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Non-random distribution of cations in $Sn_{1-x}Ti_xO_2$ $(0.0 \leqslant x \leqslant 1.0)$: a ^{119}Sn MAS NMR study

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Mixed oxide samples of $Sn_{1-x}Ti_xO_2$ $(0.0 \leqslant x \leqslant 1.0)$, prepared by the co-precipitation method followed by heating at variable temperatures, have been investigated by powder X-ray diffraction and ^{119}Sn MAS NMR spectroscopy. Based on powder X-ray diffraction studies, the formation of solid solutions has been observed for samples annealed up to ≈800 °C. Annealing of the samples with $0.2 \leqslant x \leqslant 0.8$ at higher temperatures led to their decomposition into two phases with a rutile structure, one being rich in Sn^{4+} and the other in Ti^{4+}. Based on the comparison of the ^{119}Sn MAS NMR spectra of the single phase and phase separated compositions, it is inferred that the cation distribution is non-random even for the samples which exhibited single phase formation.

Introduction

Both SnO_2 and TiO_2 are technologically very important[1–3] because of their wide applications as catalyst support and adsorption materials. SnO_2 exists in cassiterite form which has a tetragonal structure with $a = 0.4738$ and $c = 0.3188$ nm. TiO_2 exists in two forms, namely, the lower temperature anatase form with $a = 0.3785$ and $c = 0.9514$ nm, which on heating transforms to the tetragonal rutile form with $a = 0.4593$ and $c = 0.2959$ nm. The exact temperature of this phase transformation is significantly affected by the preparation conditions, extent of impurities present in the system and the type of substitution made in place of Ti^{4+} cations. The temperature region over which this phase transition occurs is in the range of 600 to 925 °C.[4,5] Addition of SnO_2 to TiO_2 is known to facilitate the rutile phase formation even at room temperatures during the co-precipitation process.[6] Although a number of studies dealing with the phase equilibria between SnO_2 and TiO_2 system with a rutile phase have been reported, some discrepancies still exist regarding the solid solution formation at lower temperatures, particularly for the samples prepared by co-precipitation or sol–gel techniques. In a number of studies[7–9] it has been reported that there exists a miscibility gap for these two oxides with a critical temperature above which the system exists as a solid solution. In an earlier phase equilibrium study, Yuan and Virkar[10] have shown that the solid solutions, when annealed below this critical temperature, decompose spinodally into tin and titanium rich oxide phases. These authors also investigated samples prepared by the co-precipitation method and suggested that the co-precipitated samples, when annealed up to 800 °C, showed the formation of a single phase with a rutile structure, and annealing at 900 °C and above for different time duration led to phase separation. Based on X-ray diffraction studies of $Sn_{1-x}Ti_xO_2$ samples, which had been annealed at different temperatures, these authors also demonstrated the existence of compositionally modulated structures during the phase separation process, as revealed by the appearance of satellite diffraction peaks along with the main peaks corresponding to (110) and (101) Bragg reflections. In a recent study, Naidu and Virkar[11] have demonstrated the existence of spinodal decomposition for this system down to 400 °C by using LiCl–KCl eutectic as the molten salt bath which facilitated the diffusion of Sn^{4+} and Ti^{4+} cations. Bastow *et al.*,[12] based on ^{119}Sn MAS NMR study of $Sn_{1-x}Ti_xO_2$ samples (with $x = 0.75$, 0.80 and 0.85), prepared by the sol–gel technique and annealed at different temperatures $(200 \leqslant T \leqslant 800\ °C)$, have reported a random distribution of cations for these samples as they observed a number of peaks in the ^{119}Sn MAS NMR patterns, which they interpreted in terms of varying next nearest neighbour configurations around ^{119}Sn nuclei. However, the relative intensity of different NMR signals could not be accounted for in terms of the calculated probability of the formation of different configurations. Thus, with a view to determining the microscopic nature of cation distribution in these mixed oxides, the environment of the Sn^{4+} nuclei has been monitored using ^{119}Sn MAS NMR techniques for a large number of $Sn_{1-x}Ti_xO_2$ samples $(0.0 \leqslant x \leqslant 1.0)$, prepared by the co-precipitation technique and annealed at different temperatures.

In the present work the results of powder X-ray diffraction and ^{119}Sn MAS NMR investigations for $Sn_{1-x}Ti_xO_2$ $(0.0 \leqslant x \leqslant 1.0)$ samples, prepared by the co-precipitation method and annealed at different temperatures, are reported to show a non-random distribution of Sn^{4+} and Ti^{4+} ions, even for the samples which exhibited X-ray diffraction patterns characteristic of a single phase rutile structure. A comparison of the ^{119}Sn MAS NMR spectra of the single and biphasic mixed oxide samples, prepared by heating the same samples at higher temperatures, $1050 \leqslant T \leqslant 1200\ °C$, has provided additional support to our inferences regarding the non-random distribution of cations in these samples.

Experimental

Mixed oxides of Sn and Ti having the general formula $Sn_{1-x}Ti_xO_2$ $(0.0 \leqslant x \leqslant 1.0)$ were prepared by the co-precipitation technique from metal chloride solutions containing Sn^{4+} and Ti^{4+} in the required molar ratio. NH_4OH was used as the precipitating agent. The precipitates were repeatedly washed with water and dried in an oven at 150 °C. These dried samples were calcined at different temperatures from 200 to 1200 °C in air for 16 h duration. X-Ray diffraction patterns were recorded by using monochromatic Cu-Kα radiation to identify the phases present in these samples and unit cell parameters have been derived by least-square fitting the observed *d* values. ^{119}Sn

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MAS NMR experiments were carried out using a Bruker Avance DPX 300 machine having a standard bore (SB) MAS accessory with a basic frequency of 111.92 MHz. The samples were packed in 7 mm diameter zirconia rotors and subjected to a spinning speed of 5 kHz. Typical 90° pulse duration for MAS experiments without side band suppression was 5 µs with a relaxation delay of 4 s. A modified version of the TOSS pulse sequence with five 180° pulses applied at different delay times, related to the 180° pulse duration and spinning speed, were employed for the side band suppression experiments.[13] The pulse widths of the 90 and 180° pulses were accurately calculated for each sample before performing the side band suppression experiments. The relaxation delay employed in the side band suppression experiments was 6 s. Around 500 to 800 scans were sufficient for samples having more than 50 mol percent of SnO_2 and for lower SnO_2 contents, around 1500–2000 scans were recorded to obtain the spectra with a reasonable signal-to-noise ratio. TOSS pulse sequences assume that the chemical shift anisotropies for tin nuclei with different structural configurations are comparable. This assumption is reasonable as the ionic radii of Sn^{4+} and Ti^{4+} are 0.071 nm and 0.068 nm, respectively, and hence the values of cationic field strength (*Z*/*r*) are comparable, thereby leading to comparable values of chemical shift anisotropy. Chemical shift values are reported with respect to tetramethyl tin (TMT) as the standard. The chemical composition of the mixed oxide samples was ascertained by X-ray fluorescence measurements and was found to be quite similar to the starting compositions suggesting the complete precipitation of both Sn^{4+} and Ti^{4+} ions.

Results and discussion

Fig. 1 shows the powder X-ray diffraction patterns for a few representative samples of $Sn_{1-x}Ti_xO_2$ heated at 800 °C for 16 h and slowly cooled to room temperature. These patterns suggest the formation of a single phase with the rutile structure over the entire composition range. The estimated values of unit cell parameters *a* and *c* are plotted in Fig. 2, along with the results reported by Yuan and Virkar[10] for the samples which exhibited a single phase. The agreement between these results is very good. The variation of both *a* and *c* parameters is quite monotonic and shows good linear dependence on the composition of the samples. The unit cell volume decreases systematically with increase in Ti^{4+} content (Fig. 2). Based on these observations, the formation of a single phase solid solution with a rutile structure is well established for these samples over the entire composition range. The width of diffraction peaks is found to be slightly more for Sn^{4+} rich samples because of their poor crystallinity. Some of the diffraction peaks for the samples with comparable concentrations of Ti^{4+} and Sn^{4+} exhibited a slight asymmetry in their peak profile, possibly because of the onset of phase separation. Fig. 3 shows the powder X-ray diffraction patterns of the samples prepared by heating different portions of a representative composition $Sn_{0.6}Ti_{0.4}O_2$ sample at variable temperatures for a fixed duration of 16 h. Heated up to 950 °C, the samples showed the existence of a single phase with $a = 0.4686$,

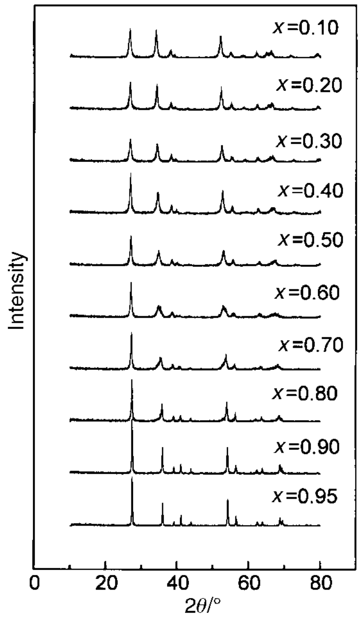

Fig. 1 Powder X-ray diffraction patterns for $Sn_{1-x}T_xO_2$ samples heated at 800 °C for 16 h.

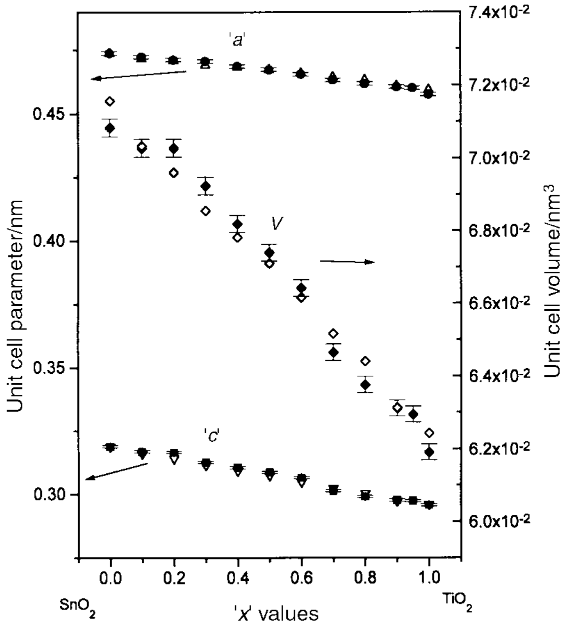

Fig. 2 Variation of lattice parameters *a* and *c* and unit cell volume *v* for $Sn_{1-x}Ti_xO_2$ samples heated at 800 °C for 16 h. Solid symbols correspond to our results and open symbols represent the data reported by Yuan and Virkar.[10]

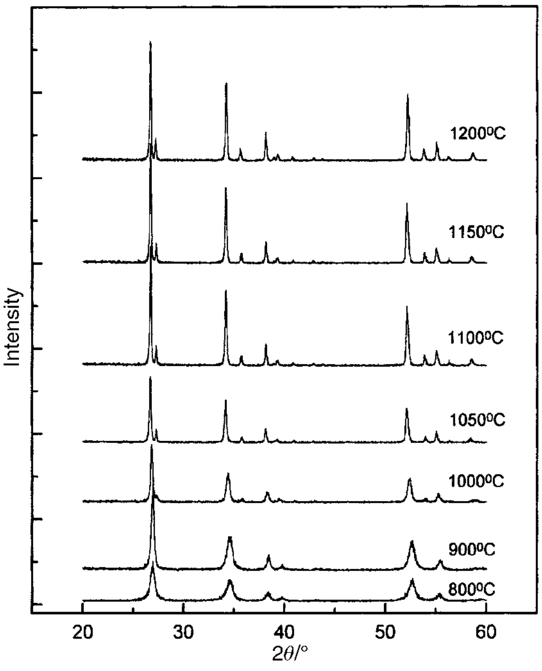

Fig. 3 Powder X-ray diffraction patterns of $Sn_{0.6}Ti_{0.4}O_2$ samples annealed at different temperatures for a fixed duration of 16 h.

$c = 0.3105$ nm and $c/a = 0.663$. Heated at ≈1000 °C and above, the samples clearly exhibited phase separation and the indexing of this diffraction pattern suggested the formation of two phases having the rutile structure with unequal intensity. These two phases can be characterized with $a = 0.4713$ and $c = 0.3150$ nm for the more abundant phase and $a = 0.4627$ and $c = 0.30015$ nm for the less abundant phase. From comparison of these values with the unit cell parameters obtained for individual SnO_2 and TiO_2 samples and their single phase solid solutions, it is clear that the more abundant phase is richer in Sn^{4+} and the less abundant phase is richer in Ti^{4+}. The values of unit cell parameters for these two phases and their relative intensity ratio did not show appreciable change for annealing temperatures above 1100 °C and attained a saturation value as can be seen from Fig. 3. Furthermore, on heating the width of the diffraction peaks was found to decrease slightly due to improved crystallinity. Similar phase separation has been observed for all $Sn_{1-x}Ti_xO_2$ samples with $0.2 \leqslant x \leqslant 0.8$, when heated at *ca.* 1000 °C and above. The actual temperature of such a phase separation was found to vary slightly with the composition of the sample. Based on the comparison of unit cell parameters and the relative intensity of these two phases, it is inferred that the solubility of Ti^{4+} ions in SnO_2 is better than that of Sn^{4+} ions in TiO_2, which is consistent with the slightly smaller ionic radius of Ti^{4+} as compared to that of Sn^{4+}. These observations are in conformity with the results reported by Yuan and Virkar.[10] However, no such phase separation was observed for $Sn_{1-x}Ti_xO_2$ samples with $0.9 \leqslant x \leqslant 0.1$, when heated at different temperatures.

The ^{119}Sn MAS NMR spectra of pure SnO_2 and $Sn_{0.5}Ti_{0.5}O_2$ samples heated at 800 °C with and without side band suppression, are shown in Fig. 4 (b and d) and (a and c), respectively. For SnO_2, the isotropic peak is characterized by a chemical shift of $\delta = -604$ with respect to TMT and a line width of approximately 330 Hz. This value of δ is in good agreement with the results reported earlier by Cossement *et al.*[14] A very weak signal, present at $\delta \approx -609$, is attributed to the presence of a hydroxy tin oxide species on the surface as the intensity of this peak decreased significantly when the NMR spectrum was recorded immediately after heating the sample at about 300 °C for about one hour.[15] From the intensity analysis of the side bands the principal components of the chemical shift anisotropy tensor were calculated as $\sigma_{11} = -557$, $\sigma_{22} = -575$ and $\sigma_{33} = -678$ ppm (with an error of ±4 ppm). The large chemical shift anisotropy for SnO_2 arises from the distortion of O^{2-}–Sn^{4+}–O^{2-} bond angles present in the cassiterite structure, wherein the Sn^{4+} ions are placed at crystallographically equivalent sites. Each Sn^{4+} is surrounded by six nearest neighbour oxygen anions, forming a slightly distorted octahedron with axial and equatorial Sn^{4+}–O^{2-} distances being almost equal at 0.2057 and 0.2052 nm, respectively. The next nearest neighbours are eight Sn^{4+} ions, placed at a distance of 0.2855 nm, forming a cube and another two tin ions are placed along the *c*-axis at a distance of 0.3188 nm. This leads to the distortion of cubic symmetry around Sn^{4+} cations and results in an asymmetric chemical shift anisotropy tensor. The ^{119}Sn MAS NMR spectra of $Sn_{0.5}Ti_{0.5}O_2$ annealed at 800 °C for 16 h, recorded with and without side band suppression are shown in Fig. 4 (c and d) which clearly establishes the effectiveness of these side band suppression experiments. From the spectrum shown in Fig. 4(d), the existence of varying next nearest neighbour configurations of ^{119}Sn nuclei, characterised by different chemical shift values, is well established.

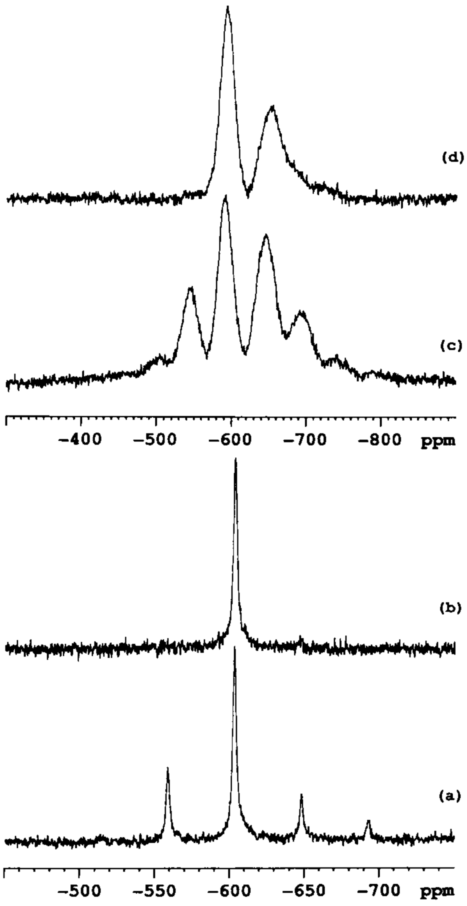

Fig. 4 ^{119}Sn MAS NMR spectra of SnO_2 samples heated at 800 °C for 16 h (a) without and (b) with side band suppression. The corresponding patterns for $Sn_{0.5}Ti_{0.5}O_2$ are shown as (c) and (d).

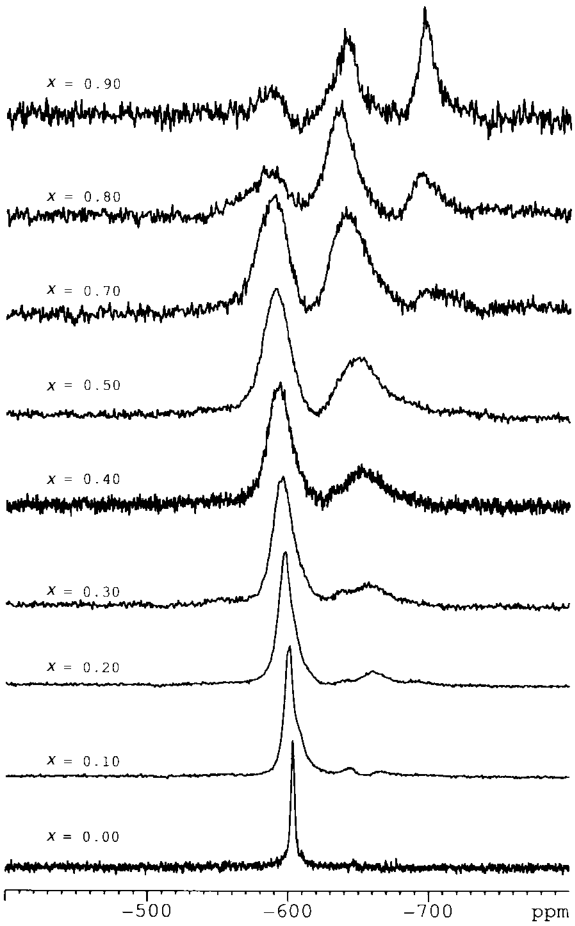

Fig. 5 Side band suppressed ^{119}Sn MAS NMR spectra of $Sn_{1-x}Ti_xO_2$ samples heated at 800 °C for 16 h.

The side band suppressed ^{119}Sn MAS NMR spectra of some representative samples of $Sn_{1-x}Ti_xO_2$ ($0.0 \leqslant x \leqslant 0.8$) which were annealed at 800 °C for a fixed duration of 16 h and exhibited the formation of a single phase (Fig. 1), are shown in Fig. 5. With increase in Ti^{4+} concentration, the observed spectra become complex and in general the line width was found to increase. The important observations, which are apparent from this figure, are the appearance of additional peaks in the region of $\delta = -630$ to -690 whose number and relative intensity increased with increasing Ti^{4+} concentration. The peak observed at $\delta = -604$ for pure SnO_2 becomes asymmetric and continuously shifts towards more positive values (less shielded) with the addition of Ti^{4+}. Both these features can be clearly seen even for 10 mol% substitution of Sn^{4+} by Ti^{4+} in SnO_2. The appearance of a number of additional peaks with varying intensities is attributed to the varying number of Ti^{4+} as the next nearest neighbours of Sn^{4+} in these mixed oxides. The shift in the peak positions can be understood in terms of the overall compression of the unit cell volume brought about by Ti^{4+} substitution and the smaller value of the electronegativity of Ti^{4+} in comparison to Sn^{4+}. Due to the partial substitution of Ti^{4+}, the Sn^{4+}–O^{2-}–Ti^{4+} bonds become compressed resulting in reduced electron density around Sn^{4+}, leading to the downfield shift of the corresponding NMR peaks. The additional peaks exhibiting more negative chemical shifts are attributed to the structural units of Sn^{4+} having varying numbers of Ti^{4+} as its next nearest neighbours. Due to the lower electronegativity of Ti^{4+} compared to Sn^{4+}, there is better shielding of Sn^{4+} nuclei for the Sn^{4+}–O^{2-}–Ti^{4+} configuration as compared to that of Sn^{4+}–O^{2-}–Sn^{4+}. Thus the NMR patterns of Ti^{4+} substituted samples clearly reveal the existence of varying types of next nearest neighbour configurations around Sn^{4+}. However, the relative intensity of different peaks does not suggest a random distribution of Sn^{4+} and Ti^{4+} in the mixed oxide lattice, as is apparent from the discussion given later.

Fig. 6 shows the powder X-ray diffraction patterns for two representative samples of $Sn_{0.9}Ti_{0.1}O_2$ and $Sn_{0.1}Ti_{0.9}O_2$ heated to 800 and 1180 °C for 16 h. These patterns clearly show the existence of a single phase with a rutile structure, which is in keeping with the reported phase diagram of the $Sn_{1-x}Ti_xO_2$ system.[11] Fig. 7 shows the side band suppressed ^{119}Sn MAS NMR spectra of these four samples. The observed peak profile for the $Sn_{0.1}Ti_{0.9}O_2$ composition is significantly affected by heating at 800 or 1180 °C. The NMR pattern of a $Sn_{0.1}Ti_{0.9}O_2$ sample, heated at 800 °C, was least-square fitted into three Gaussian curves. The fitted peak positions are at $\delta = -588$, -642 and -699 with relative intensities 0.13 : 0.44 : 0.43. The NMR spectrum of the same composition sample heated at 1180 °C showed mainly two peaks placed at $\delta = -646$ and -701 with relative intensities 0.63 : 0.37. Thus, the relative intensities of different peaks are appreciably affected by changing the annealing temperature, indicating that the Ti^{4+} ions present around different Sn^{4+} structural units are redistributed depending on the thermal treatment of the sample. For the $Sn_{0.9}Ti_{0.1}O_2$ composition, the NMR patterns of the two samples, annealed at 800 and 1180 °C, did not reveal such pronounced effects because of the relatively smaller concentration of Ti^{4+}. This pattern is characterised by an intense peak at $\delta \approx -601$ followed by two very low intensity peaks placed at $\delta \approx -642$ and -666 whose intensity distribution changed appreciably on annealing at 1180 °C. This is in accordance with the results expected for this composition, where the major constituent is tin, the number of Sn^{4+} structural units having varying numbers of Ti^{4+} as their next nearest neighbours will be fewer and hence their effect on the overall ^{119}Sn MAS NMR pattern will be of lesser significance. Further, from the comparison of the observed spectra of $Sn_{0.9}Ti_{0.1}O_2$ and SnO_2 samples heated at 800 °C, it is clear that as a result of even 10 mol% of Ti^{4+} substitution, the main peak is shifted from $\delta = -604$ to -601 and additional low intensity peaks, placed at $\delta \approx -642$ and -666, are clearly visible. For both spectra of $Sn_{0.9}Ti_{0.1}O_2$, the shoulder peak appearing in the region of $\delta = -610$ along with the intense peak, is attributed to the presence of hydroxy tin oxide species present on the surface as

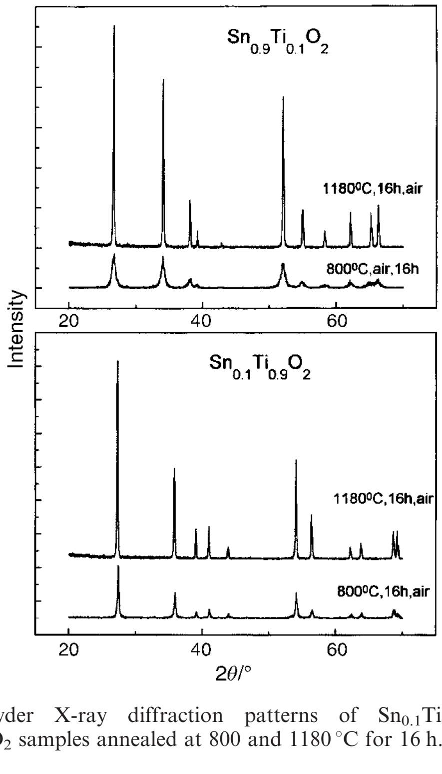

Fig. 6 Powder X-ray diffraction patterns of $Sn_{0.1}Ti_{0.9}O_2$ and $Sn_{0.9}Ti_{0.1}O_2$ samples annealed at 800 and 1180 °C for 16 h.

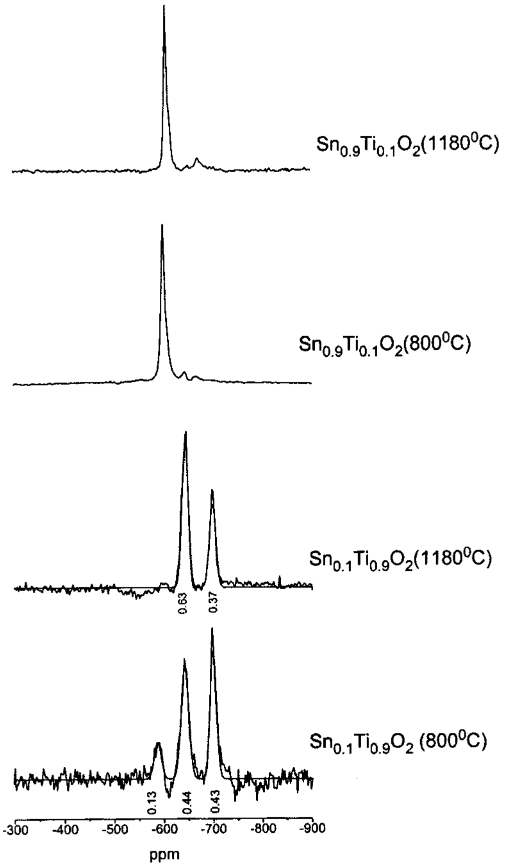

Fig. 7 Side band suppressed ^{119}Sn MAS NMR spectra of representative samples of $Sn_{0.1}Ti_{0.9}O_2$ and $Sn_{0.9}Ti_{0.1}O_2$ annealed at 800 and 1180 °C for 16 h. The numbers, mentioned below certain peaks, represent their relative intensity.

has been observed for pure SnO_2. The most intense peak arises due to those Sn^{4+} nuclei which are surrounded by ten Sn^{4+} cations as their next nearest neighbours and the low intensity peaks are arising due to those Sn^{4+} nuclei which have varying number of Ti^{4+} as their next nearest neighbours. For $Sn_{0.9}Ti_{0.1}O_2$, the slight increase in the value of chemical shift for the main peak, as compared to SnO_2, arises due to the reduction of the unit cell volume.

Assuming a binomial distribution of Ti^{4+} and Sn^{4+} for this mixed oxide system, it is possible to calculate the relative probability of different Sn^{4+} configurations with varying number of Ti^{4+} ions as its next nearest neighbours, with the assumption that all ten next nearest neighbours can be treated as identical irrespective of the slight difference in their interatomic separations. For $Sn_{0.9}Ti_{0.1}O_2$, the relative probabilities (${}^{i}P_{10}$) for the formation of the Sn^{4+} configuration, with i the number of Ti^{4+} and $(10-i)$ the number of Sn^{4+} ions as next nearest neighbours, have been calculated and the prominent values are ${}^{0}P_{10}=0.349$, ${}^{1}P_{10}=0.387$, ${}^{2}P_{10}=0.194$, ${}^{3}P_{10}=0.057$ and ${}^{4}P_{10}=0.011$. However the observed intensity ratio for the different NMR peaks does not follow such a distribution for either of the samples of $Sn_{0.9}Ti_{0.1}O_2$ which have been heated at 800 and 1180 °C, respectively and exhibit a single phase rutile structure. In contrast, for the Ti^{4+} rich composition, $Sn_{0.1}Ti_{0.9}O_2$, the most intense peak is placed at $\delta \approx -699$ which is due to those Sn^{4+} nuclei which are surrounded by ten Ti^{4+} ions. The other low intensity peaks, exhibiting a more positive chemical shift, are due to those probe Sn^{4+} nuclei which are surrounded by varying numbers of Sn^{4+} and Ti^{4+} cations as next nearest neighbours. The relative probability of the formation of prominent configurations has been calculated as ${}^{10}P_{10}=0.349$, ${}^{9}P_{10}=0.387$, ${}^{8}P_{10}=0.194$, ${}^{7}P_{10}=0.057$ and ${}^{6}P_{10}=0.011$. These values are not consistent with the relative intensity of different NMR peaks observed for both the samples of $Sn_{0.9}Ti_{0.1}O_2$ that had been heated at 800 and 1180 °C, respectively, and exhibit single phase formation. Both these observations suggest that the distribution of Ti^{4+} and Sn^{4+} in these samples is non-random in nature although they exhibit the formation of a solid solution with a rutile structure. Similarly, the probability of the formation of different Sn^{4+} configurations with varying numbers of Ti^{4+} and Sn^{4+} as its next nearest neighbours, have been calculated for other compositions of $Sn_{1-x}Ti_xO_2$ and these values have been qualitatively compared with the NMR results reported in Fig. 5. The comparison between the calculated probabilities and experimental observations is not at all satisfactory.

Fig. 8 shows the powder X-ray diffraction patterns for the two samples of $Sn_{0.7}Ti_{0.3}O_2$ and of $Sn_{0.3}Ti_{0.7}O_2$ each, prepared by heating at 800 and 1200 °C for 16 h. For both these compositions, the X-ray diffraction pattern is characteristic of a single phase formation for the samples heated at 800 °C and phase separation, with unequal intensity ratio, is clearly seen for the samples heated at 1200 °C. Based on the values of the unit cell parameters, it is observed that one of these two phases is richer in Sn^{4+} and the other in Ti^{4+}. The side band suppressed ^{119}Sn MAS NMR spectra of these samples are shown in Fig. 9. For the single phase $Sn_{0.3}Ti_{0.7}O_2$ sample, prepared by heating at 800 °C, the NMR pattern consists of three predominant peaks placed at $\delta \approx -590$, -642 and -704. Unlike this, the NMR spectrum of the same sample after heating at 1200 °C for 16 h consists of three predominant signals placed at $\delta \approx -606$, -646 and -704. In addition to this shift in the peak positions, the relative intensity of different peaks is also found to be altered by heat treatment as the resultant spectrum arises due to the superposition of a number of spectra originating from different Sn^{4+} configurations whose relative intensity is altered due to phase separation. The NMR spectrum of the single phase $Sn_{0.7}Ti_{0.3}O_2$ sample is found to consist of one predominant peak placed at $\delta \approx -596$ along with a broad peak centered around -659 having a shoulder around -640. On heating this sample at 1200 °C, the prominent peak shifted to $\delta = -607$ along with the appearance of a less intense broad peak around -671, having two shoulders around -653 and -701. Thus for both these compositions the NMR patterns show significant change on

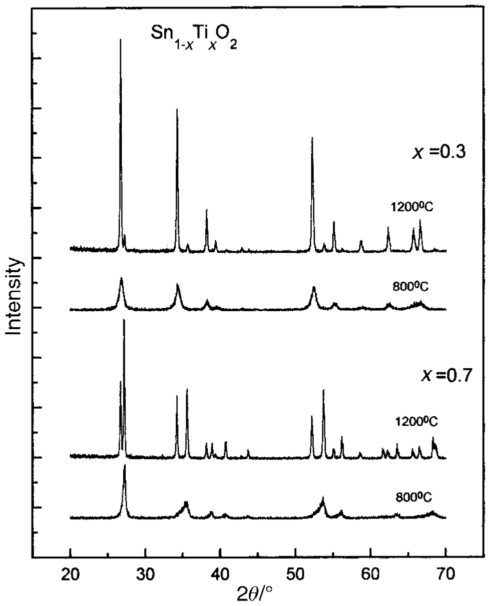

Fig. 8 Powder X-ray diffraction patterns for the representative samples of $Sn_{0.7}Ti_{0.3}O_2$ and $Sn_{0.3}Ti_{0.7}O_2$ annealed at 800 and 1200 °C for 16 h.

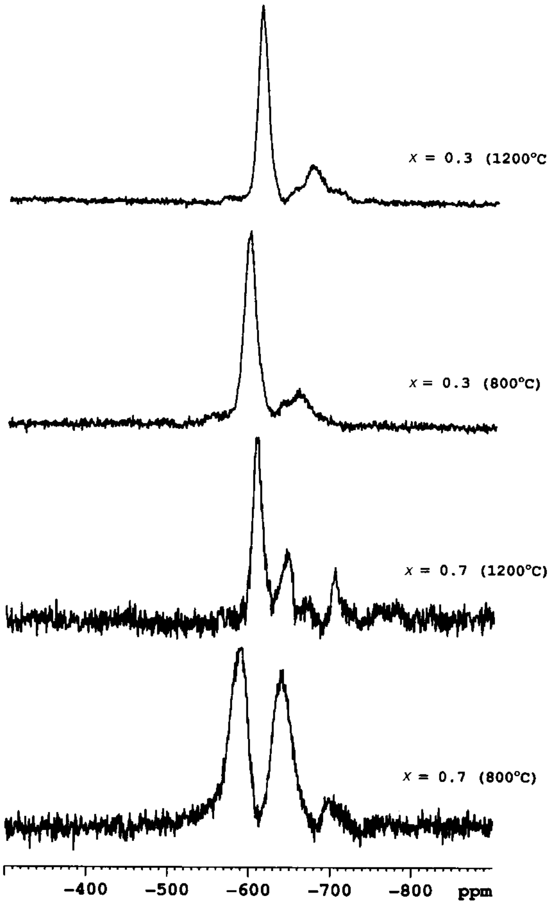

Fig. 9 Side band suppressed ^{119}Sn MAS NMR spectra for the representative samples of $Sn_{0.7}Ti_{0.3}O_2$ and $Sn_{0.3}Ti_{0.7}O_2$ annealed at 800 and 1200 °C for 16 h.

annealing the samples at higher temperature indicating significant change in cation distribution due to phase separation. These NMR observations are qualitatively similar to those of $Sn_{0.1}Ti_{0.9}O_2$ and $Sn_{0.9}Ti_{0.1}O_2$ samples, wherein no phase separation was observed, suggesting that the cation distribution in these samples is affected by annealing the samples at different temperatures, irrespective of the fact that the sample exists as a single phase solid solution or as a mixture of two phases with a rutile structure. For the phase separated samples, as the exact distribution of Sn^{4+} in the two phases is not known, it is difficult to comment about the relative intensity contributions of different Sn^{4+} configurations present in these two phases. It may specifically be mentioned that for both these compositions the observed NMR spectra of the samples annealed at 800 °C, where the existence of a single phase has been observed by X-ray diffraction studies, can not be simulated in terms of the binomial distribution of Sn^{4+} and Ti^{4+} cations. This once again suggests that the distribution of both Sn^{4+} and Ti^{4+} is non-random in nature even for the samples exhibiting single phase formation.

Based on the results presented above, it is inferred that for a number of $Sn_{1-x}Ti_xO_2$ compositions that exhibit a single phase solid solution, as revealed by powder X-ray diffraction studies, the ^{119}Sn MAS NMR spectra did not suggest the existence of a completely random distribution of cations. These results are understandable as in the NMR experiments, monitoring is at the atomic level and the effect of different types of structural configurations present around the probe nucleus is reflected in the values of hyperfine interaction parameters. For the rutile structure, the first nearest neighbours around the ^{119}Sn, probe nucleus, are six oxygen anions and the next nearest neighbours are ten Sn^{4+} or Ti^{4+} cations whose relative number will depend on the composition of the mixed oxide sample and the nature of the cation distribution. In contrast, to observe a well defined X-ray diffraction pattern, the long range periodicity of the crystal structure is required. The fact that the relative intensity of the NMR signals for different structural configurations of Sn^{4+} is not in the ratio expected for a completely random distribution of cations and is also affected by heat treatment even for $Sn_{0.1}Ti_{0.9}O_2$ and $Sn_{0.9}Ti_{0.1}O_2$ samples which are exhibiting single phase formation, it is inferred that for these mixed oxides the cation distribution is non-random in nature. This is further substantiated from the ^{119}Sn NMR study of the samples exhibiting the formation of a two-phase mixture with rutile structures. From these observations it is inferred that the two types of cations are exhibiting some kind of clustering behaviour during the formation of these mixed oxides by the co-precipitation method.

In conclusion, we would like to mention that in the present work we have reported the details of powder X-ray diffraction and ^{119}Sn MAS NMR studies for the mixed oxide system $Sn_{1-x}Ti_xO_2$. Based on the ^{119}Sn MAS NMR study of single phase $Sn_{1-x}Ti_xO_2$ compositions, it is seen that the distribution of Sn^{4+} and Ti^{4+} cations is not completely random as revealed from the relative intensity of different configuration of Sn^{4+} present in this mixed oxide system. The ^{119}Sn MAS NMR results obtained for phase separated samples of $Sn_{1-x}Ti_xO_2$ also support these inferences.

References

1 S. Matsuda and A. Kato, *Appl. Catal.*, 1983, **8**, 149.
2 M. M. Gadgil, R. Sasikala and S. K. Kulshreshtha, *J. Mol. Catal*, 1994, **87**, 297.
3 K. N. P. Kumar, K. Keizer, A. J. Burggraff, T. Okubo, S. Morooka and H. Nagamoto, *Nature (London)*, 1992, **358**, 48.
4 H. Izutsu, P. K. Nair and F. Mizukami, *J. Mater. Chem.*, 1997, **7**, 855.
5 K. N. P. Kumar, K. Keizer and A. J. Burggraff, *J. Mater. Chem.*, 1993, **3**, 1741.
6 K. N. P. Kumar, K. Keizer, A. J. Burggraff, T. Okubo and H. Nagamoto, *J. Mater. Chem.*, 1993, **3**, 923.
7 M. Park, T. E. Mitchell and A. H. Heuer, *J. Am. Ceram. Soc.*, 1975, **58**, 43.
8 S. Nambu and M. Oiji, *J. Am. Ceram. Soc.*, 1991, **74**, 1910.
9 J. Jakahazhi, M. Kuwayama, R. Kamiya, M. Takatste, T. Oota and I. Ymai, *J. Mater. Sci.*, 1988, **23**, 337.
10 T. C. Yuan and A. V. Virkar, *J. Am. Ceram. Soc.*, 1988, **71**, 12.
11 H. P. Naidu and A. V. Virkar, *J. Am. Ceram. Soc.*, 1998, **81**, 2176.
12 T. J. Bastow, L. Murgaski, M. E. Smith and H. J. Whitfield, *Mater. Lett.*, 1995, **23**, 117.
13 W. T. Dixon, J. Schaefer, M. D. Sefcik, E. O. Stejskal and R. A. McKay, *J. Magn. Reson.*, 1982, **49**, 341.
14 C. Cossement, J. Darville, J. M. Gilles, J. B. Nagy, C. Fernandez and J. P. Amoureux, *Magn. Reson. Chem.*, 1992, **30**, 263.
15 S. K. Kulshreshtha, R. Sasikala and V. Sudarsan, to be published.