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Pressure induced valence and structural phase transition in $Ba_2PrRu_{0.8}Ir_{0.2}O_6$

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Abstract

The crystal structure of the ordered double perovskite $Ba_2PrRu_{0.8}Ir_{0.2}O_6$ was investigated as a function of pressure at room temperature. High-resolution synchrotron powder diffraction measurements have revealed the occurrence of a first order phase transition at a critical pressure of about 0.5 GPa. Structural refinements indicate that $Ba_2PrRu_{0.8}Ir_{0.2}O_6$ transforms from an ambient pressure monoclinic ($P2_1/n$) to a high-pressure tetragonal ($P4/mnc$) structure. The transition is consistent with a valence change of the Pr ions.

1. Introduction

Valence transitions where the formal valence level of an atom or ion exhibits strong temperature or pressure effects are of considerable interest. A small number of rare-earth intermetallic compounds exhibit first-order valence transitions, including the $\alpha \rightarrow \gamma$ transition in Ce metal, $Sm_{1-x}Ln_xS$ (Ln = La, Gd), $CeNi_{1-x}Co_xSn$ and $YbInCu_4$ [1–6]. In $YbInCu_4$ it has been established that the application of external pressure favours the formation of the lower volume Yb^{3+} state relative to the Yb^{2+} state [6–10]. There are considerably fewer examples of valence transitions in metal oxides, one notable example being $TlReO_4$ where the Tl ion changes its valence from Tl^+ to Tl^{3+} and Re from Re^{7+} to Re^{5+} [11]. In metal oxides valence transitions are more commonly observed as valence averaging, for example the formerly Fe(IV) in the orthorhombic perovskite $CaFeO_3$ disproportionates to the valence ordered $Ca_2Fe^{V}Fe^{III}O_6$ monoclinic structure at low temperatures [12]. Here the valence transition induces a structural phase transition as a consequence of the difference in the size of the iron cation in the three oxidation states. Similar valence averaging transition is observed in $CsAuCl_3$ [13].

The ordered double perovskites A_2LnMO_6 (A = alkaline earth cation, Ln an lanthanide and M a 4d or 5d transition metal) display an array of interesting and unusual magnetic and electronic properties. For example monoclinic Ba_2PrRuO_6 contains trivalent Pr and pentavalent Ru and exhibits an antiferromagnet transition near 120 K, whereas in tetragonal Ba_2PrIrO_6 both the Pr and Ir cations are in the tetravalent state [14, 15]. Clearly in the Ba

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Table 1. Structural parameters for $Ba_2PrRu_{0.8}Ir_{0.2}O_6$ refined using powder neutron diffraction data collected at ambient pressure. $a = 5.9810(5)$ Å, $b = 5.9908(5)$ Å, $c = 8.4259(7)$ Å; $\beta = 90.39(1)°$; R_p 6.51, R_{wp} 8.09, R_{exp} 3.14, R_{Bragg} 3.38.

Atom	x	y	z	B_{iso}
Ba	0.496(3)	0.509(4)	0.240(1)	0.67(7)
Pr	0	0.5	0	0.58(12)
Ru	0.5	0	0	0.46(7)
Ir	0.5	0	0	0.46(7)
O1	0.263(2)	0.228(4)	−0.009(1)	0.5(2)
O2	0.277(2)	0.760(3)	0.006(1)	1.1(2)
O3	0.501(3)	0.001(5)	0.238(1)	2.0(2)

containing double perovskite structure, Pr is on the edge of a valence instability and it has been reported that partially replacing Ru with Ir in $Ba_2PrRu_{1-x}Ir_xO_6$ induces a first order valence transition from Pr^{3+} to Pr^{4+}. The second B-site cation (Ru or Ir) also changes its valence state, so as to maintain charge neutrality. It has been established that the valence transitions in the rare-earth intermetallics are sensitive to applied pressure, with the smaller, higher valence state being favoured at higher pressures [8, 9]. Here we report the results of a high-resolution synchrotron powder diffraction study of a representative member of the series $Ba_2PrRu_{1-x}Ir_xO_6$, namely $Ba_2PrRu_{0.8}Ir_{0.2}O_6$, as a function of pressure. A first order phase transition from a monoclinic to tetragonal structure is observed just above ambient pressure. This transition appears to be driven by the valence transition from Pr^{3+} to Pr^{4+}.

2. Experimental details

A polycrystalline sample of $Ba_2PrRu_{0.8}Ir_{0.2}O_6$ was prepared by reaction of the appropriate stoichiometric mixture of $BaCO_3$, Pr_4O_{11}, Ru and Ir. The reactants were intimately mixed in an agate mortar under acetone, placed in an alumina crucible and heated at temperatures of up to 1200 °C for three days with intermediate grindings. A modified Merrill–Bassett diamond-anvil cell was used for the x-ray studies in the pressure range 0–6.0 GPa. The powdered sample, together with a few small ruby chips, was loaded into a 200 μm hole in a steel gasket. A methanol–ethanol–water (16:3:1) mixture was used as the hydrostatic pressure-transmitting medium. The pressure was calibrated by measuring the shift of the R_1 fluorescence line of ruby before and after each run. The x-ray diffraction data were collected using synchrotron radiation at the bending magnet beamline X7A, at the National Synchrotron Light Source in Brookhaven National Laboratory [16]. A wavelength of 0.6939(1) Å was selected using a channel cut Ge 111 monochromator and diffraction patterns were recorded in 0.01° steps up to $2\theta = 45°$ using a curved position sensitive detector [17]. Powder neutron diffraction data were collected on the HRPD at ANSTO's HIFAR reactor using 1.4925 Å neutrons [18]. Structural parameters were refined by the Rietveld method using the program RIETICA [19].

3. Results and discussion

In figure 1 we show a typical high pressure x-ray diffraction pattern for $Ba_2PrRu_{0.8}Ir_{0.2}O_6$ as well as selected regions of the patterns collected as a function of pressure. At ambient pressure the sample is single phase with no impurities obvious in the synchrotron diffraction profile. The structure was refined in the monoclinic space group $P2_1/n$, this space group being confirmed by a high-resolution powder neutron diffraction study. Table 1 presents

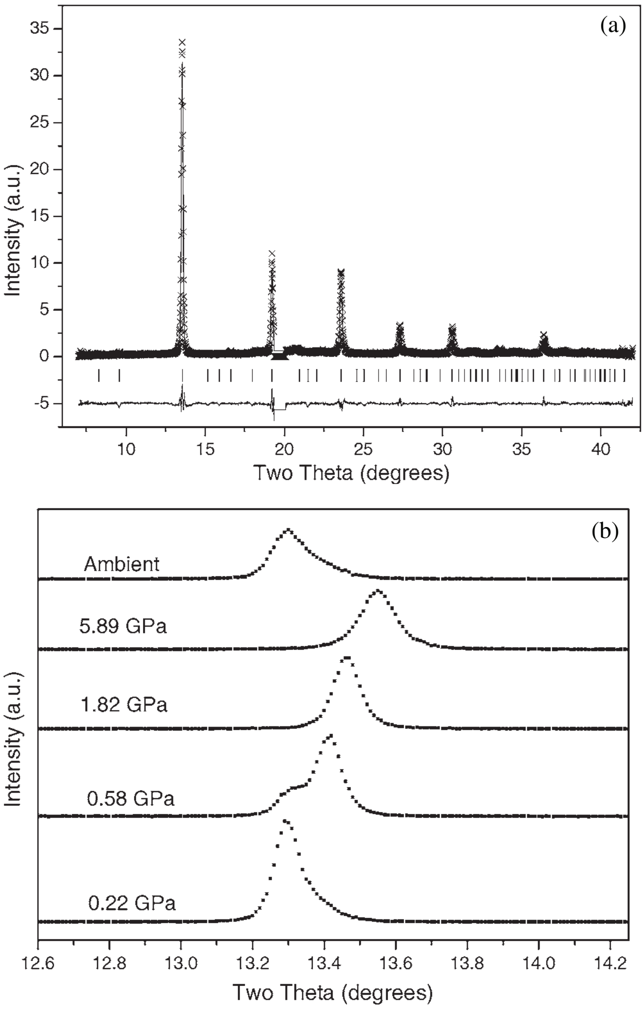

Figure 1. (a) Observed, calculated and difference synchrotron diffraction profile for $Ba_2PrRu_{0.8}Ir_{0.2}O_6$ at 1.82 GPa. The area near $2\theta = 20°$ contains reflections from the sample holder and was excluded in the refinement. The structure was refined in the tetragonal space group $P4/mnc\, a = 5.9154(6)$ Å, $c = 8.370(2)$ Å. R_p 12.9, R_{wp} 14.7, R_{exp} 13.1, R_{Bragg} 10.3. (b) Portions of the synchrotron powder diffraction profiles highlighting the transition to the tetragonal phase. The pressure in each profile is indicated. The trace at ambient was recorded after releasing the pressure.

the final refined structural parameters. In the refinement of the monoclinic structure from the synchrotron diffraction data it was necessary to fix the oxygen coordinates at the values determined in the powder neutron diffraction study. The refinements tended to be unstable if the oxygen parameters were allowed to freely vary. In the monoclinic $P2_1/n$ structure the Ba^{2+} cations are at the centre of a distorted dodecahedron and are coordinated to 12 oxygen atoms. The Pr and Ru/Ir cations are at the centre of two distorted MO_6 octahedra and these have a rock-salt like ordering as is illustrated in figure 2. The displacement parameters for the three cations refined from an ambient pressure data set are unremarkable, and there appears to be little if any mixing of the Pr and Ru/Ir cations over the two available sites. As the pressure

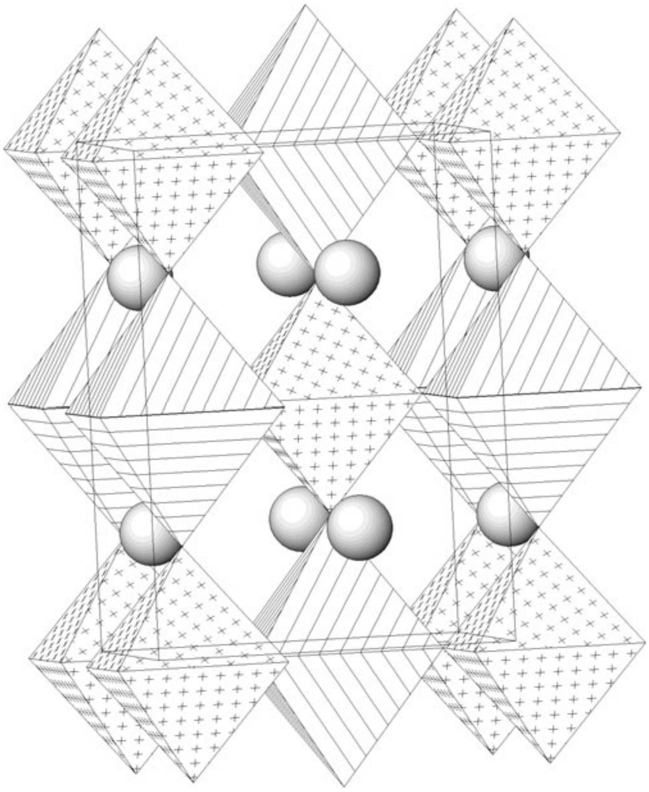

Figure 2. Representation of the $A_2BB'O_6$ double perovskite structure illustrating the rock-salt ordering of the two BO_6 octahedra. The A-type cations are represented as spheres.

increased a second phase was observed and the diffraction patterns between 0.2 and 0.9 GPa could only be adequately described in terms of a two-phase mixture. At pressures above 1 GPa only a single ordered double phase perovskite-like phase was again observed. Releasing the pressure caused a similar sequence of events and once the pressure was totally released the lattice parameters rapidly return to those found prior to the pressure cycle. This behaviour is typical of a first order phase transition from the low pressure monoclinic to a high-pressure tetragonal structure.

Refinements of the high pressure structures always showed $a/\sqrt{2} = c/2$ and $\beta = 90°$ within one esd. Hence it was concluded that the high pressure structures were no longer monoclinic but tetragonal. We have recently demonstrated that at higher Ir contents the structures in the series $Ba_2PrRu_{1-x}Ir_xO_6$ transform to a tetragonal structure with space group $P4/mnc$ [20]. In this tetragonal structure the rock-salt ordering of the Pr and Ru/Ir cations persists but the nature of the tilting of the BO_6 octahedra changes. The monoclinic structure has a $a^+b^-b^-$ tilt system (using Galzers notation), whereas the tetragonal $P4/mnc$ structure is $a^0a^0c^+$ [21, 22]. This tetragonal model adequately describes the high-pressure structure observed here for $Ba_2PrRu_{0.8}Ir_{0.2}O_6$. Similarly a model containing a mixture of the monoclinic $P2_1/n$ and tetragonal $P4/mnc$ phases was satisfactory in the analysis of the diffraction data in the two-phase region. The smaller number of variable parameters in the higher symmetry tetragonal structures, generally, resulted in more stable structural refinements, and a typical example is given in table 2.

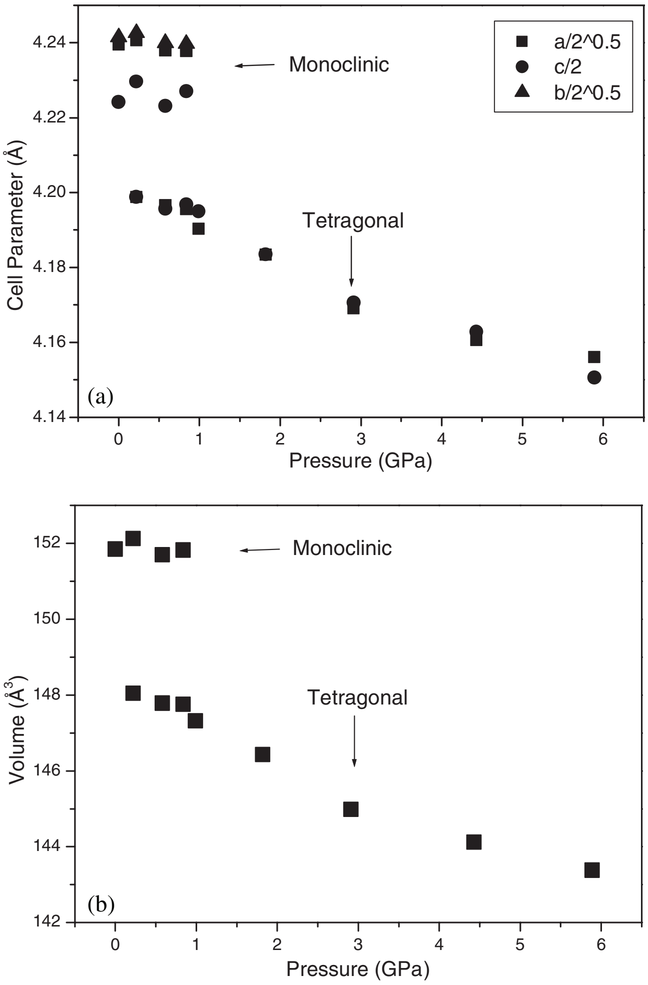

Figure 3. (a) Pressure dependence of the unit cell parameters for $Ba_2PrRu_{0.8}Ir_{0.2}O_6$. The low pressure monoclinic and high pressure tetragonal structures co-exist between 0.22 and 0.9 GPa. (b) Pressure dependence of the volume for $Ba_2PrRu_{0.8}Ir_{0.2}O_6$. The low pressure monoclinic and high pressure tetragonal structures co-exist between 0.22 and 0.9 GPa.

Table 2. Structural parameters for $Ba_2PrRu_{0.8}Ir_{0.2}O_6$ refined using powder synchrotron diffraction data collected at 1.82 GPa. $a = 5.9166(4)$ Å, $c = 8.365(1)$ Å; R_p 12.9, R_{wp} 14.7, R_{exp} 13.1, R_{Bragg} 10.3.

Atom	x	y	z	B_{iso}
Ba	0	0.5	0.25	4.2(1)
Ru	0	0	0	0.3(1)
Ir	0	0	0	0.3(1)
Pr	0	0	0.5	4.1(2)
O1	0	0	0.237(21)	2
O2	0.231(14)	0.756(12)	0	2

The variations in the refined lattice parameters and cell volumes as a function of pressure are illustrated in figure 3. The cell volumes of the low pressure monoclinic structure are clearly larger that those of the high pressure tetragonal form. This is similar to the variations observed in the series $Ba_2PrRu_{1-x}Ir_xO_6$ first described by Wakeshima *et al* [23]. The composition induced monoclinic to tetragonal transition is apparently first order and both cells co-exist [20, 23]. At those compositions where both cells co-exist the tetragonal cell has a smaller volume than the corresponding monoclinic cell. These authors [23] noted that the decrease in ionic radii for Pr^{3+} to Pr^{4+} (0.14 Å) is much larger than the rate of increase for M^{5+} (M = Ru, Ir) to M^{4+} (0.055 Å) [23, 24] and proposed that the transition to the smaller cell was a result of a valence transition of the type $Ba_2Pr^{3+}M^{5+}O_6$ to $Ba_2Pr^{4+}M^{4+}O_6$. Such a transition is expected to result in a contraction in the cell volume, since the volume of the PrO_6 octahedron should decrease much more rapidly than the increase in the volume of the MO_6 octahedron. Examination of the volumes of the PrO_6 and MO_6 octahedra in the high and low-pressure phases demonstrate this to be the case, with the volumes for the PrO_6 octahedra decreasing from 43.2 Å^3 (determined from the neutron diffraction pattern) to 38.6 Å^3 at 5.89 GPa (synchrotron diffraction data) as the pressure is increased, whereas that of the MO_6 octahedra remains essentially constant over the same pressure range, 32.4–33.0 Å^3. It is apparent that the Pr valence transition can be driven either by altering the Ru:Ir composition of the double perovskite or increasing the pressure.

The bulk modulus of B_0 of 139(10) GPa obtained by fitting a second-order Birch–Murnagham [25] equation of state with V_0 of 148.8(2) Å^2 and $K' = 4$ (by definition) to the pressure dependence of the reduced unit cell volume for the tetragonal phase is comparable to that found for $LaCoO_3$ (150(2) GPa) [26]. As noted by Vogt and co-workers [26] this value for $LaCoO_3$ is unusually low for a perovskite-type oxide, comparable perovskites $LaAlO_3$ [27] and $PrAlO_3$ [28] have values of 190(5) and 205(8) GPa, respectively, and is indicative of an unusually large volume compressibility. In $LaCoO_3$ it is apparently associated with the spin state change [26], whilst in the present case it is associated with the valence state change.

Following Teraoka *et al* [29] we have estimated the fitness factor, Ω, for the two valence states where $\Omega = \frac{\sqrt{2}r_A}{(r_B+r_O)}$, where r_A is the radii of the A-type cation, r_B the average radii of the two B-type cations and r_O the radii of the oxygen anion. We find the fitness factor for the Pr^{4+}/M^{4+} state $\Omega = 0.974$ is higher than that for the Pr^{3+}/M^{5+} state $\Omega = 0.957$. Teraoka *et al* [29] proposed that the fitness factor is a more sensitive measure of the tendency for double perovskites to adopt a distorted structure than the more usual tolerance factor. They concluded that higher values of Ω favour higher symmetry structures. The conclusion that the high-pressure tetragonal structure is the Pr^{4+}/M^{4+} state is consistent with this analysis. The finite width of the first order phase transition possibly results from the fact that each fluctuating valence ion has a somewhat different local environment due to the random Pr^{3+}, Pr^{4+} distribution as well as due to imperfections (distortions imperfections, etc) in the lattice.

In summary we have shown that the representative member of the Ba_2PrRuO_6–Ba_2PrIrO_6 solid solutions $Ba_2PrRu_{0.8}Ir_{0.2}O_6$ undergoes a pressure induced first-order phase transition near 0.5 GPa. The increase in pressure results both in a valence and structural phase transition. We note that although a continuous transition between the $P2_1/n$ and $P4/mnc$ structures is allowed, our experience with simple ABX_3 perovskites demonstrates that, in the absence of electronic or other effects, lower symmetry compounds are favoured by high pressures but destabilized by high temperatures. The precise temperature and pressure needed to observe such transitions are obviously dependent on the tolerance factor based on the size of the two cations. In the present case we would anticipate that the monoclinic structure would be favoured at higher pressures if the valence of the metal cations, and hence tolerance factor, were to remain the same.

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