Thermochimica Acta, 147 (1989) 109–117
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMOANALYTICAL CHARACTERIZATION (DTA AND TG) OF $RBa_2Cu_3O_{7-x}$ ($R \equiv Y$, Gd, Nd) SUPERCONDUCTORS

DENIS NOËL and LUC PARENT

Industrial Materials Research Institute, National Research Council Canada, 75 bd. de Mortagne, Boucherville, Québec J4B 6Y4 (Canada)

(Received 1 November 1988)

ABSTRACT

Differential thermal analysis (DTA) and thermogravimetric (TG) analysis were used to characterize $RBa_2Cu_3O_{7-x}$ ($R \equiv Y$, Gd, Nd) superconductors. Even if the resistivity–temperature curves are similar for the three compounds, DTA shows that the behavior of these materials during synthesis and sintering is different. Of the three systems, the Nd–Ba–Cu–O system is the most favorable for the formation of the 123 superconductor because secondary phases are present in smaller quantities. TG curves suggest the presence of a transition from the orthorhombic phase to the tetragonal phase in a nitrogen atmosphere at about 550–600 ° C for the three perovskites. The energy required to insert oxygen atoms in the crystal structure is smaller for the neodymium and gadolinium compounds than for the yttrium compound ($Gd < Nd < Y$). There is also a proportional relation between the ionic radius of the rare earth element and the onset melting temperature.

INTRODUCTION

According to preparation conditions and stoichiometry, it is well known that the system Y–Ba–Cu–O can have superconductive properties. The $YBa_2Cu_3O_{7-x}$ compound has a crystal structure which can be superconducting (orthorhombic) or non-superconducting (tetragonal) depending on the oxygen stoichiometry. A sharp superconducting transition, characterized by an abrupt decrease in resistivity, is observed at about 90 K. Although yttrium has been widely adopted for the fabrication of superconductors, different rare earths have been substituted for yttrium in order to verify if they have an effect on the superconducting temperature. Unfortunately, the superconducting temperature is almost insensitive to the nature of the rare earth element [1–3]. However, the replacement of yttrium by other rare earths may cause a variation in the reactivity of these perovskites.

In this work, various cuprate perovskites with the composition $RBa_2Cu_3O_{7-x}$ ($R \equiv Y$, Gd, Nd) were prepared and characterized using differential thermal analysis (DTA) and thermogravimetric (TG) analysis. It has been shown that the behavior of these materials during synthesis and sintering is different [3], and thermoanalytical characterization can reveal the presence of impurities or secondary phases in $RBa_2Cu_3O_{7-x}$ compounds which explain these variations.

EXPERIMENTAL

Compounds $RBa_2Cu_3O_{7-x}$ ($R \equiv Y$, Gd, Nd) were prepared following a standard ceramic technique. Appropriate amounts of CuO, $BaCO_3$, Y_2O_3, Gd_2O_3 and Nd_2O_3 (all of purity 99.999%) were mixed and calcined at 950 °C for 12 h in alumina crucibles. The resulting compacts were crushed and sieved to pass through a 400 mesh screen. The heating and crushing steps were repeated a second time, and pellets were pressed from these powders at a pressure of 390 MPa. The pellets were sintered at 950 °C for 6 h, cooled to 500 °C in 1 h, held at this temperature for 2 h and, finally, cooled to room temperature in about 2 h. All the thermal treatments were carried out in a flowing oxygen atmosphere.

The thermal analyzer (DTA and TG) used was a Model B70 from Setaram (Caluire, France) equipped with a carbon resistance furnace. Data were collected via a Hewlett-Packard system. The balance was accurate to ± 30 μg over a long period of time. The loss of weight was measured within 0.3%. Samples were analyzed in alumina crucibles. The heating rate was maintained constant at 10 °C min^{-1}.

RESULTS AND DISCUSSION

$YBa_2Cu_3O_{7-x}$

The yttrium perovskite was analyzed in an oxygen atmosphere using DTA and the thermogram is shown in Fig. 1. There are three large endothermic peaks at 945, 970 and 1030 °C. There are also three small endothermic deflections at about 550, 750 and 810 °C.

Gabelica et al. [4] have also observed three endothermic peaks at 945, 980 and 1032 °C associated with a loss of weight but without a definitive identification. Clearly at 1030 °C, $YBa_2Cu_3O_{7-x}$ begins to melt [5,6]. The endothermic peak at 1030 °C is associated with the decomposition of $YBa_2Cu_3O_{7-x}$ into Y_2BaCuO_5, $BaCuO_2$ and a liquid [7,8]. The presence of multiple peaks in the DTA curve is probably related to impurities. Using X-ray diffraction, impurities such as $BaCuO_2$ and CuO have been detected in pellets made from the $YBa_2Cu_3O_{7-x}$ powder used in this study [3]. At 810 °C, the small endothermic peak is caused by the α–β transition of $BaCO_3$ [5,9]. DTA peaks at 945 and 970 °C are also probably related to

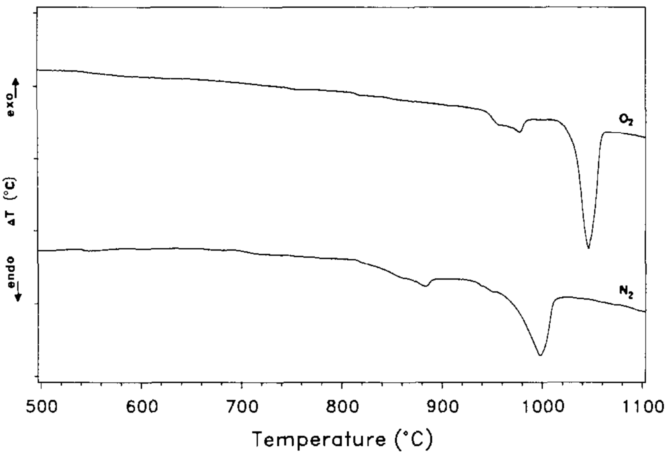

Fig. 1. DTA curves of $YBa_2Cu_3O_{7-x}$ in oxygen and nitrogen atmospheres.

reactions involving carbonates. In air, a similar reaction peak (not identified) at about 940 °C has been observed in an impure material [5]. An endothermic peak at 957 °C has also been reported for the yttrium compound in an oxygen atmosphere and it has been suggested that it may be associated with the formation of a eutectic of the ternary $Y_{0.15}$–BaO–CuO system.

Figure 1 also shows the DTA curve of $YBa_2Cu_3O_{7-x}$ obtained in a nitrogen atmosphere. There is displacement towards lower temperatures of the main peaks observed in oxygen. The largest endothermic effect occurs at 965 °C and corresponds to the melting of the compound [6]. Clearly, DTA shows the presence of secondary phases which are dependent on the preparation conditions. Owing to the complexity of the chemical reactions involved in these cuprate perovskites, more work will be necessary to identify all these secondary phases.

Figure 2 shows a thermogravimetric curve of $YBa_2Cu_3O_{7-x}$ obtained in a nitrogen atmosphere on heating. There is a significant loss of weight starting at about 440 °C. There is also a small change in slope detected at about 600 °C followed by a more important loss of weight at 830 °C. The overall decrease in weight is attributed to loss of oxygen. The change in slope at 600 °C corresponds to the orthorhombic–tetragonal transition. The transition temperature depends on the oxygen partial pressure and occurs when the stoichiometry is near $YBa_2Cu_3O_{6.5}$ [6,10,11]. Transition temperatures of 700–750 °C [7] and 850 °C [4,12] have been reported in air and oxygen respectively. However, in oxygen, no loss of weight was observed at the orthorhombic–tetragonal transition [4]. In our case, there is an important loss of weight of 830 °C which is probably due to decomposition of the sample.

Figure 3 illustrates the TG curve on heating of $YBa_2Cu_3O_{7-x}$ in an oxygen atmosphere. There is an increase in weight beginning at 325 °C with

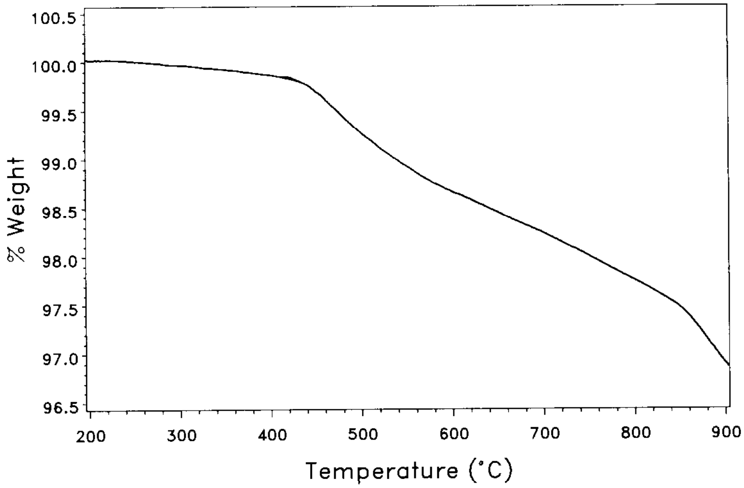

Fig. 2. TG curve of $YBa_2Cu_3O_{7-x}$ in a nitrogen atmosphere on heating.

a maximum at about 490 °C (about 1.2%). Thus the difference between the start of the increase in weight and the maximum corresponds to a change in temperature ΔT of 165 °C. From 500 °C to 800 °C, there is a gradual decrease in weight.

$GdBa_2Cu_3O_{7-x}$

The crystal structure of $YBa_2Cu_3O_{7-x}$ is slightly modified when yttrium is substituted by gadolinium [13,14]. Basically, both compounds have a distorted, oxygen-deficient, perovskite structure. Thus this substitution has

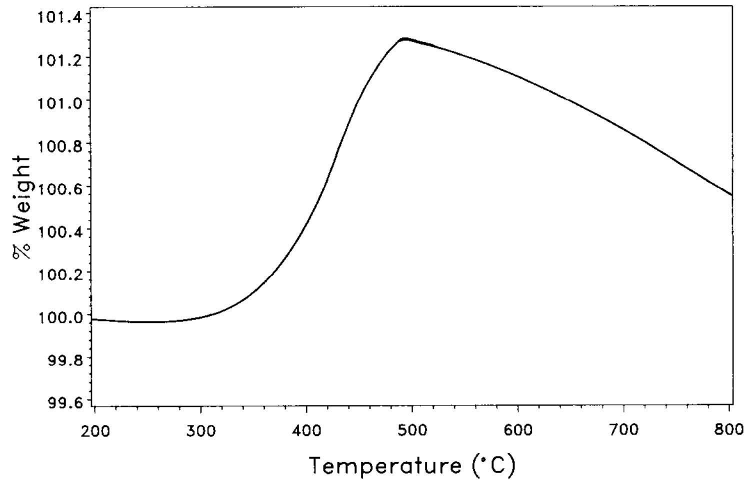

Fig. 3. TG curve of $YBa_2Cu_3O_{7-x}$ in an oxygen atmosphere on heating.

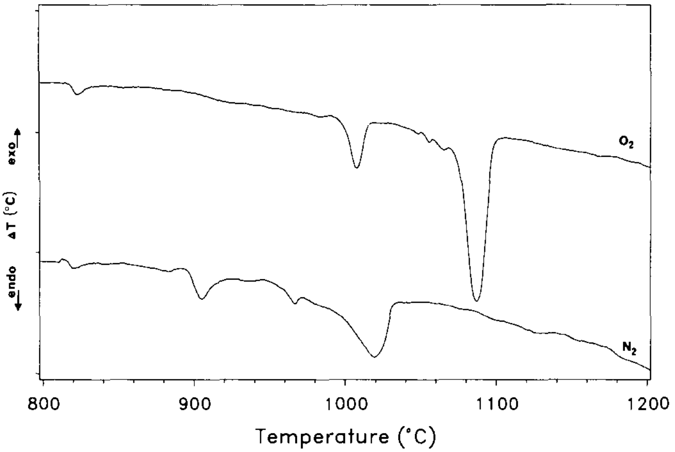

Fig. 4. DTA curves of $GdBa_2Cu_3O_{7-x}$ in oxygen and nitrogen atmospheres.

almost no effect on the superconducting transition temperature [1–3]. However, the DTA curve of $GdBa_2Cu_3O_{7-x}$ in an oxygen atmosphere, shown in Fig. 4, is different from the thermogram of the yttrium perovskite. Many endothermic peaks are detected with onset temperatures of 818, 980, 998, 1038, 1050, 1055 and 1075 °C. The presence of these peaks indicates that $GdBa_2Cu_3O_{7-x}$ is impure and contains many secondary phases. As for $YBa_2Cu_3O_{7-x}$, the peak at 818 °C probably corresponds to the α–β transition of $BaCO_3$. At 980 °C, there is probably another transformation of $BaCO_3$ to the cubic α form [9]. The presence of $BaCO_3$ has been confirmed using Fourier-transform IR spectroscopy.

The peak at 998 °C is assumed to be due to the presence of $BaCuO_2$ [7,8]. In fact, X-ray diffraction has shown that a significant amount of this product is present in $GdBa_2Cu_3O_{7-x}$ [3]. With a sintering temperature of 950 °C, the replacement of yttrium by gadolinium modifies the equilibrium conditions and the stability of the superconductor. The melting of $GdBa_2Cu_3O_{7-x}$ in an oxygen atmosphere begins at about 1075 °C. As for yttrium, there is probably an incongruent melting of $GdBa_2Cu_3O_{7-x}$ into Gd_2BaCuO_5 and a liquid.

The DTA curve of $GdBa_2Cu_3O_{7-x}$ in a nitrogen atmosphere is given in Fig. 4. As for $YBa_2Cu_3O_{7-x}$, there is a displacement of the peaks towards lower temperatures compared with the thermogram obtained in an oxygen atmosphere. In an inert atmosphere, the gadolinium perovskite begins to melt at about 990 °C.

The pattern of the TG curve (heating) in a nitrogen atmosphere for the gadolinium compound is shown in Fig. 5 and is similar to that obtained with yttrium. There is a sudden loss of weight starting at about 400 °C (which is at a slightly lower temperature than for $YBa_2Cu_3O_{7-x}$) accompanied by a change in slope at about 560 °C. Thus the orthorhombic to tetragonal

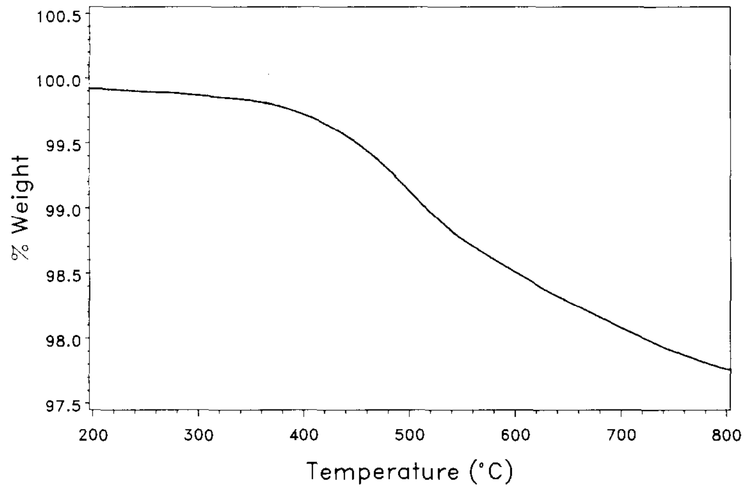

Fig. 5. TG curve of $GdBa_2Cu_3O_{7-x}$ in a nitrogen atmosphere on heating.

transition is also probably present in $GdBa_2Cu_3O_{7-x}$ as it has a similar crystal structure to $YBa_2Cu_3O_{7-x}$. However, this transition occurs at a lower temperature compared with the yttrium compound.

The TG curve of $GdBa_2Cu_3O_{7-x}$ in an oxygen atmosphere on heating is shown in Fig. 6 and indicates that this compound captures oxygen at a lower temperature (250 °C) than the yttrium compound (325 °C). The maximum increase in weight (330 °C) is also achieved more rapidly than with $YBa_2Cu_3O_{7-x}$ with a ΔT value of 80 °C. The increase in weight is similar (about 1.3%). Thus the energy required to insert oxygen atoms into the crystal structure is smaller for the gadolinium compound than for the yttrium compound.

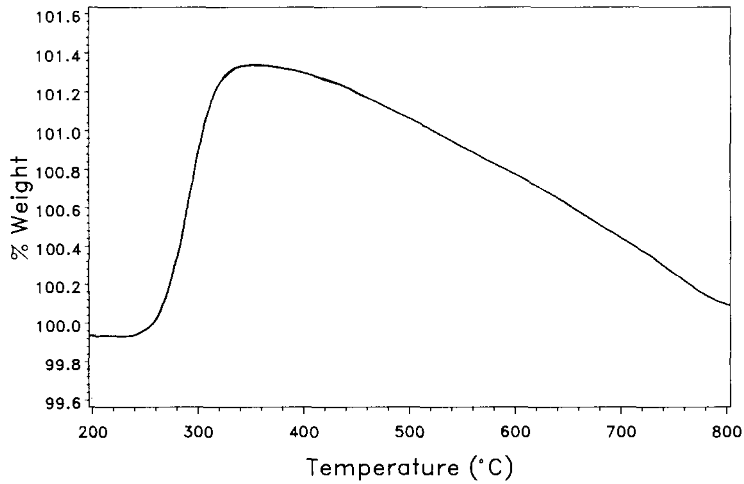

Fig. 6. TG curve of $GdBa_2Cu_3O_{7-x}$ in an oxygen atmosphere on heating.

$NdBa_2Cu_3O_{7-x}$

The superconductor prepared using neodymium has a higher superconducting transition temperature T_c than the yttrium or gadolinium superconductors [3,15]. Figure 7 shows the DTA curve of $NdBa_2Cu_3O_{7-x}$ in an oxygen atmosphere. Clearly, there are less impurities and secondary phases in this compound since there are few peaks in the thermogram. As for the previous perovskites, the endothermic peak at about 815 °C is probably caused by the α–β transition of $BaCO_3$.

$NdBa_2Cu_3O_{7-x}$ begins to melt at about 1107 °C in an oxygen atmosphere which is a higher temperature than for the yttrium or gadolinium perovskites. There is a linear trend between the ionic radius of the rare earth element and the cell volume [15]. There is also a relation between T_c and the ionic radius, and our results indicate that there is a relation between the ionic radius and the onset melting temperature. For the three rare earths used in this study, an increase in the ionic radius is proportional to an increase in the onset melting temperature. In a nitrogen atmosphere, $NdBa_2Cu_3O_{7-x}$ begins to melt at about 1035 °C as shown in Fig. 7.

The TG curve of $NdBa_2Cu_3O_{7-x}$ in a nitrogen atmosphere on heating is similar to the curve obtained with $GdBa_2Cu_3O_{7-x}$ (Fig. 8). The loss of weight starts at about 400 °C and there is a change in slope at about 550 °C. Thus it is highly probable that the transition involving the orthorhombic structure is also present in the neodymium compound. The TG curve obtained in an oxygen atmosphere, illustrated in Fig. 9, indicates that the compound captures oxygen at about 330 °C with a maximum at about 420 °C. This corresponds to a ΔT value of 90 °C, but the increase in weight is about 1.7% which is higher than for the yttrium or gadolinium com-

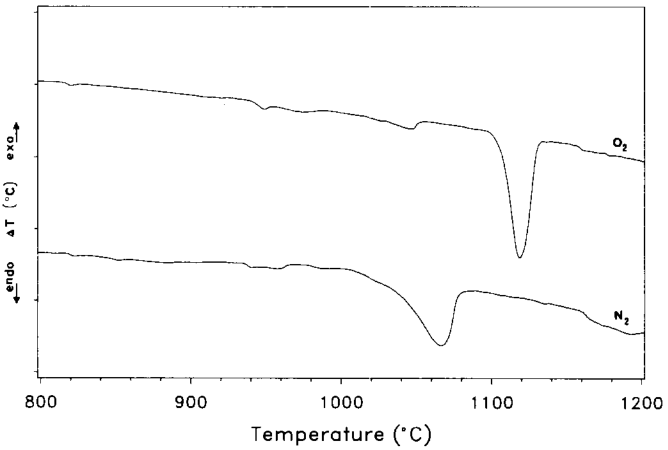

Fig. 7. DTA curves of $NdBa_2Cu_3O_{7-x}$ in oxygen and nitrogen atmospheres.

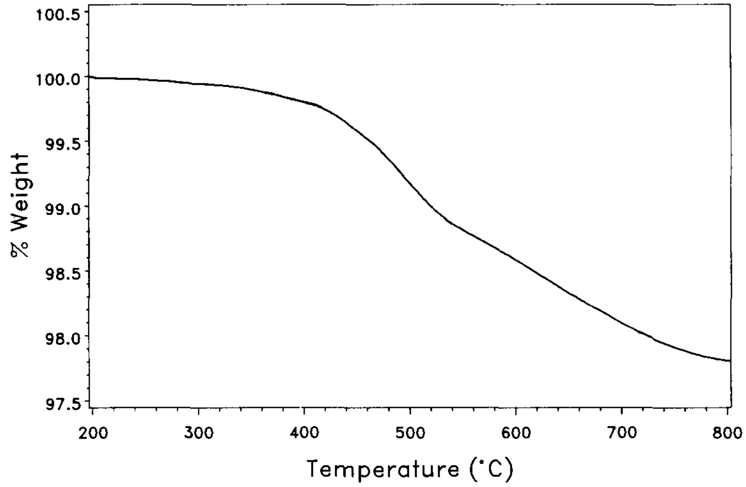

Fig. 8. TG curve of $NDBa_2Cu_3O_{7-x}$ in a nitrogen atmosphere on heating.

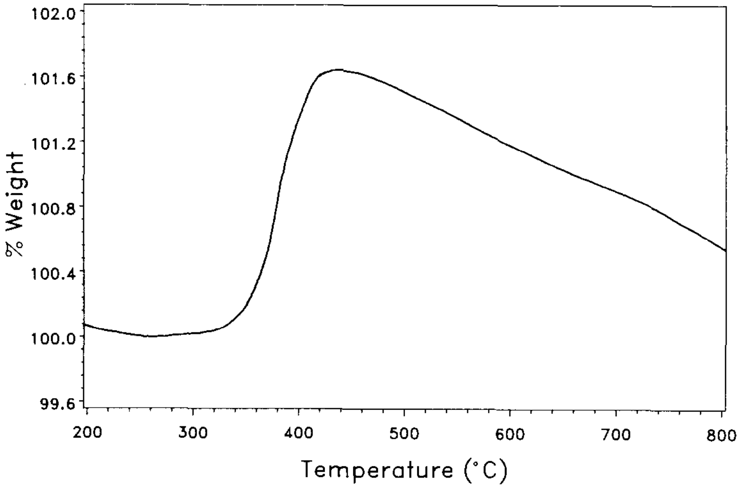

Fig. 9. TG curve of $NdBa_2Cu_3O_{7-x}$ in an oxygen atmosphere on heating.

pounds. As for gadolinium the energy required to incorporate oxygen is smaller than for the yttrium compound.

CONCLUSIONS

The DTA curves of the cuprate perovskites studied are relatively similar. In an oxygen atmosphere, $YBa_2Cu_3O_{7-x}$, $GdBa_2Cu_3O_{7-x}$ and $NdBa_2Cu_3O_{7-x}$ begin to melt at 1030 °C, 1075 °C and 1107 °C respectively. In a nitrogen atmosphere, these values are shifted to 965 °C, 990 °C and 1035 °C respectively. There is a relation between the ionic radius of the rare earth and the onset melting temperature. The DTA curves indicate the presence of impurities or secondary phases in the perovskites. Based on our results, $YBa_2Cu_3O_{7-x}$, $GdBa_2Cu_3O_{7-x}$ and $NdBa_2Cu_3O_{7-x}$ behave differently during sintering and the neodymium compound is the most easily synthesized. At 950 °C, under the conditions of this study, the system Nd–Ba–Cu–O is the most favorable for the formation of the 123 superconductor; this is followed by the yttrium system and, finally, by the gadolinium system.

Thermogravimetric experiments suggest the presence of an orthorhombic to tetragonal transition (550–600 °C) in the three compounds. In addition, TG curves show that $GdBa_2Cu_3O_{7-x}$ reacts with oxygen at a lower temperature than $YBa_2Cu_3O_{7-x}$ or $NdBa_2Cu_3O_{7-x}$. However, the absorption–desorption cycle of oxygen is reversible for the three compounds.

ACKNOWLEDGMENT

We wish to thank K.C. Cole for performing the IR spectroscopy.

REFERENCES

1 P.H. Hor, R.L. Meng, Y.Q. Wang, L. Gao, Z.J. Huang, J. Bechtold, K. Forster and C.W. Chu, Phys. Rev. Lett., 58 (1987) 1891.
2 J.M. Tarascon, W.R. McKinnon, L.H. Greene, G.W. Hull and E.M. Voget, Phys. Rev. B, 36 (1987) 226.
3 L. Parent, C. Moreau, D. Noël, S. Dallaire and B. Champagne, Mater. Lett., 7 (1989) 367.
4 Z. Gabelica, G. Demortier, G. Deconninck, F. Bodart, A.A. Lucas, M. Renier, Ph. Lambin, J.-P. Vigneron and E.G. Derouane, Solid State Commun., 64 (1987) 1137.
5 A. Bhargava, M. Heuberger and R.L. Snyder, Mater. Lett., 5 (1987) 495.
6 P.K. Gallagher, Adv. Ceram. Mater., 2(3B) (1987) 632.
7 R.S. Roth, K.L. Davis and J.R. Dennis, Adv. Ceram. Mater., 2(3B) (1987) 303.
8 M. Nevriva, E. Pollert, J. Sestak and A. Triska, Thermochim. Acta, 127 (1988) 395.
9 P. Kishan, L.K. Nagpaul and S.N. Chatterjee, Solid State Commun., 65 (1988) 1019.
10 P.K. Gallagher, H.M. O'Bryan, S.A. Sunshine and D.W. Murphy, Mater. Res. Bull., 22 (1987) 995.
11 J.D. Jorgensen, M.A. Beno, D.G. Hinks, L. Soderholm, K.J. Volin, R.L. Hitterman, J.D. Grace, I.K. Schuller, C.U. Segre, K. Zhang and M.S. Kleefisch, Phys. Rev. B, 36 (1987) 3608.
12 Z. Gabelica, E.G. Derouane, J.-P. Vigneron, Ph. Lambin, M. Renier, A.A. Lucas, G. Deconninck, F. Bodart and G. Demortier, Solid State Commun., 64 (1987) 1221.
13 J.B. Boyce, F. Bridges, T. Claeson, R.S. Howland and T.H. Geballe, Phys. Rev. B, 36 (1987) 5251.
14 H. Mazaki, M. Takano, R. Kanno and Y. Takeda, Jpn. J. Appl. Phys., 26 (1987) L1752.
15 T.J. Kistenmacher, Solid State Commun., 65 (1988) 981.