Structural and magnetic features of high performance Ca₃₋ₓInₓVO₈ ceramic synthesized via mixed oxalates-citrates precursors

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Received: 18ᵗʰ February, 2009 ; Accepted: 23ʳᵈ February, 2009

ABSTRACT

Indium-doped vanadate ceramic samples with general formula Ca₃₋ₓInₓVO₈ were synthesized by using solution route technique depending upon two different precursors (oxalate and citrates) to get maximum homogeneity inside the bulk of the material where x = 0.05 and 0.25 mole. Structural and microstructural properties were monitoring by using both of XRD and SEM evaluating that indium doped-calcium vanadate ceramic has the semiconducting classical doubly perovskite phase as proved in the X-ray diffractogram, grain size of the material bulk was found to be in between 1.57-2.23μm which are lower than those reported in literatures.Magnetic measurements indicated that the In- doped- calcium vanadate ceramic exhibits an semiconducting behavior confirming that indium-hole dopings enhance the paramagnetic character and semi-conduction mechanism of the hexagonal perovskite phase.   © 2009 Trade Science Inc. - INDIA

INTRODUCTION

Based on the electrical, magnetic and other related properties, there has been rapid progress in developing new materials of different structural families (i.e., perovskite, tungsten bronze, layer structure, etc.) for different devices, such as capacitors, actuators, pyroelectric detectors, transducers, electro-optic, ferroelectric random access memory and display, etc.[1-7]. Out of the materials developed only a few can be used in wireless communication technologies such as cellular phones, microwave multilayer integrated circuits, etc. [8-10]. In this attempt physical properties of some materials have been tailoredeither by substituting suitable elements at different atomic sites of the structure of the material or fabricating complex/composite systems[11-13]. Though a lot of complex systems now-a-days are available for the purpose, CaO–Nb₂O₅, BaO–Nb₂O₅, SrO–Nb₂O₅ binary systems[14] have been found very interesting and useful because of diversity of their crystal structural, stability and physical properties.

Some mixed metal oxides containing vanadium (V⁺⁴) with perovskite-related structure have recently been found interesting as transition metal analogs of the cuperate superconductors and ionic conductors[15-25].

Although Nb⁺⁵, Ta⁺⁵ and V⁺⁵ containing systems have recently been studied in details for different applications, not much has been reported on structural and electrical properties of Ca-O-V₂O₅ which is the subject of this paper. The major goal in the present article

is to investigate the effect indium-dopings on;
a. Structural and micro-structural properties of In-doped $Ca_{3-x}In_xVO_8$ ceramics.
b. Electrical conduction and Magnetic properties of In-doped- $Ca_{3-x}In_xVO_8$ samples.

EXPERIMENTS

A. Samples preparation

The In-doped-vanadates ceramics with general formula $Ca_{3-x}In_xVO_8$ were selected from another study for authors to be the target of this investigation where x = 0.05 and 0.25 mole.The preparation was attempted by applying solution route and sintering procedure using the molar ratios of In_2O_3, V_2O_3, and $CaCO_3$ each of highly pure chemical grade purity. The mixture were ground carefully then solublize in few drops of concentrated nitric acid forming nitrate extract which diluted by distill water. The nitrate solution was neutralized by using 30 % urea solution and pH becomes ~6. Mixture I was for calcium solution and mixture II was for (indium + vanadium) nitrates. Mixture I was diluted by distill water to be 100 ml then pH was adjusted to be 8.5 concentrated solution of oxalic acid was added carefully till heavy white precipitate from calcium oxalates is obtained and the pH must be higher than 8.The oxalate precursor is filtered and washed by 5 % ammonium nitrate solution.Mixture II of indium and vanadium was passing through the same treatment but citric acid was applied instead of oxalic in present of ethylene glycol as complexing agent to produce gelatinous precipitate of indium-vanadium citrates that formaing citrates precursor.

The calcium oxalate and In/V-citrates precursors were forwarded to muffle furnace and calcinations process was performed at 780⁰C under a compressed O_2 atmosphere for 10 hrs then reground and pressed into pellets (thickness 0.2 cm and diameter 1.2 cm) under 6 Ton /cm². Sintering was carried out under oxygen stream at 900⁰C for 20 hrs.The samples were slowly cooled down (20⁰C /hr) till 500⁰C and annealed there for 8 hrs under oxygen stream. The furnace is shut off and cooled slowly down to room temperature. Finally the materials are kept in vacuum desiccator over silica gel dryer

B. Phase identiication

The X-ray diffraction (XRD) measurements were carried out at room temperature on the fine ground samples using Cu-Kα radiation source,Ni-filter and a computerized STOE diffractometer/Germany with two theta step scan technique.

Scannig Electron Microscopy (SEM) measurements were carried out at different sectors in the prepared samples by using a computerized SEM camera with elemental analyzer unit (PHILIPS-XL 30 ESEM / USA).

C. Magnetic measurements

The cryogenic AC-susceptibility of the prepared materials was undertaken as a function of temperature recorded in the cryogenic temperature zone down to 30 K using liquid helium refrigerator.

RESULTS AND DISCUSSION

1. Phase identification

Figure (1a-c) displays the X-ray powder diffracto metry pattern for In-doped-vanadates ceramics with general formula $Ca_{3-x}In_xVO_8$ where x = 0.0, 0.05 and 0.25 mole respectively. Analysis of the corresponding 2θ values and the interplanar spacings d (Å) were carried out and indicated that, the X-ray crystalline struc-
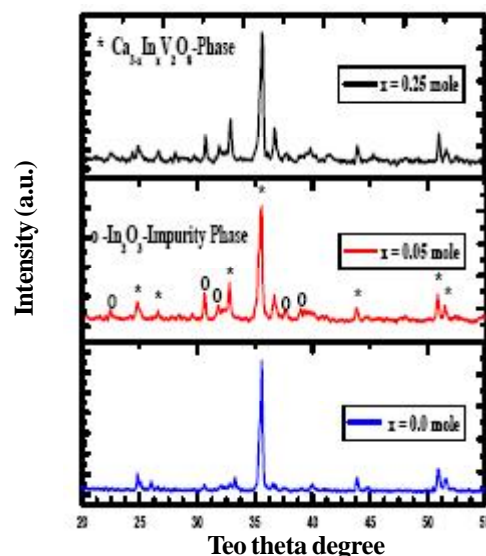

Figure 1 : X-ray diffraction pattern recorded for In-doped-vanadates ceramics with general formula $Ca_{3-x}In_xVO_8$ where x = 0.0, 0.05 and 0.25 mole

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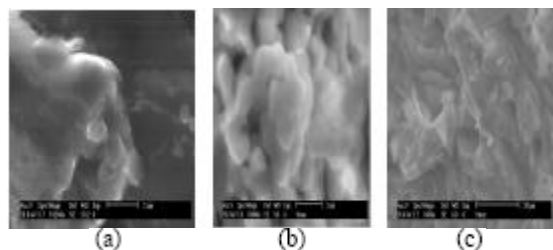**Figure 2(a-c) : SE-Micrographs recorded for in-doped-vanadates ceramics with general formula $Ca_{3-x}In_xVO_8$ where; (a) x = 0.0, (b) x = 0.05 and (c) x = 0.25 mole, with different magnification factors 2 and 20μm**

TABLE 1 : EDX-elemental analysis recorded for Ca_3VO_8 system

Element	Ca_3VO_8 Wt %	At %	K-ratio	Z	A	F
O K	65.38	60.15	0.1037	1.1119	0.7131	1.0019
V K	7.29	9.139	0.0159	1.2443	0.2253	1.0011
CaK	23.26	30.48	0.1831	1.0336	0.5507	1.0313

TABLE 2 : EDX-elemental analysis recorded for $Ca_{2.95}In_{0.05}VO_8$ system

Element	$Ca_{2.95}In_{0.05}VO_8$ Wt %	At %	K-ratio	Z	A	F
O K	65.38	60.15	0.1037	1.1119	0.7131	1.0019
V K	7.29	9.139	0.0159	1.2443	0.2253	1.0011
CaK	23.26	30.48	0.1831	1.0336	0.5507	1.0313
In L	0.1606	0.145	0.0332	0.9481	1.0218	1.0118

TABLE 3 : EDX-elemental analysis recorded for $Ca_{2.75}In_{0.25}VO_8$ system

Element	$Ca_{2.75}In_{0.25}VO_8$ Wt %	At %	K-Ratio	Z	A	F
O K	63.32	61.15	0.1247	1.1259	0.8131	1.0022
V K	8.21	9.189	0.0149	1.1563	0.2252	1.0021
CaK	21.26	29.87	0.1731	1.0126	0.5607	1.0213
In L	0.706	0.645	0.0352	0.8721	1.0518	1.0123

ture mainly belongs to a single hexagonal doubly pervoskite phase $Ca_{3-x}In_xVO_8$ in major besides few peaks of In_2O_3 as secondary phase in minor. The lattice parameters of the unit cell were refined using the least-squares sub-routine of a standard computer program these refined lattice parameters are: a = b = 16.8312Å, c = 40.3783 Å with estimated standard deviation in parenthesis. These unit cell parameters are in good agreement with those of the reported ones for $Ca_3Nb_2O_8$ structure[26].

The unit cell dimensions were calculated using the most intense X-ray reflection peaks which is fully agreement with those mentioned in the literature[27-29].

It is obviously that, the additions of In_2O_3 has a

negligible effect on the main crystalline structure hexagonal doubly pervoskite phase $Ca_{3-x}In_xVO_8$ with In-content (x = 0.25) as shown in figure 1c.

From figures 1a,b one can indicate that hexagonal pervoskite phase $Ca_{3-x}In_xVO_8$ is the dominating phase by ratio exceeds than 90 % confirming that In-ion substitutes successfully on the Ca-sit at low concentration x = 0,0.05 mole without damaging the original-pervoskite hexagonal phase.

TABLES 1 and 2 explain EDX-elemental analysis data recorded for $Ca_{3-x}In_xVO_8$ where x = 0.05 and 0.25 mole that prepared via solution route.It is clear that the atomic percentage recorded is approximately typical with the molar ratios of the prepared sample emphasizing the quality of preparation through solution technique.

On the basis of ionic radius In-ion can substitute on the ca-sites causing slight shrinkage in the lattice without destroying it as clearly appears in the x-ray diffractogram figure 1. Since $Ca_{3-x}In_xVO_8$ hexagonal phase is clearly assigned in our x-ray patterns by * as shown in figure 1.

2. SE-microscopy measurements

Figure (2a-c) show the SEM-micrographs recorded for In-doped-vanadates ceramics with general formula $Ca_{3-x}In_xVO_8$ where x = 0.0, 0.05 and 0.25 mole. The estimated average of grain size was calculated and found in between 1.57- 2.23μm supporting the data reported in[23].

The EDX examinations for random spots in the same sample confirmed and are consistent with our XRD analysis for polycrystalline In-doped-vanadates ceramic sample,such that the differences in the molar ratios EDX estimated for the same sample is emphasized and an evidence for the existence of hexagonal phase with good approximate to molar ratios see (TABLES 1-3).

From figure (2a-c), it is so difficult to observe inhomogeneitiy within the micrograph due to that the powders used are very fine and the particle size estimated is too small.

This indicates that, the actual grain size in the material bulk is smaller than that detected on the surface morphology. Furthermore, in our EDX (energy disperse X-ray) analysis, In^{3+} was detected qualitatively with good approximate to the actual molar ratio but not ob-
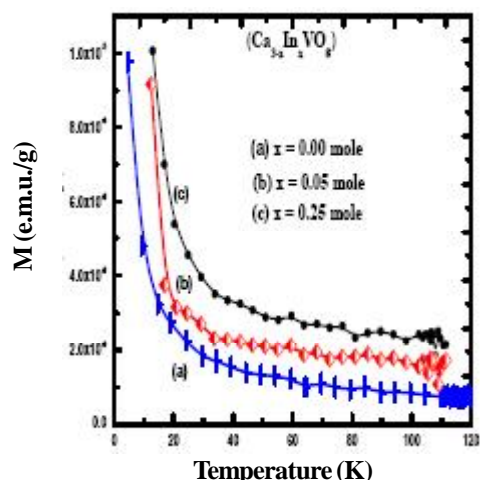
Figure 3(a-c): Magnetic susceptibility curve recorded for In-doped – vanadates ceramics with general formula Ca$_{3-x}$ In$_x$VO$_8$ where; (a) x = 0.0, (b) x = 0.05 and (c) x = 0.25 mole
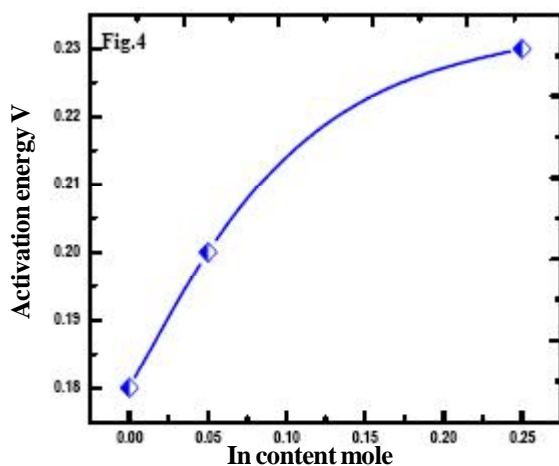

Figure 4 : Activation energies calculated for indium doped ceramics versus in-content

served at vanadates ceramics grain boundaries which confirm that, indium (III) has diffused regularly into material bulk of superconducting vanadates ceramics-phase and In-ion induces in the crystalline structure through solid state reaction by some extent.The inclusion of In-ion is confirmed also by the enhancing the semiconducting behavior of vanadates ceramics semi-conductor.

3. Magnetic and electrical properties

Figure 3 exhibits magnetic susceptibility curve recorded as a function of absolute temperatures for vanadates ceramics samples synthesized via solution route.It is clear that the conduction increases as temperatures raise reflecting semiconductor behavior for vanadates

ceramic sample. Although the indium dopant has metallic behavior as reported in literatures[22-25] it enhances semi-conduction mechanism inside material bulk of vanadates ceramics. From this point of view indium as dopant element with metallic character expected to make a shift towards semiconducting behavior as achieved in our investigation.

Transport properties of the materials obeying Arrhenius equation $\sigma_{ac} = \sigma_0\exp(-E_a/K_BT)$, where the symbols have their usual meanings. It is observed that the ac conductivity of the material increases with rise in temperature, and shows the negative temperature co-efficient of resistance behavior. The values of activation energy of the compound are found to be 0.18, 0.20 and 0.23 eV for x = 0.0,0.05 and 0.25 mole respectively.

This behavior suggests that the conduction mechanism of the compound may be due to the hopping of charge carrier that enhanced by indium holes- dopings and the energy gabs between conduction and valence band increase as In-dopant concentration increase as shown in figure 4.

COCLUSIONS

The conclusive remarkes inside this article can be summarized as the follow ;
1. Solution technique exhibits structure quality as preparation technique.
2. In-dopant make a shift towards hexagonal phase.
3. SE-micrographs confirmed that In-ions distribute regularly through out the lattice structure of vanadates ceramics without destroying hexagonal-phase.
4. Magnetic order of Ca$_{3-x}$In$_x$VO$_8$ (where x = 0.05 and 0.25 mole)does not changed and still semiconducting order although indium-dopant has metallic character.
5. The values of activation energy of the In-doped-ceramics are raised as indium increases.

REFERENCES

[1] D.Szwagierczak, J.Kulawik; J.Eur.Ceram.Soc., **24**, 1979 **(2004)**.
[2] H.El Alaoui-Belghiti, R.Von der Muhll, A.Simon, M. Elaatmani; J.Ravez; Mater.Lett., **55**, 138 **(2002)**.
[3] N.Wakiya, J.K.Wang, A.Saiki, K.Shinozaki,

Full Paper

N.Mizutani; J.Eur.Ceram.Soc., **19**, 1071 **(1999)**.

[4] M.R.Raju, R.N.P.Choudhary; J.Phys.Chem.Solids, **64**, **(2003)**, 847.

[5] X.M.Chen, Z.Y.Xu, J.Li; J.Mater.Res., **15**, 125 **(2000)**.

[6] L.G.Van Uitert, S.Singh, H.J.Levinstein; Appl.Phys. Lett., **11**, 61 **(1967)**.

[7] J.J.Rubin, L.F.Van Uitert, H.J.Levinstein; J.Cryst. Growth, **1**, 315 **(1967)**.

[8] W.Wersing, B.C.H.Steele; 'Electronic ceramics', Elsevier, New York, **(1991)**.

[9] W.Wersing, Curr.Opin.Solid State Mater.Sci., **1**, 715 **(1996)**.

[10] T.Negas, G.Yeager, S.Bell, R.Amren, P.K.Davies, R.S.Roth; 'NIST Special Publication 804', NIST, 21-38 **(1991)**.

[11] R.J.Cava, J.J.Krajewski, R.S.Roth; Mater.Res. Bull., **33**, 527 **(1998)**.

[12] R.Umemura, H.Ogawa, A.Yokoi, H.Ohsato, A.Kan; J.Alloy.Compd., **424**, 388 **(2006)**.

[13] H.Ogawa, A.Yokoi, R.Umemura, A.Kan; J.Eur. Ceram.Soc., **27**, 3099 **(2007)**.

[14] L.M.D.Cranswick, W.G.Mumme, I.E.Grey, R.S. Roth, P.Bordet; J.Solid State Chem., **172**, 178 **(2003)**.

[15] H.-Zh.Li, L.-M.Liu, K.P.Reis, A.J.Jacobson; J. Alloy.Compd., **203**, 181 **(1994)**.

[16] G.Xiao, F.H.Streitz, A.Gavrin, Y.W.Du, C.L.Chien; Phys.Rev.B., **35**, 8782 **(1987)**.

[17] Y.Maeno, T.Tomita, M.Kyogoku, S.Awaji, Y.Aoki, K.Hoshino, A.Minami, T.Fujita; Nature, **328**, 512 **(1987)**.

[18] J.M.Tarascon, P.Barboux, P.F.Maceli, L.H.Greene, G.W.Hull; Phys.Rev.B., **37**, 7458 **(1988)**.

[19] H.Renevier, J.L.Hodeau, M.Marezio, A.Santoro; Pysica.C., **220**, 143 **(1994)**.

[20] R.G.Kulkarni, D.G.Kuberkar, G.J.Baldaha, G.K. Bichile; Physica.C., **217**, 175 **(1993)**.

[21] J.F.Bringley, T.M.Chen, B.A.Averill, K.M.Wong, S.J.Poon; Phys.Rev.B., **38**, 2432 **(1988)**.

[22] Y.Shimakawa, Y.Kubo, K.Utsumi, Y.Takeda, M.Takano; Jpn.J.Appl.Phys., **27**, L1071 **(2006)**.

[23] Z.Hiroi, M.Takano, Y.Takeda, R.Kanno, Y.Bando; Jpn.J.Appl.Phys., **27**, L580 **(1988)**.

[24] M.P.Delamare, M.Hervieu, I.Monot, K.Verbist, G.Tendeloo; Physica.C., **262**, 220 **(1996)**.

[25] P.N.Peters, R.C.Sisk, E.Ubran, C.Y.Huang, M.K. Wu; Appl.Phys.Lett., **52**, 2066 **(1988)**.

[26] C.Y.Huang, Y.Shapiro, E.J.McNiff, P.N.Peters, B.B.Shwatrz, M.K.Wu, R.D.Shull, C.K.Chiang; Mod.Phys.Lett., **2**, 869 **(1988)**.

[27] J.P.Singh, H.L.Leu, R.B.Poepple, E.Voorhees, G.T. Goudery, K.Winsley, D.Shi; J.Appl.Phys., **66**, 3154 **(1989)**.

[28] B.Dwir, M.Affronte, D.Pavuna; Appl.Phys.Lett., **55**, 399 **(1989)**.

[29] J.Jung, M.A.Mohammed, S.C.Cheng, J.P.Frank; Phys.Rev., **B42**, 6181 **(1990)**.