Non-random cation distribution in hexagonal $Al_{0.5}Ga_{0.5}PO_4$

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ABSTRACT

Based on powder X-ray diffraction and [31]P Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) investigations of mixed phosphate $Al_{0.5}Ga_{0.5}PO_4$, prepared by co-precipitation method followed by annealing at 900 °C for 24 h, it is shown that $Al_{0.5}Ga_{0.5}PO_4$ phase crystallizes in hexagonal form with lattice parameter $a = 0.491(2)$ and $c = 1.106(4)$ nm. This hexagonal phase of $Al_{0.5}Ga_{0.5}PO_4$ is similar to that of pure $GaPO_4$. The ^{31}P MAS NMR spectrum of the mixed phosphate sample consists of five peaks with systematic variation of their chemical shift values and is arising due to existence of P structural units having varying number of the Al^{3+}/Ga^{3+} cations as the next nearest neighbors in the solid solution. Based on the intensity analysis of the component NMR spectra of $Al_{0.5}Ga_{0.5}PO_4$, it is inferred that the distribution of Al^{3+} and Ga^{3+} cations is non-random for the hexagonal $Al_{0.5}Ga_{0.5}PO_4$ sample although XRD patterns showed a well-defined solid solution formation.

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1. Introduction

Both $AlPO_4$ and $GaPO_4$ are the derivatives of the quartz structure and obtained by replacing half of the Si^{4+} by Al^{3+}/Ga^{3+} and the other half by P^{5+} in alternate positions. Both $AlPO_4$ and $GaPO_4$ crystallize in different polymorphs of SiO_2 and exhibit a number of temperature and pressure induced phase transitions. The study of these phosphates, which contain both MO_4 and PO_4 tetrahedra, is of fundamental importance for the understanding of the bonding characteristics in these tetrahedrally coordinated compounds and the occurrence of phase transitions in these compounds, where the four oxygen of PO_4 tetrahedron are connected to the four different metal ions. Besides the properties and structural similarity with quartz, $AlPO_4$–$GaPO_4$ system, is of particular importance as its piezo-electric properties can be tuned by varying the relative concentration of Al^{3+} or Ga^{3+} in the samples. Dynamic disorder existing in such compounds is worth investigating as it decides the piezo-electric properties of the material. Based on the detailed neutron scattering studies it has been inferred that [1] dynamic disorder increases at a faster rate with increase in temperature in quartz as compared to $GaPO_4$. Further in the solid solution formed between $GaPO_4$ and $AlPO_4$, the relative concentration of Al^{3+} and Ga^{3+} has got strong influence on the extent of dynamic disorder [1]. Hence understanding the cation distribution in solid solutions of $Al_{1-x}Ga_xPO_4$

phases is quite significant for predicting the piezo-electric properties of the material.

^{31}P MAS NMR has been very widely used to understand the nature of P structural units and cation distribution present around P in a variety of phosphate based micro-porous and meso-porous materials. For example, the cation distribution around P atoms in solid solutions like $BiM_xMg_{(2-x)}PO_6$ (with $M^{2+} = Zn$ or Cd) was studied by ^{31}P MAS NMR [2] and it was inferred that in case of $BiZn_xMg_{(2-x)}PO_6$, as Zn^{2+} concentration increases at the expense of Mg^{2+}, the cationic environment of P is unaffected. Unlike this in the case of $BiCd_xMg_{2-x}PO_6$ compounds, as Mg^{2+} concentration increase, P structural units having different number of Mg and Cd as near neighbors are formed. These results were further confirmed by X-ray and neutron diffraction techniques.

In the past few years, we have carried out a number of investigations for $AlPO_4$–$GaPO_4$ system using different techniques like, XRD, NMR, neutron diffraction, thermal methods and theoretical calculations to understand the structural features of these compounds [3–9]. ^{31}P MAS NMR studies were carried out to understand the factors responsible for the wide variation in the values of ^{31}P chemical shift and its anisotropy of different phosphorus structural units existing in these compounds [3]. Based on powder X-ray diffraction and ^{31}P NMR investigations of the orthorhombic $Al_{1-x}Ga_xPO_4$ samples ($0.0 \leq x \leq 1.0$), we have established that these mixed phosphates form a solid solution for the entire composition range and the ^{31}P NMR spectrum of the mixed phosphates was found to consist of five components due to the existence of five different types of phosphorous structural configurations, formed by varying number of Al^{3+} and Ga^{3+} as its next nearest neighbors [3]. The intensity analysis of the component spectra suggested a perfectly random distribution of

Al^{3+} and Ga^{3+} cations in these mixed phosphates. Further the values of chemical shift anisotropy parameter ($\Delta\delta$) obtained from ^{31}P MAS NMR spectrum were found to be quite different for the iso-structural $AlPO_4$ and $GaPO_4$ compounds ($\Delta\delta = -36.3$ ppm for $AlPO_4$ and $\Delta\delta = -32.1$ ppm for $GaPO_4$) and the corresponding values of the asymmetry parameter (η) were found to be 0.8 and 0.3, respectively. These results are consistent with the observed ^{31}P NMR line width for these two compounds. Unlike this, in an earlier X-ray diffraction studies of the mixed oxide samples of $Sn_{1-x}Ti_xO_2$ ($0.0 \le x \le 1.0$), prepared by co-precipitation method followed by annealing at variable temperatures, it was reported that the samples annealed up to 800 °C for 16 h exhibited the formation of a solid solution with rutile structure over the entire composition range as revealed by the variation of unit cell parameters and the width of the X-ray diffraction lines [10]. However, the intensity analysis of the ^{119}Sn MAS NMR spectra of these samples suggested that the cation distribution in these mixed oxide samples is non-random [10].

In the present communication, we report the powder X-ray diffraction and ^{31}P MAS NMR investigations of the mixed phosphate sample $Al_{0.5}Ga_{0.5}PO_4$, having hexagonal structure, to establish the formation of a well-defined single phase solid solution with non-random distribution of Al^{3+} and Ga^{3+} cations in the lattice.

2. Experimental

For preparing the individual $GaPO_4$ or $AlPO_4$ samples, around 0.5 g of Ga or Al metal was dissolved in minimum amount of HCl and excess acid was evaporated out. It was then mixed with 45 ml of ethylene glycol and heated to 100 °C. To this solution stoichiometric amount of $NH_4H_2PO_4$ dissolved in 40 ml of ethylene glycol was added and finally the temperature was raised to 180 °C. The precipitate was washed many times with acetone and ethanol and dried under ambient conditions before being annealed at 900 °C for 24 h. For the preparation of mixed phosphate, both Al and Ga metals in the desired atomic ratio were taken together and converted to chloride form and subsequently the same procedure was followed as for the individual phosphates. Philips X-ray diffractometer was used to record the diffraction patterns using Ni filtered Cu$K\alpha$ radiation. ^{31}P MAS NMR patterns were recorded using a Bruker Avance DPX 300 spectrometer with Larmor frequency of 121.49 MHz. Typical 90° pulse duration, delay time and spinning speed are 3.5 µs, 4 s and 5 kHz, respectively. Pulse durations and relaxations delay times were optimized for these samples. It is observed that there is no change in the line shape and intensities for NMR patterns obtained with a relaxation delay of 4, 10 and 20 s. The chemical shift values are expressed with respect to 85% H_3PO_4. The complex NMR spectrum of the mixed phosphate was de-convoluted into five components using Gaussian peak profile to get the intensity ratio and peak position of the individual peaks.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of annealed $GaPO_4$ sample, which is characteristics of the hexagonal phase with $a = 0.490(2)$ and $c = 1.105(1)$ nm. The XRD pattern of the annealed sample of $AlPO_4$, shown in Fig. 1(b) is quite different from that of $GaPO_4$ and is characteristic of the pseudo-hexagonal tridymite phase with $a = 0.935(2)$, $b = 0.864(3)$ and $c = 1.827(2)$ nm. These results are consistent with the results reported in the literature [11]. Fig. 1(c) shows the XRD pattern for mixed phosphate sample $Al_{0.5}Ga_{0.5}PO_4$, prepared in the same manner. This pattern is quite similar to that of hexagonal $GaPO_4$ and the calculated values of unit cell
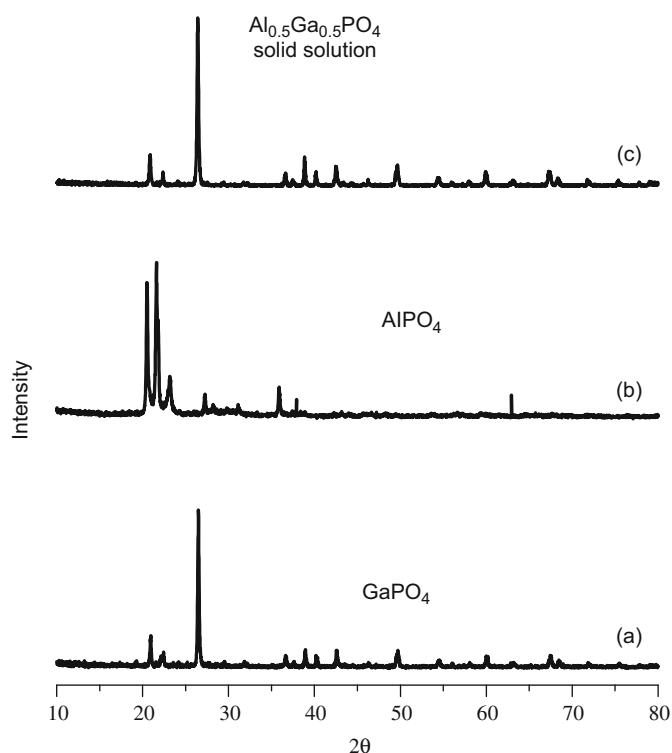

Fig. 1. XRD patterns of the 900 °C annealed samples of (a) $GaPO_4$, (b) $AlPO_4$ and (c) $Al_{0.5}Ga_{0.5}PO_4$.

parameters are $a = 0.491(2)$ and $c = 1.106(4)$ nm. The slight increase in the unit cell parameters for the mixed phosphate sample is arising due to slightly larger average value of the angle Al–O–P ($\approx 145°$) compared to the average value of Ga–O–P angle ($\approx 132°$) as reported earlier for the orthorhombic as well as the hexagonal phases of these phosphates [4,12]. For the mixed phosphate, $Al_{0.5}Ga_{0.5}PO_4$, the average value of this angle has been found to be $\approx 137°$ [7,8].

The ^{31}P MAS NMR spectra of these samples are shown in Fig. 2. The spectrum for $GaPO_4$ is a single line characterized with chemical shift $\delta = -9$ ppm and exhibits slight asymmetry in line shape. The spectrum for $AlPO_4$ is a broad asymmetric peak characterized with chemical shift $\delta = -27$ ppm. The observed increase in the chemical shift for $GaPO_4$ as compared to $AlPO_4$ can be explained in terms of the paramagnetic contribution to the phosphorus chemical shift values, which arises due to charge delocalization from the bridging oxygen atoms. The net magnetic field felt by the nucleus (B_{net}) is given by the relation $B_{net} = (1-\sigma)B_0$, where B_0 is the applied magnetic field and σ is the shielding constant. The shielding constant, σ can be considered as the sum of local diamagnetic and paramagnetic contributions, the former is a positive quantity and the latter is a negative quantity. An increase in the diamagnetic contribution decreases the net magnetic field felt by the nucleus and thereby decreases the chemical shift values. The converse is true for the paramagnetic contribution. The diamagnetic contribution is almost identical for $GaPO_4$ and $AlPO_4$ as the oxidation state of P and number of near neighbor oxygen atoms is same for both of these compounds. The paramagnetic contribution mainly arises due to the π bond character of the P–O bond, which is related to the cationic field strength of the cation attached to oxygen of the P–O bond, and can be expressed by the relation $\sigma_p \approx -(1/\Delta E)(1/r_i^3)_{2p}(\Sigma Q_{ij})$ where ΔE is the mean electronic excitation energy, r is the average radius of the phosphorus $2p_z$ orbital and Q_{ij} is the bond order of the P–O bond [13,14]. As the cationic field strength of Al^{3+} is larger than that of

Ga^{3+}, oxygen in P–O–Ga^{3+} linkages will have a higher electron density compared to P–O–Al^{3+} linkages. The higher electron density at oxygen favors a greater delocalization of electrons in the P–O bond and develops a partial double bond character, thereby increasing the Q_{ij} values. The increase in the bond order (Q_{ij}) results in an increase in σ_p values and in the value of net magnetic field felt by the nucleus, which increases the chemical shift value. In addition to this bond order effect, P–O–Al/P–O–Ga bond angles [15] are also known to affect ^{31}P MAS NMR chemical shift values. Increase in the bond angle of P–O–Al/Ga linkages leads to the increase in electron density around P, resulting in the upfield shift of ^{31}P chemical shift values. Thus based on the above discussion, the larger value of ^{31}P chemical shift in $GaPO_4$ compared to $AlPO_4$ is attributed to the increased electron density at oxygen in P–O–Ga^{3+} linkages compared to P–O–Al^{3+} linkages as
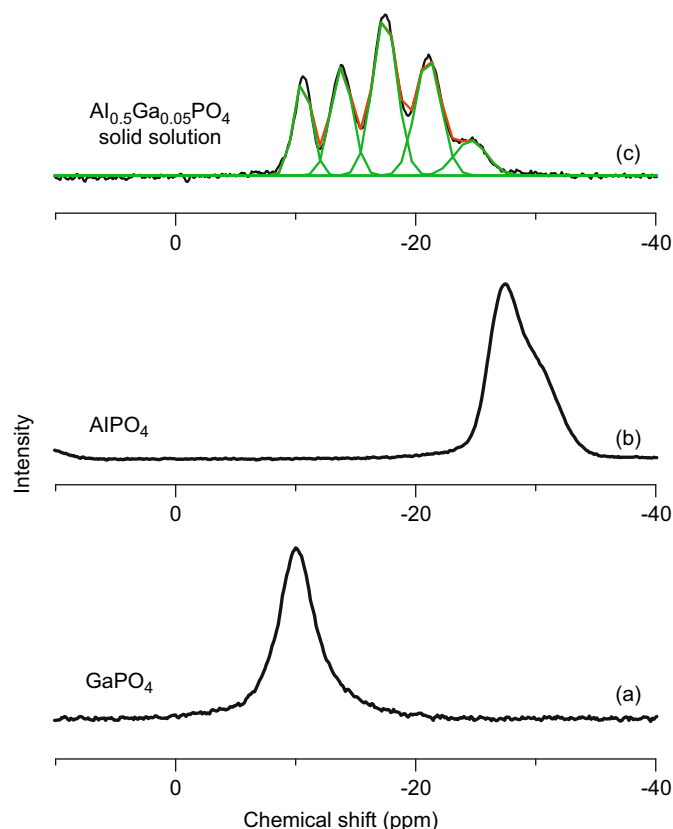
well as an increase in bond angle of P–O–Al linkages compared to P–O–Ga linkages. Further, the observed difference in the line width of the NMR spectra of these two samples is arising due to the difference in their chemical shift anisotropy values for these two compounds brought about by the combined effect of change in the extent of paramagnetic contribution and the smaller average value of the angle Ga–O–P ($\approx 132°$) as compared to that of Al–O–P ($\approx 145°$) as revealed from the crystal structure of these two compounds [4,12,14,16].

The ^{31}P MAS NMR pattern of $Al_{0.5}Ga_{0.5}PO_4$ is quite complex and consists of five well resolved peaks of varying intensities and characterized by different values of chemical shift. The chemical shift values for the five centrally placed peaks are approximately -24, -21, -17, -13 and -10 ppm. The origin of five peaks in the NMR spectrum of the mixed phosphate sample can be understood in terms of the structural configurations of ^{31}P with varying number of Al^{3+} and Ga^{3+} as its next nearest neighbors. These five configurations for ^{31}P are P_{4Ga0Al}, P_{3Ga1Al}, P_{2Ga2Al}, P_{1Ga3Al} and P_{0Ga4Al}, which are systematically exhibiting decreasing values of chemical shift, because of the significant difference in the chemical shift values of $GaPO_4$ and $AlPO_4$. For each replacement of Al^{3+} by Ga^{3+}, the ^{31}P chemical shift increases by about 4 ppm. The relative concentrations of different P structural units have been obtained based on the de-convolution of the observed NMR peak and the values are mentioned in Table 1. ^{31}P MAS NMR pattern of $Al_{0.5}Ga_{0.5}PO_4$ solid solutions, obtained from different batches are found to be identical indicating that the samples of present study are homogeneous.

Fig. 3 shows the ^{31}P MAS NMR pattern of orthorhombic $Al_{0.5}Ga_{0.5}PO_4$, where also the oxygen of PO_4 tetrahedra are bonded

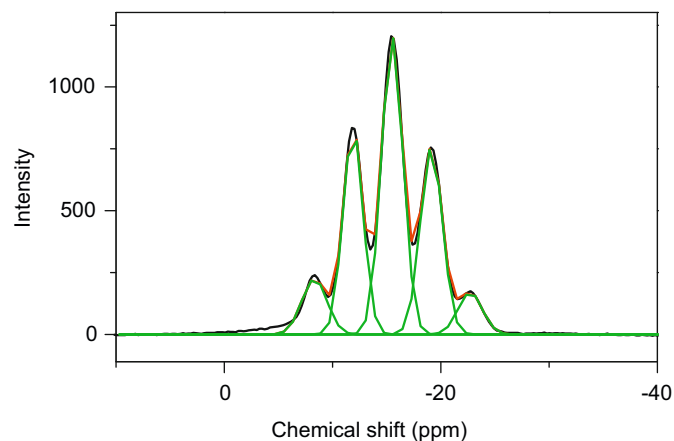**Fig. 2.** ^{31}P MAS NMR spectra of the 900 °C annealed samples of (a) $GaPO_4$, (b) $AlPO_4$ and (c) $Al_{0.5}Ga_{0.5}PO_4$. (c) The peaks with green color correspond to individual P structural units having different number of Al^{3+} and Ga^{3+} as next nearest neighbors obtained by de-convolution of the composite peak. Overall fit is shown in red color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. ^{31}P MAS NMR pattern of orthorhombic $Al_{0.5}Ga_{0.5}PO_4$ sample annealed at 1300 °C. The peaks with green color correspond to individual P structural units having different number of Al^{3+} and Ga^{3+} as next nearest neighbors obtained by de-convolution of the composite spectrum. Overall fit is shown in red color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Relative concentration of P structural units having different number of Ga and Al atoms present in $Al_{0.5}Ga_{0.5}PO_4$ solid solutions obtained at 900 °C (hexagonal) and 1300 °C (orthorhombic).

Relative concentration of different structural configurations of P	%$P_{4Al,0Ga}$	%$P_{3Al,1Ga}$	%$P_{2Al,2Ga}$	%$P_{1Al,3Ga}$	%$P_{0Al,4Ga}$
Hexagonal $Al_{0.5}Ga_{0.5}PO_4$	9.2 (6.25)	24.8 (25.0)	32.1 (37.5)	19.3 (25.0)	14.6 (6.25)
Orthorhombic $Al_{0.5}Ga_{0.5}PO_4$	6.0 (6.25)	24.1 (25.0)	37.4 (37.5)	24.2 (25.0)	8.3 (6.25)

The values in brackets are the relative concentration of P structural units having different number of Ga and Al atoms calculated assuming a binomial distribution of cations.

to the Al^{3+}/Ga^{3+} cations, the observed NMR pattern consisted of five well resolved symmetrically placed peaks, similar to what has been observed for the hexagonal phase of $Al_{0.5}Ga_{0.5}PO_4$. However, the observed intensity ratio of these five peaks for the two phases of $Al_{0.5}Ga_{0.5}PO_4$ is found to be significantly different as can be seen from the relative concentration of different P structural units shown in Table 1. For the orthorhombic phase the intensity ratio is in excellent agreement with what is expected from the binomial distribution of cations assuming a perfectly random distribution of Al^{3+} and Ga^{3+}.

From the comparison of the relative intensity of the component ^{31}P NMR spectra of the hexagonal and orthorhombic phases of $Al_{0.5}Ga_{0.5}PO_4$ samples, it is clear that the relative fraction of ^{31}P with varying structural configurations is different for these two samples. For the hexagonal sample of $Al_{0.5}Ga_{0.5}PO_4$, prepared by co-precipitation method followed by annealing at $900\,^\circ C$ for 24 h, the observed intensity ratio of the different configurations is significantly different from what is calculated based on the binomial distribution of the cations, implying a non-random distribution of Al^{3+} and Ga^{3+} in the lattice for this sample. Unlike this the intensity ratio for different P structural units in the orthorhombic phase prepared by annealing at $1300\,^\circ C$, showed a completely random distribution of P structural units. The observed non-random distribution of P structural units in $900\,^\circ C$ heated sample has been attributed to the difference in the crystal structure of $GaPO_4$, $Al_{0.5}Ga_{0.5}PO_4$ and $AlPO_4$ samples subjected to a heat treatment temperature of $900\,^\circ C$. The former two exists in the hexagonal form, whereas the latter exists in the pseudo-hexagonal or orthorhombic form at $900\,^\circ C$. The above results clearly demonstrate that the NMR studies, which are probe specific and monitor at atomic scale, where the chemical shift values provide valuable information about the nearest and next nearest neighbors around the probe atom, are able to discern the effect of the short range order. Unlike this, from the X-ray diffraction studies which reveal the long range periodicity of the lattice, it is not possible to get information about the effect of varying nearest and next nearest neighbors and consequently the short range order is averaged out in diffraction studies.

4. Conclusions

Based on the ^{31}P MAS NMR studies, the relative concentration of different P structural units present in hexagonal $Al_{0.5}Ga_{0.5}PO_4$ phase has been estimated. From these studies, it is inferred that unlike in orthorhombic $Al_{0.5}Ga_{0.5}PO_4$ phase, the A^{13+} and Ga^{3+} cations are not randomly distributed in the lattice of hexagonal $Al_{0.5}Ga_{0.5}PO_4$ phase. From the present study it is clear that the ^{31}P MAS NMR can be effectively used to understand the cation distribution in such solid solutions.

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