for superconductivity in new copper oxide systems, Praseodymium (Pr) containing cuprates have been examined for the presence of superconductivity and/or magnetic ordering, and for explaining the anomalous behaviour of the Pr compounds. Among all known RBa₂Cu₂O_{7-y} (in short RBCO), where *R* is a rare earth metal, PrBCO is nonsuperconducting in combination with an unusually high Néel temperature, *T_N*=17 K, compared with the other members of the RBCO series. In a new series, RBa₂Cu₂NbO_{8-y} (RBCNO), NbO₂ planes are replacing the CuO chains. *R*=Pr again appears to be the most interesting compound, because of its high Néel temperature, *T_N*=12 K. Based on this analogy with the RBCO series, it is anticipated that PrBCNO may not be superconducting [1]. The Sr analogues, RSr₂Cu₂NbO_{8-y} (RSCNO), also exist. From the viewpoint of magnetic ordering, PrSCNO is interesting, since the Pr ions are squeezed into a smaller CuO₂-Pr-CuO₂ block than in the Pr compounds mentioned above.

The elastic properties of materials showing superconductivity are important because of the effect of pressure on the critical temperature *T_c* [2]. For the YBCO compounds the orthorhombic structure is associated with superconductivity. The present work is high-pressure X-ray diffraction study of PrBCNO and Pr_{1.2}SCNO. The principal aims have been to determine the equation of state of these compounds and to look for possible phase transformations from the tetragonal to the orthorhombic crystal system.

2. Experimental procedure

Appropriate amounts of high-purity dry powders of Pr₆O₁₁, CuO, Nb₂O₅, BaCO₃ and SrCO₃ were thoroughly mixed and ground. The mixture was heated to a temperature of 1000 °C, followed by 4-5 grinding-heat treatment cycles. A typical heat treatment was carried out at 1025-1070 °C in air for about 12 hours. The resultant product was examined with X-ray powder diffraction. The final heat treatment was followed by a slow cooling. More details can be found in Ref. [3].

The PrBCNO powder was found to be phase pure. The expected PrSCNO crystal structure (tetragonal, *P4/mmm*), however, was found only for the non-stoichiometric composition Pr_{1+x}Sr_{2-x}Cu_{2+x}Nb_{1-x}O_{8-y} (Pr_{1+x}SCNO) with *x*=0.2.

X-ray powder diffraction spectra were recorded using synchrotron radiation and the white-beam energy-dispersive method. High pressures were obtained in a diamond-anvil cell

of the Syassen-Holzapfel type [4]. A 4:1 methanol-ethanol mixture was used as the pressure transmitting medium. The actual pressure was determined using the ruby fluorescence method. The experiments were performed at the Hamburg Synchrotron Radiation Laboratory (HASYLAB) using radiation in the 15-70 keV photon energy range. The diffractometer, working in the energy-dispersive mode has recently been described by Otto [5]. Some experiments were performed at the Synchrotron Radiation Source of the Daresbury Laboratory, UK.

3. Results and Discussion

3.1. Pr_{1.2}SCNO

Fig. 1. Diffraction spectrum of Pr_{1.2}SCNO at ambient pressure, indexed according to a tetragonal unit cell.

The diffraction spectrum of Pr_{1.2}SCNO at ambient pressure is shown in Fig. 1. From the peak positions on the photon energy scale we obtain the refined lattice parameters *a*₀=3.891(1) Å and *c*₀=11.664(2) Å in good agreement with the previous determination [3]. The goodness of the fit is characterized by the reliability factor *R*, defined as

$$R = \frac{\sum |d_{\text{obs}} - d_{\text{calc}}|}{\sum d_{\text{obs}}} \quad (1)$$

where d_{obs} and d_{calc} are the observed and calculated interplanar spacings, respectively. For the spectrum shown in Fig. 1 we obtain $R=0.07\%$, which is highly satisfactory in high-pressure diffraction work.

The tetragonal phase of $\text{Pr}_{1.2}\text{SCNO}$ has been found to be stable in the whole pressure range investigated, i.e. at least up to 60 GPa. The compression of the sample can be described by the Murnaghan equation of state:

$$P = \frac{B_0}{B'_0} \left[\left(\frac{V_0}{V} \right)^{B'_0} - 1 \right] \quad (2)$$

where V is the volume at pressure P , and V_0 is the zero-pressure volume; B_0 and B'_0 are the bulk modulus and its pressure derivative, evaluated at zero pressure. A least-squares fit of Equation (2) to the experimental pressure-volume data gives $B_0=212(11)$ GPa, and $B'_0=2.8(4)$.

3.2. PrBCNO

From the zero-pressure diffraction spectrum we obtain $a_0=3.959(2)$ Å, and $c_0=11.926(8)$ in good agreement with Ref. [3]. Fig. 2 shows the high-pressure diffraction spectrum at $P=58$ GPa. The reliability factor for the tetragonal fit is $R=1\%$. This value is considered too large for a proper fit. Instead, we have assumed an orthorhombic structure. For the orthorhombic fit, the reliability factor was then found to be reduced by a substantial amount. For the spectrum shown in Fig. 2 we obtain $R=0.2\%$. By way of contrast, a similar calculation for $\text{Pr}_{1.2}\text{SCNO}$ did not show any significant decrease of the R-factor for an orthorhombic unit cell as compared to a tetragonal one.

Fig. 2. Diffraction spectrum of PrBCNO at $P=58$ GPa. Orthorhombic structure (see text).

Fig. 3. Reliability factor as function of pressure. Solid line: tetragonal structure; dashed line: orthorhombic structure.

Fig. 4. Relative volume, V/V_0 , as a function of pressure for PrBCNO . The full curve is the equation of state.

For PrBCNO it is observed that the reliability factor for the tetragonal fit worsens considerably for pressures above 13 GPa. Assuming an orthorhombic high-pressure structure, the R-factor can be kept below 0.4% in the whole pressure range as seen in Fig. 3. We interpret this result as a clear indication of a tetragonal to orthorhombic phase transformation at the transition pressure $P_t=13$ GPa.

It may be argued that the observed differences in the reliability factor for the tetragonal and orthorhombic fit, respectively, is caused by the freezing of the methanol-ethanol mixture, resulting in non-hydrostatic pressure. However, we think that the observed effect is a genuine one, because no similar effect was observed for $\text{Pr}_{1.2}\text{SCNO}$, which was studied under identical conditions as described above. Unfortunately, the expected splitting of the tetragonal diffraction lines is too small

to be observed by the low-resolution energy-dispersive method applied in the present work. Further studies are under way, using a high-resolution monochromatic method based on the image-plate detector.

Fig. 4 shows the compression curve of PrBCNO. It is seen that there is no volume discontinuity at the phase transition. The pressure-volume data can be described by Equation (1) with the parameters $B_0=215(13)$ GPa, and $B_0'=1.8(6)$. It is noticed that the bulk moduli of Pr_{1.2}SCNO and PrBCNO are larger than the corresponding values, around 160 GPa, for the RBCO superconductors [6].

Acknowledgments

We would like to thank HASYLAB-DESY for use of the synchrotron radiation facility, and Daresbury Laboratory for use of the Synchrotron Radiation Source under the EU Large Facilities Programme. Financial support from the Danish National Science Research Council is gratefully acknowledged (LG, JSO & SS).

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