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Abstract
Amorphous to crystalline transition in pressure quenched $Zr_{0.5}Hf_{0.5}W_2O_8$ has been studied with respect to local structures of ZrO_6 using the perturbed angular correlation technique. In an untreated crystalline sample close to 0.7 fraction of the probe atoms occupy Zr sites of regular ZrO_6 while the remaining three fractions are understood to be associated with contracted and distorted octahedra. The existence of six distinct ZrO_6 could be deduced based on perturbed angular correlation studies in the pressure amorphized sample. In the amorphous sample these ZrO_6 are associated with appreciable octahedral distortions. Isochronal annealing measurements show that these octahedra remain structurally quite stable up to 800 K. Values of quadrupole frequencies tend to become close to those experienced by probe atoms in a crystalline sample for annealing at 870 K, implying that around this temperature there is an onset of amorphous to crystalline transition. Complete restoration of quadrupole parameters to those of the untreated crystalline sample is seen subsequent to annealing at 975 K.

1. Introduction

Zirconium tungstate is a ceramic material that exhibits isotropic negative thermal expansion from 4 to 1050 K [1]. At normal temperature and pressure it is a cubic compound with an interconnected framework of ZrO_6 octahedra and WO_4 tetrahedra, with the latter having one nonbridging (terminal) oxygen. Apart from negative thermal expansion, zirconium tungstate is found to exhibit many interesting properties such as pressure-induced amorphization and an increase in entropy while the system undergoes an amorphous to crystalline transition [2, 3]. Recent perturbed angular correlation (PAC) studies show that the contracted and distorted ZrO_6 octahedra [4] provide an additional contribution and mechanism to negative thermal expansion (NTE). This is in addition to the phononic contribution from the low energy rigid unit mode due to tilting of nearly rigid oxygen polyhedra [5] and the bending modes of WO_4 tetrahedra [6]. Even the ambient temperature cubic phase is reported to have orientational disorder of WO_4 ions that is not allowed by crystallographic symmetry [7]. A number of experimental and theoretical results have been reported addressing different important aspects of NTE [1, 8–19] and pressure-induced amorphization [20–24].

Crystalline to amorphous transitions were first reported in zirconium tungstate for pressures exceeding 3 GPa based on x-ray diffraction and Raman data [2]. The amorphous phase was found to be quenchable to ambient upon the release of pressure. Across amorphization a remarkable densification of 26% has been reported to occur [23]. Similar results were reported by other researchers subsequently [24]. Due to short range ordering in pressure amorphized zirconium tungstate by means of studying the local structure of WO_4/ZrO_6 one could deduce the degree of contraction and distortions, if any, associated with these polyhedra. The average W–O bond length increase suggesting an increase in average coordination number of W has been reported using synchrotron x-ray diffraction and x-ray absorption spectroscopy measurements in ZrW_2O_8 subjected to pressures up to 7 GPa [23]. Increase in the coordination number of W has been suggested based on the modelling of neutron and x-ray total scattering data [25]. As ZrO_6 is less rigid than WO_4 due to higher W–O covalency [1], a detailed study of the local structure of octahedra in the densified pressure amorphized sample might provide a better understanding of pressure-induced amorphization.

In the present work, the local structure(s) of ZrO_6 has been studied in a detailed manner in the pressure amorphized zirconium tungstate by means of perturbed angular correlation

Table 1. Results of PAC measurements in pressure amorphized zirconium tungstate.

| Sample treatment	i	ν_{Qi} (MHz)	η_i	δ_i	f_i
Untreated crystalline sample at 303 K	1	334 ± 5	0.12 ± 0.05	0.05 ± 0.02	0.6 ± 0.04
	2	678 ± 15	0.89 ± 0.25	0.15 ± 0.04	0.2 ± 0.04
	3	770 ± 12	0.26 ± 0.04	0.04 ± 0.01	0.1 ± 0.02
	4	850 ± 28	0.28 ± 0.05	0.04 ± 0.01	0.1 ± 0.01
Pressure amorphized (PA)	1	230 ± 35	0.55 ± 0.08	0.08 ± 0.02	0.30 ± 0.04
	2	437 ± 21	0.78 ± 0.28	0.14 ± 0.04	0.28 ± 0.04
	3	1039 ± 42	0.28 ± 0.12	0.08 ± 0.03	0.16 ± 0.04
	4	1289 ± 33	0.58 ± 0.17	0.07 ± 0.03	0.10 ± 0.03
	5	1467 ± 22	0.29 ± 0.04	0.05 ± 0.01	0.09 ± 0.02
	6	1797 ± 38	0.68 ± 0.06	0.06 ± 0.01	0.07 ± 0.01
PA and annealed at 773 K	1	265 ± 25	0.55 ± 0.08	0.10 ± 0.02	0.32 ± 0.04
	2	454 ± 24	0.74 ± 0.28	0.2 ± 0.04	0.26 ± 0.04
	3	1039 ± 38	0.28 ± 0.08	0.11 ± 0.02	0.11 ± 0.04
	4	1258 ± 35	0.6 ± 0.11	0.16 ± 0.04	0.16 ± 0.04
	5	1406 ± 34	0.29 ± 0.04	0.12 ± 0.01	0.08 ± 0.02
	6	1667 ± 29	0.58 ± 0.06	0.12 ± 0.02	0.07 ± 0.01
PA and annealed at 975 K	1	354 ± 5	0.15 ± 0.04	0.04 ± 0.02	0.65 ± 0.04
	2	686 ± 20	0.86 ± 0.19	0.09 ± 0.03	0.17 ± 0.04
	3	731 ± 15	0.28 ± 0.05	0.04 ± 0.01	0.09 ± 0.01
	4	881 ± 22	0.25 ± 0.04	0.04 ± 0.02	0.09 ± 0.02

spectroscopy (PAC) [4, 26] using ^{181}Hf/Ta radioactive probe atoms. PAC is based on studying the time dependence of the angular correlation of two distinct γ-rays emitted in cascade by the probe atoms caused by the hyperfine interaction between probe nuclear moments with electromagnetic fields at the sites of their occupation. In this non-magnetic system the hyperfine interaction is between the nuclear quadrupole moment of the probe atoms with electric field gradient at the sites of probe atoms. By this study non-zero electric field gradient (EFG) tensor(s) if the symmetry of the distribution of charges around the probe atom is non-spherical or non-cubic at the site of occupancy of probe atoms (i.e. Zr sites) are deduced [26].

The principal component of the EFG tensor (V_{zz}) is proportional to the experimentally measured quadrupole frequency. As V_{zz} is inversely proportional to the cubic distance of the Zr–O bond, any change in the quadrupole frequency could be used to roughly quantify the variation in Zr–O bond length and hence the rigidity of ZrO_6. The asymmetry parameter of the EFG in the principal axis system is given as $\eta = (V_{xx} - V_{yy})/V_{zz}$ (where V_{xx}, V_{yy} and V_{zz} are elements of the EFG tensor in its principal axis system) with its value $0 \leqslant \eta \leqslant 1$ describing the deviation of the EFG from axial symmetry. Hence the asymmetry parameter η is sensitive to orientation distortion if any is associated with ZrO_6. Thus the EFG is a very important short range parameter used to characterize the local structures around the occupancy of probe atoms, mainly its nearest-neighbour surroundings, irrespective of the crystalline or amorphous nature of the matrix [27]. Also angular distribution of near neighbours could be explained based on the EFG at a given atomic site that is sensitive to local atomic coordination [27]. Based on ^{181}Hf/Ta PAC equilibrium measurements at different temperatures on untreated crystalline $Zr_{0.5}Hf_{0.5}W_2O_8$ it is deduced that there exist four distinct Zr sites. It is seen that as high as 0.7 fraction of probe atoms are associated with regular octahedra for temperatures close to 250 K [4]. The present work mainly

addresses the local structural aspects of ZrO_6 by ^{181}Hf/Ta PAC measurements in a pressure amorphized sample and across the bulk amorphous to crystalline transition with isochronal annealing treatments in $Zr_{0.5}Hf_{0.5}W_2O_8$.

2. Experimental details

$Zr_{0.5}Hf_{0.5}W_2O_8$ samples (isostructural to those of pure ZrW_2O_8 in the cubic phase with $P2_13$ space group) both as-synthesized and pressure-quenched from 5 GPa were neutron irradiated at BARC to produce ^{181}Ta probe nuclei. PAC measurements have been carried out at the isomeric state of the ^{181}Ta probe separating 133–482 keV γ–γ cascade using a BaF_2-based three-detector PAC spectrometer. The spectrometer has a time resolution of 660 ps (FWHM) [28] when the detectors are set for the above energies. From the measured coincidence spectra at 90° and 180°, namely W(90°, t) and W(180°, t), the time-dependent anisotropy function $R(t) = 2[\text{W}(180°, t) - \text{W}(90°, t)]/[\text{W}(180°, t) + 2\text{W}(90°, t)]$ is evaluated and this contains information on the hyperfine parameters of interest. Further details of the spectrometer and data acquisition have been reported [28, 29]. The time-dependent anisotropy function $R(t)$ [30] is analysed with the following expression for extraction of hyperfine interaction parameters, i.e. $R(t) = A_2 \sum_{i=1}^{n} f_i \sum_{m=0}^{3} S_{2m}^i(\eta_i) \cos(g_n(\eta_i)\omega_m^i t) \exp(-g_n(\eta_i)\delta_m \omega_m^i t)$, where n is determined by the number of frequency components. Quadrupole frequency $\nu_Q^i = eQV_{zz}^i/h$, asymmetry parameter η_i, f_i the fraction experiencing corresponding ν_Q^i with a width of the Lorentzian distribution of quadrupole frequencies, δ_i, are deduced. PAC measurements have been carried out at room temperature subsequent to each step of the isochronal annealing treatment with a step time of 30 min in the pressure amorphized sample. All annealing treatments have been carried out in air.
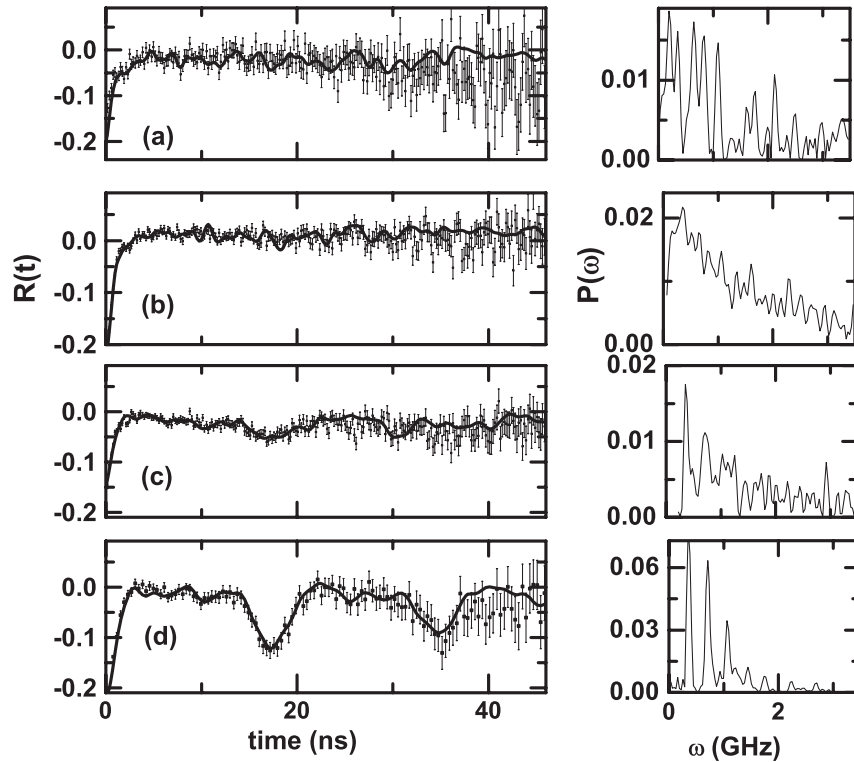
Figure 1. Representative anisotropy spectra and the Fourier transforms for PAC measurements carried out at room temperature (a) as pressure amorphized while (b)–(d) refer to pressure quenched sample subsequent to isochronal annealing at various temperatures, namely 773, 875 and 975 K respectively.

3. Results and discussion

As Zr and Hf ions are of 4+ valence and with ionic radii 0.86 and 0.85 Å, respectively, each atom of Zr or Hf can freely substitute for the other without affecting their local environments. As far as the structure of the systems ZrW_2O_8 and HfW_2O_8 are concerned both are of cubic symmetry with almost similar lattice parameters. Therefore the occurrence of more than one fraction in the untreated crystalline sample with 50% doping of Hf for Zr in zirconium tungstate could not be due to local distortion caused by the substitution of Zr by Hf atoms. Based on the values of quadrupole parameters and their variation with temperature obtained in PAC measurements on untreated crystalline $Zr_{0.5}Hf_{0.5}W_2O_8$ samples (cf table 1) it is deduced that the fraction (f_1) of probe atoms occupy regular octahedra while the remaining fractions are associated with contracted octahedra of varying degrees of octahedral distortion [4]. Further, these measurements imply the equilibrium configurations of these distinct octahedra in terms of their variation in structure and concentrations with temperature. Results of equilibrium temperature measurements show the variations of quadrupole parameters in terms of the changes in the magnitudes of fractions experiencing different quadrupole frequencies and the fraction of probe atoms associated with regular octahedra is seen to increase to the value of 0.7 at the cost of other fractions at 250 K. PAC measurements at different temperatures evidently show that these are equilibrium $Zr(Hf)O_6$ configurations occurring in the sample with fractions of probe atoms

associated with these configurations exhibiting changes in quadrupole parameters [4].
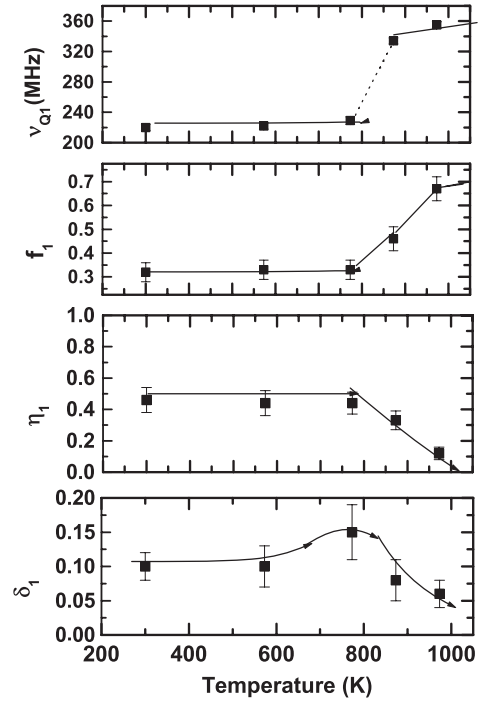
PAC results in the pressure amorphized sample show that the obtained anisotropy spectra in the pressure amorphized sample is non-vanishing (cf figure 1(a)), though dampened compared to the untreated crystalline sample [4]. Dampening implies the degree of non-uniqueness in the local structures of the octahedra due to the distribution in bond lengths and bond angles caused by the distortions of octahedra. The short range order observed in amorphous systems are in general explained either by dense random packing of ions or a random unit network [27]. Probe atoms associated with a dense random packed matrix lead to a total vanishing of spectra with the complete absence of any periodic features. On the other hand, probe atoms occupying an amorphous system with a near-crystalline-like local order do not result in a completely damped anisotropy spectra [27]. Therefore the anisotropy spectra obtained in the pressure quenched sample with corresponding peaks in the Fourier transform (cf figure 1) implies that the short range ordering can be explained in terms of a random network of structural units. The deduced quadrupole parameters as experienced by probe atoms associated with distinct octahedra are shown in the table. These quadrupole parameters are seen to be different from those of the untreated crystalline sample. Further, compared to the untreated crystalline sample the values of ν_{Q1} and ν_{Q2} are smaller, while the remaining quadrupole frequencies are much higher in the amorphized sample. This implies that in the amorphized sample most of the fractions associated with ZrO_6 exhibit an appreciable degree of contraction and distortion.
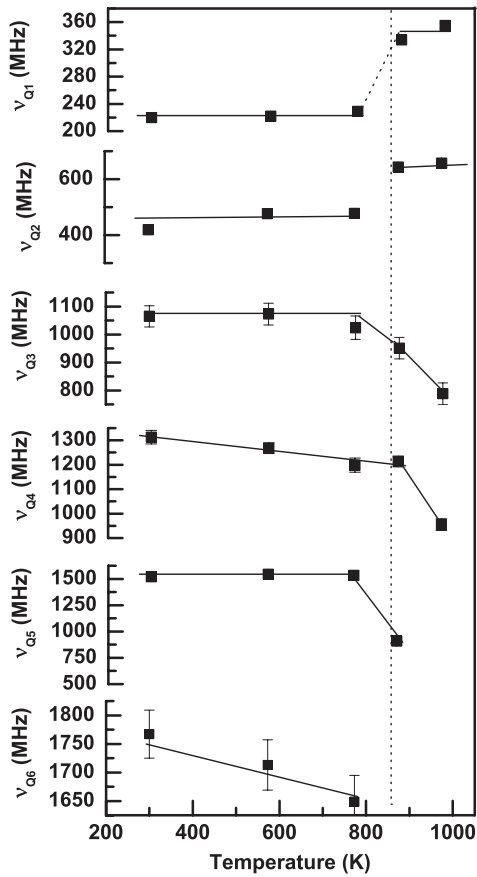
Figure 2. Variation of quadrupole frequencies associated with different fractions in pressure amorphized sample with isochronal annealing temperature. Dotted vertical line shows the temperature beyond which the values of quadrupole frequencies tend to become close to those of untreated crystalline sample.

Figure 3. Variation of the quadrupole parameters of the fraction f_1 in terms of its quadrupole frequency, magnitude, asymmetry parameter and the width of the Lorentzian distribution of quadrupole frequencies with annealing temperature in pressure quenched sample.

Variation of quadrupole frequencies with isochronal annealing temperature is shown in figure 2. It can be seen that below 875 K, apart from ν_{Q6} which exhibits a small change, all the other quadrupole frequencies remain constant. Subsequent to annealing at 875 K ν_{Q1} and ν_{Q2} exhibit an increase while ν_{Q3}, ν_{Q4} and ν_{Q5} decrease. As the fractions f_5 and f_6 disappear beyond 875 and 775 K, respectively, variation of the corresponding quadrupole frequencies is shown only up to these temperatures. From figure 2 it can be seen that beyond 875 K the values of ν_{Q1}, ν_{Q2}, ν_{Q3} and ν_{Q4} tend to become close to those of untreated crystalline samples (cf table 1). Hence this temperature might mark the onset of the amorphous to crystalline transition. PAC being a short range technique could detect the onset of long range ordering around 875 K. Complete restoration of quadrupole parameters to those of the untreated crystalline sample is seen subsequent to annealing at 975 K commensurate with the bulk amorphous to crystalline transition as deduced using XRD measurements [23, 24].

As the evolution of local structures across the amorphous to crystalline transition could be followed by the evolution of the fractions of probe atoms associated with regular octahedra, variation of quadrupole parameters such as the quadrupole frequency asymmetry parameter, the dampening parameter and the magnitude of fraction with annealing temperature is shown in figure 3. f_1 remains constant up to 775 K while it starts increasing following annealing beyond 850 K and almost remains constant around 0.65 for annealing beyond 975 K. The value of η_1 remains close to 0.55, which is much higher than that of the untreated crystalline sample. A decrease in the value of η_1 and δ_1 beyond 875 K is concomitant with the increase in f_1. Quadrupole parameters of different fractions do not vary below 800 K, which imply (cf table 1 and figure 2) that the structural configurations of ZrO_6 octahedra remain stable in the PA sample. This experimental observation points to the inference that the terminal oxygen of WO_4 has got bonded with the other tetrahedra leading to the frozen configurations of ZrO_6 up to 800 K, as rotational and/or translational motion of polyhedra are coupled. This is consistent with the suggestion made by Keen *et al* on the bonding of terminal oxygen of WO_4 leading to O–W–O links based on the modelling of neutron scattering data [25]. There is an overall increase in the dampening of the anisotropy spectra and its Fourier transform for the measurement subsequent to 775 K, while the frequencies and other quadrupole parameters remain almost the same as those of the PA sample. This implies that around this temperature there is a tendency for relaxation of the frozen-in configurations due to PIA. This is understood to be due to weakening of the bonds connecting terminal oxygen of WO with other tetrahedra around this temperature. For annealing beyond 850 K the quadrupole parameters clearly tend to reach values the same as those of the untreated crystalline sample, while the complete restoration of the parameters to those of the untreated crystalline sample is observed following

the annealing treatment at 975 K commensurate with the amorphous to crystalline transition.

The fraction f_1 in the untreated crystalline sample at 300 K decreases at the cost of other fractions, while the variation in ν_{Q1} is smaller than that of other frequencies with respect to the application of pressure, as reported in the present work or equilibrium measurements carried out at different temperatures [4]. This might imply that the octahedra associated with the fraction of probe atoms f_1 are more rigid than the others. A higher number of frequency components and hence ZrO_6 of distinct local structures are seen in the pressure amorphized sample (cf table 1), implying that the number of distinct octahedra increases with increasing volume contraction of the sample. The observed changes in quadrupole parameters in equilibrium measurements is understood to be due to the flexibility of the polyhedra caused by the terminal oxygen of WO_4 and the correlation between the inward rotation of WO_4 and ZrO_6, as the inward rotation of polyhedra is supposed to be one of the important mechanisms of NTE [31–37].

Increase in the coordination number of Zr, if any, in the pressure amorphized sample is quite likely to result in an appearance of a low quadrupole frequency. Quadrupole frequencies (low in magnitude) occurring in pressure amorphized samples are closer in values to those observed in equilibrium measurements at elevated temperatures on an untreated crystalline sample [37]. There are no additional low frequency components appearing in the pressure amorphized sample which are not present in the equilibrium measurements. This observation therefore indicates that there may not be any increase in the coordination number of Zr. Invariance of quadrupole frequencies in the PA sample for annealing below 800 K implies the locking up of polyhedra due to bonding of terminal oxygens of WO_4. Restoration of quadrupole parameters to those of the untreated crystalline sample for annealing beyond 950 K might imply that there might not be any breaking of bonds due to amorphization. Thus these results of isochronal annealing measurements on the pressure amorphized sample might support, to a large extent, the rigidity and stability of WO_4 and ZrO_6 polyhedra.

ZrW_2O_8 and HfW_2O_8 are isostructural and physical properties such as NTE and phase transition of these systems were reported to be nearly the same [11, 12, 38] though subtle changes in terms of smaller lattice parameter and absolute value of negative thermal expansion coefficients are seen in HfW_2O_8 compared to ZrW_2O_8. Based on the similar properties of these systems Evans *et al* [35, 1] conclude that the observed NTE in these materials is not due to subtle structures of Zr–O or Hf–O. ZrW_2O_8 and HfW_2O_8 undergo pressure-induced amorphization at 1.5 and 2 GPa, respectively [39, 40]. As both these systems are isostructural the mechanism of negative thermal expansion and pressure-induced amorphization are the same in both systems. The present system $Zr_{0.5}Hf_{0.5}W_2O_8$ is quenched from a pressure of 5 GPa to obtain the frozen amorphous structure at room temperature and atmospheric pressure. The temperature at which the complete restoration of the amorphous to crystalline transition closely matches with that of the crystallization temperature of pressure amorphized

zirconium tungstate. These above points might imply that the results obtained in the present study on $Zr_{0.5}Hf_{0.5}W_2O_8$ might be largely representative of ZrW_2O_8 as far as the evolution of local structures of $Zr(Hf)O_6$ octahedra are concerned.

Summarizing this atomic scale study shows the existence of highly distorted octahedra in the pressure amorphized sample. Invariance of quadrupole parameters in the pressure amorphized sample implies that the structures of these distorted octahedra remain stable up to 800 K. This is understood to be caused by the locking up of polyhedra due to bonding of the terminal oxygen of WO_4 with other tetrahedra. This study also suggests that there may not be any increase in the coordination number of Zr atoms in the pressure quenched sample. The onset of relaxation of the octahedra occurs at 870 K while the restoration of quadrupole parameters to those of the untreated crystalline sample is observed subsequent to annealing at 975 K. Bulk amorphous to crystalline transition in pressure quenched ZrW_2O_8 was reported to occur beyond 900 K.

Acknowledgments

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