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Microwave-Assisted Solid-State Synthesis of Oxide Ion Conducting Stabilized Bismuth Vanadate Phases

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A microwave-assisted method for the preparation of substituted bismuth vanadates has been described. The method consists of starting with the respective oxides mixed in stoichiometric proportions and exposing the mixture to microwaves. Substitution takes place at the vanadium sites and it has been possible to prepare Ag^+-, Mn^{4+}-, Ga^{3+}-, Y^{3+}-, and Ce^{4+}-substituted compounds with up to 10% substitution. Mn^{4+}- and Ag^+-substituted compounds are found to exhibit better oxygen ion conductivities than any reported so far in the literature.

I. Introduction

Oxide ion electrolytes are of great importance due to their promising applications in solid oxide fuel cells, water-vapor electrolyzers, and oxygen sensors. Though stabilized zirconias are known to be good oxide ion conductors, the operating temperatures are high (≥950 K).[1] This necessitates the development of new materials possessing high oxygen ion conductivity at lower temperatures.[2] To synthesize such compounds, various chemical strategies have been adopted in the literature.[2] One of them has been to engineer three-dimensional oxide materials that can support a high concentration of disordered oxygen ion vacancies in the oxygen sublattice. Ba_2InO_5, which is a perovskite-related brownmillerite, typifies this class of materials.[3] An oxide of the formula $Bi_4V_2O_{11}$, which belongs to the Aurivillius layered-perovskite family, has been reported to be a good oxide ion conductor in its high-temperature γ-phase[4] (Figure 1). It is found that substitution of aliovalent cations in α-bismuth vanadate (orthorhombic structure) stabilize the high-temperature γ-$Bi_4V_2O_{11}$ (tetragonal) phase. These tetragonal bismuth vanadates exhibit high oxide ion conductivity (around 770 K), especially if the substituent is copper[4] or titanium.[5] A large number of cations such as Li^+, Zr^{4+}, Mg^{2+}, Al^{3+}, Ni^{2+}, Pb^{2+}, Co^{2+}, and Nb^{5+} have been substituted for vanadium in α-$Bi_4V_2O_{11}$ structure in order to stabilize the high-temperature γ-phase at room temperature.[6,7] These metal-substituted bismuth vanadate samples are designated by the acronym BIMEVOX.[8] The conventional ceramic method of synthesizing these complex oxides is both tedious and time-consuming owing to the low diffusion rates involved in the solid-state reactions.[5,6] For example, the Pb-substituted sample required a stepwise heating schedule of about 24 h.[9] Li- and Ti-substituted compounds were prepared by heating appropriate amounts of constituent oxides at 923 K for 24 h with intermittent cooling and grinding.[5,10] Microwave irradiation has been known to provide an alternate and

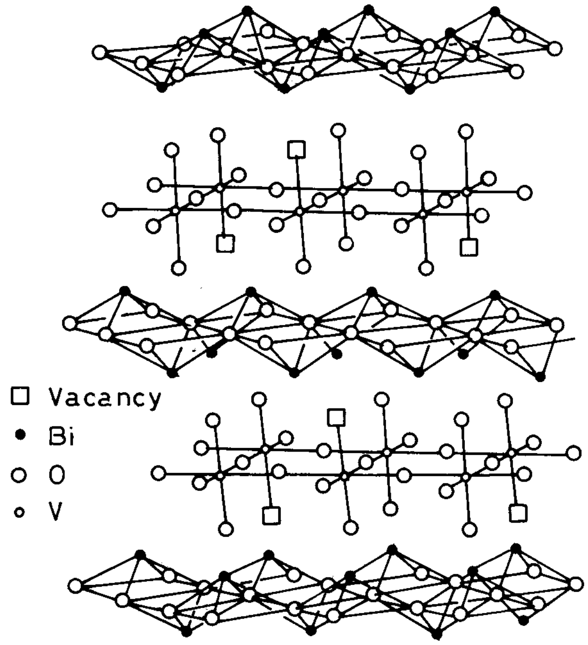

Figure 1. Structure of γ-$Bi_4V_2O_{11}$ phase.

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* Corresponding author.

(1) Etsell, T. H.; Flengas, S. N. *Chem. Rev.* **1970**, *70*, 339.

(2) Goodenough, J. B.; Shukla, A. K. *Solid State Ionic Devices*; Chowdary, B. V. R., Radhakrishna, S., Eds.; World Scientific: Singapore, 1988; p 573 and references therein.

(3) Goodenough, J. B.; Ruiz-diaz, J. E.; Zhen, Y. S. *Solid State Ionics* **1990**, *44*, 21.

(4) Abraham, F.; Boivin, J. C.; Mairesse, G.; Nowogrocki, G. *Solid State Ionics* **1990**, *40/41*, 934.

(5) Sharma, V.; Shukla, A. K.; Gopalakrishnan, J. *Solid State Ionics* **1992**, *58*, 359.

(6) Goodenough, J. B.; Manthiram, A.; Paranthaman, M.; Zhen, Y. S. *Mater. Sci. Eng. B* **1992**, *12*, 357.

(7) Yan, J.; Greenblatt, M. *Solid State Ionics* **1995**, *81*, 225.

(8) Iharada, T.; Hammouche, A.; Fouletier, J.; Kleitz, M.; Boivin, J. C.; Mairesse, G. *Solid State Ionics* **1991**, *48*, 257.

(9) Vannier, R. N.; Mairesse, G.; Nowogrocki, G.; Abraham, F.; Boivin, J. C. *Solid State Ionics* **1992**, *53−56*, 713.

(10) Sharma, V. Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1993; p 11.

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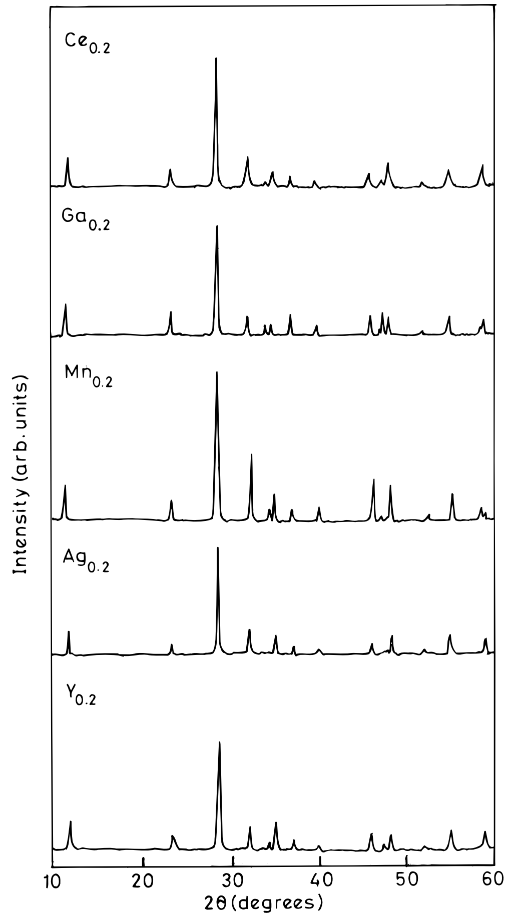

Figure 2. X-ray diffractograms of the microwave prepared stabilized bismuth vanadate phases ($Bi_4V_{1.8}M_{0.2}O_{11-\delta}$, where M = Ce, Ga, Mn, Ag, and Y).

Table 1. Lattice Parameters and Conductivity of the Microwave-Prepared BIMEVOX Compounds

composition	x	a^a (Å)	c^a (Å)	σ (at 573 K) (S cm^{-1})
$Bi_4V_{1.8}Cu_{0.2}O_{10.7}$[b]	0.3	3.920	15.340	4.55×10^{-6}
$Bi_4V_{1.8}Zn_{0.2}O_{10.7}$	0.3	3.930	15.380	8.16×10^{-6}
$Bi_4V_{1.8}Ti_{0.2}O_{10.9}$	0.1	3.934	15.320	1.44×10^{-5}
$Bi_4V_{1.8}Mn_{0.2}O_{10.7}$	0.3	3.906	15.409	7.46×10^{-5}
$Bi_4V_{1.8}Ag_{0.2}O_{10.6}$	0.4	3.924	15.221	3.06×10^{-5}
$Bi_4V_{1.8}Ga_{0.2}O_{10.8}$	0.2	3.918	15.401	1.52×10^{-5}
$Bi_4V_{1.8}Y_{0.2}O_{10.8}$	0.2	3.947	15.279	4.78×10^{-7}
$Bi_4V_{1.8}Ce_{0.2}O_{10.9}$	0.1	3.912	15.299	3.32×10^{-7}

[a] The accuracy of lattice parameters is 0.001 Å. [b] Reported in the literature.

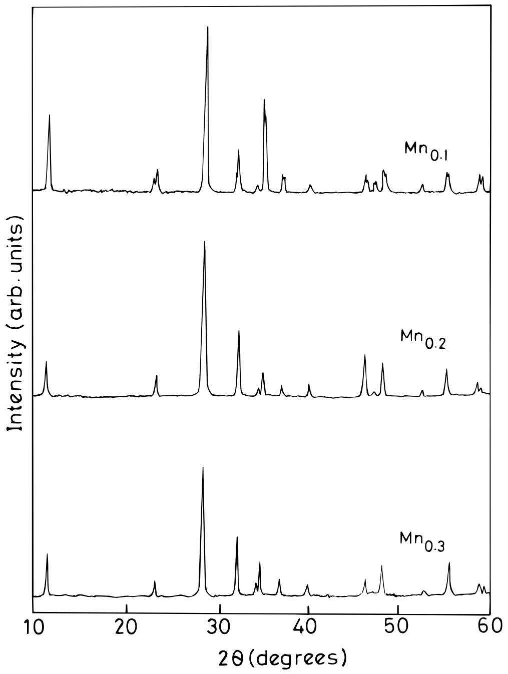

Figure 3. Powder X-ray diffraction patterns of Mn-substituted bismuth vanadate phases, indicating clearly that 10% dopant concentration is necessary for the complete stabilization of γ phase.

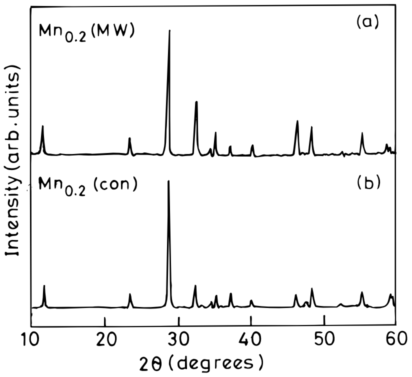

Figure 4. X-ray diffractograms of (a) microwave-prepared and (b) conventionally prepared Mn-substituted γ-bismuth vanadate phases (the good agreement is evident).

facile route for reactions in solid state.[11−15] Microwave-induced reactions are generally very fast and often occur at lower temperatures than the corresponding reactions in conventional heating procedures. This has been reported earlier in several cases such as the preparation of SiC,[16] todorokite, bixbyte and cryptomelane,[17] etc. Also, products of good structural uniformity are obtained in microwave reactions.[12,13] Preparation of bismuth and lead vanadates by using microwaves has been earlier reported from this laboratory.[18] We have now examined the possibility of preparing stabilized bismuth vanadate phases by a microwave method. In the present work, we have employed aliovalent substitution of V^{5+} in $Bi_4V_2O_{11}$ with 10% Mn^{4+}, Ce^{4+}, Ga^{3+}, Y^{3+}, and Ag^{+} ions. Substitution of these ions has not been examined earlier. In this paper we report a successful preparation of stabilized γ-phase of substituted bismuth vanadates. The microwave synthesis of BIMEVOX compounds is accomplished in just 15 min.

II. Experimental Section

Appropriate amounts of oxide constituents (Bi_2O_3, V_2O_5, MnO_2, CeO_2, Ga_2O_3, Y_2O_3, and Ag_2O) were thoroughly mixed

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(11) Mingos, D. M. P.; Baghurst, D. R. *Chem. Soc. Rev.* **1991**, *20*, 1.

(12) Landry, C. C.; Barron, A. R. *Science* **1993**, *260*, 1653.

(13) Baghurst, D. R.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1988**, 829.

(14) Vaidhyanathan, B.; Rao, K. J. *Chem. Mater.* **1997**, *9* (5), 1196.

(15) Vaidhyanathan, B.; Ganguli, M.; Rao, K. J. *J. Solid State Chem.* **1994**, *113*, 448.

(16) Ramesh, P. D.; Vaidhyanathan, B.; Ganguli, M.; Rao, K. J. *J. Mater. Res.* **1994**, *9*, 3025.

(17) Suib, S. L.; Vileno, E.; Zhang, Q.; Marun, C.; Conde, L. D. *Microwave: Theory and Application in Materials Processing IV*; Clark, D. E., Sutton, W. H., Lewis, D. A., Eds.; *Ceram. Trans.* **1997**, *80*, 331.

(18) Vaidhyanathan, B.; Ganguli, M.; Rao, K. J. *Mater. Res. Bull.* **1995**, *30* (9), 1173.

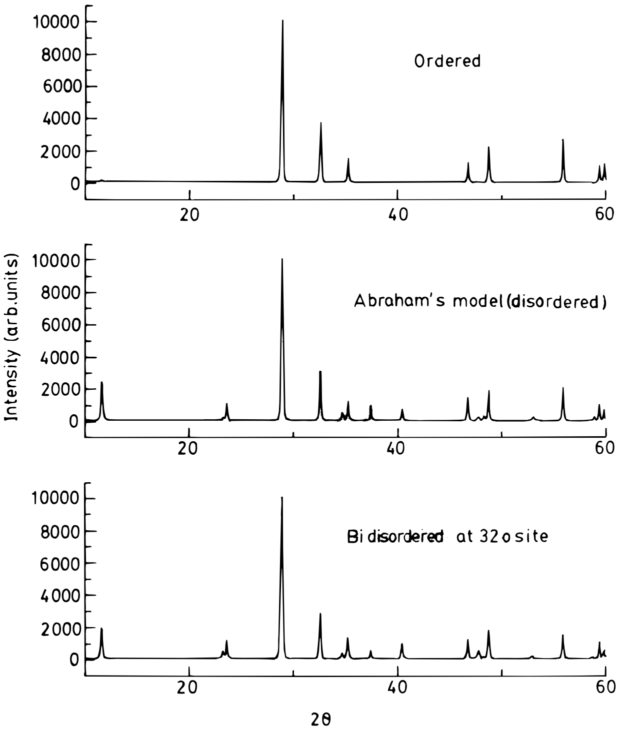

Figure 5. Simulated X-ray diffraction patterns of ordered and disordered Mn substituted bismuth vanadate phases.

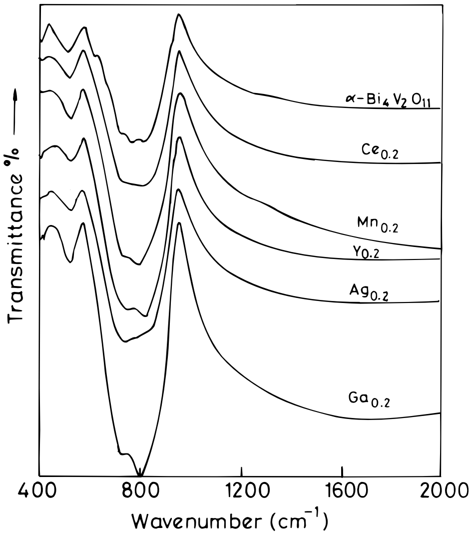

Figure 6. Infrared spectra of microwave-prepared $Bi_4V_{1.8}M_{0.2}O_{11-\delta}$ (M = Ce, Ga, Mn, Ag, and Y) phases. The IR spectrum of the parent bismuth vanadate phase is given for comparison.

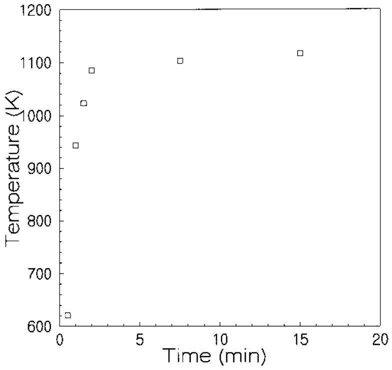

Figure 7. Time−temperature profile for the microwave heating pattern of V_2O_5.

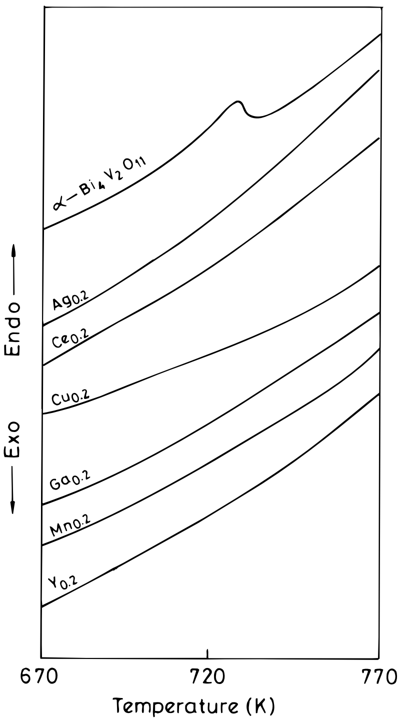

Figure 8. DSC thermograms of the microwave-prepared substituted γ-bismuth vanadate phases (no structural transition is observed, indicating that the materials are already stabilized in the high-temperature phase). The DSC trace of low-temperature α-$Bi_4V_2O_{11}$ phase is also given for comparison.

and pelletized. Pellets were made by applying an uniaxial pressure of 5 tons without using any binder. The pellets were placed in silica crucibles and irradiated with microwaves for about 10−15 min in a domestic microwave oven at a power level of 980 W as described earlier. The pellets turned red-hot within 2−3 min of microwave exposure. By a few trial experiments, it was found that a 15 min exposure was enough to ensure the completion of the reaction. The maximum temperature reached by the reaction mixtures were recorded in some of the preparations. Temperatures were measured by interrupting microwave irradiation and inserting a thermocouple into the charge. Details have been discussed elsewhere.[16] After 15 min of irradiation, the crucible was taken out of the oven and the samples were allowed to cool in air. The products were characterized by X-ray diffraction (XRD) (Philips X-ray diffractometer, model PW 1050/70), differential scanning calorimetry (DSC) (Perkin-Elmer DSC 2), Fourier transform infrared spectroscopy (FTIR) (Bio-Rad FTIR spectrometer), and electron paramagnetic resonance spectroscopy (EPR) (X-band EPR spectrometer; Varian model). Some of the substituted vanadate samples were also prepared by a conventional method (by heating the reactants in an electric furnace to 923 K for 24 h and then at 973 K for 8 h with intermittent grindings) for comparison. The conductivity measurements were carried out on sintered pellets (sintering was carried out in air at 973 K for 4 h). The flat surfaces of these pellets were coated with gold for electrical contacts. A two-probe conductivity cell has been used for impedance measurements. Impedance data on various substituted vanadates in the frequency range 100 Hz−1 MHz were obtained at 573 K employing a HP 4192 A LF−impedance analyzer. The temperature of the cell was controlled to within ±1 K. The DC conductivity values for the stabilized bismuth vanadates were obtained from impedance plots.

III. Results and Discussion

XRD patterns of the microwave-prepared BIMEVOX compounds are presented in Figure 2. The XRD mea-

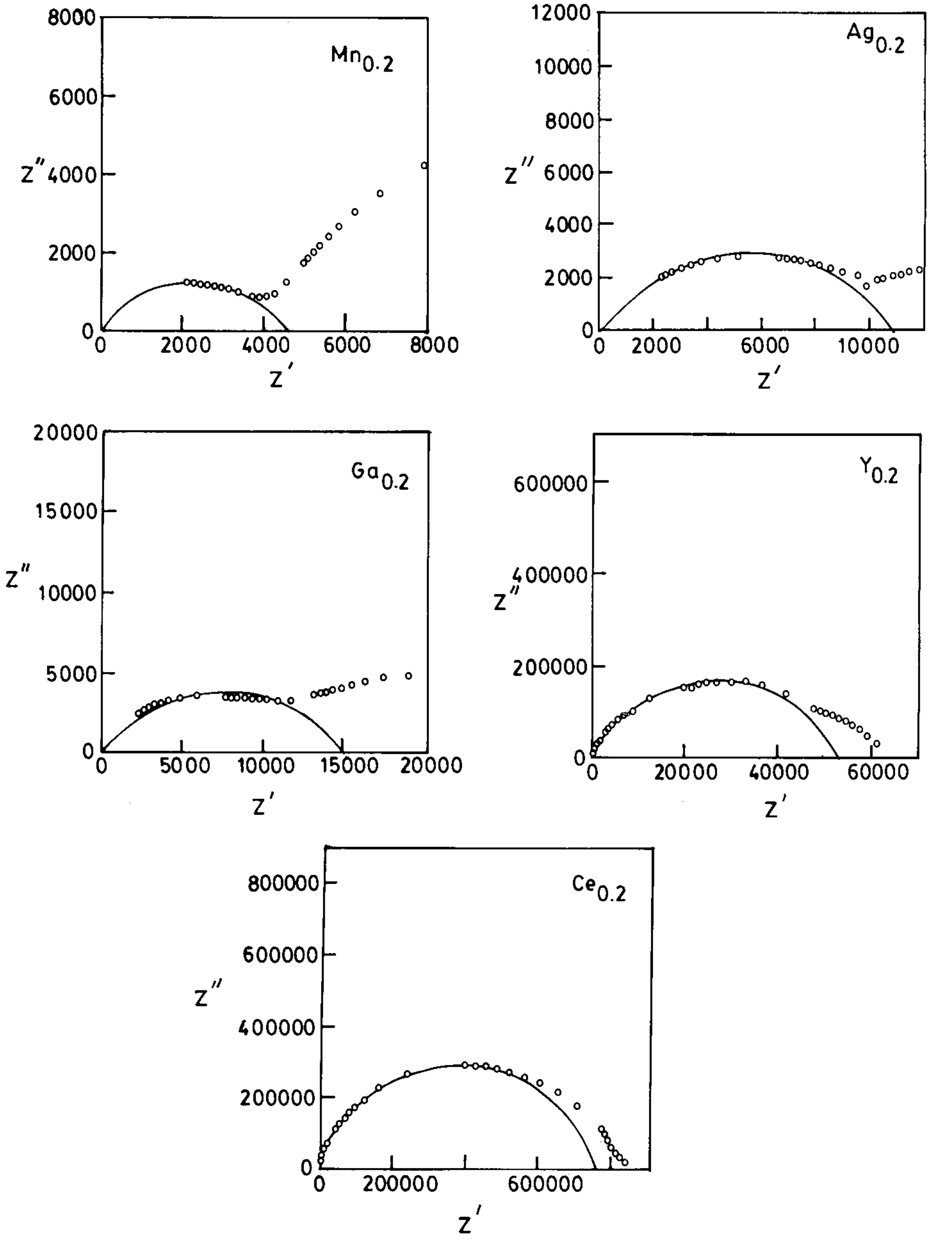

Figure 9. Typical impedance plots for the substituted bismuth vanadates at 573 K.

surements reveal that all the substituted products are stabilized in the high-temperature γ-phase (tetragonal) of bismuth vanadate. The calculated lattice parameters of the stabilized phases match well with the reported values (Table 1).[5,10,19] At the 5% doping level ($Mn_{0.1}$-doped BIMEVOX), the structure of the resulting product is shown in Figure 3, which reveals clearly that the phase is orthorhombic. It was found that the dopant concentration should be 10% or more for the complete stabilization of the structure of the γ-phase (Figure 3). An examination of the XRD patterns of microwave and conventional preparation (Figure 4) reveals excellent comparison in peak positions for the case of Mn^{4+}-doped samples. However, the (006) peak (and a few others) exhibit a significantly higher intensity in microwave-prepared samples than in the conventionally prepared compounds. This is thought to be due to better ordering of both V^{5+} and Mn^{4+} ions in the (006) plane.[20] The better ordering could be a consequence of the lower temperature of the microwave reaction (886 K) compared to the temperature in conventional preparation (temperatures exceeding 923 K).[5] This aspect of influence of the ordering of V^{5+} and Mn^{4+} ions in the (006) plane has been examined by generating powder XRD profiles of the ordered and disordered phases of the 10% Mn-doped BIMEVOX using the *Theo* package of the STOE diffraction system (Figure 5). In the ordered phase, vanadium atom occupies 2b site with site symmetry $4/mmm$,[19] which is the center of inversion in the space group $I4/mmm$, whereas bismuth atom is present at 4e site with a $4mm$ symmetry. The simulated pattern for the ordered phase shows a more intense (006) peak when compared to that of the disordered phase. The simulated pattern for this ordered phase

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(19) Abraham, F.; Debreuille-Gresse, M. F.; Mairesse, G.; Nowogrocki, G. *Solid State Ionics* **1988**, *28–30*, 529.

(20) Sooryanarayana, K.; Guru Row: T. N.; Varma, K. B. R. *Mater. Res. Bull.* **1997**, *32* (12), 1651.

has $I(002) < I(006)$. In the disordered phase both V and Bi are removed from their respective sites to 8h and 16m, 4e, respectively. However, one set of Bi atoms upon disordering retains the 4e positions, thus making $I(002) > I(006)$. Indeed, by moving Bi from 4e to 32o site a significant reduction in $I(002)$ has been observed. Therefore this analysis suggests the requirement of further modifications of the structural model proposed by Abraham et al. Nevertheless, the origin of higher intensities of (006) (and other higher angle) reflections in the XRD of microwave-prepared samples appears to be very much related to the disordering of V^{5+} and Mn^{4+}. The infrared spectra of the microwave-prepared BIMEVOX compounds are given in Figure 6. The IR spectrum of the orthorhombic $Bi_4V_2O_{11}$ (α-phase) exhibits sharp features, all of which compare well with the literature reports.[5,10] Substituted compounds show a broadening of the otherwise sharp features. However, this is consistent with the expected changes in the local structures and environments of the perovskite layers in the tetragonal phase. Electron paramagnetic resonance (EPR) measurements on the substituted bismuth vanadates showed the presence of only a very weak resonance (at very high gains) due to V^{4+}, indicating that there can be only insignificant amount of V^{4+} present in these samples. The fast rates of microwave-induced reactions seem to effectively prevent any reduction of V^{5+} to V^{4+}.

Although V_2O_5 and Bi_2O_3 are the major reactants in the microwave preparation, only V_2O_5 is the dominant microwave susceptor. The time−temperature ($t-T$) profile of the reactions is therefore dominated by the microwave heating of V_2O_5. The $t-T$ plot of pure V_2O_5 is shown in Figure 7 for the purpose of illustration. It was found that the maximum temperatures recorded during the reaction were 823 and 886 K, respectively, during the preparation of pure $Bi_4V_2O_{11}$ and $Mn_{0.2}Bi_4V_{1.8}O_{11}$. Some of these reactions could have reached completion in well under 15 min but we made no efforts to quantify these times for the reaction. The DSC thermograms of the doped samples do not exhibit the endothermic feature (Figure 8) corresponding to the $\alpha \rightarrow \beta$ transformation of the parent $Bi_4V_2O_{11}$.[4] This clearly establishes the stabilization of the tetragonal phase. In conventional methods of preparation a β-phase (which is also tetragonal) stabilization is often noted[5,6] and a high-temperature thermal transition from β to γ (at 723 K) has been reported. However, in the present microwave procedure, we have achieved a single-step stabilization of the γ-phase (we do not observe any thermal events up to 850 K even in DTA measurements). This was possible due to the rapid reaction rates involved in the present procedure. Stabilized bismuth vanadates (γ-phases) are expected to show high oxide ion conductivity and indeed in our preliminary electrical measurements it was found that the substituted compounds exhibit much higher ionic conductivity than the parent α-$Bi_4V_2O_{11}$. Typical impedance plots obtained at 573 K are shown in Figure 9 for all the compounds synthesized in this work. Conductivities were calculated from the Z' versus Z'' plots after semicircular curve-fitting.[21] It is interesting to note that two of the BIMEVOX compounds prepared in the present work, namely, $Bi_4V_{1.8}Mn_{0.2}O_{10.9}$ and $Bi_4V_{1.8}Ag_{0.2}O_{10.6}$, exhibit much higher oxide ion conductivity at 573 K compared to the Cu- and Zn-substituted analogues[3,5,10] (see Table 1). The conductivities of these materials are found to be even higher than those of the Ti-substitued compound, hitherto reported to have the highest oxide ion conductivity at 573K.[5,10] Y^{3+}- and Ce^{4+}-substituted BIMEVOX compounds exhibit lower conductivities. Indeed it is very interestingly the lowest for the Ce^{4+}-substituted compound. Further detailed measurements on the transport behavior of these materials are in progress.

IV. Conclusions

Thus, a simple, fast, single-step method is made possible for the preparation of BIMEVOX-type compounds by the use of microwaves. The method is quite general and it yields products of good crystallinity and phase purity. Also the microwave-prepared Mn^{4+}- and Ag^{+}-substituted BIMEVOX compounds are found to exhibit very high oxide ion conductivity as compared to the other reported compounds of this family.

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[21] Boukamp, B. A. *Equivalent Circuit Users' Manual*, University of Twente, 1989.