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Low temperature structural and thermal expansion studies on α-cristobalite type $Al_{0.5}Ga_{0.5}PO_4$ by powder neutron diffraction

S.N. Achary [a], A.K. Tyagi [a], P.S.R. Krishna [b], A.B. Shinde [b],
O.D. Jayakumar [c], S.K. Kulshresththa [c,*]

[a] Applied Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India
[b] Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India
[c] Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

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Abstract

The orthorhombic (α) low-cristobalite type $Al_{0.5}Ga_{0.5}PO_4$, prepared by co-precipitation followed by high-temperature annealing of the amorphous precipitate has been investigated by powder X-ray diffraction (XRD) at room temperature and variable temperature neutron diffraction technique down to 20 K. In the temperature range of 20–300 K, the crystal structure of this compound has been analyzed by Rietveld refinements of powder neutron diffraction data. This composition crystallizes in the orthorhombic lattice with unit cell parameters: $a = 7.030(1)$, $b = 7.015(1)$, $c = 6.923(1)$ Å and $V = 341.4(1)$ Å^3 (space group $C222_1$) (at ambient temperature). The unit cell parameters show a gradual decrease with decreasing temperature and the Al^{3+} and Ga^{3+} ions are statistically distributed over a single crystallographic site forming an ideal solid solution of $AlPO_4$ and $GaPO_4$ down to 20 K. The structural details and low-temperature thermal expansion behavior of this compound are reported in this communication. The results are also compared with our earlier thermal expansion studies of cristobalite type phosphates above ambient temperature.
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Keywords: Thermal expansion; Phosphates; Cristobalite; Neutron diffraction

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1. Introduction

The structural variations of the framework architect crystalline lattices under non-ambient conditions have been of recent interest due to their flexible crystal structure allowing low energy rotation of polyhedra leading to various displacive phase transitions [1–9]. The classic example of framework architect, SiO_2, is known to exist in different polymorphs, namely quartz, tridymite, and cristobalite structures, depending on the temperature [10]. Each of these polymorphs of silica undergoes various displacive type phase transitions at higher temperature [10]. Several phosphates of trivalent cations are also known to crystallize in various silica analogue structures. $AlPO_4$ and $GaPO_4$ are such examples where all the ambient pressure silica polymorphs have been reported [11–15]. The different polymorphs formed by reconstructive phase transitions can be retained at ambient temperature by optimizing the preparation conditions. For both of these compounds, the cristobalite type phases are reported at higher temperatures. The low-cristobalite (orthorhombic) form of $AlPO_4$ and $GaPO_4$ can be retained at ambient temperature by annealing above the cristobalite transition temperature [15–19].

The detailed temperature induced phase transitions of the quartz type $GaPO_4$ and $AlPO_4$ have been reported in literature [20–22]. Haines et al. [23] have recently reported the ideal solid solution of quartz type $GaPO_4$ and $AlPO_4$ in the complete range of compositions. Kulshreshtha et al. [17] have shown the formation of perfectly random solid solution between the low-cristobalite type $AlPO_4$ and $GaPO_4$ phases from ^{31}P NMR and powder X-ray diffraction (XRD) investigations. Later by combined XRD and neutron diffraction studies on $Al_{0.5}Ga_{0.5}PO_4$ an ideal distribution of Al^{3+}

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* Corresponding author. Fax: +91 22 2550 5151/2551 9613.
E-mail address: kulshres@magnum.barc.ernet.in (S.K. Kulshresththa).

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and Ga^{3+} was further confirmed [18]. The details of the high-temperature structural and thermal expansion behavior of their solid solutions have been reported earlier by high-temperature XRD and differential thermal analysis (DTA) [16,19]. At higher temperatures, the low-cristobalite type $Al_{1-x}Ga_xPO_4$ ($0.00 \leq x \leq 1.00$) (orthorhombic) transforms to high-cristobalite (cubic) lattice [19]. Thermal expansion coefficients of the high-cristobalite type structures are significantly lower then those of the low-cristobalite type structures [16,24,25].

Similar to the above-mentioned temperature induced phase transitions, several pressure-induced displacive and reconstructive phase transitions in such framework type compounds have also been reported in literature [6–8]. Cristobalite and quartz type $GaPO_4$, $AlPO_4$ or SiO_2 were reported to transform to orthorhombic lattice with the transformation of tetrahedral coordination of Ga^{3+}, Al^{3+}, and Si^{4+} to octahedral coordination under high pressure [6,7,26–29]. However, all these compositions show a memory effect on releasing the pressure. The change in coordination number brought out by the high pressure is reflected in decrease of unit cell volume. Often the lowering of temperature may results in the formation of high-pressure phases, as both the processes lead to decrease in unit cell volume. Earlier low-temperature diffraction study of quartz type $GaPO_4$ showed a systematic decrease in unit cell volume on lowering the temperature but no phase transformation corresponding to any high-pressure modifications was observed [19]. However, below and above the ambient temperature drastic differences in the thermal expansion behavior of this compound was reported. To the best of our knowledge, no low-temperature diffraction studies have been reported for cristobalite type $AlPO_4$ and their solid solutions. The present study is aimed to explore the existence of any phase transition due to either temperature or ordering of the metal ions in the cristobalite type solid solution composition $Al_{0.5}Ga_{0.5}PO_4$.

2. Experimental

The $Al_{0.5}Ga_{0.5}PO_4$ composition was prepared by heating amorphous precipitate of stoichiometric phosphates as reported earlier [16–19]. The phase purity of the product was ascertained from powder XRD patterns recorded on a Philips Powder X-ray diffractometer (model PW1710) using the Cu Kα radiation. The neutron powder diffraction (ND) data was collected with the linear 5-PSD based powder diffractometer at 100 MW Dhruva Research Reactor at BARC, Mumbai, in the 2θ range of $6°$–$138°$. The total range of data was collected in 4 h. The sample was packed in a vanadium can (6 mm diameter and 5 cm height). At lower temperatures, the ND patterns of this sample were recorded by using an APD make closed cycle helium refrigerator. The sample was cooled to desired temperature and equilibrated for 5 min and then the diffraction data were collected. The Rietveld refinements of the observed data at various temperatures were carried out using the Fullprof-2K software package [30].

3. Results and discussion

The analysis of room temperature X-ray diffraction data of this compound showed the formation of orthorhombic low-cristobalite lattice ($C222_1$ No. 20) [18]. The observed neutron diffraction data was refined with the starting model based on the earlier reported low-cristobalite crystal structure of $Al_{0.5}Ga_{0.5}PO_4$ [18]. The Al and Ga atoms are statistically distributed over the 4*b* sites and the P atoms are placed in 4*a* sites of the space group $C222_1$. There are two different kinds of oxygen atoms, namely O1 and O2, present in the general positions (8*c* sites) of this space group. The profile was fitted with Pseudo–Voigt profile function. The profile refinement was started with scale and background parameters followed by the unit cell parameters. The typical half width, mixing and peak asymmetry parameters were also refined. After getting a proper match, the positional parameters and isotropic thermal parameters of various atoms were refined. The crystal structure analysis of $Al_{0.5}Ga_{0.5}PO_4$, at ambient temperature was found to agree with the earlier reported powder neutron and XRD studies [16,18]. The observed diffraction patterns at other temperatures were refined in a similar manner with the starting model based on the present ambient temperature refined parameters. The goodness of the refinements was assessed by the residuals (*R*-values). The typical observed and calculated neutron diffraction patterns of $Al_{0.5}Ga_{0.5}PO_4$ at 300 and 20 K are shown in Fig. 1 and the details of the refined structural parameters observed at various temperatures for $Al_{0.5}Ga_{0.5}PO_4$ are listed in Tables 1 and 2.

The refined unit cell parameters obtained from the present neutron diffraction studies of $Al_{0.5}Ga_{0.5}PO_4$ at 300 K are: $a = 7.030(1)$, $b = 7.015(1)$ $c = 6.923(1)$ Å, and $V = 341.4(1)$ Å^3, which are in agreement with our earlier reported values [16,18] and the corresponding parameters at 20 K are: $a = 7.009(2)$, $b = 6.993(2)$, $c = 6.892(2)$ Å, and $V = 337.8(2)$ Å^3. The variation of unit cell parameters with temperature is shown in Fig. 2, which indicates a gradual decrease of all unit cell parameters with decrease in temper-

Table 1
Refined unit cell parameters for $Al_{0.5}Ga_{0.5}PO_4$ at various temperatures

Temperature (K)	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å)^3
20	7.009(2)	6.993(2)	6.892(1)	337.8(1)
50	7.014(2)	6.993(2)	6.895(1)	338.2(1)
125	7.014(2)	6.999(2)	6.900(1)	338.7(1)
175	7.018(2)	6.003(2)	6.907(1)	339.4(2)
225	7.024(2)	7.006(2)	6.912(1)	340.1(2)
250	7.030(2)	7.008(2)	6.913(1)	340.6(2)
300	7.030(1)	7.015(1)	6.923(1)	341.4(1)
300[a]	7.030(1)	7.017(1)	6.922(1)	341.4(1)
373[a]	7.038(1)	7.027(1)	6.934(1)	343.0(1)
473[a]	7.049(1)	7.044(1)	6.954(1)	345.3(1)
573[a]	7.066(2)	7.061(2)	6.980(1)	348.2(1)

[a] Data taken from ref. [16].

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