Structural and unique magnetic properties of $PrBa_2Fe_3O_8$

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Tetragonal $PrBa_2Fe_3O_8$ exhibits a unique magnetic behavior and behaves differently from both $PrBa_2Cu_3O_7$ and all $RBa_2Fe_3O_8$ materials. Magnetic-susceptibility study reveals two anomalies at 23 and 55 K which are sensitive to oxygen concentration, but no specific heat anomaly was observed at either temperature. Mössbauer studies reveal two inequivalent iron sites, which order antiferromagnetically at ≈230 K, in contrast to 670 K in $RBa_2Fe_3O_8$. X-ray absorption spectra indicate that Pr is trivalent. In contrast to $PrBa_2Cu_3O_7$ [$T_N(\mathrm{Pr})=17$ K] Pr in $PrBa_2Fe_3O_8$ does not order magnetically. The anomalies at 23 and 55 K are probably related to spin reorientation of Fe moments. [S0163-1829(96)05837-7]

Complete replacement of Cu^{2+} by Fe^{3+} in $RBa_2Cu_3O_7$ (RBCO) (R=rare earth), leading to $RBa_2Fe_3O_8$ (RBFO), has been reported recently.[1–3] The tetragonal structure of $YBa_2Fe_3O_8$ (YBFO) was studied by neutron diffraction.[1] The space group is $P4/mmm$, and the configuration of the atoms in the unit cell are similar to those of RBCO. In YBFO, the Fe(2) layers have fivefold oxygen coordination and Fe in the Fe(1) site is in a distorted octahedral oxygen environment. dc magnetic susceptibility and Mössbauer-spectroscopy (MS) measurements on RBFO (R=Y, Eu, Gd and Er) show two different subspectra for the Fe(1) and Fe(2) sites which are antiferromagnetically (AFM) ordered, at $T_N \approx 670$ K, regardless of R.[2,3] $PrBa_2Cu_3O_7$ ($PrBCO_7$) is an AFM insulator with a high $T_N(\mathrm{Pr})=17$ K.[4] T_N drops to 10 K in tetragonal $PrBCO_6$.[5] The preferable model for the absence of superconductivity (SC) in $PrBCO_7$ and for the appearance of a high $T_N(\mathrm{Pr})$ assumes that Pr is primarily trivalent, and there is a strong hybridization of the Pr-$4f$ ground states with the Cu-O valence bands.[6] Due to the loosely bound electrons, this hybridization produces the destruction of SC by a pair-breaking mechanism and generates large AFM exchange interactions rather than hole filling. In addition, using the MS technique, we have shown that the Cu(2)-O_2 layers are AFM ordered at 325 and 350 K for $PrBCO_7$ and $PrBCO_6$, respectively.[4] In this paper, we report the magnetic properties of the tetragonal $PrBa_2Fe_3O_8$ (PrBFO) which are differently from both RBFO and $PrBCO_7$. Magnetic susceptibility and MS reveal that both Fe sites are AFM ordered at $T_N \sim 230$ K. Specific-heat measurements provide no indication for magnetic ordering of the Pr sublattice, and the electronic coefficient $\gamma^* = 10$ mJ/mol K^2 obtained is substantially lower than $\gamma = 200$ mJ/mol K^2 found in $PrBCO_7$.[7] X-ray absorption near-edge study (XANES) of Pr-L_{II} shows that Pr is trivalent, in contrast to $PrBCO_7$ where the hybridization leads to a weak Pr-$4f^1$ admixture in the final state.[8]

$PrBa_2Fe_3O_8$ samples were prepared by a solid state reaction.[2] The constituents were preheated under oxygen at 1000 °C for 1 day, and then reground and sintered at 1200 °C for 72 h under oxygen for PrBFO, or at 1125 °C for 96 h (Ref. 9) for PrBFO(AW). Powder x-ray diffraction (XRD) measurements (Fig. 1) indicate that PrBFO is nearly single phase (~98%), whereas the PrBFO(AW) contains about 8% of the cubic $BaFeO_x$ material, with a ~4.11 Å. dc magnetic measurements in the range of 2–320 K were performed in a commercial superconducting quantum interference device magnetometer. ^{57}Fe MS studies were carried out using a conventional constant acceleration spectrometer, with a 50 mCi ^{57}Co:Rh source. Specific heat measurements were performed, at $H=0$ and 9 T, in the range 1.5–100 K, in an automated adiabatic calorimeter employing the Nernst step

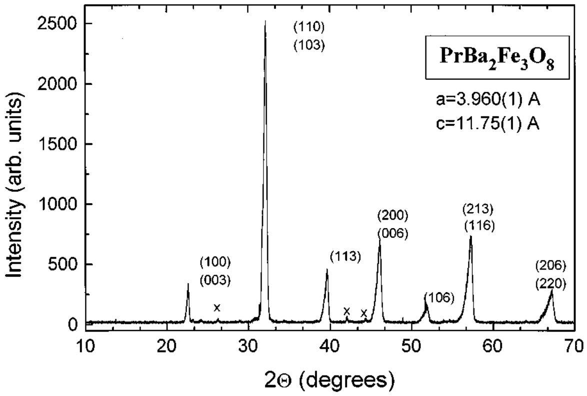

FIG. 1. XRD pattern of the tetragonal $PrBa_2Fe_3O_8$. The extra peaks are marked by (×).

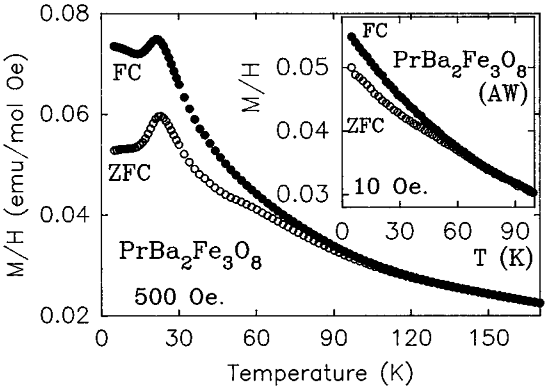

FIG. 2. Temperature dependence of ZFC and FC magnetization for $PrBa_2Fe_3O_8$ measured at 500 Oe and for $PrBa_2Fe_3O_8$(AW) measured at 10 Oe in the inset.

heating method. The XANES measurements were performed at the EXAFS-II beam line of HASYLAB/DESY (Hamburg).

XRD studies show that both compounds are tetragonal with the space-group $P4/mmm$. Figure 1 shows the pattern of PrBFO. For PrBFO the lattice parameters are $a=3.960(1)$ and $c=11.75(1)$ Å, and for PrBFO(AW) $a=3.955(1)$ and $c=11.82(1)$ Å.[10] The a of PrBFO(AW) differs slightly from that of PrBFO, while the c lattice parameter increases by about 0.7%. The atomic positions determined by Rietveld analysis are in excellent agreement with data published for YBFO.[1] In PrBFO, the apical O(1) moves away from its original position in YBCO toward the Fe(2) layers by ~0.4 Å. Determination of the oxygen content in these materials is difficult, and it is proposed that the different sintering temperature causes a small difference in oxygen concentrations in the two materials.

Zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility measurements $[\chi(T)=M/H]$ of PrBFO were performed at 5, 500, and 5000 Oe. The $\chi(T)$ curves for all applied fields exhibit basically the same feature. Figure 2 shows the typical magnetic behavior of $\chi(T)$ obtained at 500 Oe. Three distinct anomalies are readily observed, of which two are field independent: (1) the peak in both branches, around 22–23 K, (2) a small deflection around 55 K in the ZFC branch, and (3) the irreversibility between the ZFC and FC branches. The irreversibility temperature (T_{irr}), defined as the temperature in which the difference between the branches exceeds $\Delta\chi=1\times10^{-4}$ emu/mol Oe, is field dependent. As H is increased from 5 to 500 and to 5000 Oe, T_{irr} is shifted from 144(2) to 130(2) and to 82(2) K, respectively. No other anomalies were observed at higher temperatures. The isothermal magnetization at 4.5 and 40 K up to 5 T are linear and no hysteresis loops are observed when the field is decreased, suggesting an AFM behavior for PrBFO. The anomalies are sensitive to oxygen concentration. For PrBFO(AW), with a different oxygen concentration, the ZFC and FC susceptibility presented in Fig. 2 (inset) indicate clearly that the peak at 23 K is absent, and the deflection in the ZFC branch and T_{irr} are shifted to ~40 and to 78(2) K, respectively. The Pr sublattice does not order magnetically down to 1.5 K (see below), therefore, all magnetic anomalies in Fig. 2 are related to the AFM alignment of the Fe sublattices. T_N (Fe) in PrBFO is *not* at T_{irr}. The $\chi(T)$ curves do not lend themselves to an easy determination of T_N(Fe). Using the MS technique, we find T_N(Fe)~230 K, a value which is much lower than T_N(Fe)=670 K found in *R*BFO compounds.[2,3] The weak ferromagnetic component at T_{irr} arises as a result of an antisymmetric exchange coupling of the Dzyaloshinski-Moriya (DM) type between neighboring Fe moments induced by a local distortion that breaks the tetragonal symmetry of the Fe-O planes. Due to this DM interaction, the field causes the spins to cant slightly out of their original direction and to align a component of the moments with the direction of the H. The dependence of T_{irr} on H is easily understood by recognizing this as a typical characteristic of weak ferromagnetic behavior.

Above T_N(Fe)=230 K, $\chi(T)$ can be well described by the Curie-Weiss (CW) law: $\chi=\chi_0+C/(T-\theta)$, where χ_0 is the temperature independent part of χ, C is the molar Curie constant, and θ is the CW temperature. The fit at $240<T<330$ yields $\chi_0=4.3\times10^{-3}$, $C=3.43$ emu/mol Oe, and $\theta=23.1$ K. Assuming an effective moment $P_{\text{eff}}=3.58\ \mu_B$ for Pr^{3+} (according to Hund's rule), an average $P_{\text{eff}}=2.21\ \mu_B$ for Fe is extracted. It is possible that due to influence of crystal field (CF) effects, P_{eff} for Pr^{3+} is lower, and the average P_{eff} for Fe is higher.

In Fig. 3 the ^{57}Fe MS spectra of PrBFO below and above T_N are presented. All spectra exhibit a superposition of two subspectra with relative intensity of 2:1 which are related to Fe(2) and Fe(1) sites. The spectrum at 240 K shows the presence of about 8% of a magnetic impurity phase (probably $BaFeO_z$), and the fit made on all spectra takes into account this contribution. The spectra at various temperatures obtained for the PrBFO(AW) sample are (within the limit of uncertainty) similar to those of PrBFO. The spectrum at 330 K is composed of two doublets, which are identified by their hyperfine parameters: the isomer shift (IS) relative to Fe metal, and quadrupole splitting ($\Delta=\frac{1}{2}eqQ$) values, with a common line width of 0.42(2) mm/s. Doublet *A* accounts for 61% of the spectral area, with IS=0.26(1) and $\Delta=0.60(2)$ mm/s, and is attributed to a pyramidal configuration of the Fe(2) sites. Doublet *B* (31%) with IS=0.24(1) and $\Delta=1.03$ mm/s is attributed to the distorted octahedral configuration of the Fe(1) site. Qualitative first-nearest-neighbor point-charge calculations of the electric-field gradients for the two sites confirm this interpretation.

At low temperatures all spectra display magnetic hyperfine splitting which is a clear evidence for long-range magnetic ordering. The interpretation of the spectra was made to be consistent with the site assignment obtained at 330 K. At 4.1 K (Fig. 3), the well defined sextet [62 (2)%] which corresponds to doublet *A* indicates that the Fe(2) ions are equivalent with respect to their oxygen environment. The fitting parameters are IS=0.47(1) and linewidth=0.44(1) mm/s, magnetic hyperfine field $H_{\text{eff}}=463(3)$ kOe, and an effective quadrupole splitting $\Delta_{\text{eff}}=-0.01(1)$ mm/s. This H_{eff} is lower than 530 kOe at 4.1 K obtained for the Fe(2) site in YBFO.[2] For the minor broad sextet (31%), which is attributed to the Fe(1) site, IS=0.27(1) and $\Delta_{\text{eff}}=0.03(2)$ mm/s, and the fit yields a distribution of H_{eff} with an average value of $H_{\text{eff}}=269(10)$ kOe. Due to the low Δ_{eff} value, this distribution is needed only for H_{eff}. This broadening probably arises from the fact that the oxygen content in PrBFO is very

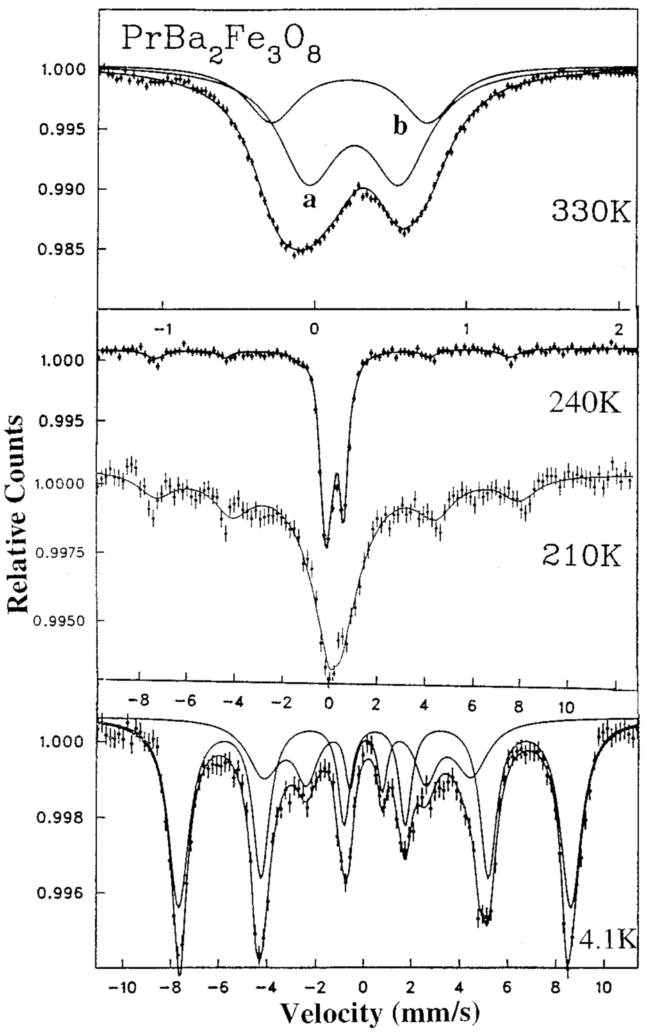

FIG. 3. Mössbauer spectra of PrBa$_2$Fe$_3$O$_8$ measured at various temperatures. Note (a) the magnetic impurity sextet at 240 K and (b) the extended scale of the spectrum at 330 K.

close to eight, and the Fe(1) site misses oxygen as first-nearest neighbors. Using the relation $\Delta_{\mathrm{eff}}=\Delta/2(3\cos^2\Theta-1)$, we obtained for both sites the magnetic hyperfine field orientation $\Theta=0°$ indicating that the Fe magnetic moments lie along the *c* axis. The spectrum also containes a third sextet [7(2)%] which belongs to an extra phase (not shown) with hyperfine parameters: IS=0.38, $\Delta_{\mathrm{eff}}=0.26$ mm/s, and $H_{\mathrm{eff}}=500$ kOe. These values vary very little with temperature.

As the temperature is raised, the magnetic splittings decrease and disappear completely above $T_N=230$ K. The H_{eff} values obtained at 90, 120, and 150 K are 453(3), 455(5), and 424(3) kOe for the major sextet, and 226(5), 222(5), and 163(5) kOe for the minor one. At higher temperatures, due to a distribution of T_N, resulting from inhomogeneity in the local environment of Fe throughout the Fe(1) site, a paramagnetic doublet and a distribution in H_{eff} of both sites had to be assumed. At 210 K (Fig. 3), 64% of the spectral area is still magnetically split with an average value of $H_{\mathrm{eff}}=24$ kOe. For the sake of clarity, the subspectra are not shown. At 240 K, no magnetic splitting is observed (except for the impurity phase) and the spectrum is similar to that obtained at 300 and 330 K. Regardless of the model used to fit the spectrum at 210 K, we may say with high confidence that in PrBFO [as well as in PrBFO(AW)], both Fe sites are magnetically ordered with the same $T_N\approx 230(10)$ K.

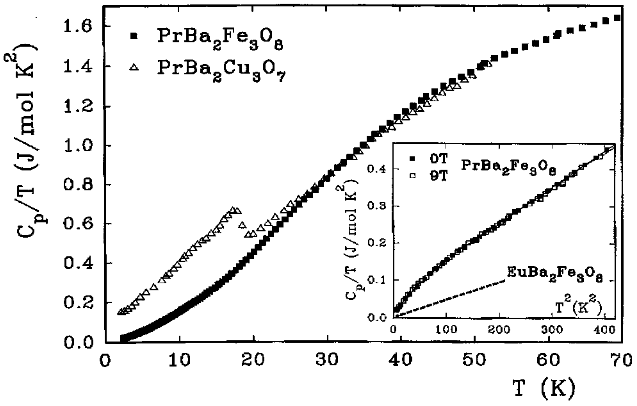

FIG. 4. Temperature variation of the specific-heat curves for PrBa$_2$Fe$_3$O$_8$ and PrBa$_2$Cu$_3$O$_7$ measured at $H=0$. The inset shows the $C_p/(T)$ versus T^2 curves of PrBa$_2$Fe$_3$O$_8$ at $H=0$ and 9 T and of EuBFO at $H=0$ T.

Specific heat (C_p) measurements performed at $H=0$ and 9 T are displayed in Fig. 4. In the vicinity of the anomalies, at about 23 and 55 K (Fig. 2), *no* features indicative of magnetic origin can be observed. For a comparison, we include the data for PrBCO$_7$, in which a pronounced anomaly occurs at $T_N(\mathrm{Pr})=17$ K.[6,7] Both curves merge at about 30 K indicating a rather similar lattice contribution to C_p at least at elevated temperatures. The influence of H is negligible in the whole temperature range and in particular in the more sensitive region at low temperatures (Fig. 4 inset), where the C_p/T versus T^2 curves are plotted. Estimation of linear electronic γ^* and the lattice contributions to C_p is difficult, because the CF contribution to C_p is rather ambiguous. We include in Fig. 4 (inset) the low temperature data of EuBFO,[2] which demonstrate the enhancement of C_p of PrBFO, presumably due to the population of low lying crystal field levels. Nevertheless, a tentative low temperature extrapolation yields $\gamma^*\approx 10(2)$ mJ/mol K^2 which is of the same magnitude as that of YBFO but still larger than 2.5 mJ/mol K^2 obtained for EuBFO.[2] Because of CF contribution to $C_p(T)$ the estimate of the Debye temperature (250 K) is unreasonably small as compared to 400 K deduced in *R*BFO (*R*=Y, Eu).

The local electronic structure of the Pr ions in PrBFO was studied by XANES at the Pr-L_{II} thresholds, and we also compare the results obtained for PrBCO$_x$ (x=6,7) compounds. The Pr=L_{III} and Pr=L_{I} edges were also measured, but only the Pr=L_{II} is presented (Fig. 5) since the Pr=L_{III} is somewhat disturbed by the Ba-L_{I} threshold and no more information is observed in Pr=L_{I} edge. Detailed comparison reveals that all spectra exhibit a dominant white line position at 6440 eV, typical for Pr^{3+}. Only the PrBCO$_7$ sample exhibits additional structure (~15%) at the high energy side, corresponding to an admixture of Pr^{4+} in the final state.[8] This admixture is absent in both PrBFO and PrBCO$_6$ compounds, and the Pr ions are in trivalent state.

The susceptibility measurements of PrBFO can be compared with that of PrBFO(AW) despite the fact that the two samples differ slightly in their oxygen content. The specific anomalies observed in the $\chi(T)$ curves of PrBFO (Fig. 2)

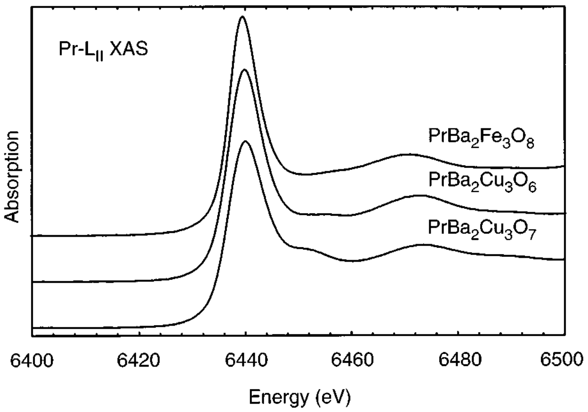

FIG. 5. Pr-$L_{\rm II}$ XANES spectra of PrBa$_2$Fe$_3$O$_8$, PrBa$_2$Cu$_3$O$_7$, and PrBa$_2$Cu$_3$O$_6$ measured at 300 K. Note the similarity between PrBa$_2$Fe$_3$O$_8$ and PrBa$_2$Cu$_3$O$_6$ spectra.

were not observed in PrBCO$_x$ or in other *R*BFO compounds. The peak at 23 K is not observed in PrBFO(AW) indicating that the oxygen concentration has a drastic effect on its appearance. The interpretation of this peak is not straightforward, and we suggest two scenarios that could lead to this peak. We may assume that in PrBFO, Pr orders AFM near 23 K, analogous to Pr ordering in PrBCO$_7$ at 17 K, and PrBa$_2$NbCu$_2$O$_8$ at ~12 K.[10] Supporting evidence for this determination is that the position of this peak is independent on H. But the absence of an anomaly in the C_p curve (Fig. 4) and the absence of this peak in $\chi(T)$ of PrBFO(AW) sample cast some doubt on this interpretation, because a sizable magnetic entropy $S=R\ln 3=9.2$ J/mol K is normally expected for the ordering of Pr^{3+} ions in similar compounds.[6] One approach to reconcile this difficulty is to dope PrBFO with ^{155}Gd and through MS to reveal the magnetic properties of Pr as reported previously for PrBCO$_7$.[5] However, we believe that such measurements will not shed light on this problem, because our MS performed on pure GdBFO (Ref. 3) at various temperatures yield complicated spectra and their interpretation is not yet conclusive.

A more preferable second interpretation can be made that invokes an analogy to Pr$_2$CuO$_4$ and Pr$_{1.5}$Ce$_{0.5}$NbSr$_2$Cu$_2$O$_{10}$ (Ref. 11) or to the PrBa$_{2-x}$Sr$_x$NbCu$_2$O$_8$ system,[12] where clear anomalies are observed in $\chi(T)$ curves, but no indication for AFM order of the Pr sublattice can be deducted from C_p measurements. We tend to believe that the peak at 23 K (Fig. 2) is *not* associated with AFM order of Pr. The Fe moments in PrBFO are AFM ordered below 230 K and lie parallel to the c axis. At $T_{\rm irr}$, due to the DM interaction mentioned above, H aligns a component of the moment with the direction of the field. At low temperatures the Fe-Fe and/or Pr-Fe interactions begin to dominate, leading to reorientation of the Fe moments and the anomalies in $\chi(T)$ are observed. This scenario is supported by (1) the absence of this peak in the PrBFO(AW) sample; (2) the lack of deflection in the FC branch for both materials, where the aligned component of Fe moments along the field direction inhibits the reorientation; (3) these reorientations lead to a negligibly small latent heat which cannot be observed in the C_p curve; and (4) the low linear terms ($\gamma^*=10$ mJ/mol K^2) obtained for PrBFO as compared to $\gamma^*=200$ mJ/mol K^2 observed in PrBCO$_7$.[7] It is reasonable to imply that there is a connection between the AFM ordering of PrBCO$_7$ and its heavy-fermion-like behavior.

The absence of magnetic ordering of Pr sublattice in PrBFO may be explained as follows. What sets apart the Pr in PrBCO$_7$ from other R ions in RBCO is the hybridization of the localized Pr $4f$ and CuO$_2$ valence-band states. It is proposed[13] that the large AFM exchange interactions in PrBCO$_7$ are generated by this hybridization. It is speculated that such a hybridization does not exist in PrBFO because of (1) the pure trivalent state of Pr (Fig. 5) and (2) due to the higher Fe^{3+} valence, the nature of the O $2p$ states in the FeO$_2$ planes are completely different from those of the CuO$_2$ layers, and the loose oxygen electrons are now more tightly bound. The intriguing question arises as to why T_N(Fe) in PrBFO remains as low as 230 K. On one hand, in PrBCO$_x$ the CuO$_2$ planes order at T_N~325 and 350 K for $x=7$ and 6, respectively; thus T_N(Cu) varies little with oxygen concentration. On the other hand, T_N(Fe)=670 K was obtained for *R*BFO materials, and our Rietveld analysis indicates that the Fe-O(1) and Fe(1)-Fe(2) distances in PrBFO and YBFO are similar.

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