JOURNAL OF MATERIALS SCIENCE 30 (1995) 5644–5648

# Study of the effect of Na/Cu substitution in $Bi_4Sr_3Ca_3Cu_4O_{16}$ glass-ceramic superconductor

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The composition $Bi_4Sr_3Ca_3Cu_{4-x}Na_xO_{16}$ for $x=0.2$, 0.4, 0.6, 0.8 and 1.0 was examined, in order to study the effect of Na/Cu substitution on both the glass-forming ability as well as the superconducting properties of the glass-ceramic (GC) phase. Because the GC phase of the composition $Bi_4Sr_3Ca_3Cu_4O_{16}$ (4334) showed superconducting properties below 78.5 K, the crystalline phases formed after heat treatment were identified by X-ray diffraction. This suggests that $Na^+$ substituted the $Cu^+$ cations. The GC phases were studied by X-ray diffraction, differential thermal analysis, infrared absorption, d.c. electrical conductivity and low-temperature a.c. magnetic susceptibility in the temperature range 77–300 K. The present results support the considerations that the addition of sodium enhances the crystallization of the 4334 phase while sacrificing the glass-forming ability. The crystalline phases precipitated from the rapidly quenched glasses in the Bi–Sr–Ca–Cu–Na–O system were greatly dependent on the heat-treatment time as well as the treatment temperature. The stability and crystallization process of the glass differ greatly depending on the sodium content which acted as fluxing agent. Considering that the formation of the 4334 phase is largely enhanced in sodium-doped samples, it is concluded that the lowering of the partial melting temperature is very important for the enhancement of the formation of the 4334 phase, as well as in raising the critical transition temperature. Infrared spectroscopy measurements indicate that part of the ceramic phase is non-metallic. The two-probe method and the standard four-point probe method electrical resistivity indicate that Bi–Sr–Ca–Cu–Na–O superconductor formation was greatly dependent on heat-treatment time as well as treatment temperature. The superconducting crystalline phase, which grew upon heat treatment, was identified as a quasi-tetragonal phase 4334. Electrical resistance measurements together with thermopower results indicate that the electrical properties move from a metal region to a semiconducting region according to the magnetic phase diagram of oxide superconductors. Superconducting 4334 phase with $T_c=84$ K could be successfully prepared by the GC techniques within 1-2 h thermal cycling, which renders a great saving in processing costs and is a simple method of moulding superconducting articles.

## 1. Introduction

It is well established that the solid-state reaction method for processing superconducting (SC) ceramics is associated with three main drawbacks, namely, poor homogeneity, high porosity and brittleness, which make it very difficult for processing. In order better to control these drawbacks, the processes of melt texture [1], and glass-ceramics (GC) seem to offer distinct advantages over the solid-state reaction method. GC methods have been employed by various workers [2–5], specially for the high-temperature superconductors (HTSC) of the Bi–Cu compounds series. Recent reports claim high-temperature superconductors which have broken the record and reached a critical temperature as high as 250 K in Hg–Ba–Ca–Cu–O [6] and Bi–Sr–Ca–Cu–O [7] compounds. The recent report of Laguqs *et al.* [7] encourages further research on the Bi–Sr–Ca–Cu–O system, together with the other important features of the bismuth compound, that is its ability to be formed as a glass as well as ceramics and GC.

One type of these glasses, Bi–Sr–Ca–Cu–O, could be devitrified to high-temperature superconductors if proper heat treatment is achieved [2–4]. $Bi_2O_3$ has been known for a long time as a conditional glass former. In the present work the composition $Bi_4Sr_3Ca_3Cu_{4-x}Na_xO_{16}$ ($x = 0.2$–1.0) has been selected for our studies, to establish the process of glass formation, fluxing and modifying action of sodium addition, which as in silicate glasses may reduce the melting point and improve the glass quality. On the other hand a reduction in melting point, $T_m$, would enhance the SC transition temperature, $T_c$, a phenomena observed by Scheel *et al.* [8] and independently also by Bahgat [9]. Because of

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charge neutrality of the doped composition, the concentration of holes in the Cu–O layer may also show a change, and the $T_c$ (critical transition temperature to the SC state) may be increased according to the magnetic phase diagram [10] owing to the existence of $Na^+$ cations which may substitute $Cu^+$ cations, as both have the same ionic size and charge. The GC phases were studied by X-ray diffraction, differential thermal analysis (DTA), infrared (IR) absorption, d.c. electrical conductivity and low-temperature a.c. magnetic susceptibility in the temperature range 77–300 K.

## 2. Experimental procedure

### 2.1. Preparation of the glass and glass-ceramic

In the present work, the composition $Bi_4Sr_3Ca_3Cu_{4-x}Na_xO_{16}$ was examined, in order to study the effect of Na/Cu substitution on both the glass-forming ability and the superconducting properties of the GC phase, because the GC phase of the composition (4334) showed superconducting properties below 78.5 K [3,4]. Appropriate amounts of $Bi_2O_3$, $SrCO_3$, $CaCO_3$, $Na_2CO_3$ and CuO for $x = 0.2$, 0.4, 0.6, 0.8 and 1.0, were thoroughly mixed and ground in an agate mortar. The mixture was then melted in a platinum crucible in air at 950 °C for 0.5–1 h, during which the melt was occasionally stirred to ensure complete mixing, fusion and complete decomposition of carbonates. The melt was then poured and rapidly quenched by pressing between two copper plates, resulting in opaque black sheets of glass about 0.5 mm thick. The glass was examined visually, as well as by X-ray diffraction for traces of crystallinity.

The GC phase was produced by heat treatment of the glass samples at 820 ± 5 °C for 0.5 h, following the DTA results, as well as on a trial and error procedure. This was found to be the most appropriate condition under which to obtain SC phase, otherwise the sample exhibits partial melting and shape deformation or the superconducting phase will not be precipitated. However, it was found helpful not to discard samples which may show a certain degree of crystallinity. The crystalline phases formed after heat treatment were identified by X-ray diffraction patterns (XRD). In the XRD patterns most of the peaks could be identified on the basis of an orthorhombic unit cell with lattice constants $a = 0.537$ nm, $b = 0.540$ nm and $c = 3.087$ nm, showing the same reflection reported previously for bismuth compound 4334 [3,4], and some other combined traces of CuO, $SrCO_3$ and $CaCO_3$. It was clear that the diffraction peaks became sharper and more intense with increasing sodium contents, indicating that the 4334 phase grew with increasing sodium contents. Another observation made during this study was that no shift occurred in the position of the main peaks in the XRD patterns of the 4334 phase. This suggests that $Na^+$ substituted for the $Cu^+$.

### 2.2. Techniques

In the present work several experimental tools were used to identify and study both the glass and the GC phases. X-ray diffraction was used to estimate the crystalline phases which were grown upon heat treatment; the crystalline phases shown were identified by comparison with ASTM cards, as well as those reported previously for ceramic phases of similar composition [1–4]. Differential thermal analysis (DTA, DuPont Model 990 thermal analyser), was used to define the glass transition temperature, $T_g$, the crystallization temperature, $T_{cr}$, and melting temperature, $T_m$, of the glass phase. Qualitative thermopower using the hot-probe method was used to determine the carrier type where it is often necessary to determine whether an extrinsic sample is p-type or n-type as an important requirement for cuprate HTSC. IR spectra, using a computerized spectrophotometer type Shimadzu IR440, were recorded in the range 300–1500 $cm^{-1}$. Electrical resistance measurements using the standard four-point probe technique and the low-temperature a.c. magnetic susceptibility, as measured by the mutual inductance method at 400 Hz frequency in the temperature range 77–300 K, were used to determine the existence of superconductivity in the ceramic phases, these two sets of equipment are home made.

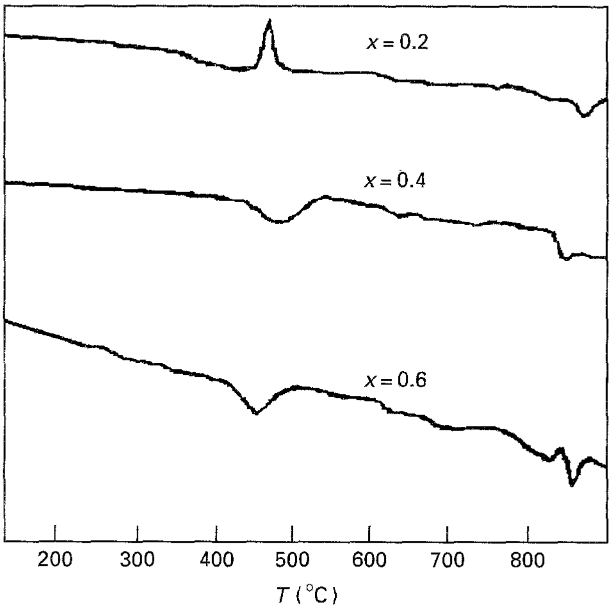

*Figure 1* DTA thermograms for the glass and glass-ceramic phases of the as-quenched composition $Bi_4Sr_3Ca_3Cu_{4-x}Na_xO_{16}$, with $x = 0.2$, 0.4 and 0.6.

## 3. Results and discussion

### 3.1. Differential thermal analysis

DTA curves in the temperature range 30–900 °C for the composition $Bi_4Sr_3Ca_3Cu_{4-x}Na_xO_{16}$ where $x = 0.2$, 0.4 and 0.6, respectively, are shown in Fig. 1. Generally, the curves show an endothermic drop around 400 °C, indicating a glass transition temperature, $T_g$. This is followed by an exothermic peak of crystallization. $T_g$, $T_{cr}$ and $T_m$ are summarized in Table I. For a sodium-free sample [3,4], melting is observed at $T_m = 839$ °C, as a very weak endothermic dip. The ratio $T_g/T_m = 0.5$ and the difference $(T_o - T_g) = 65$ °C indicates the good quality of the

TABLE I Thermal and superconducting parameters

| $x$ | $T_c$ (K) | $T_g$ (°C) | $T_o$ (°C) | $T_x$ (°C) | $T_m$ (°C) | State |
|---|---|---|---|---|---|---|
| 0.0 | 78.5 | 420 | 485 | 514 | 839 | Superconducting |
| 0.2 | – | 400 | 448 | 470 | 838 | Non-superconducting |
| 0.4 | 80 | 420 | – | – | 816 | Superconducting |
| 0.6 | 84 | 424 | – | – | 806 | Superconducting |
| 0.8 | 81 | – | – | – | – | Super + semiconducting |

glass. In the sample containing 0.6 Na, two endothermic peaks were detectable after a diffused exothermic reaction; these two peaks may be explained as actual melting at 806 °C followed by a decomposition at 860 °C. The compositions with $x = 0.4$ and 0.6 seem to be composites of glass and polycrystals and the crystallization is a very slow process, as seen from the DTA curve. It can be said that this transition is of a second-order type, where a well-defined exothermic peak is not recognized. The present results indicate that the partial melting temperature is lowered by the addition of $Na_2O$. One further important experimental observation is that the glass-forming tendency decreased as the sodium contents increased, although the SC transition temperature, $T_c$, was increased by the substitution of sodium.

### 3.2. IR spectroscopy measurements

The results of i.r. spectroscopy measurements are considered in order to discuss the basic vibrations of the building units of the studied GC. Fig. 2 shows the i.r. spectra of the system $Bi_4Sr_3Ca_3Cu_{4-x}Na_xO_{16}$ for $x = 0.2$–1.0. It can be seen that the spectra consist of several absorption bands and humps mainly at 400–500, 860, 1000 and 1400 cm$^{-1}$. The first band may be related to the overlapped peaks of Cu–O, Ca–O and Bi–O vibrations [11]. Bishay and Maghrabi [12] assigned the peak at 860 cm$^{-1}$ in the infrared spectra to a totally symmetric stretching vibration mode of the $BiO_3$ pyramidal point group $C_{3v}$. Considering that three-coordinated bismuth has not been found in any crystals, the formation of $BiO_3$ pyramidal units in the glasses is doubtful [13]. Bismuth atoms generally form distorted $BiO_6$ octahedra in most oxide crystals, such as $Bi_2O_3$ and $Bi_4Si_3O_{12}$. It is well established that the six Bi–O bonds in a $BiO_6$ octahedron are classified into two groups of short (0.2–0.22 nm) and long (0.25–0.28 nm) Bi–O on the basis of Bi–O interatomic distances. It is proposed that the distorted $BiO_6$ octahedron involves a BiO species, when three Bi–O distances in the $BiO_6$ octahedron are nearly equal and its intensity depends on the amount of nearest neighbour Sr–O [13]. The bands at 1000 and 1400 cm$^{-1}$ could be assigned to stretching vibrations of C–O [10] with nearest neighbour Sr–O or Ca–O, respectively, as confirmed from the XRD. This indicates that, although the melting was done properly, there remain traces of carbonyl groups. It can be seen that the sample containing 0.2 Na seems to retain its amorphous state even after heat treatment. However, from the i.r. spectra of the ceramic phases, it is clear that the metallization is not achieved completely, indicating that part of these phases is non-metallic. This is in agreement with the electrical resistivity and a.c. susceptibility measurements.

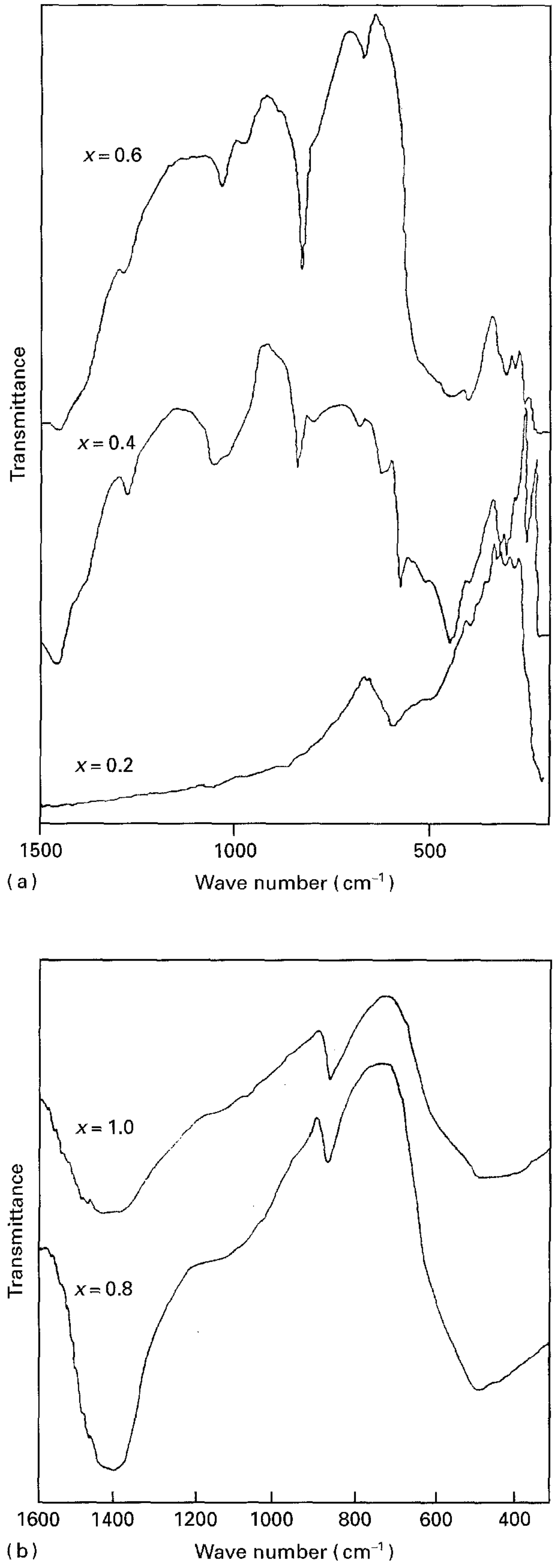

*Figure 2* IR spectra for the glass and glass-ceramic phases of the as-quenched composition $Bi_4Sr_3Ca_3Cu_{4-x}Na_xO_{16}$, with (a) $x = 0.2$, 0.4 and 0.6, and (b) $x = 0.8$ and 1.0.

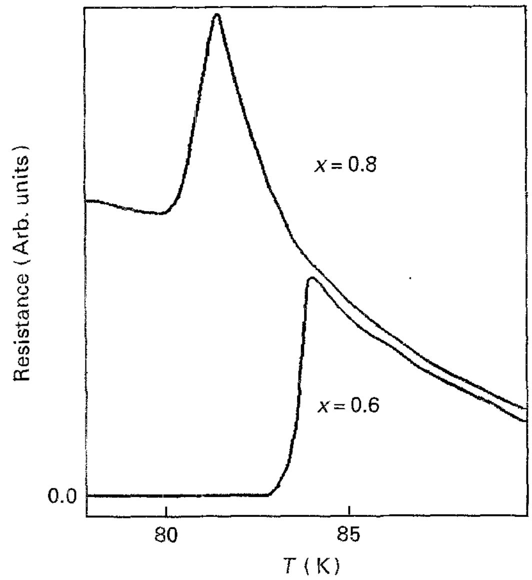

*Figure 3* Low-temperature electrical resistance of the glass-ceramic phase of the composition $Bi_4Sr_3Ca_3Cu_{4-x}Na_xO_{16}$, with $x = 0.6$ and 0.8.

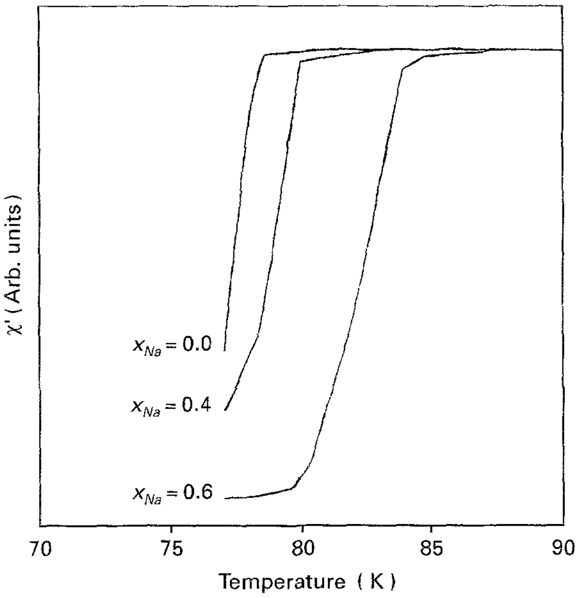

*Figure 4* Effect on the a.c. magnetic susceptibility of the Cu/Na substituted glass-ceramic phases of the composition $Bi_4Sr_3Ca_3Cu_{4-x}Na_xO_{16}$, with $x = 0.4$ and 0.6.

## 3.3. Study of superconductivity of the $Bi_4Sr_3Ca_3Cu_{4-x}Na_xO_{16}$

In order to study the effect of the crystallization process on resistivity, the two-probe method as well as the standard four-point probe method were used for electrical resistance measurements of the as-quenched glass and the GC phases at room temperature. It is seen that after crystallization, the resistivity of the GC samples is reduced by about $10^{10}$ times. Fig. 3 shows a representation of the temperature dependence of electrical resistance for samples with $x = 0.6$ and 0.8. The sample containing 0.6 Na showed a resistance drop at onset $T_c = 84$ K, while the sample containing 0.8 Na showed a semiconducting behaviour and a transition temperature at 81 K, and had a long tail continuing down to 77 K and which did not reach zero. These transitions are due to a mixture of semiconductor and superconductor phases as shown. Fig. 4 shows a representation of the temperature dependence of the real susceptibility $\chi'$ for samples with $x = 0.4$ and 0.6, where the diamagnetic drop is clearly apparent and the onset $T_{on}$ as given in Table I. The relations between the transition temperature, $T_c$, melting temperature, $T_m$, and sodium concentration, $x$, are shown in Fig. 5. It is obvious that $T_c$ increases systematically with increasing sodium content and it reaches a maximum value of 84 K for $x = 0.6$, and then drops with further increase in sodium, while the melting temperature is lowered as shown. On the other hand it is evident from the present qualitative thermopower measurements that all our samples exhibit p-type behaviour. Generally speaking, because the state of the Cu–O layers has been recognized as an essential part for superconductivity, a quite useful approach is to modify the charge-carrier concentration in the active Cu–O layers for any compound family, where the superconducting transition temperature is maximized in a narrow range of hole (or electron) concentration [10]. The magnetic phase diagram for cuprates [10], illustrates how magnetic and transport properties vary as the hole concentration is changed. Metallic transport and superconductivity both appear when the electron concentration deviates from the undoped phase of Cu–O layer. In this range, the absence of a normal metal phase as $T$ approaches 0 K, that is the compounds are either spin glass or insulating at low doping levels, is noted. On the right of the superconducting range with high hole-doping level, the materials are metallic but not superconducting, and their properties resemble those of ordinary metals. According to the above results and those obtained from the present electrical resistance

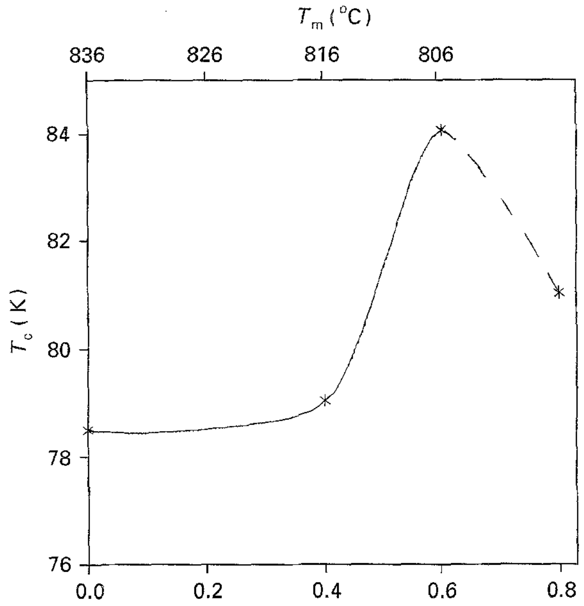

*Figure 5* The relation between the fraction, $x$, of sodium substituting for copper in the glass-ceramic phases of the $Bi_4Sr_3Ca_3Cu_{4-x}Na_xO_{16}$, and both the apparent SC transition, $T_c$, and the melting, $T_m$, temperatures.

measurements it can be said that our samples move from a metal region to a semiconducting region as the sodium content increases, i.e. the hole concentration decreased as sodium content increased, and this may explain why $T_c$ drops for 0.8 Na.

## 4. Conclusions

1. The present results support the postulation that the addition of sodium enhances the crystallization of the 4334 phase while sacrificing the glass-forming ability.

2. The crystalline phases precipitated from the rapidly quenched glasses in the Bi–Sr–Ca–Cu–Na–O system were greatly dependent on the heat-treatment time as well as the treatment temperature.

3. The stability and crystallization process of the glass differ greatly depending on the sodium content which acted as fluxing agent.

4. Considering that the formation of the 4334 phase is largely enhanced in sodium-doped samples, it is concluded that the lowering of the partial melting temperature is very important for the enhancement of the formation of the 4334 phase, also confirming the raising of the critical transition temperature.

5. IR spectroscopy measurements indicate that part of the ceramic phase is non-metallic.

6. The two-probe method and the standard four-point probe method electrical resistivity indicate that Bi–Sr–Ca–Cu–Na–O SC formation is greatly dependent on heat-treatment time as well as treatment temperature.

7. The SC crystalline phase which grew upon heat treatment is identified as a quasi-tetragonal phase 4334.

8. Electrical resistance measurements together with thermopower results indicate that the electrical properties move from a metal region to a semiconducting region, according to the magnetic phase diagram of oxide superconductors.

9. Superconducting 4334 phase with $T_c = 84$ K could be successfully prepared by the GC techniques within 1–2 h thermal cycling, which renders a great saving in processing costs, as well as being a simple method of moulding SC articles.

## References

1. S. X. DOU, H. K. LIU, W. M. WU, W. X. WANG, C. C. SORRELL, R. WINN and N. SAVVIDES, *Phys. C* **172** (1990) 295.
2. F. GAN and G. LI, *J. Non-Cryst. Solids* **130** (1991) 67.
3. A. A. BAHGAT, S. A. EISSA and S. H. SALAH, *J. Mater. Sci. Lett.* **13** (1994) 826.
4. A. A. BAHGAT, *Mater Sci. Eng.* **B26** (1994) 103.
5. N. BANSAL, *J. Appl. Phys.* **68** (1990) 1143.
6. J.-L. THOLENCE, B. SOULETIE, O. LABORDE, J.-J. CAPPONI, C. CHAILLOUT and M. MAREZIO, *Phys. Lett.* **A184** (1994) 215.
7. M. LAGUQS, X. M. XIE, H. TEBBJI, X. Z. XU, V. MAIRET, C. HATTERE, C. F. BEURAN and C. DEVILLE-CAVELLIN, *Science* **262** (1993) 1850.
8. H. J. SCHEEL, M. BERKOWSKI and B. CHABOT, *J. Crystal Growth* **115** (1991) 19.
9. A. A. BAHGAT, *High Tc UpDate* **6**(19) (1992) 5, presented at the XVI Solid State Conference, El-Menia, Egypt, January 1993.
10. R. J. BIRGENEAU, *Am. J. Phys.* **58** (1990) 28.
11. N. NAKAMOTO, "Infrared spectra of inorganic and coordination compounds" (Wiley, New York, 1963).
12. A. BISHAY and C. MAGHRABI, *Phys. Chem. Glasses* **10** (1969) 1.
13. F. MIYAJI, T. YOKO and S. SAKKA, *J. Non-Cryst. Solids* **126** (1990) 170.

*Received 10 November 1994*
*and accepted 24 May 1995*