

## Microstructure of $\text{Bi}_{2212}$ and $(\text{Bi}/\text{Pb})_{2212}$ single crystals and effect of electron donors and acceptors

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### Abstract

Pure and lead doped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  ( $\text{Bi}_{2212}$ ) single crystals were grown and their structures were studied by several methods, especially by resistivity measurements, electron microprobe and Raman micro-spectroscopy. The microstructure and the Raman spectrum of  $\text{Bi}_{2212}$  were analyzed in comparison to those of  $\text{Bi}_{2201}$  and  $\text{Bi}_{2223}$  single crystals. In these structures, the existence of close, staggered and antiparallel Bi-O bonds leads to a Raman doublet at 653 and 627  $\text{cm}^{-1}$  which corresponds to coupled motions in these bonds. The intercalation of iodine in  $\text{Bi}_{2212}$  suppresses this staggered configuration and gives a more homogeneous vertically aligned distribution of  $(\text{Bi})\text{O}(\text{Cu})$  bonds. In these intercalations, the presence of unsymmetrical  $\text{I}_3^-$  ion is demonstrated. Similar bond-ordering was observed on intercalation with chloranil and tetrahydrofuran. By lead doping, the staggered bonds are no longer identical and the decoupling leads to a single phonon around 623  $\text{cm}^{-1}$  and confirms that Pb occupies Bi position.

### 1 - Introduction

In the recent years, many papers have appeared concerning the physical properties of bismuth-based superconductors. But the impurities and intergrowth of different phases often give controversial results and wrong interpretations. Having a large series of samples, mostly single crystals of undoped  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  ( $n = 1,2,3$ ) systems, we are attempting to give a coherent analysis of their Raman spectra in relation to their microstructure. The bond-ordering in lead-doped materials, as well as in iodine or other electron donor and acceptor intercalated compounds will help to clarify the correlation between Raman spectra and structure.

### 2 - Experimental

Before undertaking Raman studies, each sample was selected and checked with different methods such as X-Ray pattern, resistivity and magnetic susceptibility measurements, electron micro-probe analysis (EMPA). With systematic use, Raman spectroscopy also becomes a powerful technique for identification.

All the samples do not have their composition rigorously identical to  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  ( $n = 1,2,3$ ). For instance, the  $\text{Bi}_{2212}$  used<sup>(1)</sup> as starting material is revealed by EMPA as having  $\text{Bi}_{1.87}\text{Sr}_{1.84}\text{Ca}_{1.00}\text{Cu}_{1.96}\text{O}_8$  composition.

The Raman spectra were recorded on Raman micro-spectrometers Dilor/Omars equipped with a multichannel photodiode detector and Dilor/Z24 triple monochromator<sup>(2,3)</sup>.

### 3 - Results and discussion

#### 3.1 - Raman spectra and microstructure

The observed phonons from polarized Raman spectra of  $\text{Bi}_{2201}$ ,  $\text{Bi}_{2212}$ ,  $\text{Bi}_{2223}$  are displayed in Table 1 along with those of lead doped  $(\text{Bi}/\text{Pb})_{2212}$  and  $(\text{Bi}/\text{Pb})_{2223}$ .

All these materials present *strong anisotropy*, with very strong Raman bands around 630  $\text{cm}^{-1}$  for ZZ scattering geometry (along the *c*-axis), in contrast with weak features in the other geometries (Fig.1). This property is particularly helpful in the determination of the orientation of surfaces and thin films<sup>(4,5)</sup>.

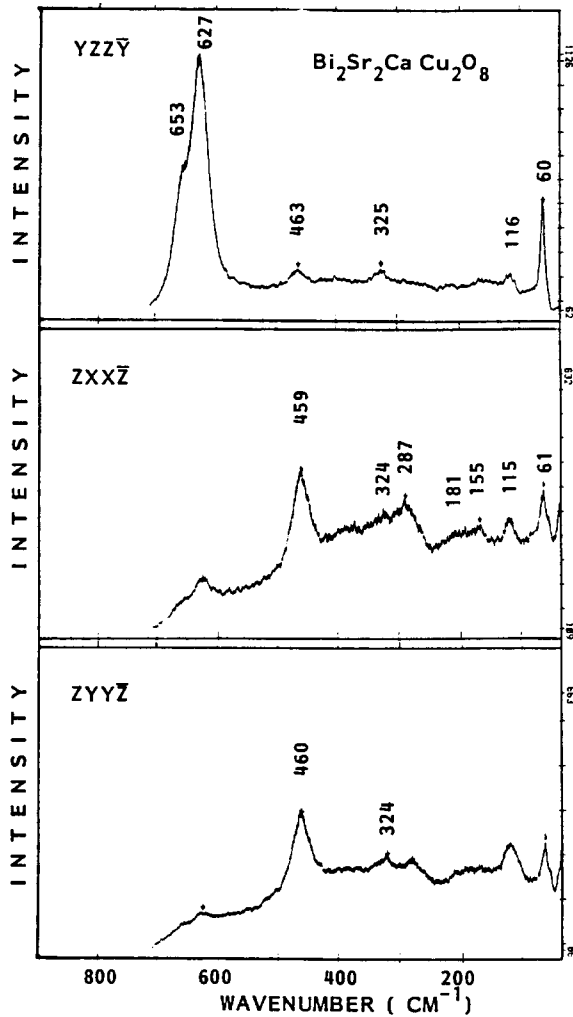


Fig.1 - Polarized Raman spectra of  $\text{Bi}_{2212}$ .

The XX and YY Raman spectra are very similar for each material. This is in agreement with a nearly tetragonal structure (Fig.2). Of course, these figures represent only ideal and limiting structures.

With the  $I4/mmm$  space group<sup>(6-8)</sup> for these materials, for instance for  $\text{Bi}_{2212}$ , the phonon modes are:

- $6A_{1g} + B_{1g} + 7E_g$  : Raman active
- $6A_{2u} + 7E_u$  : infrared active
- $B_{2u}$  : silent.

The highest frequency  $A_{1g}$  phonons appear as a doublet at 653 and 627  $\text{cm}^{-1}$ . These two bands are found in all compounds presenting close, staggered and antisymmetrical Bi-O bonds<sup>(9-13)</sup>. They could correspond to the coupled motions in these bonds in the solid network. As the higher frequency band disappears in  $\text{Bi}_{1212}$ <sup>(14)</sup> where the

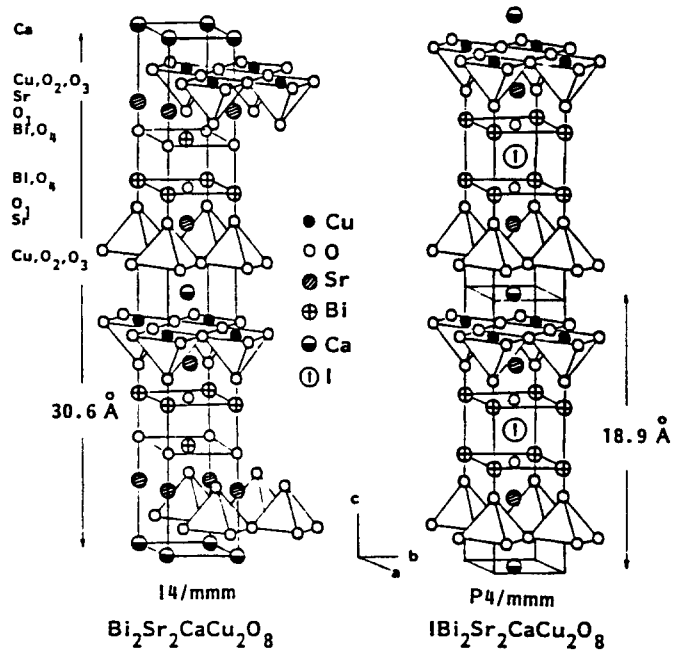


Fig.2 - Scheme of spatial structures of  $\text{Bi}_{2212}$  and  $I.\text{Bi}_{2212}$ .

Bi-O planes are in mirror image without any staggered configuration, we call it "staggered Bi-O motion". Note that in lead-doped materials, this mechanical coupling disappears, and only the lower frequency band remains as the staggered and antiparallel bonds are no longer identical<sup>(9)</sup>. This also indicates that *Pb occupies Bi position*.

The very low frequency  $A_{1g}$  mode in  $\text{Bi}_{2212}$  is located at 60  $\text{cm}^{-1}$  and represents Sr c-axis

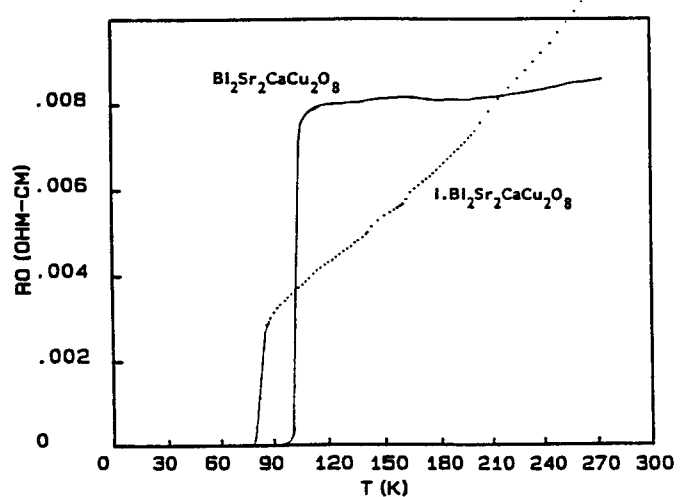


Fig.3 - Resistivity of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  and  $I.\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  versus temperature.

Table 1 - Observed Raman Shifts and Assignment for Bi-based High-Tc Superconductors Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>2n+4</sub> (n = 1,2,3).

Bi <sub>2201</sub>	Bi <sub>2212</sub>	Bi <sub>2223</sub>	(Bi/Pb) <sub>2212</sub>	(Bi/Pb) <sub>2223</sub>	Scattering geometry	Symmetry & Assignment
651	653	650			ZZ	A <sub>1g</sub> (Bi)O(Cu) staggered
623	627	625	623	624	ZZ	A <sub>1g</sub> (Bi)O(Cu)
	463		459	464	ZZ	A <sub>1g</sub> O(Sr)
325	325		328	326	ZZ	A <sub>1g</sub> O(Cu) <sub>z</sub> in phase
				170	ZZ	
	150		149		ZZ	A <sub>1g</sub> Cu <sub>z</sub>
	116				ZZ	A <sub>1g</sub> Bi <sub>z</sub>
			85		ZZ	
70	60	51	58	52	ZZ	A <sub>1g</sub> Sr <sub>z</sub>
37	37				ZZ	
455	460	459	457	451	XX,YY	B <sub>1g</sub> O(Cu) <sub>z</sub> out of phase
288	287	292	276	275	XX,YY	
		217		217	XX,YY	
	181		173		XX,YY	
	155				XX,YY	
117	115	116	103	108	XX,YY	
	60	52	58	51	XX,YY	
37	37				XX,YY	
					XX,YY	
					XX,YY	

vibration. The frequency of this Sr mode is strongly affected by the lightening or the weighting in its neighborhood : it changes to 70 cm<sup>-1</sup> in Bi<sub>2201</sub> and to 51 cm<sup>-1</sup> in Bi<sub>2223</sub>.

The assignment of the other Raman bands are given in the Table.

### 3.2 - Iodine intercalation : presence of I<sub>3</sub><sup>-</sup>

The intercalated compound, obtained by exposing Bi<sub>2212</sub> single crystals in saturated I<sub>2</sub> vapor in a sealed silica tube at 170°C during three days, shows T<sub>c</sub> at 78 K (Fig.3) -lowered by 19 K compared to that of the parent crystal (T<sub>c</sub> = 97 K)- and gives a Raman spectrum (Fig.4) with a single (Bi)O stretching band at 621 cm<sup>-1</sup>. This fact is in agreement with the disappearance of the staggered configuration of the Bi-O bonds which become far apart from one to another<sup>(15)</sup>, leading to a single formula unit cell (Fig.2). Strong Raman bands are observed at 149 and 107 cm<sup>-1</sup> and may correspond to unsymmetrical I<sub>3</sub><sup>-</sup> as the ν<sub>3</sub> and ν<sub>1</sub> stretching modes of this ion generally lie in the same range<sup>(16)</sup>. They can not be associated with I<sub>5</sub><sup>-</sup> or longer ions as their stretching motions are located at much higher frequencies<sup>(17)</sup>. Another fact against the presence of I<sub>5</sub><sup>-</sup> is the absence of resonance Raman

effect when changing the excitation laser line from 514.5 to 457.9 nm and 647.1 nm. In particular, with the latter excitation which locates exactly at the absorption maximum of I<sub>5</sub><sup>-</sup>, its resonance effect could be very strong, but it is not experimentally the case.

Another strong support for the presence of I<sub>3</sub><sup>-</sup> is its pre-resonance effect giving the progression of its ν<sub>1</sub> fundamental mode with its overtones 2ν<sub>1</sub>, 3ν<sub>1</sub> and 4ν<sub>1</sub> respectively at 107, 214, 321 and 427 cm<sup>-1</sup> and its ν<sub>3</sub> fundamental rendered Raman active at 149 cm<sup>-1</sup> and the overtone 2ν<sub>3</sub> at 298 cm<sup>-1</sup>.

A small decrease in the Bi-O stretching phonon from 627 to 621 cm<sup>-1</sup> reflects that the *interaction between I<sub>3</sub><sup>-</sup> and the adjacent Bi-O layers is relatively weak*. Moreover the broadening of all observed bands suggests *inhomogeneous distribution of I<sub>3</sub><sup>-</sup> ions in the lattice with more than one I atom being off-centered*.

The absence of strong anisotropy of ν<sub>1</sub> and ν<sub>3</sub> bands in the three scattering geometries suggests that the I<sub>3</sub><sup>-</sup> is neither parallel nor perpendicular to the *ab* plane but has an inclined orientation. We must mention that we cannot exclude the presence of I<sup>+</sup> and I<sup>-</sup> ions as mono-atomic species have no vibration in Raman scattering.

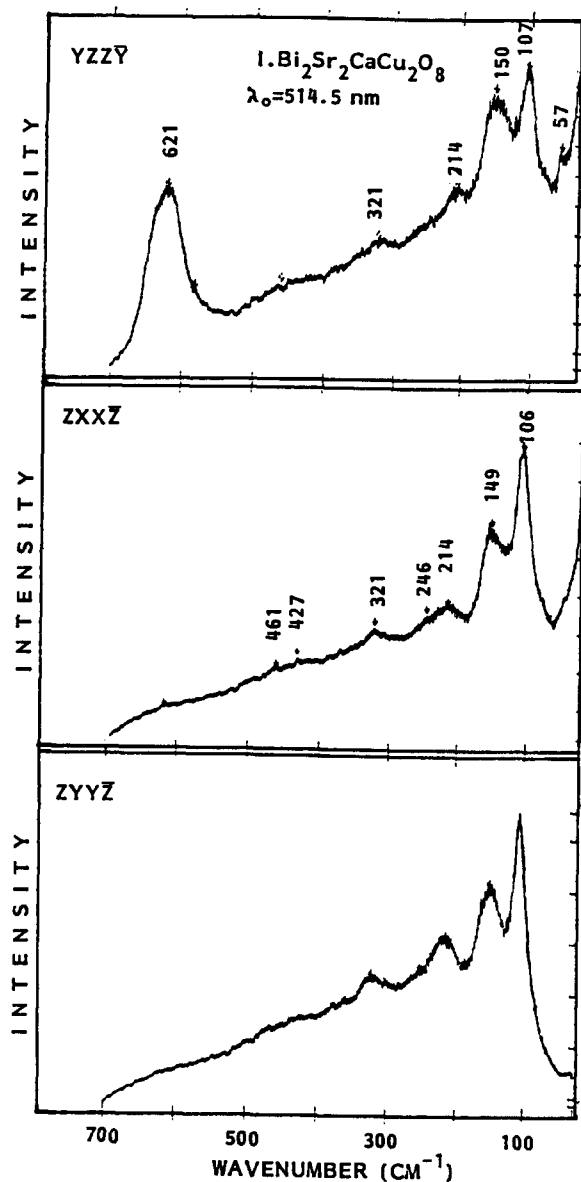


Fig.4 - Polarized Raman spectra of  $\text{I. Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ .

With chloranil and tetrahydrofuran doped  $\text{Bi}_{2212}$  we observe similar collapse of the Bi-O stretchings into only one band. This could also correspond to the disappearance of the staggered configuration of the Bi-O planes and the increase of the distance between the two layers. Thus, the spectral and micro-structure changes are mostly induced by intercalation and are much less dependent on the donor acceptor interactions although these forces exist.

### Acknowledgment

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