

# XRD and micro Raman characterization of epitaxial Bi-2201, Bi-2212 and Bi-2223 thin films.

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Micro Raman characterization is performed on high quality thin films of  $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$  (2201),  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  (2212),  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$  (2223) made by dc-sputtering. Single crystal x-ray measurements reveal the full epitaxy of the films, which allows for polarized Raman spectra to be obtained.

## 1. XRD CHARACTERIZATION

Thin films of the three phases of the superconducting series  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  ( $n=1,2,3$ ), prepared [1] by dc-sputtering on  $\text{SrTiO}_3$  (100) substrates and having transition temperatures  $T_c(2212)=83\text{K}$  and  $T_c(2223)=90\text{K}$  (the 2201 thin film is not superconducting until 4K), are investigated by single-crystal x-ray analysis. As can be seen in the pole figures of Fig.1, only 4 distinct peaks appear for each reflection when rotating the sample by angle  $\phi$ , which shows that the films are epitaxial, their c-axis being normal to their surface. Knowing the exact directions of the a, b axes of the films, an investigation with polarized Raman spectroscopy is carried out.

## 2. RAMAN CHARACTERIZATION

Raman spectra are obtained for the three films, using a Jobin Yvon T64000 triple spectrometer equipped with a microscope employing a 488.0nm  $\text{Ar}^+$  line. Within the  $I4/mmm$  space group (we adopt this, as a simplifying model, though the Bi-series are well known to exhibit orthorhombic distortion and b-axis modulation), the following Raman active modes are expected (all involving c-axis vibrations): **2201 phase:**  $4A_g$  (concerning Bi, Sr,  $\text{O}_{\text{Bi}}$ ,  $\text{O}_{\text{Sr}}$  atoms). **2212 phase:**  $6A_g$  (concerning Bi, Sr, Cu,  $\text{O}_{\text{Bi}}$ ,  $\text{O}_{\text{Sr}}$ ,  $\text{O}_{\text{Cu}}$  atoms) and  $1B_{1g}$  (out-of-phase, vibrations of the  $\text{O}_{\text{Cu}}$  atoms). **2223 phase:**  $7A_g$  (Bi, Sr, Cu, Ca,  $\text{O}_{\text{Bi}}$ ,  $\text{O}_{\text{Sr}}$ ,  $\text{O}_{\text{Cu}}$  atoms) and  $1B_{1g}$  (out-of-phase vibrations of the  $\text{O}_{\text{Cu}}$  atoms).

However, it is to be noted that orthorhombic distortion and 110-axis modulation will result in the appearance of extra, weaker modes, which are not expected in the tetragonal  $I4/mmm$  scheme.

In Figs.2,3,4 the polarized Raman spectra of the 2201, 2212 and 2223 thin films taken at room

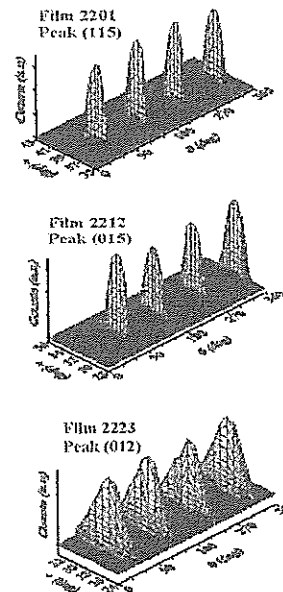


Fig.1 normally assigned to the lowest frequency peak of the spectrum. The Bi-mode is observed at  $69\text{cm}^{-1}$  in the 2201 phase (Fig.2) and at  $61\text{cm}^{-1}$  in the 2212 phase (Fig.3), while in the 2223 case it cannot be resolved.

**The Sr- phonon.** The c-axis Sr- phonon does not change frequency in the three phases and it is observed at  $119\text{cm}^{-1}$  in all three compounds (Figs.2,3,4). This is a natural consequence of the surrounding of the Sr atom being the same in the three compounds. The shoulder in the lower frequency side of the Sr peak occurs at  $109\text{cm}^{-1}$  in all three compounds and may be attributed to an extra Sr mode, due to the modulation in the BiO planes.

**The  $B_{1g}$  phonon.** The  $293\text{cm}^{-1}$  peak in the 2212 spectra of Fig.3 and the  $252\text{cm}^{-1}$  peak in the 2223

temperature are shown. ( $x'x'$ ) denotes polarizations parallel to the 110 direction, while ( $x'y'$ ) denotes cross polarizations along the 110 and  $1\bar{1}0$  directions. Also, polarized Raman spectra at temperature 77K are taken for the 2212 and 2223 films and are shown in Figs.5,6.

**The Bi- phonon.** Differences are observed in the frequency of the Bi-mode, which is

spectra of Fig.4, that are observed in all of the parallel and in only the (x'y') of the cross polarizations, can unambiguously be assigned to the out-of-phase vibrations of the Oxygen atoms of the CuO<sub>2</sub> layers (noted as O<sub>Cu</sub>), predicted from group theoretical analysis to have B<sub>1g</sub> symmetry. The difference in frequencies is due to the different couplings between the CuO<sub>2</sub> planes in the two phases, owing to the extra CuO<sub>2</sub> and Ca planes (similar case is observed in YBCO [3]).

**The O<sub>Sr</sub>- and the O<sub>Bi</sub>-phonon.** The particularly intense peaks at 463cm<sup>-1</sup> of Fig.2 (2201 phase), 466cm<sup>-1</sup> of Fig.3 (2212 phase) and 471cm<sup>-1</sup> of Fig.4 (2223 phase) are attributed to the c-axis vibrations of the O atom of the SrO planes (noted as O<sub>Sr</sub>), contrary to other works that assign it to the O<sub>Bi</sub> atom [2 and references within]. The motivation for this is that in our low temperature data (Figs.5,6), where the lattice vibrations are clarified, this phonon exhibits simple structure, in contrast to the 600-670cm<sup>-1</sup> zone, which splits in components (615, 636, 667cm<sup>-1</sup> in 2212 in Fig.5 and 607, 631, 668cm<sup>-1</sup> in 2223 in Fig.6). Thus, the zone 600-670cm<sup>-1</sup> of Figs.2-6 is attributed to the vibrations of the Oxygen atom of the BiO planes, where Oxygen disorder dominates. Another observation which supports the above assignment is the existence of a shoulder peak on the low frequency side of the 466cm<sup>-1</sup> peak (seen more clearly in the low temperature spectra of Figs.5,6), similar to the shoulder of the 119cm<sup>-1</sup> peak of Sr.

**Continuous background of low Temperature data.** In Fig.5 one can see that there is a significant decrease in the intensity of the background (especially at low frequencies), when the temperature is reduced. This behavior strongly suggests a phononic type background, though it cannot be resolved if it is one-phonon scattering or two-phonon scattering.

#### References

1. M. Holiastou et. al. (to be published).
2. M. Kakihana, Phys.Rev.B. 53 (1996) 11796.
3. N. Poulakis et al. Phys.Rev.B. 53 (1996) R534

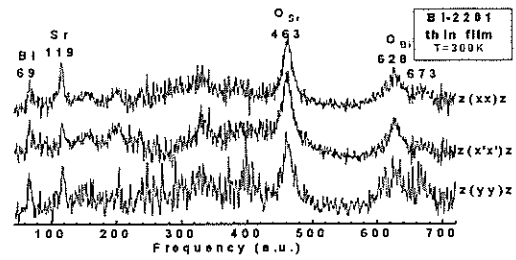


Fig.2

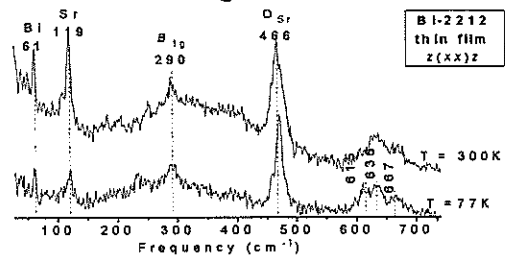


Fig.3

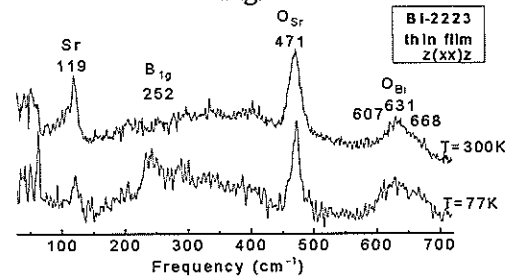


Fig.4

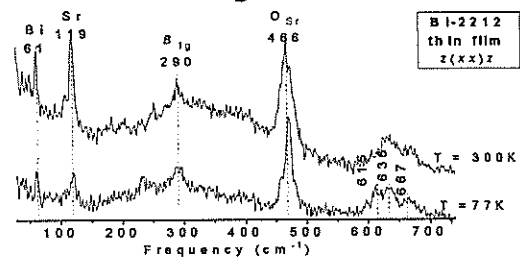


Fig.5

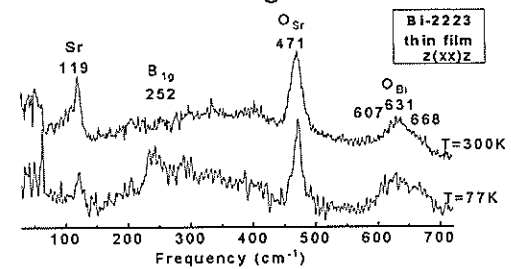


Fig.6