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Raman scattering and transmission electron microscopy studies of commensurate modulated $\text{Bi}_{2+x}\text{Sr}_{3-x}\text{Fe}_2\text{O}_{9.2}$ isostructural to $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.21}$

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Abstract. The polarized Raman spectra from $\text{Bi}_{2.4}\text{Sr}_{2.6}\text{Fe}_2\text{O}_{9.6}$, which is isostructural to the superconducting $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.6}$, are reported. The crystals have been characterized by TEM analysis, confirming the existence of commensurate modulation and giving evidence for a weak misorientation of the a - b planes. The number and symmetries of Raman phonon modes have been analysed within the $Amaa$ space group. In close comparison with previous reports on the scattering from $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.6}$, the Raman lines of $\text{Bi}_{2.4}\text{Sr}_{2.6}\text{Fe}_2\text{O}_{9.6}$ at 116, 157, 190, 247, 285-300, 310-330, 365, 460 and 614 cm^{-1} have been assigned to definite modes of A_g symmetry. Much weaker lines of B_{1g} (160 and 290 cm^{-1}) and B_{3g} (about 240 cm^{-1}) symmetries have also been observed. The commensurate modulation of the structure seems to have no effect on the Raman spectra.

1. Introduction

The antiferromagnetic insulator $\text{Bi}_2\text{Sr}_3\text{Fe}_2\text{O}_{9.6}$ (sometimes called $\text{Bi}_2\text{Sr}_2\text{Sr}^1\text{Fe}_2\text{O}_{9.6}$ (BSSFO)) has a structure very similar to that of the Bi-based 2:2:1:2 superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.6}$ (BSCCO) [1-3]. BSCCO (BSSFO) consists of sequential Bi-O, Sr-O, Cu-O (or Fe-O), Ca (or $\text{Sr}^1\text{-O}$), Cu-O (Fe-O), Sr-O and Bi-O layers and as a first approximation could be characterized by an orthorhombic unit cell (space group, $Amaa$; $a \approx b \approx 5.4\text{ \AA}$ and $c \approx 31.7\text{ \AA}$). In the refined structure this cell has to be considered as a subcell as there is an additional modulation along the a axis, which is incommensurate for BSCCO and commensurate for BSSFO, with 4.76 and five times the subcell period, respectively, along a . It is commonly accepted that the modulation is caused by the insertion of extra oxygen atoms in the double Bi layers, resulting in periodic rearrangement of the oxygen atoms in these layers [3]. Therefore, the oxygen content per formula unit should correspond to 8.21 and 9.20 for BSCCO and BSSFO, respectively.

The Raman spectra of BSCCO have been studied intensively [4-10] and the positions and symmetries of the most intense Raman lines at 115-120, about 300, 460-465 and $625\text{-}635\text{ cm}^{-1}$ have been firmly established. There is, however, little consensus concerning the assignment of observed lines to definite atomic vibrations.

It is reasonable to expect that the comparison of the polarized spectra of BSSFO and BSCCO could help the assignment of the Raman lines, as the substitution of Fe for Cu should affect most strongly the Raman modes involving mainly vibrations of atoms in Cu–O (Fe–O) planes. It was also of interest whether any effects of phonon branch folding due to the commensurate modulation of $\text{Bi}_2\text{Sr}_2\text{Sr}^{\text{I}}\text{Fe}_2\text{O}_{9.2}$ could be observed in the Raman spectra.

To our knowledge the only report on the Raman scattering of BSSFO is that of Farrow *et al* [11]. Raman lines have been observed at 44, 84, 112, 464 and 662 cm^{-1} . The sample used in [11], however, has not been characterized with respect to exact elemental composition and crystallographic orientation.

In this work we present the polarized Raman spectra in various exact scattering geometries of single crystals of $\text{Bi}_{2+x}\text{Sr}_{3-x}\text{Fe}_2\text{O}_{9+\delta}$ with well defined elemental content and structural characteristics. The results are compared with those for BSCCO single crystals and the assignment of Raman lines of both compounds to definite phonon modes is discussed.

2. Sample characterization and experimental details

Mica-like single crystals of $\text{Bi}_{2+x}\text{Sr}_{3-x}\text{Fe}_2\text{O}_{9+\delta}$ (up to 3 mm in the longest dimension) have been prepared following procedures described elsewhere [12]. The crystallographic structure was confirmed by means of x-ray analysis. The morphology and composition tests were carried out on a Philips SEM 515 scanning electron microscope, equipped with an EDAX 9100/72 energy-dispersive x-ray (EDX) spectrometer with Si/Li detector. The SEM–EDX microanalysis showed that the actual composition was $\text{Bi}_{2.4}\text{Sr}_{2.6}\text{Fe}_2\text{O}_{9+\delta}$, i.e. some of the Sr atoms are replaced by Bi. It is worth noting that similar substitution of Bi for Sr (Ca) has earlier been observed for the Bi2:2:1:2 system (see, e.g., [6]). No significant differences, however, could be found between the Raman spectra of non-stoichiometric [6] and stoichiometric [7] Bi2:2:1:2 single crystals.

The transmission electron microscopy (TEM) study was carried out on a Philips EM 420T electron microscope operated at 120 keV. The samples were prepared from alcohol suspension and were deposited on a copper grid covered with a holey carbon film. It was found that as a rule the samples consist of thin platelets (thickness, about 100 nm) parallel to the (001) planes. Most of the platelets have a rectangular shape with edges parallel to the *a* and *b* directions. The edges parallel to {010} are kinked, with the kinked edges parallel to {110}. The lattice fringes (figure 1(b)) are curved in some areas, whereas in other areas they are displaced by different periods, displaying a domain structure with boundaries, varying in the full range from a coherent to an incoherent structure. The greater part of the crystals display moiré patterns revealing misorientation between the layers perpendicular to *c* with a typical misorientation angle of 2–3°, although angles of about 5–10° or even higher were also observed. The results of TEM studies are illustrated in figure 1 and figure 2. SAED patterns of the type shown in figures 2(a) and 2(b) prevail for the crystals of our sample.

The Raman spectra were collected at room temperature in backward-scattering geometry from the as-grown single-crystal surfaces of $\text{Bi}_{2.4}\text{Sr}_{2.6}\text{Fe}_2\text{O}_{9+\delta}$. A triple-multichannel spectrometer (Microdil 28) was used in conjunction with a microscope (objective, 100×) for both focusing the incident laser beam ($\lambda_L = 514.5$ nm; $P_L < 0.5$ mW; laser spot diameter, 1–2 μm) and collecting the scattered light. Typical acquisition times were 3000–10 000 s.

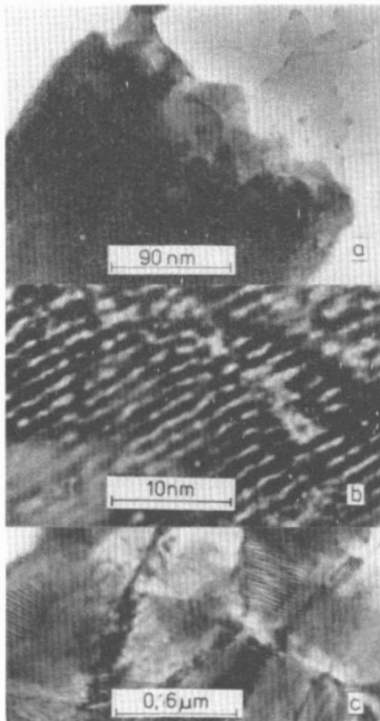


Figure 1. (a) Morphology of a thin $\text{Bi}_{2.4}\text{Sr}_{2.6}\text{Fe}_2\text{O}_{9+\delta}$ crystal platelet. The edges are parallel to a and b . The kinked structure of the (010) face shows the preferred development of the (110) faces owing to their faster growth speed. The resolved lattice fringes, corresponding to interplanar spacings $d_{200} = 1.362$ nm, are parallel to the $\{100\}$ edges of the crystal. (b) A part of the crystal shown in (a). The displacement and curvature of the lattice fringes are visualized as corresponding to domain boundaries with coherent and dislocation structures. The image contrast is enhanced by image processing and filtering. (c) A region of single crystal with moiré patterns, suggesting a misorientation between layers parallel to (001). The different spacings of the moiré patterns represent the different misorientation angles.

3. Results and discussion

Figure 3 shows the Raman spectra of a $\text{Bi}_{2.4}\text{Sr}_{2.6}\text{Fe}_2\text{O}_{9+\delta}$ single crystal. In Porto's notation (e.g. $z(yx)\bar{z}$), x , y and z correspond to the directions of a , b and c axes, respectively. The latter were determined by taking into account that following the TEM analysis the crystal surface coincides with the a - b plane and the steps on the surface are along the a or b directions. The assignment of the crystallographic directions finds additional support in the close resemblance of our spectra to those of BSCCO measured in the same exact scattering configurations [7]. We note, however, that the spectra in figure 3 differ significantly from the spectrum for $\text{Bi}_2\text{Sr}_3\text{Fe}_2\text{O}_{8+y}$ reported by Farrow *et al* [11].

LePage *et al* [3] have described the commensurate modulated structure of BSSFO by the space group $B222$ (D_2^5 ; No.21) with the axes relabelled ($Z = 4$) with the cell parameters $a = 27.246$ Å, $b = 5.4618$ Å and $c = 31.696$ Å. The subcell is

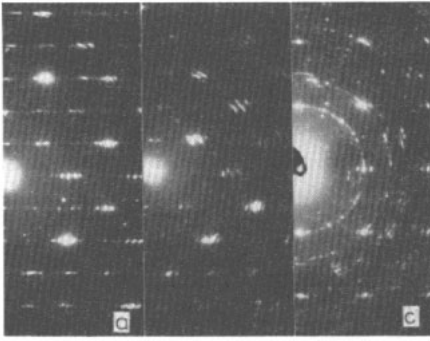


Figure 2. SAED patterns along [001] with different degrees of imperfection. (a) The diffraction pattern is taken from the crystal shown in figures 1(a) and 1(b). The splitting of the reflection suggests a misorientation of domains and layers of about $2\text{--}3^\circ$. (b) The diffraction pattern is taken from the crystal shown in figure 1(c). The misorientation is about $5\text{--}10^\circ$. (c) The ring patterns correspond to texture along c in the (001) plane.

orthorhombic $Amaa$ with $a = 5.449 \text{ \AA}$ and the same values of b and c as for the $B222$ cell. The SAED patterns in figure 2 confirm this structure.

The factor group analysis made by Farrow *et al* [11] has shown that, for BSSFO with the structure described by the $B222$ space group every atom participates in the Raman modes of every symmetry and a very large number of Raman lines ($118A + 123B_1 + 120B_2 + 125B_3$) are expected. As much fewer Raman lines have been observed experimentally, it has been suggested that most of the modes are degenerate [11].

Further, the Raman spectra of both BSSFO and BSCCO will be discussed using the orthorhombic non-symmorphic space group $Amaa$ (D_{2h}^{20}) to describe the elementary subcell. The site symmetries and Γ -point phonons are given in table 1. One expects a total of $11(12)A_g + 7(8)B_{1g} + 10(12)B_{2g} + 14(16)B_{3g}$ Raman-active phonons (the number of modes in parentheses corresponds to the case of occupied O(5) sites). The vibrations of Sr^I (Ca) and O(6) atoms are not Raman active.

Table 1. Site symmetries and Γ -point phonons for $Bi_2Sr^I Sr_2Cu_2O_9$. The numbers in parentheses correspond to the case of occupied O(5) sites.

Atom	Site symmetry	Γ -point phonon modes
Bi,Sr,Fe,O(3)	$C_s(8)$	$2A_g + B_{1g} + B_{2g} + 2B_{3g}$ $+A_u + 2B_{1u} + 2B_{2u} + B_{3u}$
O(1),O(2),O(4),O(5)	$C_2(8)$	$A_g + B_{1g} + 2B_{2g} + 2B_{3g}$ $+A_u + B_{1u} + 2B_{2u} + 2B_{3u}$
Sr^I ,O(6)	$C_{2h}(4)$	$A_u + 2B_{1u} + 2B_{2u} + B_{3u}$
Total, $Bi_2Sr_2Sr^I Cu_2O_9$	$11(12)A_g + 7(8)B_{1g} + 10(12)B_{2g}$ $+14(16)B_{3g} + 9(10)A_u + 15(16)B_{1u}$ $+18(20)B_{2u} + 12(14)B_{3u}$	
Raman active	$11(12)A_g + 7(8)B_{1g} + 10(12)B_{2g}$ $+14(16)B_{3g}$	

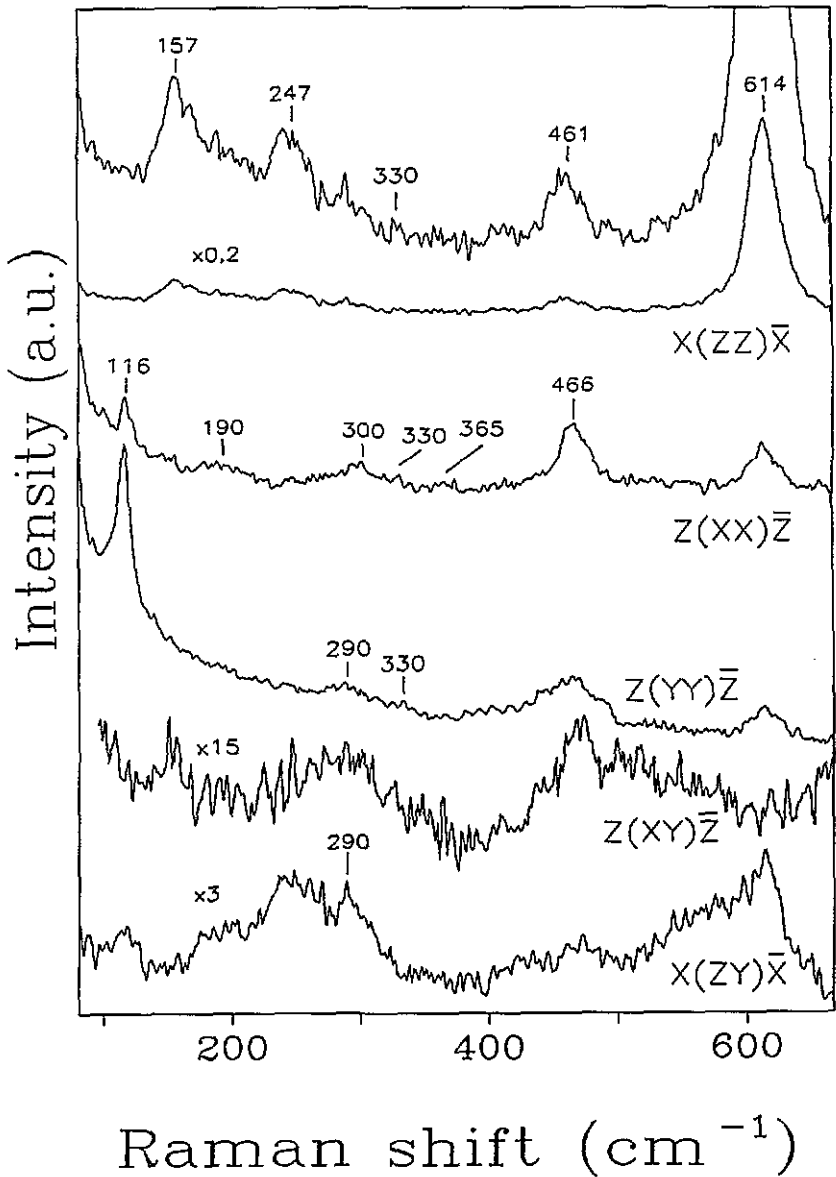


Figure 3. Polarized Raman spectra of $\text{Bi}_{2+x}\text{Sr}_{3-x}\text{Fe}_2\text{O}_{9.2}$ for various scattering configurations (a.u., arbitrary units).

The xx/yy -polarized line at 116 cm^{-1} in BSSFO is obviously of the same origin as that at 120 cm^{-1} in BSCCO. It remains almost unshifted, which is consistent with its assignment to an A_g mode involving vibrations of either mainly Sr [7] or mainly Bi [5, 8] along the c axis. We shall argue below that the latter assignment is more reasonable, as the Sr lines appear at higher wavenumbers. The a - b anisotropy could even be larger than observed if one takes into account the misorientation of the a - b planes (figure 2).

The zz -polarized line at 157 cm^{-1} for BSSFO cannot be unambiguously related

to a corresponding feature in BSCCO. For the latter compound a weak line near 160 cm^{-1} has been reported earlier [5, 7] and controversially assigned to either Cu or Sr vibrations. Recently a line at 155 cm^{-1} has also been observed for Bi₂:2:0:1 [8] and assigned to Sr atom vibrations. The insensitivity of the mode frequency to Fe for Cu substitution supports the latter assignment. The enhancement of this line in BSSFO may be due to changes in the resonant conditions.

The xx -polarized line at 190 cm^{-1} has its counterpart in the spectrum of BSCCO. A peak at 184 cm^{-1} , also xx polarized, has been reported in [5] and assigned to either Sr or Cu vibrations along the c axis. A weak peak at 188 cm^{-1} of A_g symmetry has also been reported by Kirillov *et al* [9]. Ran Liu *et al* [8] observed a line at 180 cm^{-1} , which is stronger in the yy polarization. (Because of the different assignment of the lattice parameters used in [8] (*Bbmb* space group instead of the *Amaa* space group used in this work), the y axis in [8] corresponds to the x axis in our assignments and vice versa.) It has been assumed in [8] that the frequencies of the two Raman modes related to Sr vibrations are close to 180 cm^{-1} . We also assign the line at 190 cm^{-1} for BSSFO to Sr vibrations, taking into account the closeness of its frequency to that of its counterparts in the BSCCO. Within the alternative assignment to Fe vibrations (Cu vibrations in BSCCO), stronger hardening of the mode has to be expected upon substitution of Fe for Cu.

It is reasonable to assume that the A_g mode involving mainly vibrations of Fe (Cu) along the c axis is represented by the line at 247 cm^{-1} for BSSFO and at 220 cm^{-1} [5, 6] for BSCCO. Taking into account only the mass ratio $(m_{\text{Cu}}/m_{\text{Fe}})^{1/2} \simeq 1.05$, hardening of this line by $10\text{--}12\text{ cm}^{-1}$ is expected in the case of BSSFO. The stronger shift of 27 cm^{-1} could be due to the sixfold coordination of Fe atoms (compared with the fivefold coordination of Cu atoms in BSCCO).

The broad structure of A_{1g} symmetry that can be seen in the xx/yy spectra at $285\text{--}300\text{ cm}^{-1}$ (figure 3) has its analogue in the spectrum for BSCCO [7]. The structure observed near $310\text{--}330\text{ cm}^{-1}$ for BSCCO, however, is very weak in our case (also of A_g symmetry). These structures have been controversially assigned either to bond-bending vibrations of O(4) and O(5) atoms of the Bi-O layers [5, 7] or to the two A_g modes of O(1) and O(2) atoms of the Cu-O layers [10]. Since upon substitution of Fe for Cu one expects a shift of the O(1) and O(2) vibration frequencies (which is not the case), the latter assignment is less reasonable.

The weak line at 365 cm^{-1} in the xx spectrum in figure 3 is similar to the Raman lines observed at 360 cm^{-1} [9] and 355 cm^{-1} [8] for BSCCO. Ran Liu *et al* [8] have assigned this line to O(1) and O(2) a -axis vibration, because of the shift in the frequency upon doubling the CuO₂ layer. This assignment is consistent with observed hardening upon substitution of Fe for Cu. The shift is weaker than expected, accounting only for the Cu to Fe mass ratio (17 cm^{-1}).

The origin of the line at about 460 cm^{-1} in BSCCO has often been discussed and controversially assigned to either O(3) stretching vibrations along c [5] or in-phase vibrations along c of O(1) and O(2) atoms of the Cu-O planes [7]. The same frequency of this mode for BSSFO is consistent with an assignment to oxygen vibrations related to O(3) rather than to O(1) and O(2) atoms.

The high-frequency line at 614 cm^{-1} for Bi_{2.4}Sr_{2.6}Fe₂O_{9+δ} and that at 630 cm^{-1} for BSCCO are obviously of the same origin in both compounds. It has been assigned to the A_g out-of-BiO-plane vibrations of O(4) and O(5) atoms [5]. The insensitivity of this line to the substitution of Fe for Cu is consistent with such an assignment.

We note, however, that the frequency of this line obtained for our samples differs significantly from that reported by Farrow *et al* [11]. The difference could reflect the sensitivity of this mode to partial substitution of Bi for Sr.

From the cross polarized spectra in figure 3, one cannot unambiguously identify the lines of B_{1g} , B_{2g} or B_{3g} symmetry, as some of the structures could be due to 'polarization leakages' of A_g modes. Nevertheless, the 160 cm^{-1} line and the broad structure centred at 290 cm^{-1} in the $z(xy)\bar{z}$ spectrum seem to represent B_{1g} modes whereas the peak at 240 cm^{-1} in the $x(zy)\bar{x}$ spectrum could be a B_{3g} mode.

Finally, we shall tentatively propose an alternative assignment of the two most prominent high-frequency Raman lines, namely those at 460 and 614 cm^{-1} . If the statement of Heyen *et al* [13] that only the Cu–O stretch in the z direction generates Raman tensors with strong zz components is valid for the Bi-based layered compounds too, the high-frequency line could be assigned to O(3) (z) vibration. The line at 460 cm^{-1} should then be assigned to O(4) and O(5) (z) vibrations, which is in agreement with the insensitivity of its position upon substitution of Fe for Cu. The splitting of this line observed in the yy spectrum may be caused by the defective structure of Bi–O planes. This structure may be the reason for an inexact A_g symmetry of the modes involving motions of the oxygen atoms in the Bi–O planes and, hence, could be responsible for the stronger 'leakage' of the 290 and 465 cm^{-1} peaks in the xy spectrum.

4. Conclusion

We have performed Raman and electron microscopy studies on insulating $\text{Bi}_{2.4}\text{Sr}_{2.6}\text{Fe}_2\text{O}_{9.2}$ isostructural to superconducting BSCCO. TEM results have confirmed the existence of a commensurate modulation of five times along a . The particular single crystals showed structural defects between separate layers as well as within the layers. The defects of the structure have no significant effect on the Raman spectra. On the basis of comparison of the Raman spectra of isomorphous BSSFO and BSCCO compounds, the main Raman lines have been assigned to definite atomic vibrations and some earlier assignments of the Raman lines of BSCCO have been reconsidered.

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