Role of vanadium in Bi-2223 ceramics

D R MISHRA*, S V SHARMA and R G SHARMA

National Physical Laboratory, Dr K.S. Krishnan Road, New Delhi 110 012, India
*Corresponding author

Abstract. The effect of substitution of vanadium in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta$ ceramic at Bi and Cu sites has been investigated for the resistivity, a.c. susceptibility, XRD and a.c. magnetization studies. Enhancement in T_c for the smaller concentrations of V at either of the two sites was observed which followed an expected lattice distortion and decrease in T_c for higher V concentrations. V plays a role of substituting element more than just a sintering agent as reflected in the more rapid decrease in T_c at Cu-site and further in the magnetization values that are higher compared to the values at the Bi-site. It indicates higher magnetization scattering at the Cu site. The results were explained keeping in mind the liquid phase mechanism behind the formation of the 2223 phase and the possibility of magnetic scattering.

Keywords. Superconductors; crystal growth; X-ray diffraction; magnetic properties.

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1. Introduction

The BSCCO ceramic system is known [1–7] to have large number of existing and co-existing crystal structures or phases. 2201 with nominal composition as Bi:Sr:Ca:Cu= 2:2:0:1 is a monoclinic phase with a rather low T_c of $\sim 10\,\text{K}$, while the other phases so far reported seem to have average orthorhombic crystal structure and with the nominal compositions can be summarized as Bi:Sr:Ca:Cu=1:1:1:2 ((1112) phase, $T_c < 80$ K), 2:2:1:2 ((2212) phase, $T_c \sim 80\,\text{K}$) and 2:2:2:3 ((2223) phase, $T_c \sim 110\,\text{K}$). The (2201), (2212) and (2223) phases have single, double and triple layers of CuO_2 plane in the subunit cell respectively, and more CuO_2 planes are believed to be associated with higher values of T_c. Out of these three, 2223 phase has always been of interest because of its highest T_c (~ 110 K). There are too many experimental parameters which determine the quality of the specimens and control their T_c values. It has been reported by various groups [8] that Pb at Bi site up to an optimum concentration of 0.3–0.4 has proven useful in enhancing the 2223 superconducting phase and thus facilitating its isolation. Double substitutions of lead with other elements [2] are being attempted for the further improvements in these materials especially if we could affect the properties of these materials such as phase composition, T_c or the critical current density (J_c), etc. This paper reports results of our exploration of the V-substituted Bi-2223 ceramics.

Previous reports ([1–7] and also, [9]) on V-substituted samples of $Bi_2Sr_2Ca_2Cu_3O_\delta$ have mostly pointed out that V when substituted at Bi-site, the 110 K phase is significantly enhanced. However the T_c ($R = 0$) value is still around 90 K. Also, there is a wide range of combinations of Pb and V associated with T_c ($R = 0$) in the range (90–103 K). Fung *et al* [9] have shown that addition of V to the Bi-system is much like the role of Pb in the pure Bi–Sr–Ca–Cu–O samples, i.e. it acts like a catalyst and enhances the formation of high T_c 2223 phase. Also Xin *et al* [2] report a structure $Bi_{1.3}Pb_{0.5}V_{0.2}Sr_2Ca_2Cu_3O_\delta$ which consists of about 90% 2223 phase. Our studies on samples of Bi-2223 prepared by substitution of V at two different sites; viz. Bi-site and the Cu-site lead us to believe that V has played significant role in enhancing the liquid phase during the formation of the 2223 phase and thereby leading to enhancement in the 2223 phase.

2. Experimental

Two series of V-substituted samples were prepared by partial replacement of V at two different sites; viz. the Bi-site according to $Bi_{1.6-x}V_xPb_{0.4}Sr_2Ca_2Cu_3O_\delta$ (where $x = 0.05$ to 0.5, samples are labelled as VBi-1 to VBi-7) and at Cu-site according to $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3-y}V_yO_\delta$ (where $y = 0.05$ to 0.5, samples are labelled as VCu-1 to VCu-7) (refer tables 1 and 2). The standard ceramic route was adopted for this purpose in which appropriate quantities of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO and V_2O_5 all of $4N$ purity were thoroughly mixed, ground and calcined at $810°C$ followed by regrinding, and re-calcination at $815°C$ for 24 h. It was found for both the series of samples that the melting temperature was considerably reduced when V_2O_5 was added to the system. All the samples were ground, pelletised and finally sintered in air at $830°C$ for 30 h and furnace-cooled to room temperature.

To observe the superconducting transition, d.c. resistivity of the specimens was measured as a function of temperature by the four-probe method and the real part of susceptibility (χ') was measured as a function of temperature using the mutual inductance bridge.

Table 1. Sample composition, T_c values and summary of XRD results.

Sample denomination, stoichiometry and sintering conditions		$T_c(R=0)$. (K)	$T_c(\chi')$ in (K)		%HTP .(χ')	%HTP (XRD)
			2223	2212		
Pure	$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3$ ($830°C \times 30$ h for all)	100.6	100	80	42.1	30.1
VBi-1	$Bi_{1.55}V_{0.05}Pb_{0.4}Sr_2Ca_2Cu_3$	102	101	76	60	65.3
VBi-2	$Bi_{1.5}V_{0.1}Pb_{0.4}Sr_2Ca_2Cu_3$	103	102	78	64.2	72.1
VBi-3	$Bi_{1.45}V_{0.15}Pb_{0.4}Sr_2Ca_2Cu_3$	97	95	76	68.2	70.0
VBi-4	$Bi_{1.4}V_{0.2}Pb_{0.4}Sr_2Ca_2Cu_3$	95	92	74	57.8	69.6
VBi-5	$Bi_{1.3}V_{0.3}Pb_{0.4}Sr_2Ca_2Cu_3$	89	89	61	54.5	55.1
VBi-6	$Bi_{1.2}V_{0.4}Pb_{0.4}Sr_2Ca_2Cu_3$	melted	–	–		–
VCu-1	$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{2.95}V_{0.05}$	102.5	102	82	38.6	32.0
VCu-2	$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{2.9}V_{0.1}$	101	100	78	45.5	49.0
VCu-3	$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{2.85}V_{0.15}$	99	99	77	73.7	>80.0
VCu-4	$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{2.8}V_{0.2}$	97	93	75	70.0	75.4
VCu-5	$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{2.7}V_{0.3}$	80	82	74	55.0	48.3
VCu-6	$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{2.6}V_{0.4}$	63	–	–		–
VCu-7	$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{2.5}V_{0.5}$	melted	–	–		–

Table 2. Magnetization data.

Sample	Applied field		Loop shape	ΔM per unit thickness (Oe)	Loop area/ volume (emu/cc)	$J_c = 2\Delta M/d$ (A/cm^2)
	Coil-curr (mA)	Hae (Oe)				
Pure	75	1.15	ellipse	11.89	0.035	95.1
	150	1.95	ellipse	13.25	0.082	106.0
	300	3.70	ellipse	15.33	0.208	122.6
	500	6.15	ellipse	16.98	0.354	135.8
	800	9.70	distorted	18.65	0.754	149.2
VBi-1	75	1.15	ellipse	5.94	0.013	47.5
	150	1.95	ellipse	9.83	0.048	78.7
	300	3.70	ellipse	12.74	0.115	102.0
	500	6.15	distorted	13.30	0.144	106.4
	800	9.70	distorted	13.38	0.254	107.0
VBi-2	75	1.15	ellipse	5.55	0.011	44.4
	150	1.95	ellipse	10.25	0.036	82.0
	300	3.70	ellipse	12.65	0.082	101.2
	500	6.15	distorted	14.72	0.107	117.7
	800	9.70	distorted	13.96	0.159	111.7
VBi-3	75	1.15	ellipse	4.70	0.012	37.6
	150	1.95	ellipse	6.07	0.036	48.5
	300	3.70	ellipse	9.77	0.118	78.2
	500	6.15	ellipse	13.01	0.249	104.1
	800	9.70	distorted	15.57	0.278	124.6
VBi-4	75	1.15	ellipse	5.30	0.009	42.4
	150	1.95	ellipse	8.33	0.034	66.7
	300	3.70	ellipse	11.96	0.096	95.7
	500	6.15	near ellipse	13.04	0.122	104.3
	800	9.70	distorted	14.15	0.189	113.2
VBi-5	75	1.15	ellipse	1.48	0.011	11.8
	150	1.95	ellipse	2.34	0.039	18.7
	300	3.70	ellipse	4.29	0.136	34.4
	500	6.15	ellipse	6.81	0.365	54.5
	800	9.70	ellipse	9.50	0.816	76.0
VCu-1	75	1.15	ellipse	17.97	0.033	143.8
	150	1.95	ellipse	18.55	0.053	148.4
	300	3.70	near ellipse	17.22	0.125	137.8
	500	6.15	distorted	17.70	0.225	141.6
	800	9.70	distorted	18.19	0.438	145.5
VCu-2	75	1.15	ellipse	17.69	0.026	141.5
	150	1.95	near ellipse	16.92	0.041	135.4
	300	3.70	near ellipse	16.40	0.089	131.2
	500	6.15	distorted	16.96	0.154	135.7
	800	9.70	distorted	16.52	0.239	132.1
VCu-3	75	1.15	ellipse	16.96	0.057	135.6
	150	1.95	ellipse	17.45	0.141	139.6
	300	3.70	ellipse	19.14	0.346	153.1
	500	6.15	ellipse	19.51	0.711	156.1
	800	9.70	distorted	19.73	0.631	157.8

contd...

Sample	Applied field		Loop shape	ΔM per unit thickness (Oe)	Loop area/ volume (emu/cc)	$J_c = 2\Delta M/d$ (A/cm^2)
	Coil-curr (mA)	Hae (Oe)				
VCu-4	75	1.15	ellipse	11.31	0.036	90.5
	150	1.95	ellipse	12.86	0.093	102.9
	300	3.70	ellipse	13.88	0.212	111.0
	500	6.15	ellipse	13.98	0.342	111.8
	800	9.70	distorted	15.38	0.374	123.0
VCu-5	75	1.15	ellipse	2.10	0.006	16.8
	150	1.95	ellipse	3.19	0.011	25.5
	300	3.70	ellipse	4.86	0.075	38.9
	500	6.15	ellipse	9.73	0.198	77.9
	800	9.70	ellipse	13.27	0.420	106.1
VCu-6	75	1.15	ellipse	0.61	0.003	4.9
	150	1.95	ellipse	1.01	0.011	8.1
	300	3.70	ellipse	1.63	0.040	13.0
	500	6.15	ellipse	3.24	0.126	25.9
	800	9.70	ellipse	6.57	0.341	52.5

Room temperature XRD spectra were obtained on all specimens for crystal structure de-termination on a Siemen's D-500 diffractometer using CuK_α radiation. Zero field cooled a.c. magnetization measurements at 77 K were carried out on samples $\sim$3 mm in width and approx. 16×1.8 mm^2 in cross-section at a frequency of 317 Hz at fixed applied fields (shown in table 2) in the range of 1 to 10 Oe. Hysteresis loops observed on the oscilloscope screen were plotted using the attached plotter and for the pure (as representative sample) is shown in figure 7.

3. Results and discussion

3.1 T_c behaviour and XRD analysis

The T_c $(R = 0)$ values of our different samples with compositions $(BiPb)_2Sr_2Ca_2Cu_3O_\delta$ with V substituted at Bi- and Cu-site along with the relative phase composition of the 2223 and 2212 phases and the lattice parameters as evaluated from XRD patterns are being shown in table 1.

Figure 1a, 1b and 1c shows the resistivity behaviour of different samples with V sub-stituted at Bi- and Cu- sites in accordance with the general compositions $Bi_{1.6-x}V_x$ $Pb_{0.4}Sr_2Ca_2Cu_3O_\delta$ (VBi series) and $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3-y}V_yO_\delta$ (VCu series) respec-tively. In case of VBi series it is seen that T_c improves with initial increase in the dopant concentration (up to $x = 0.1$). Similar is the case for VCu samples T_c initially shows a slight improvement followed by a decrease much faster than that in VBi samples with T_c 97 K for $x = 0.2$, 80 K for $x = 0.3$ and about 63 K for $x = 0.4$. This is identical to the observation in the case of Nb substitution in 2223 [10]. It can be an indication that in the VCu samples V gets incorporated in the CuO$_2$ layers in which presence of any impurity element has a dramatic effect on the T_c of the superconductor. The details of how this takes place is described later in the section on the role of V after discussing
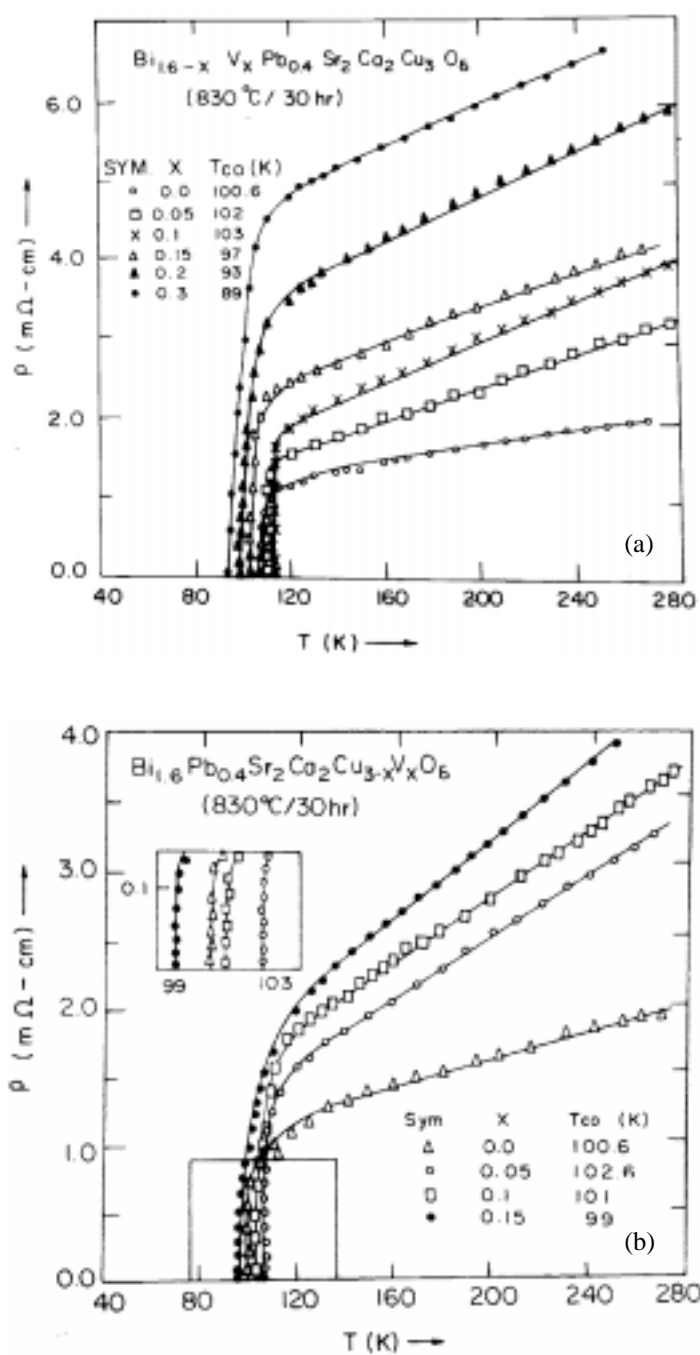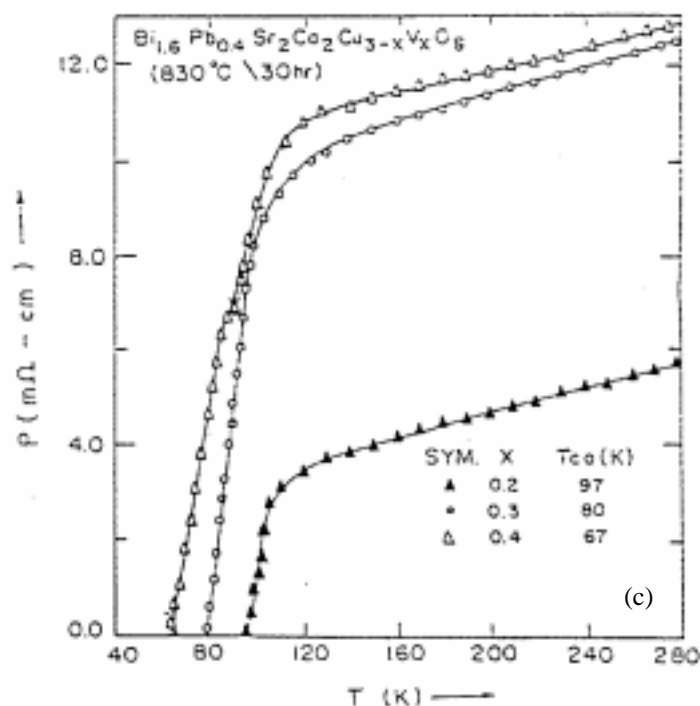
Figure 1a, b.

Figure 1. Resistance versus temperature curves for V-substituted samples of Bi-2223. (**a**) V-substitution at Bi-site, i.e. $(Bi_{1.6-x}V_xPb_{0.4})Sr_2Ca_2Cu_3O_\delta$ (VBi) series; (**b** and **c**) V-substitution at Cu-site, i.e. $(Bi_{1.6}Pb_{0.4})Sr_2Ca_2Cu_{3-x}V_xO_\delta$ (VCu) series.

the magnetization results. The samples with higher concentrations did not show any sign of superconductivity at $T > 77$ K. The normal state resistivity as generally observed for pure Bi samples has been found to increase with the increase in the dopant concentration. The normal state resistivity increases with increase in the temperature and all the samples follow the same trend. The samples not showing superconductivity above 77 K, also follow this behaviour. This shows, no indication of a semiconducting behaviour which leads to a metal–insulator transition typically observed in materials doped with other elements such as Y, Tm etc. [11].

Most of the samples are showing the double transition in a.c. susceptibility vs temperature curves indicating the presence of both the 2223 and the 2212 phases. However T_c values obtained from these transitions (see table 1) are slightly lower than those obtained by resistivity measurements. Here also it is visible that the reduction in T_c follows an initial enhancement at either of the two sites, more prominent in case of VCu samples than in VBi ones. Figure 2a, 2b shows the variation of the real part of a.c. susceptibility (χ') with the temperature of the samples having V concentration of 0.15 at both Bi- and Cu-sites respectively.

XRD patterns of the V-substituted samples of $(BiPb)_2Sr_2Ca_2Cu_3O_\delta$, at the Bi site and the Cu site are being shown in figures 3a–d (for VBi) and 4a–d (for VCu) respectively. The XRD spectra of the un-doped Bi-2223 sample shows the presence of both the phases,
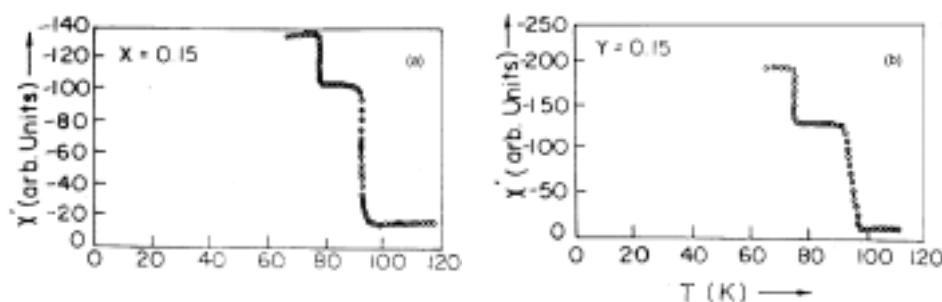
Figure 2. A.c. susceptibility (χ') as a function of temperature for V-substituted samples of Bi-2223. (**a**) V-substitution at Bi-site; (**b**) V-substitution at Cu-site.

the 110 K 2223 phase and the 80 K 2212 phase. Most of the substituted samples of both the series show peaks corresponding to 2223 and 2212 phases. However the peaks observed are invariant and are present in all samples indicating the absence of the formation of any new phase or compound. That means V is taking a position in the interstitial or the substitutional site thereby becoming part of the lattice. There are steep transitions in susceptibility corresponding to the two phases indicating rare possibility of some other phase being present in these specimen. No peak corresponding to phases other than these two was observed. There is a consistent variation in the intensity and the positions of the peaks indicating the change in the phase composition and the lattice parameters of our samples. However the shifting of the peak was not large enough to indicate any new phase formation. Smaller variations can be because of the off-stoichiometry of the lattice, V(+3 or +5) being substituted at the Cu(+2) and Bi(+3) sites or may be held somewhere in the interstitial sites. (As in generally believed and widely reported, different atoms have the valence states as being shown in the parentheses.) Furthermore off-stoichiometry develops because of the difference in ionic radii of the substituted and the host atoms. For example, Bi(+3) and Cu(+2) are having ionic radii of 1.20Å and 0.69Å while that of V(+3), V(+5) is 0.74Å and 0.59Å respectively. However the variation in the phase composition as reflected in the intensities of the peaks was more consistent and noteworthy. Using intensity of the prominent peaks [12] from the XRD spectra of these specimens, a percentage composition of 110 K high T_c (2223) and 82 K low T_c (2212) phase was estimated with, %HTP (high T_c (2223) phase) also shown in the table 1. To confirm our observations, we also evaluated the phase composition on the basis of our susceptibility plots. This has also been given in table 1 for comparison. In both the series we observed an enhancement of the 2223 phase percentage. In XRD patterns, in case of VBi series 2223 phase percentage increases up to 72.12% for concentration $x = 0.1$ and then remains almost constant i.e. 70.06% and 69.64% respectively for the next two concentrations i.e. for the $x = 0.15$ and $x = 0.2$. In case of VCu series, this percentage goes still higher; almost no peak of 2212 phase was observed in the sample with V concentration of $y = 0.15$, then there is good amount ($\sim$75%) of 2223 phase present in the next higher concentration i.e. $y = 0.2$. For higher concentrations, however this percentage rapidly falls down. The initial enhancement in the 2223 phase indicates the catalytic action of V which is somewhat similar to Pb. This we suppose because of the reasoning in the following paragraph. We detected no line corresponding to any compound formation due to V, in higher concentrations, that can be well because its presence if any, is less than the observable limits of XRD.
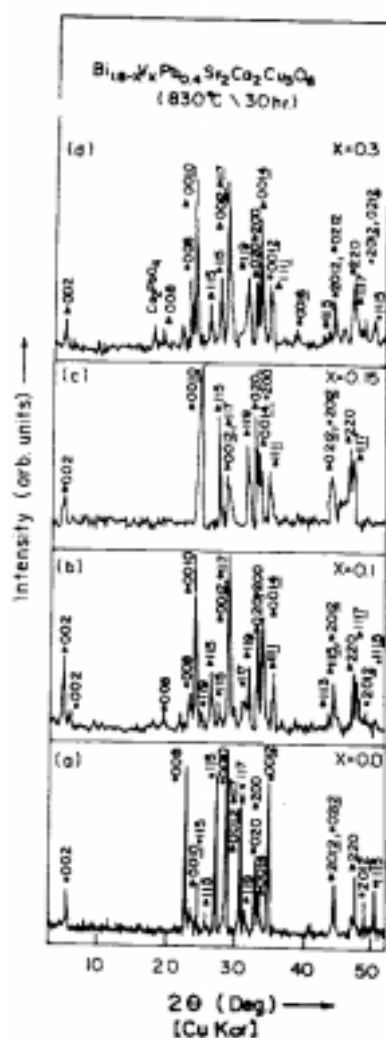
Figure 3. XRD patterns of $(Bi_{1.6-x}V_xPb_{0.4})Sr_2Ca_2Cu_3O_\delta$ (VBi) series (**a**) –(**d**).

As being known [12,13], the 2223 phase formation in the pure Bi specimen is an extremely slow process. However its rapid growth via improved mobility of the ions, can be catalysed through the formation of a liquid phase which is believed to be Ca_2PbO_4, Sr_2PbO_4, or an eutectic of 2201 and Ca_2PbO_4. Partial melting of our V substituted samples for low dopant concentrations and melting of these at higher dopant concentrations $(x, y > 0.4)$, at only 830°C suggests that addition of V_2O_5 further extends the range of the liquid phase, thus increasing the possibility of the substituents occupying the positions (interstitial or substitutional sites) in the crystal structure, which may well get precipitated out if subjected to prolonged annealing. Now if the substituent is helpful in the formation of CuO_2 layer, it is expected that the mobility of ions will just favour the formation of
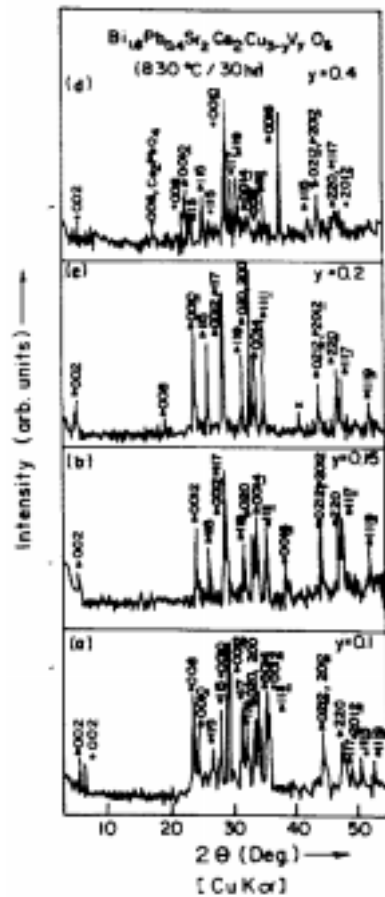
Figure 4. XRD patterns of $(Bi_{1.6}Pb_{0.4})Sr_2Ca_2Cu_{3-x}V_xO_\delta$(VCu) series (**a**)–(**d**).

2223 as the dominant phase. In our case V unlike Nb [10], exists in both +3, +5 states and quite possibly in the reducing atmosphere of carbon or carbon monoxide (which is possible as we have used mainly the carbonates), V_2O_5 be getting reduced to V_2O_3. So V as V(+3) (undoubtedly V(+5) is also there in small proportion) may easily insert into host site of Cu atoms making the system equillibria shift in the direction of greater use of Cu atoms i.e. favouring the formation of 2223 phase. Normal state resistivity behaviour of our samples, however, indicate some possibility of V-atoms being actually retained in the lattice. Corresponding to higher concentration samples show slight shifting of the peak positions that suggests a small distortion of the crystal structure either due to the presence of the substituted atoms (mainly V(+5)) or due to the off-stoichiometry of the compound, thus these samples have very low T_{c0}. This decrease may well because of the magnetic scattering due to the presence of 'V', an empty d-band transition element which we shall discuss in detail, on the role of V.

We notice that in VBi samples, the effect of V-doping is not as prominent especially at

higher concentrations, as compared to the case of VCu samples where it appears to lower the T_c by magnetic scattering. This observation is quite similar to what was observed for Nb substitution [10]. In case of VBi samples; the initial increase of T_c is similar to the VCu samples (see table 1). Here also, $x = 0.15$ appears to be the optimum concentration for the growth of the 2223 phase as was the case in VCu samples. But with higher concentrations, T_c decreases less rapidly as discussed in the beginning of the discussion on the T_c behaviour. This relatively less insensitivity of the T_c of VBi samples to the dopant concentration suggests the possibility of V occupying an out-of-CuO_2 plane position in the crystal structure or just getting segregated in the grain-boundaries. However we observed deviations in the 2Θ positions of the important (00L and 11L) reflections in the XRD pattern (figure 3c). It indicates that some dopant ions have occupied the lattice-sites thereby causing a shift in the plane positions. For cuprate superconductors, it is generally observed that substitution in the planes other than CuO_2 which create a charge imbalance and are expected to modify the formal valence of Cu through charge-transfer can result in the variation of their T_c. Presence of V in the $+3, +5$ state in the Bi–O layer could be causing such a degradation effect because of the replacement of Bi^{3+}. There is, however, some experimental evidence [14] that Bi is not always present as Bi^{3+} and oxygen non-stoichiometry of the Bi-O layers can alter its valence state to Bi^{5+}, and thus induces a variation of T_c even in the un-doped samples. Since the ionic radii of Bi^{5+} (0.74Å) slightly higher than the ionic radii of V^{5+} (0.59Å), there is a good possibility of V occupying positions in Bi–O layers; i.e. a substitution which will not affect the charge-balance and, therefore the T_c of the material.

The grain morphology of the specimens are shown in figure 5a–c. Figure 5a is for undoped specimen. It shows very small size grains with thin flake like structures, indicating poor formation of the superconducting phase. However the size of grains is on increase in figures 5b and 5c which are for the specimens showing optimum 2223 phase, the difference is visible. The size of the grains is quite large and long – elongated grains of 2223 phase are dominantly present. Other specimen (not shown) have mixed grain growth of needle shaped as well as thin flake like grains.

3.2 *Magnetization and low field hysteresis*

It is interesting in HTSC materials that they generally have the low value of this critical field, $\mathbf{H}_{cl}$ and so these materials easily come into the mixed state. Opening up of loops by our samples indicate low value of $\mathbf{H}_{cl}$ for these samples. It is observed, in general, the loops are elliptical in shape, however, for the higher fields, the shape distorts to near rectangular or a parallelogram like figure (as can be seen in figure 7). We find near rectangular loops obtained for higher field values. This well resembles with the theoretical loops of figure 6 that have been obtained giving 'a', very low values of 0 to 0.02 in the following equations:

$$4\pi\mathbf{M} = 4\pi\mathbf{M}_{\mathrm{Bean}} - a\mathbf{H}.$$

Here, the $a\mathbf{H}$ term accounts for the diamagnetism of the grains [15], which are still in the Meissner state.

$$4\pi\mathbf{M}_{\mathrm{Beam}} = \mathbf{B} - \mathbf{H}, \qquad \text{where} \quad \mathbf{B} = \frac{\int H(x)\mathrm{d}x}{\int \mathrm{d}x}.$$
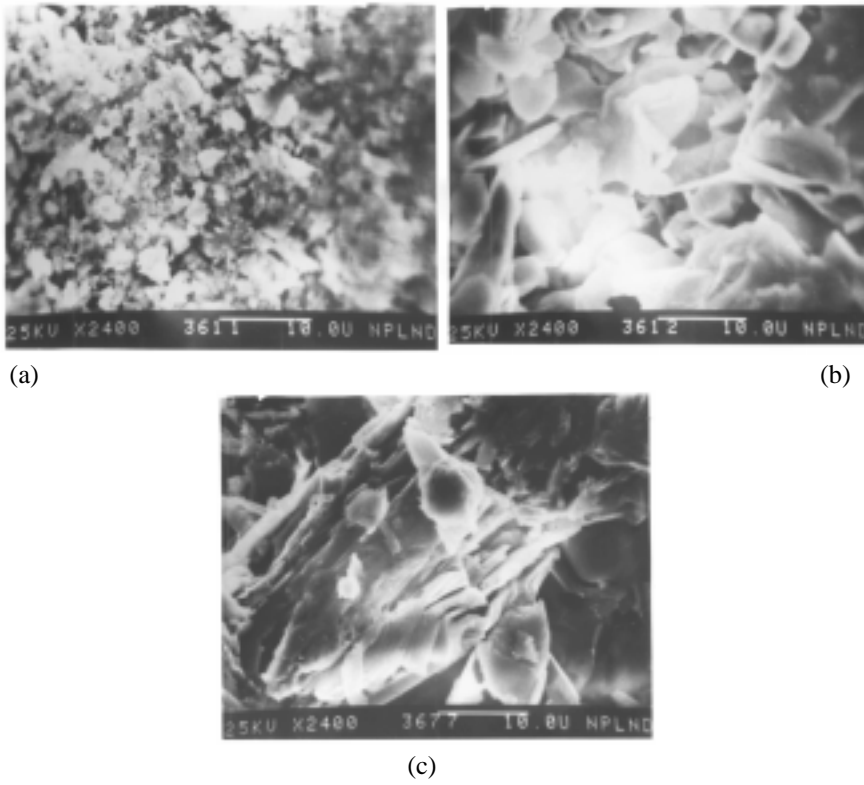
(a)

(b)

(c)

Figure 5a–c. SEM micrographs of pure and samples with $y, x = 0.15$ showing an improvement in the formation of 2223 phase (**a**)–(**c**).
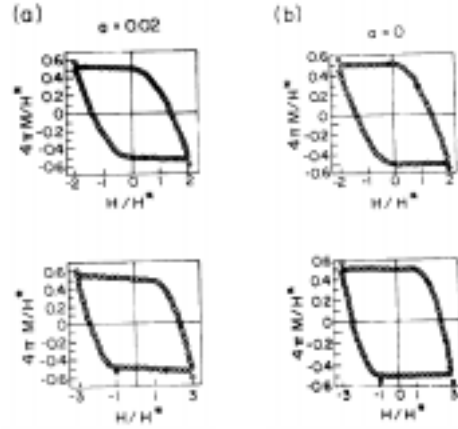

Figure 6. Hysteresis loops predicted by the formulae (after ref. [16]): (**a**) $4\pi\mathbf{M} = 4\pi\mathbf{M}_{\text{Bean}} - (0.02)\mathbf{H}$; (**b**) $4\pi\mathbf{M} = 4\pi\mathbf{M}_{\text{Bean}}$.

That means the proportion of the grains in the Meissner state is quite low i.e. below 2%. The field has penetrated all the grains (besides the intergranular regions) which is quite expected to happen at the higher fields. The loops are elliptical in case grain contribution is there and a is well above zero and tends to rectangular shapes as soon as a approaches the value zero.

Therefore the Bean's model appears to be sufficient to explain the shape of the experimental loops obtained.

We tried to fit the same model to get an idea of $\mathbf{J}_c$ for our samples. We evaluated the magnetization values $\mathbf{M}^+$ and $\mathbf{M}^-$ corresponding to the zero field value for the different loops observed at the different maximum a.c. fields and then $\mathbf{J}_c$ was evaluated substituting in the formula $\mathbf{J}_c = 2\Delta\mathbf{M}/d$; d being the thickness of the sample. The magnetization, $\Delta\mathbf{M}$ values, the corresponding $\mathbf{J}_c$ values and area of the loops, as evaluated by us, at different applied fields, has been shown in table 2.
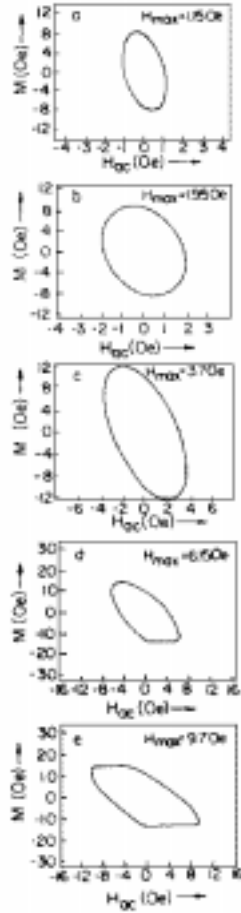

Figure 7. A.c. magnetization hysteresis loops of $(Bi_{1.6}Pb_{0.4})Sr_2Ca_2Cu_3O_\delta$ at 77 K in different $\mathbf{H}_{\max}$ at 317 Hz.

For samples with the substitution of V at Cu site, we observe maximum ΔM and J_c values corresponding to the sample for $y = 0.05$ followed by a decrease for the samples with the higher concentrations. Area of the loops increases with field for the same sample thus indicating the increase in the hysteresis losses with the increase in the field.

In the case of VBi samples, we observed a decrease for the sample with $x = 0.05$ unlike in VCu samples with the same V concentration, then a slight increase possibly because of the increase in the 2223 phase and then almost no change for the next two concentrations. For the sample with the highest concentration i.e. $x = 0.3$ because low T_c and also lesser 2223 phase proportion has low ΔM values and corresponding J_c values only 11.8 to 76.0 A/cm^2. This is quite similar to what we observed in VCu samples where the last two samples show very less magnetization as well as the corresponding J_c values.

We can observe a clear contrast between magnetization values of VBi and VCu samples especially for higher concentration where VCu samples have very high magnetization as compared to the VBi samples with the same V concentration. For example, magnetization values (in Oe) for VCu-4 sample varies from 90.5 to 123 as compared to the magnetization values for VBi-4 sample that varies from 42.4 to 113.2 and similar is the case for VCu-5 and VBi-5 samples as can be seen from table 2. It appears there are mainly two factors that are determining the magnetization and the corresponding J_c values: firstly the 2223 phase percentage in the sample and secondly, the site of V doping. VCu samples have relatively higher magnetization compared to the VBi samples with the same V concentration. One possible region is that defects interacting and thereby hindering the motion of the flux-threads, are less dominant in VBi samples.

One useful observation that was drawn from these loops was the small asymmetry in their shapes after distortion from the ellipse. There was observed a flatness in the loops especially in VCu samples which can be because of the Bean–Livingstone effect [16] or the various viscous effects [17] present in these superconductors. The formation of 2223 phase is a sort of surface reaction in which the 2223 phase forms initially at the surface and then the core is slowly converted to the 2223 lattice. During this process, there is a good possibility for the formation of surface defects. These surface defects put a sort of friction to the entry and exit of the fluxoids, thereby leading to the observed flatness in the loops.

4. Conclusions

Our studies on V shows that it plays a double role: as a sintering agent and as a substituent element which has typical transition element magnetic properties due to the presence of an empty d-band. The above discussions strengthens our belief that the addition of d-band elements to the $(BiPb)_2Sr_2Ca_2Cu_3O_\delta$ superconductor firstly, assist in the formation of the liquid phase (which is believed to be Ca_2PbO_4, Sr_2PbO_4, or a eutectic of 2201 and Ca_2PbO_4 and is considered responsible for the growth of 2212 and 2223 phases via improved mobility of the ions) during the sintering process of these materials. V, catalyses the liquid phase and helps in the formation of a 2223 phase whose T_c initially improves. Both T_c and the 2223 phase formations are affected at higher V concentrations because of the off-stoichiometry of the substituent and the host site. Secondly, it causes magnetic scattering responsible for the pair-breaking effect near the Fermi level, a well-known effect [10] that the magnetic impurities usually play in these materials and thereby causes a decrease in the T_c of the Bi-2223 phase. The effect due to magnetic scattering, is more

pronounced and increases with the dopant concentration when V is substituted at the Cu-site and is accompanied with an increase in magnetization values of the samples that are higher compared to the VBi samples with the corresponding V concentration.

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