

## Structure and Raman spectrum of $\text{BiSr}_2\text{CaCu}_2\text{O}_7$ ( $\text{Bi}_{1212}$ ) superconductor

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### Abstract

*$\text{BiSr}_2\text{CaCu}_2\text{O}_7$  ( $\text{Bi}_{1212}$ ) is prepared and characterized by various methods in particular by Raman spectroscopy. The material is found to be very anisotropic. The identity between the polarized Raman spectra along XX and YY axes is in agreement with a tetragonal structure  $P4/mmm$ . The collapse of the stretching  $(\text{Bi})\text{O}(\text{Cu})$  from two Raman bands in  $\text{Bi}_{2212}$  into only one band in  $\text{Bi}_{1212}$  reflects a vertically aligned bond ordering, similar to that observed when converting from  $\text{YBa}_2\text{Cu}_4\text{O}_8$  into  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and from  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  into  $\text{TlBa}_2\text{CaCu}_2\text{O}_7$ .*

### 1 - Introduction

The easy structural conversion by thermal treatment<sup>(1-3)</sup> from  $\text{YBa}_2\text{Cu}_4\text{O}_8$  ( $\text{Y}_{124}$ ) into  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $\text{Y}_{123}$ ) and from  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  ( $\text{Tl}_{2212}$ )<sup>(4)</sup> into  $\text{TlBa}_2\text{CaCu}_2\text{O}_7$  ( $\text{Tl}_{1212}$ ) and their analogy with the bismuth cuprate superconductors suggest that the same conversion could happen from  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  ( $\text{Bi}_{2212}$ ) into  $\text{BiSr}_2\text{CaCu}_2\text{O}_7$  ( $\text{Bi}_{1212}$ ). The Bi series also have their interest in practical applications. The working temperature of a superconducting device must be at least 25% lower than its  $T_c$ , due to losses of various nature<sup>(5)</sup>. So, yttrium series have too low  $T_c$  for liquid nitrogen temperature cooling devices. On the other hand, thallium is rather toxic ; its handling is thus delicate, especially in the synthesis phase. The bismuth series do not present such disadvantages. Nevertheless if the two or three BiO layers compounds are well studied, it is not the case for one BiO layer series.

Recently  $(\text{Bi}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCa}_2\text{O}_7$  was obtained by Ehmann *et al.*<sup>(6)</sup> and identified as having  $P4/mmm$  structure.

In this paper, we present our study on  $\text{BiSr}_2\text{CaCu}_2\text{O}_7$  ( $\text{Bi}_{1212}$ ) containing only one BiO chain/layer. The material was characterized by several physical methods especially by Raman spectroscopy, this latter technique has been

revealed to be very helpful in the structural study of superconductors.

### 2 - Experimental

$\text{Bi}_{1212}$  was prepared by sintering a calcinated lyophilized precursor as follows. Fine drops of about one hundred  $\mu\text{m}$  in diameter of a stoichiometric aqueous solution (15 g/l) of nitrates (Bi, Sr, Ca, Cu) were pulverized in liquid nitrogen. After detente, the frozen powder was then lyophilized progressively from  $-30$  to  $+80^\circ\text{C}$  during 24 h under  $10^{-3}$  atm. pressure. A further calcination at  $520^\circ\text{C}$  during 18 h is managed to decompose the nitrates and to avoid the re-hydration. This temperature was respected to prevent the eutectic ( $0.9\text{Bi}_2\text{O}_3-0.1\text{CuO}$ ) which melts at  $570^\circ\text{C}$  and induces irreversible microstructural defects<sup>(7,8)</sup>. After pelleting under uni-directional pressure, the sample was sintered at  $800^\circ\text{C}$  in air for 100 h followed by a final annealing at  $500^\circ\text{C}$  in an oxygen flow.

The Raman spectra were recorded on a microspectrometer Dilor/Omars equipped with a multichannel photodiodes detector and an ion/argon laser source Spectra-Physics, model 2016. The spatial resolution was around  $1 \mu\text{m}^2$ , the laser power was some microwatts and the spectral resolution was  $3 \text{ cm}^{-1}$ .

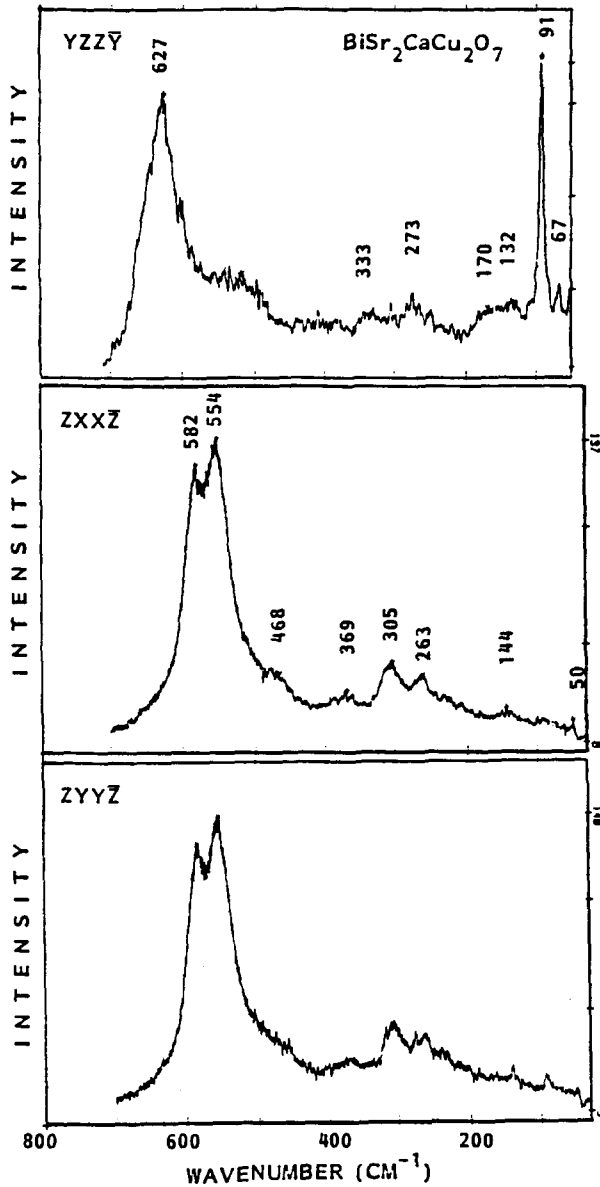


Fig.1 - Polarized Raman spectra of  $\text{Bi}_{1212}$ .

### 3 - Results and discussion

#### 3.1 - Optical anisotropy

The polarized Raman spectra of  $\text{BiSr}_2\text{CaCu}_2\text{O}_7$  present strong anisotropy along the different axes of the crystal. Strong bands are observed at 627 and 91  $\text{cm}^{-1}$  along the  $\text{ZZ}$  geometry and they are nearly absent in the  $\text{XX}$  and  $\text{YY}$  configurations (Fig.1). On the contrary, in the latter two geometries, strong features are apparent at 582 and 554  $\text{cm}^{-1}$ .

As we already mentioned in the case of  $\text{Bi}_{2212}$  and  $\text{Bi}_{2223}$  and their lead doped compounds this anisotropy can help in the determination of the orientation of any surface or thin film(9,10).

#### 3.2 - Tetragonal structure of $\text{Bi}_{1212}$

If the  $\text{ZZ}$  polarized spectrum of  $\text{Bi}_{1212}$  is quite different from the  $\text{XX}$  and  $\text{YY}$  spectra, the latter two are nearly identical. This result is similar to that we already observed for  $\text{TlBa}_2\text{CaCu}_2\text{O}_7$  ( $\text{Tl}_{1212}$ )(11-13). This is in agreement with a tetragonal structure  $\text{P4}/\text{mmm}$  for both materials. In such a case, when passing from  $\text{Bi}_{2212}$  into  $\text{Bi}_{1212}$ , there is a reduction of the two formula unit cell into one formula unit cell with a  $\frac{1}{2}(a+b)$  gliding. In particular, the pyramids which are at staggered positions in  $\text{Bi}_{2212}$  become in mirror image in  $\text{Bi}_{1212}$  (Fig.2). Note that the figure 2 represents only ideal limiting structures.

#### 3.3 - Bond ordering in $\text{Bi}_{1212}$

It is well known that in the Raman spectra of  $\text{Bi}_{2212}$  as well as of  $\text{Bi}_{2223}$ , the  $(\text{Bi})\text{O}(\text{Cu})$  stretching is represented by a doublet around 650 and 625  $\text{cm}^{-1}$ . This doublet is due to the in-phase and out-of-phase  $\text{O}(\text{Bi})$  unharmonic motions in two close, staggered and antiparallel  $\text{O}-\text{Bi}$  bonds along the  $c$ -axis; these oxygen atoms occupying the apical position of the pyramids. The band at 650  $\text{cm}^{-1}$  appears in all structures where the pyramidal networks are in staggered position(14-17) and where the antiparallel bonds are close and identical. We can call it "staggered  $(\text{Bi})\text{O}(\text{Cu})$  motion". Note that the structural modulation incommensurability, which is well evidenced in

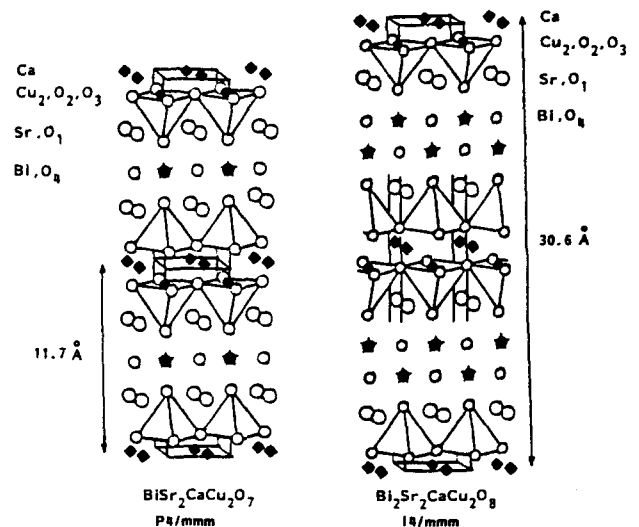


Fig.2 - Scheme of the spatial structure of  $\text{Bi}_{1212}$  and  $\text{Bi}_{2212}$ .

TABLE 1 - PHONONS WAVENUMBERS OF BiSr<sub>2</sub>CaCu<sub>2</sub>O<sub>7</sub> AND TlBa<sub>2</sub>CaCu<sub>2</sub>O<sub>7</sub>.

BiSr <sub>2</sub> CaCu <sub>2</sub> O <sub>7</sub>			TlBa <sub>2</sub> CaCu <sub>2</sub> O <sub>7</sub>		
Wave-number cm <sup>-1</sup>	Scattering geometry	Symmetry & Assignment	Wave-number cm <sup>-1</sup>	Scattering geometry	Symmetry & Assignment
627	ZZ	A <sub>1g</sub> (Bi)O(Cu)	518	ZZ	A <sub>1g</sub> (Tl)O(Cu)
519	ZZ				
333	ZZ	A <sub>1g</sub> (Cu)O <sub>z</sub> in phase	395	ZZ	A <sub>1g</sub> (Cu)O <sub>z</sub> in phase
273*	ZZ		280*	ZZ	
170	ZZ				
132	ZZ	A <sub>1g</sub> Cu <sub>z</sub>	143	ZZ	A <sub>1g</sub> Cu <sub>z</sub>
91	ZZ				
67	ZZ	A <sub>1g</sub> Sr <sub>z</sub>	116	ZZ	A <sub>1g</sub> Ba <sub>z</sub>
582	XX,YY		516	XX,YY	
554	XX,YY	O(Sr)	400	XX,YY	O(Ba)
469	XX,YY	O(Bi,Sr)	282	XX,YY	O(Tl,Ba)
305	XX,YY	B <sub>1g</sub> (Cu)O <sub>z</sub> out of phase			B <sub>1g</sub> (Cu)O <sub>z</sub> out of phase
263	XX,YY		144*	XX,YY	
144	XX,YY		116*	XX,YY	
50	XX,YY				

\*component from the other geometry.

these materials as having strong consequences on the properties out of the Brillouin zone center, has no direct effect on our Raman spectrum.

Such a *staggered motion* disappears in the Raman spectrum of Bi<sub>1212</sub> where only one (Bi)O(Cu) band is observed at 627 cm<sup>-1</sup> which represents the motion of oxygen between the Bi and Cu atoms on the same *c*-axis.

We want to mention that the same bond-ordering with only one single (Bi)O(Cu) band is also observed in LBi<sub>2212</sub> where the structure is similarly reduced to only one formula unit cell<sup>(18)</sup> and where the O-Bi bonds become far apart from one to another.

In the case of lead-doped Bi<sub>2212</sub>, the mechanical coupling also disappears as the antiparallel bonds are no longer identical and therefore only one O(Bi) stretching band is observed along the ZZ scattering symmetry.

### 3.4 - Other spectra-structure correlations

In one formula unit cell tetragonal structure with space group P4/mmm, the irreducible representation of Bi<sub>1212</sub> is<sup>(19-21)</sup>:

$$4A_{1g} + B_{1g} + 5E_g + 7A_{2u} + B_{2u} + 8E_u$$

where :

$$\begin{array}{ll} 4A_{1g} + B_{1g} + 5E_g & \text{are Raman active} \\ 6A_{2u} + 7E_u & \text{are infrared active} \\ B_{2u} & \text{is silent.} \end{array}$$

The A<sub>1g</sub> modes include the motions of Ba, Cu, O<sub>1</sub> and O<sub>2</sub> atoms while the B<sub>1g</sub> modes represent O<sub>2</sub> motions and the E<sub>g</sub> modes involve the motions of Ba, Cu, O<sub>1</sub>, O<sub>2</sub> atoms.

The ZZ polarized spectrum gives all four vibrations expected for A<sub>1g</sub> symmetry, which represent the motions of Oxygen, Cu and Sr along the *c*-axis respectively at 627, 132 and 67 cm<sup>-1</sup> and in-phase oxygen motion in the Cu-O plane at 333 cm<sup>-1</sup>. Note that the motion of Bi is not active.

From the XX and YY geometries, by comparison with the Raman spectrum of Tl<sub>1212</sub>, the oxygen (Sr) motion along the *c*-axis can be located at 554 cm<sup>-1</sup> and the out-of-phase oxygen motion in the Cu-O plane, with B<sub>1g</sub> symmetry, is found at 305 cm<sup>-1</sup>. All remaining phonons can be assigned to components of E<sub>g</sub> symmetry although the E<sub>g</sub> modes may totally appear in the ZX and ZY scattering geometries.

The correspondance of the phonons of

$\text{BiSi}_2\text{CaCu}_2\text{O}_7$  and their assignment with those of  $\text{TlBa}_2\text{CaCu}_2\text{O}_7$  are displayed in Table 1. As also indicated in the Table, some unassigned weak features could be due to a component from the other scattering symmetry.

#### 4 - Conclusion

$\text{BiSr}_2\text{CaCu}_2\text{O}_7$  superconductor is prepared and its polarized Raman recorded and assigned by comparison with those of isostructural  $\text{TlBa}_2\text{CaCu}_2\text{O}_7$ . High optical anisotropy is found between the *c*-axis and the other axes. The identity of XX and YY polarized spectra is in agreement with a tetragonal structure. The (Bi)O(Cu) bond homogeneity along the *c*-axis in  $\text{Bi}_{1212}$  is found and contrasts with staggered and antiparallel (Bi)O bonds in  $\text{Bi}_{2212}$  where in-phase and out-of-phase (Bi)O motions along the *c*-axis was recorded. Note that the latter coupling also disappears in doped (Bi/Pb) $_{2212}$  where the staggered bonds Bi-O and Pb-O are no longer identical.

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