Thermochimica Acta, 171 (1990) 57–65
Elsevier Science Publishers B.V., Amsterdam

THERMOANALYTICAL CHARACTERIZATION (DTA AND TG) OF $RBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$ AND $RBaSrCu_3O_{7-x}$ (R ≡ Y, Gd, Sm OR 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 26 March 1990)

ABSTRACT

Differential thermal analysis and thermogravimetric analysis were used to characterize $RBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$ and $RBaSrCu_3O_{7-x}$ superconductors (R ≡ Y, Gd, Sm or Nd). It was found that the replacement of Ba by Sr increases the onset melting temperature of the perovskites. The effect is larger for compounds which contain an R atom with a small ionic radius. TG curves show that the temperature of the orthorhombic–tetragonal transition is modified by the presence of Sr.

INTRODUCTION

Yttrium has been widely adopted for the fabrication of superconductors. $YBa_2Cu_3O_{7-x}$ is certainly the most extensively studied of the 123 superconductors. It is possible to replace yttrium by different rare earths such as gadolinium, neodymium or samarium. Unfortunately, the superconducting temperature is almost insensitive to the nature of the rare earth element [1,2]. However, the replacement of yttrium by other rare earths causes a significant variation in other physical properties of these perovskites.

It has been shown that even if the resistivity–temperature curves are similar for these 123 compounds, differential thermal analysis (DTA) indicates that the behavior of these materials during synthesis and sintering is different [3]. The Nd–Ba–Cu–O system is the most favorable for the formation of a 123 superconductor because secondary phases are present in smaller quantities. Also, thermogravimetric (TG) analysis shows that the energy required to insert oxygen atoms in the crystal structure is smaller for the neodymium and gadolinium compounds than for the yttrium compound.

* Present address; Alcan International Ltée, Centre de recherches Arvida, 1955 Mellon, Jonquière, Québec G7S 4K8, Canada.

In this work, strontium has been used to replace partially the barium atom in various cuprate perovskites. The compositions of the studied compounds were $RBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$ and $RBaSrCu_3O_{7-x}$ (where R ≡ Y, Gd, Nd or Sm); they were analyzed using DTA and TG in oxygen and nitrogen atmospheres. As the ionic radius of Sr (1.13 Å) is greater than that of Ba (0.99 Å), it is expected that a slight modification of the crystal structure will occur. The purpose of this study is to determine the effect of this modification on the melting point and the oxygen lability in the new compounds.

EXPERIMENTAL

R_2O_3 and CuO (each 99.999%), BaO_2 (99%) and SrO (99.5%) powders were sieved through a 32-μm screen, then weighed and mixed in the required amount under an inert atmosphere to avoid the formation of carbonates. The mixtures were compressed at 200 MPa and the resulting green pellets were heated to 990 °C at a rate of 4 °C min^{-1}. The temperature was held constant for 36 h, and the furnace was then cooled at a rate of 2 °C min^{-1}. The heat treatment was carried out under 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. 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

Differential thermal analysis

In a first series of experiments, DTA of the eight perovskites were obtained in an oxygen atmosphere and the results are summarized in Table 1. Figures 1 and 2 show thermograms for $RBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$ and $RBaSrCu_3O_{7-x}$ compounds respectively. For comparison, DTA results obtained with $RBa_2Cu_3O_{7-x}$ [3] are also given in Table 1.

Similar thermograms are obtained for perovskites synthesized with and without Sr. When the Sr stoichiometry is 0.5, thermograms show small peaks between 950 °C and 1000 °C which are still unidentified. The higher endothermic peaks between 1050 °C and 1115 °C depend on the R atom and are associated with the incongruent melting of the compound, as for the $RBa_2Cu_3O_{7-x}$ series [3].

When the Sr content reaches 1.0, extra peaks appear on the thermograms before incongruent melting. These peaks are detected at higher temperatures than those observed for compounds with $Sr_{0.5}$, and their intensities are

TABLE 1

DTA results of $RBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$ and $RBaSrCu_3O_{7-x}$ perovskites in oxygen atmosphere

Compound	Onset melting temperature (°C)	
	Main peak	Other small peaks
$YBa_2Cu_3O_{7-x}$ [a]	1030	
$YBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$	1050	985, 965
$YBaSrCu_3O_{7-x}$	1070	1020, 1040
$GdBa_2Cu_3O_{7-x}$ [a]	1075	
$GdBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$	1090	
$GdBaSrCu_3O_{7-x}$	1095	1050, 1090
$SmBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$	1110	
$SmBaSrCu_3O_{7-x}$	1110	1075, 1085, 1135
$NdBa_2Cu_3O_{7-x}$ [a]	1107	
$NdBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$	1115	
$NdBaSrCu_3O_{7-x}$	1115	1070, 1095, 1165

[a] From ref. 3.

related to the nature of the R atom. In fact, the greater the R atom ionic radius, the higher is the relative intensity of these peaks. It is difficult to assign the peaks to specific reactions, because of lack of knowledge of these relatively complicated systems. However, it is clear that some other phases may be present, particularly in the case of $NdBaSrCu_3O_{7-x}$, for which extra peaks can be seen on the X-ray diffraction pattern.

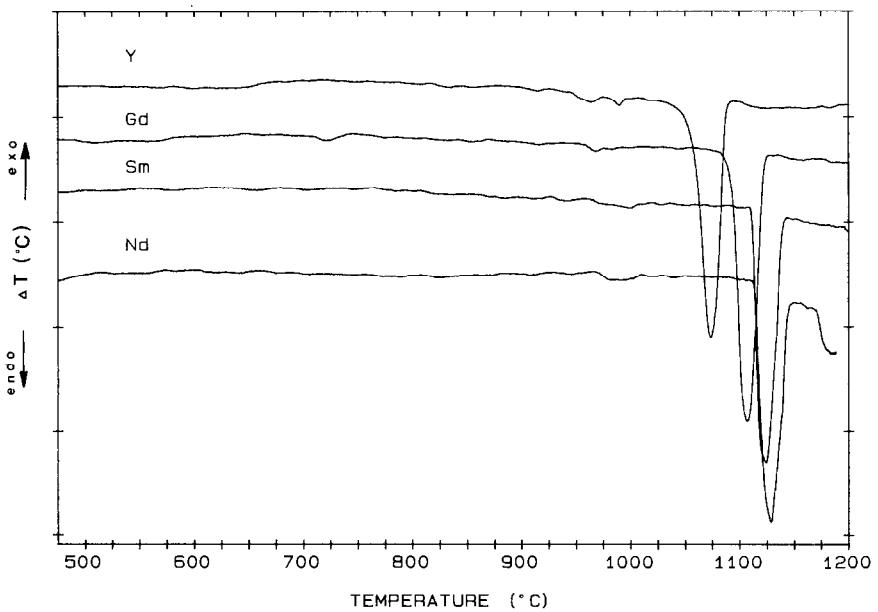

Fig. 1. DTA curves of $RBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$ in an oxygen atmosphere.

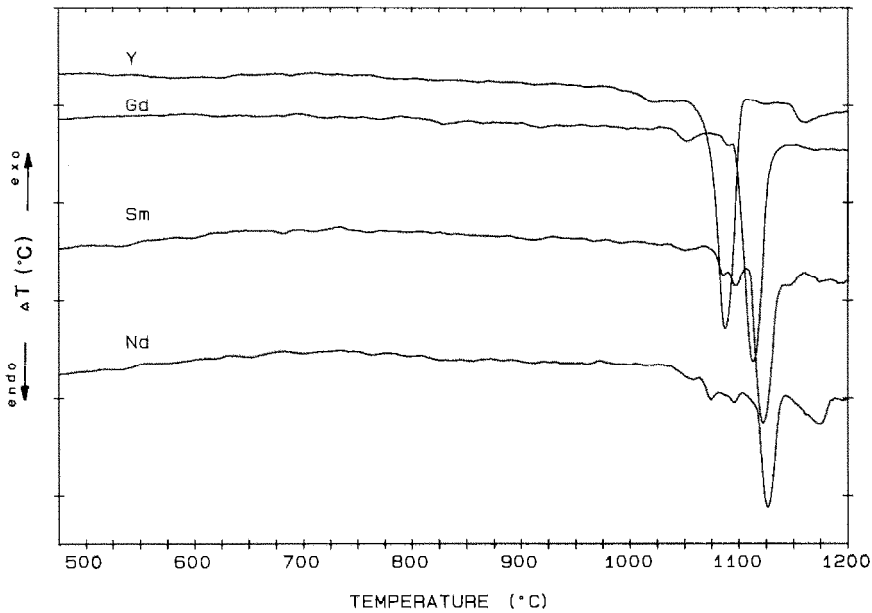

Fig. 2. DTA curves of $RBaSrCu_3O_{7-x}$ in an oxygen atmosphere.

The most interesting data obtained from the DTA are the melting point results. We have shown that a relationship exists between the ionic radius of the R atom and the onset melting temperature of a 123 compound without Sr [3]. With incorporation of Sr the relationship still exists but is less pronounced. There is a general increase in the melting point, dependent on the Sr stoichiometry and on the R atom. For example, the melting temperature of the yttrium series increases by 20 and 40 °C for $Sr_{0.5}$ and Sr

TABLE 2

DTA results of $RBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$ and $RBaSrCu_3O_{7-x}$ perovskites in nitrogen atmosphere

Compound	Onset melting temperature (°C) Main peak
$YBa_2Cu_3O_{7-x}$ [a]	965
$YBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$	990
$YBaSrCu_3O_{7-x}$	1000
$GdBa_2Cu_3O_{7-x}$ [a]	990
$GdBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$	1015
$GdBaSrCu_3O_{7-x}$	1010
$SmBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$	1030
$SmBaSrCu_3O_{7-x}$	1020
$NdBa_2Cu_3O_{7-x}$ [a]	1035
$NdBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$	1030
$NdBaSrCu_3O_{7-x}$	1030

[a] From ref. 3.

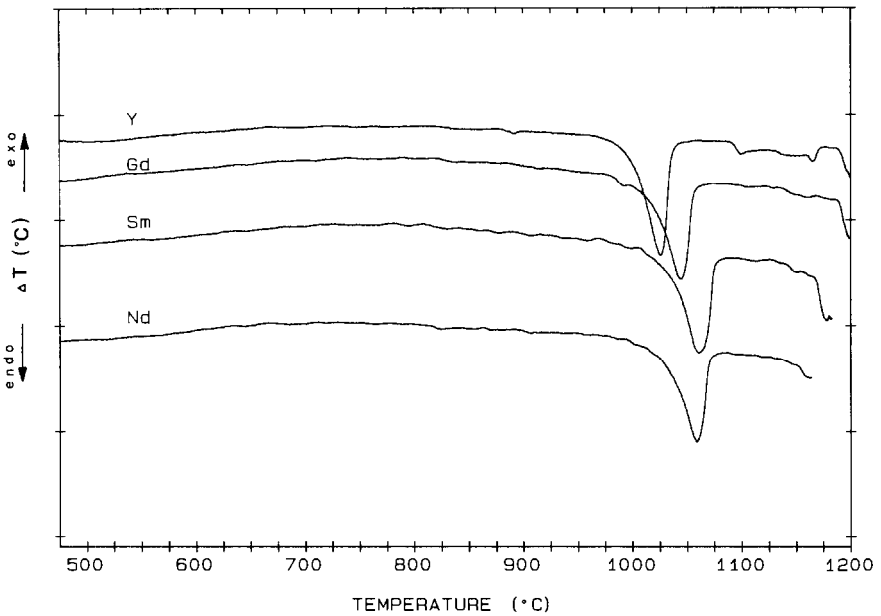

Fig. 3. DTA curves of $RBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$ in a nitrogen atmosphere.

respectively, but by only 8°C when Y is replaced by Nd, independently of the Sr content. This effect is not an advantage, as it means that a higher temperature will probably be necessary to process this material.

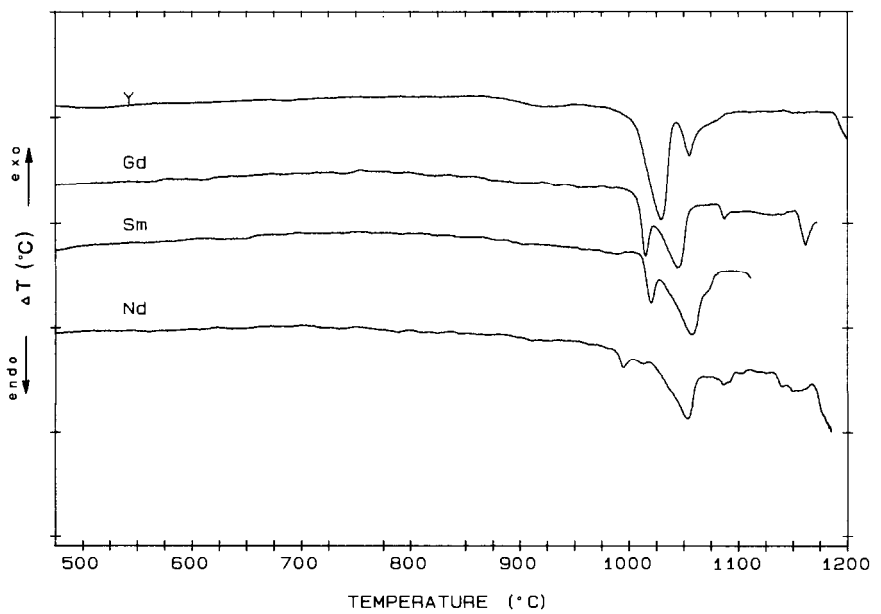

Fig. 4. DTA curves of $RBaSrCu_3O_{7-x}$ in a nitrogen atmosphere.

In a second series of experiments, DTA data for the same perovskites were obtained in a nitrogen atmosphere and the results are summarized in Table 2. Figures 3 and 4 show the thermograms for $RBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$ and $RBaSrCu_3O_{7-x}$ compounds respectively. Results obtained with $RBa_2Cu_3O_{7-x}$ [3] are also given in Table 2 for comparison.

The same remarks as for the oxygen atmosphere are applicable to the thermograms obtained in the nitrogen atmosphere, except that the onset melting temperature is lower than in the oxygen atmosphere. As observed for $RBa_2Cu_3O_{7-x}$ compounds, the melting in nitrogen is spread over a wider range of temperature than in oxygen.

For the $RBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$ series, DTA curves in nitrogen are similar to those obtained in oxygen. However, for the $RBaSrCu_3O_{7-x}$ series, two or more peaks are always present; this suggests that these compounds are very unstable during sintering and thus contain a high level of secondary phases. Owing to the complexity of the chemical reactions involved in these cuprate perovskites, more work will be necessary to identify these secondary phases.

Thermogravimetric analysis

Table 3 summarizes the thermogravimetric results obtained in oxygen and nitrogen atmospheres. Figures 5 and 6 show TG curves for $YBa_{1.5}Sr_{0.5}$

TABLE 3

TG results of $RBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$ and $RBaSrCu_3O_{7-x}$ perovskites in nitrogen and oxygen atmospheres

Compound	Nitrogen		Oxygen			
	T_{sl}	T_t	T_{sg}	T_m	%	T_d
$YBa_2Cu_3O_{7-x}$ [a]	440	600	325	490	1.2	165
$YBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$	400	540	190	450	1.8	260
$YBaSrCu_3O_{7-x}$	400	560	190	450	1.8	260
$GdBa_2Cu_3O_{7-x}$ [a]	400	560	250	330	1.3	80
$GdBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$	400	535	260	480	1.4	220
$GdBaSrCu_3O_{7-x}$	400	500	260	470	0.8	210
$SmBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$	400	500	300	480	1.3	180
$SmBaSrCu_3O_{7-x}$	390	480	280	450	0.9	170
$NdBa_2Cu_3O_{7-x}$ [a]	400	550	330	420	1.7	90
$NdBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$	400	500	340	460	1.1	120
$NdBaSrCu_3O_{7-x}$	390	490	190	420	1.5	230

[a] From ref. 3.

T_{sl}, Starting temperature for the loss of weight when heated in nitrogen.

T_t, Transition temperature.

T_{sg}, Starting temperature for the gain of weight when heated in oxygen.

T_m, Temperature of the maximum weight gain.

%, Percentage of gain in oxygen.

T_d, Difference of temperature between T_s and T_m.

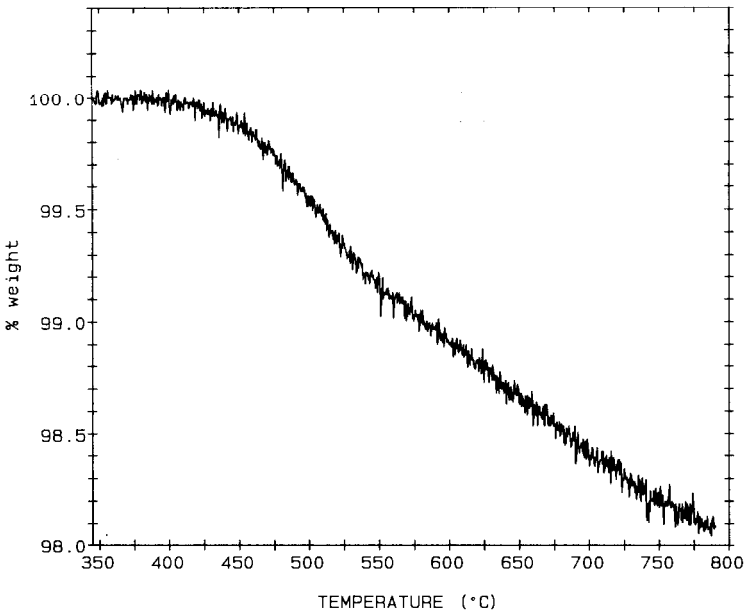

Fig. 5. TG curve of $YBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$ in a nitrogen atmosphere.

Cu_3O_{7-x} on heating in nitrogen and oxygen atmospheres respectively. Other curves are similar and do not indicate any different behavior.

There is a significant loss of weight in nitrogen on heating, starting at about 400 °C, for all the superconductors. The incorporation of Sr does not

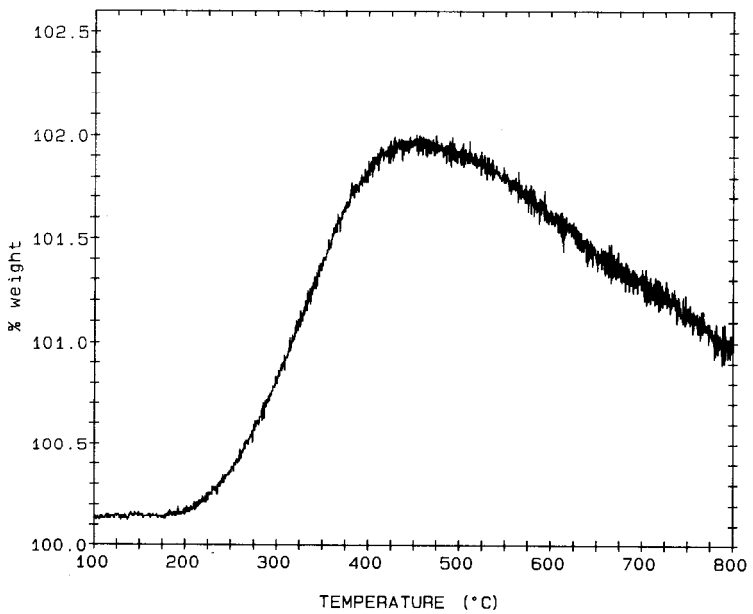

Fig. 6. TG curve of $YBa_{1.5}Sr_{0.5}Cu_3O_{7-x}$ in an oxygen atmosphere.

seem to change this behavior. There is also a small change in slope detected between 480 and 570 °C, depending on the compounds. The overall decrease in weight is a result of loss of oxygen whereas the change in slope is attributed to the orthorhombic–tetragonal transition. For $YBa_2Cu_3O_{7-x}$, the transition depends on the oxygen partial pressure and occurs when the stoichiometry is near $YBa_2Cu_3O_{6.5}$ [4–6]. It is reasonable to assume that similar behavior occurs for the compounds used in this work.

For the $RBa_2Cu_3O_{7-x}$ series, the transition temperature is affected by the R atom. Higher transition temperatures are obtained for a smaller R radius. After addition of Sr, the transition temperature is much reduced and the difference can reach 60 °C for the same R atom. This indicates that the transition occurs at a lower temperature because either the crystal is more disordered when Sr is present or the oxygen can be removed more easily in these compounds.

After heating in a nitrogen atmosphere, compounds remain oxygen deficient if they are cooled in nitrogen. It is possible to measure their reactivities with oxygen by heating them in this atmosphere. The results are shown in Table 3, where the starting temperature, the maximum temperature and the percentage of weight gain are reported. It is not clear from these results whether the incorporation of Sr helps the reactivity of a compound with oxygen or not. For example, Sr seems to help for yttrium compounds and $NdBaSrCu_3O_{7-x}$, as shown by the lower T_{sg}, but seems to have no influence or only a slight influence on the other compounds.

CONCLUSION

The replacement of a fraction of the barium atoms by strontium in the 123 compounds increases the temperature of the peritectic melting point and decreases the temperature of the orthorhombic–tetragonal transition. The increase in the melting point is more pronounced for an R atom with a small ionic radius and depends also on the Sr stoichiometry. The orthorhombic–tetragonal transition occurs at temperature 60 °C lower than for the $RBa_2Cu_3O_{7-x}$ series. The properties of the compounds which contain Sr seem not to give any advantages for the processing of these superconducting materials.

REFERENCES

1 J.M. Tarascon, W.R. McKinnon, L.H. Greene, G.W. Hull and E.M. Voget, Phys. Rev., Part B, 36 (1987) 226.
2 L. Parent, C. Moreau, D. Noël, S. Dallaire and B. Champagne, Mater. Lett., 7 (1989) 367.
3 D. Noël and L. Parent, Thermochim. Acta, 147 (1989) 109.

4 P.K. Gallagher, Adv. Ceram. Mater., 2 (3B) (1987) 632.
5 P.K. Gallagher, H.M. O'Bryan, S.A. Sunshine and D.W. Murphy, Mater. Res. Bull., 22 (1987) 995.
6 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., Part B, 36 (1987) 3608.