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On the Comparison of Stability of $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$, $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ and $YBa_2Cu_{3-x}Al_xO_{7-\delta}$ in Water for Various Concentration of Zn $(0 < X < 0.1)$, Sr $(0 < x < 0.6)$ and Al $(0 < x < 0.6)$

Research Article

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Abstract. Substitutional study of Zn on $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ $(0 < x < 0.1)$ have been carried out on polycrystalline samples to determine the effect of Zn doping in small concentration on the instability of the unit cell structure in the presence of water. $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ and $YBa_2Cu_{3-x}Al_xO_{7-\delta}$ polycrystalline samples for various concentration of Sr $(0 < x < 0.6)$ and Al $(0 < x < 0.6)$ have also been treated with water. The degree of degradation in the substituted samples is a function of the type of the dopant $Sr^{2+}/Al^{3+}/Zn^{2+}$ as well as the molar concentration of the dopant. The degradation is found to be minimum in the case of Sr^{2+} substitution at Ba^{2+} sites in $YBa_2Cu_3O_{7-\delta}$ as compared to the degradation of Al^{3+} and Zn^{2+} substitution at Cu(1) and Cu(2) sites, respectively. The degradation is maximum in the case of Zn^{2+} substitution at Cu(2) site. The studies were made using R-T measurements, X-ray diffraction technique and iodometric titration method and SEM.

Keywords. Superconductivity; Doping; Water treatment; Structural instability

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1. Introduction

The high temperature superconductors are susceptible to degradation in different environments. But relatively a few studies have been made to investigate their degradation behaviour [1–11]. The possible cause of the degradation in these material have been studied by many authors [12–17]. Briefly, the degradation particularly in $YBa_2Cu_3O_{7-\delta}$ has been attributed to its layer structure, comprising of an intergrowth of Cu(2)O−Y−Cu(2)O and BaO−Cu(1)O−BaO network [13], processing parameter [18], variable oxidation state of copper [3, 6, 7], presence of oxygen vacancies [19], ordering of chain or oxygen atoms along the b-axis [20], presence of group II elements (Ba) [1], bondlength of the Cu−O chains and planes [21], etc. Some attempts have been made earlier to reduce or control the degradation in $YBa_2Cu_3O_{7-\delta}$ [22–28]. Also Co-substitution of Ca^{2+} for Y^{3+} and La^{3+} for Ba^{2+} in $YBa_2Cu_3O_{7-\delta}$ has been reported to enhance significantly the resistance to its degradation [26]. Evidence of high stability against water corrosion of $NdBa_2Cu_3O_{7-\delta}$ relative to $YBa_2Cu_3O_{7-\delta}$ and $EuBa_2Cu_3O_{7-\delta}$ has been reported by McDevitt *et al.* [29]. Kita and Osumi [30] observed that the stability of $Y_{1-z}Ca_zBa_{2-z}La_zCu_3O_{7-\delta}$ in water is increased with degree of cation co-substitution up to $z = 0.6$. It appears that the cationic substitution relieve internal stresses in the structure caused by the bondlength mismatching and the change in the position of oxygen atoms in oxygen deficient $YBa_2Cu_3O_{7-\delta}$. Seema and Bhalla *et al.* [24, 27, 28] found that the single substitution of Sr^{2+} and Al^{3+} in $YBa_2Cu_3O_{7-\delta}$ results in the formation of corrosion resistant $YBa_{1.8}Sr_{0.2}Cu_3O_{7-\delta}$ and $YBa_2Cu_{2.8}Al_{0.2}O_{7-\delta}$ superconducting samples. The $YBa_2Cu_3O_{7-\delta}$ phase has an oxygen deficient perovskite structure with a layer sequence Cu(1)Ox−BaOCu(2)O2−Y−Cu(2)O2−BaO−Cu(1)Ox along the c-axis. The effect of water on Zn^{2+} substituted $YBa_2Cu_3O_{7-\delta}$ have been investigated by Bhalla and Seema *et al.* [31, 32]. It is therefore worth mentioning over here that the effect of Zn substitution in $YBa_2Cu_3O_{7-\delta}$ will bring about the changes in the structural stability of the superconducting compound, in addition to the changes in the superconducting properties as documented well in the high Tc literature [33–36].

The present study have led to a wealth of new insights and information about comparison of stability of $YBa_2Cu_3O_{7-\delta}$, $YBa_{2-x}Sr_xCu_3O_{7-\delta}$, $YBa_2Cu_{3-x}Al_xO_{7-\delta}$, $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ for various concentration of Sr, Al and Zn in water and the interlinked aspects of structural stability and the stability of high Tc compound in water or its corrosion reactivity with water. The effect of water on Sr, Al and Zn doped $YBa_2Cu_3O_{7-\delta}$ is examined by employing temperature dependent resistivity measurement, X-ray diffraction studies and oxygen content determination and SEM techniques.

2. Results and Discussion

The findings stemmed from the systematic analysis of the experimental data can broadly be summed up as below.

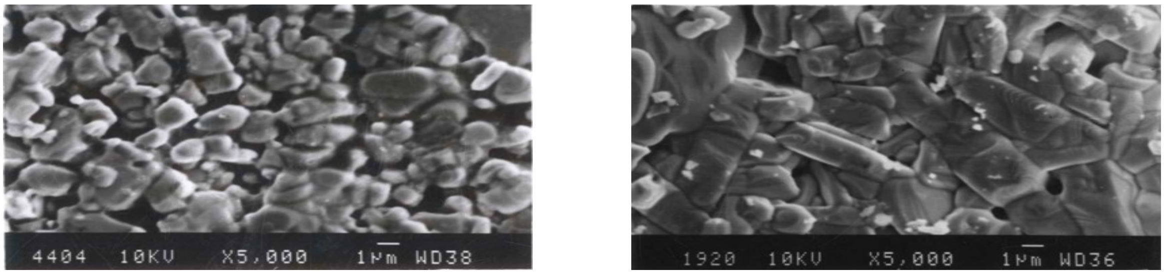
The critical transition temperature (Tc(K), $R = 0$) of $YBa_2Cu_3O_{7-\delta}$ superconductor is reduced both on doping with $Sr^{2+}/Al^{3+}/Zn^{2+}$ and on their treatment with water [24,27,28,31,32]. The reduction in Tc upon substitution and on their water treatment is a function of dopant and the concentration of dopant. The magnitude of reduction in Tc increases with increasing concentration of the dopant, except for Sr^{2+} and Al^{3+} for the molar concentration of 0.2. The reduction in Tc for the molar concentration of 0.2, both for Sr^{2+} and Al^{3+}, is found to be minimum, i.e., 3.1 K and 4.5 K, respectively, with respect to the corresponding undoped respective sample. Also, it has been observed, in the case of $YBa_{1.8}Sr_{0.2}Cu_3O_{7-\delta}$ and $YBa_{1.6}Sr_{0.4}Cu_3O_{7-\delta}$ samples, i.e., for the Sr^{2+} with molar concentration of 0.2 and 0.4 that the value of Tc (87.5 and 85.0 K) on water treatment is higher compared to the value of Tc (81.2 K) of undoped water treated $YBa_2Cu_3O_{7-\delta}$ sample [24,27]. Zn substituted $YBa_2Cu_3O_{7-\delta}$ samples on their water treatment for Zn concentration 0.025, 0.05, 0.075 and 0.1 show semi-conducting behaviour which increases with increasing concentration of Zn. In fact, the sample with Zn concentration 0.1 on water treatment becomes non-superconducting [31].

The X-ray diffractogram of $YBa_2Cu_3O_{7-\delta}$ indicates that the sample has an orthorhombic structure and also has a single phase. The lattice constants a and b decrease whereas the c increases in $Sr^{2+}/Al^{3+}/Zn^{2+}$ doped samples on their water treatment as compared to the corresponding untreated samples, except for the undoped samples where the lattice constant a infact is increased (0.015Å) and the lattice constant c in the case of Al^{3+} doped sample for the concentration of 0.05 shows a slight decrease (0.0003Å) [24,27,28,31].

The orthorhombicity is calculated from the lattice constants. The decreased in the orthorhombicity in $YBa_2Cu_3O_{7-\delta}$ sample on water treatment is found to be maximum (0.58×10^{-2}). The magnitude of decrease in the orthorhombicity in the untreated samples and the corresponding water treated samples increases with increasing concentration of the dopant, except in the case of Al^{3+} sample where the orthorhombicity for the molar concentration 0.2 and 0.3 of Al^{3+} infact increases in the untreated and the corresponding water treated samples. Also, in the case of Zn doped samples for the molar concentration of 0.075 and 0.1 the decrease in the orthorhombicity is less as compared to the lower concentrations, i.e., 0.025 and 0.05, respectively, of Zn.

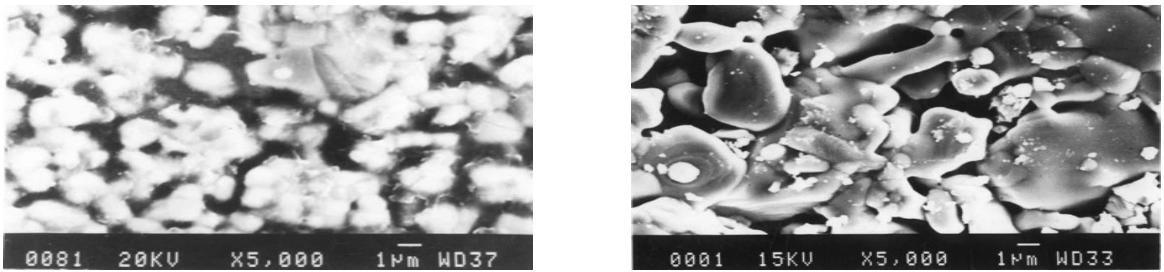
The oxygen content in water treated samples is, in general, found to be less as compared to their corresponding untreated samples. The decrease in the oxygen content in water treated samples and the corresponding untreated samples substituted with Sr^{2+} and Al^{3+} for the molar concentration 0.2 in both the cases is found to be minimum, i.e., 0.003 and 0.007, respectively.

The 2[] peaks of the X-ray diffractograms for the doped $Sr^{2+}/Al^{3+}/Zn^{2+}$ samples indicate incorporation of the respective dopant. Whereas, the X-ray diffractograms of water treated samples indicate the formation of impurity products/phases. The formation of impurity phases is further demonstrated by the surface morphological studies using the scanning electron microscope (SEM) in Figures 1(a-d) and 2(a-d).



(a) SEM of $YBa_2Cu_3O_{7-\delta}$, comprises of round and small grains with high porosity

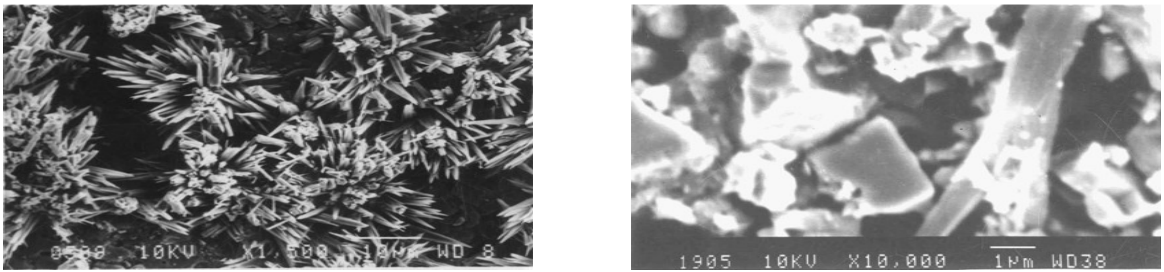
(b) SEM of $YBa_2Cu_{2.8}Al_{0.2}O_{7-\delta}$ with long and well connected grains with very few pores



(c) SEM of $YBa_{1.8}Sr_{0.2}Cu_3O_{6.882}$ showing very high porosity

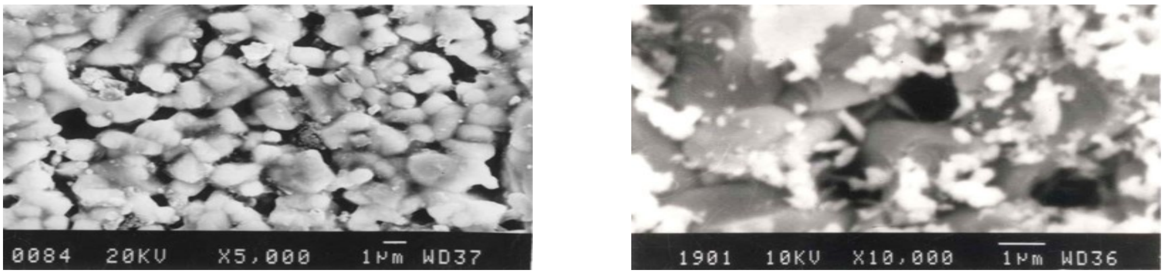
(d) SEM of $YBa_2Cu_{2.975}Zn_{0.025}O_{6.916}$ showing big and elongated grains with reduced porosity and few round shaped impurity structure

Figure 1. SEM of untreated



(a) SEM of water treated sample of $YBa_2Cu_3O_{7-\delta}$ covered with impurity phases like $BaCO_3$, CuO, and Y_2BaCuO_5

(b) SEM of Water treated $YBa_2Cu_{2.8}Al_{0.2}O_{7-\delta}$ with Y_2BacuO_5 impurity phases at high magnification



(c) SEM of Water treated $YBa_{1.8}Sr_{0.2}Cu_3O_{6.882}$ with very few impurity phases

(d) SEM of Water treated $YBa_2Cu_{2.975}Zn_{0.025}O_{6.916}$ with increased porosity and ZnO, $BaCO_3$, CuO, as impurity phases

Figure 2. SEM of water treated

3. Conclusions

Systematical and careful analysis of the experimental data of the four different types of the samples, viz., $YBa_2Cu_3O_{7-\delta}$, $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ $(0 < x < 0.6)$, $YBa_2Cu_{3-x}Al_xO_{7-\delta}$ $(0 < x < 0.3)$ and $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ $(0 < x < 0.1)$, before and after the 16h water treatment enables to draw some of the conclusions on the degradation, broadly defined as deterioration in the superconducting parameters, e.g., Tc(K), []Tc(K), oxygen content, etc., of the samples as follows:

(a) $YBa_2Cu_3O_{7-\delta}$ degrades upon substitution with $Sr^{2+}/Al^{3+}/Zn^{2+}$ at Ba^{2+}/Cu(1)/Cu(2) sites, respectively. The results are inconformity with the earlier investigations.

(b) All the substituted samples, viz., $YBa_{2-x}Sr_xCu_3O_{7-\delta}$, $YBa_2Cu_{3-x}Al_xO_{7-\delta}$ and $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ degrade consequent to the water treatment.

(c) The degree of degradation in the substituted samples is a function of the type of the dopant $Sr^{2+}/Al^{3+}/Zn^{2+}$ as well as the molar concentration of the dopant.

(d) The degradation is found to be minimum in the case of Sr^{2+} substitution at Ba^{2+} sites in $YBa_2Cu_3O_{7-\delta}$ as compared to the degradation of Al^{3+} and Zn^{2+} substitution at Cu(1) and Cu(2) sites, respectively. The degradation is maximum in the case of Zn^{2+} substitution at Cu(2) site.

(e) The degradation of Al^{3+} substituted $YBa_2Cu_3O_{7-\delta}$ is found to increase with increasing time of water treatment.

(f) It is found that the degradation of Sr^{2+} and Al^{3+} substituted samples do not continue to increase with increasing molar concentration of dopants, whereas for the Zn^{2+} substituted samples, the degradation increases with the concentration of Zn.

(g) One of the important and significant findings of the detailed study is that the degradation is minimum for the Sr^{2+} and the Al^{3+} substituted $YBa_2Cu_3O_{7-\delta}$ with molar concentration of 0.2, i.e., for $YBa_{1.8}Sr_{0.2}Cu_3O_{8.882}$ and $YBa_2Cu_{2.8}Al_{0.2}O_{6.941}$.

The investigations on the substituted $YBa_2Cu_3O_{7-\delta}$ with different dopants, i.e., Sr^{2+}, Al^{3+} and Zn^{2+} under different concentration enhance our understanding on the cause of degradation in the substituted samples and elucidate that

(1) The substitution of a smaller/bigger ionic-radius ion at the sites of a bigger/smaller ionic-radius ion seems to produce a perturbation aound the substituted sites.

(2) The perturbation around the substituted sites results in the change of critical transition temperature, transition width, change in the lattice parameters and hence change in the bond lengths, the oxygen content etc.

(3) Change in the bond lengths in between Cu(2)−O(3), Cu(2)−O(2), Cu(2)−O(4), Cu(1)−O(4), caused by perturbation is likely to reduce mis-matching of the bond length in the substituted structures which results reduction in strains within the unit cell alongwith the change in the buckling/puckering. Perhaps these factors contribute to the lesser degradation in the substituted $YBa_2Cu_3O_{7-\delta}$.

(4) The channels formed in the substituted $YBa_2Cu_3O_{7-\delta}$ structure, because of the readjustment of the oxygen along the a and b axes, parallel to the b-axis apparently reduce the penetration of the protonic species into the structure. This also seems to cause relatively a less degradation in the substituted $YBa_2Cu_3O_{7-\delta}$ as compared to the unsubstituted $YBa_2Cu_3O_{7-\delta}$.

(5) The lesser affinity of the substituted ions, viz., Sr^{2+}, Al^{3+} and Zn^{2+} for the protonic species as compared to high affinity of Ba^{2+} for the protonic species also contributes to the relative reduce degradation in the substituted $YBa_2Cu_3O_{7-\delta}$.

(6) $YBa_{1.8}Sr_{0.2}Cu_3O_{6.882} > YBa_2Cu_{2.8}Al_{0.2}O_{6.941} > YBa_2Cu_3O_{6.905} > YBa_2Cu_{2.975}Zn_{.025}O_{6.893}$.

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Competing Interests

The author declare that she has no competing interests.

Authors' Contributions

The author wrote, read and approved the final manuscript.

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