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Structure and Mössbauer Studies of F−O Ordering in Antiferromagnetic Perovskite $PbFeO_2F$

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The synthesis of $PbFeO_2F$ is achieved using a solid-state reaction under high pressure. This perovskite crystallizes in SG $Pm\bar{3}m$ (No. 221) with $a = 0.39991$ (1) nm. The Rietveld refinement using powder X-ray diffraction data shows that the mean structure of this compound can be characterized as follows: (1) the Pb ion statically shifts from the 1*a* Wyckoff position in the twelve $\langle 110 \rangle$ direction toward anions (O, F), and (2) the Fe ion is located in a single crystallographic site. In contrast, hyperfine data estimated from Mössbauer spectra at different temperatures suggest the existence of different Fe sites, and the isomer shift is consistent with the presence of high-spin (HS) Fe^{3+} ions located in FeO_4F_2 octahedral units, where anions are randomly distributed. Such a distribution thus favors two prevailing Fe sites, namely cis and trans. No evidence of O/F ordering in $PbFeO_2F$ was detected by electron diffraction experiments. Finally, in-field Mössbauer spectra unambiguously reveal that $PbFe_2OF$ behaves as an antiferromagnet, which is consistent with static magnetic measurements.

Introduction

Materials with both ferroelectric and magnetic properties have recently been of interest because their properties are expected to be coupled and tuned by external magnetic or electric fields (the so-called magnetoelectric effect). Among them, perovskite-type ferroelectric and magnetic compounds (ABX_3), which include a transition metal ion in the B-site, e.g., $BiFeO_3$, $BiMnO_3$, and their related compounds, have been investigated as candidate compounds.[1−3] Their ferroelectricities are induced by the $6s^2$ lone pair of the Bi^{3+} ion as A-site ions, as Pb^{2+} in a ferroelectric perovskite $PbTiO_3$. The entitled perovskite-type oxyfluoride $PbFeO_2F$ is therefore a potential hybrid material. As the first step in realizing the possibility suggested by $PbFeO_2F$, we investigated the structure and magnetic properties using X-ray diffraction, electron diffraction, and ^{57}Fe Mössbauer spectrometry.

Stabilization of perovskite-type oxyfluorides ($AB(O,F)_3$) has been demonstrated using high pressure by Demazeau et al.[4] ($TlTlOF_2$), Chamberland et al.[5] ($KTiO_2F$), and Troyanchuk et al.[6] ($PbFeO_2F$), although it is difficult to prepare the perovskite-type oxyfluorides under ambient pressure. Troyanchuk et al.[6] have successfully synthesized a cubic perovskite-type oxyfluoride $PbFeO_2F$ at 1000 °C under pressures as high as 5 GPa. In the perovskite-type oxyfluorides, the location of both fluorine and oxygen ions, which octahedrally coordinate B-site cations, remains an important question because their positions influence the electric and magnetic properties of these materials. We, however, encounter the difficulties in determining the ordering of O and F in oxyfluorides from X-ray and neutron diffraction experiments due to their similar scattering factors. Brink et al., however, have obtained the evidence of O/F ordering in FeOF and NbO_2F by electron diffraction.[7,8] The ^{57}Fe Mössbauer experiment for Fe-containing compounds is also a powerful technique for determining the distribution of O and F[9] as well as the magnetic properties. Indeed, the hyperfine parameters, particularly the isomer shift, are sensitive to the nature and number of F ligands. Troyanchuk et al.[6] have suggested the following from the Mössbauer and IR absorption spectra: (1) $PbFeO_2F$ is antiferromagnetic at room

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temperature; (2) there are two non-equivalent ferric iron sites, which can be ascribed to the two kinds of occupations of fluorine ions, *i.e.*, cis- and trans-type distribution in an FeO_4F_2 octahedron; and (3) there is the possibility of short-range ordering of O/F. Troyanchuk et al. have identified many important features regarding $PbFeO_2F$, as described above. Both a detailed structure analysis and Mössbauer experiments of $PbFeO_2F$ are, however, necessary to elucidate the relationship between the structure and the antiferromagnetic properties of $PbFeO_2F$.

We discuss herein the structure, including the location and ordering of O and F, and the antiferromagnetic interaction between Fe ions via anions, and their relationship based on data from X-ray diffraction and transmission electron microscopy (TEM) as well as the temperature-dependent and in-magnetic field Mössbauer spectra.

Experimental Procedure

The synthesis of perovskite $PbFeO_2F$ was carried out by a solid-state reaction under high pressure. The starting materials were PbO (3N), PbF_2 (4N), and Fe_2O_3 (3N). The mixture of starting materials was dried by evacuating at approximately 200 °C overnight prior to the reaction to prevent the influence of moisture in the air, as the reagent PbF_2 is slightly sensitive to moisture. This drying process is necessary to synthesize the single phase, and without it small amounts of impurities are observed. The stoichiometric mixture of the powders was sealed in a gold capsule (0.2 mm thick, 4 mm inner diameter, and 4 mm deep), which was placed in a NaCl sleeve. They were inserted into a pyrophyllite cube block ($15 \times 15 \times 15$ mm^3) with a cylindrical graphite heater. The mixture of powders was allowed to react in a TRY cubic multianvil-type high-pressure apparatus (NAMO 2001) at 6 GPa and 1173−1373 K for 30 min, and then was quenched down to room temperature. No weight loss was detected in the sample after the high pressure and heat treatment.

The phase identification and determination of lattice parameters for the sample were carried out by the powder X-ray diffraction method using a Rigaku RINT 2100 diffractometer (graphite-monochromatized Cu Kα). The crystal structure was refined using the Rietveld method with the RIETAN 2000 program.[10] The X-ray diffraction data for Rietveld analysis were collected in the range $2\theta = 20-120°$ at 0.02° intervals at room temperature. The valence was calculated from interatomic distances based on the concept of bond valence.[11,12]

The microstructure analysis of the sample was performed with a JEOL 2010 transmission electron microscope operating at 200 kV. The powder was crushed into small particles in an agate mortar and suspended in ethanol. A Cu grid with a holey carbon film was covered with one drop of the resulting suspension, leaving randomly oriented crystallites after drying. The grid was set in a side-entry, double-tilt specimen holder with the tilting limited to a maximum of ±30° in two directions. Selected-area electron diffraction (SAED) was performed.

The magnetization at 5 K was measured under a maximum magnetic field of 1 T using a SQUID magnetometer (Quantum Design MPMS system).

The transmission ^{57}Fe Mössbauer spectra of $PbFeO_2F$ were obtained by means of a standard constant acceleration spectrometer using a ^{57}Co source. The powdered samples were placed either in a bath cryostat for temperatures ranging from 4.2 to 300 K, or in a cryofurnace for measurements from 300 up to 363 K. A spectrum at 10 K was also recorded under an external magnetic field of 6 T applied parallel to the γ radiation. The Mössbauer spectra were least-squares fitted using the MOSFIT program[13] while the isomer shift values are quoted from that of α-Fe at 300 K.

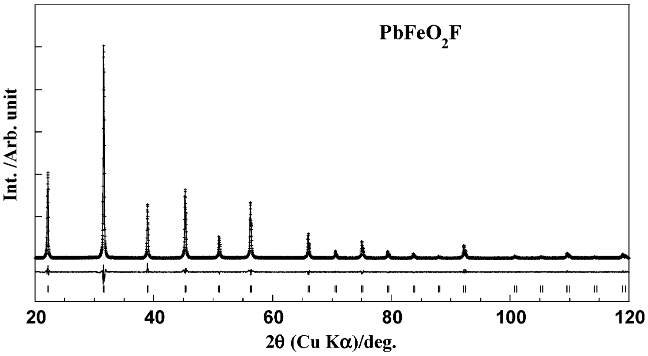

Figure 1. Observed (+) and calculated (solid line), powder X-ray diffraction patterns, difference (solid line on the bottom), and peak positions (|) of $PbFeO_2F$ at room temperature.

Results and Discussion

1. Structure. The observed powder X-ray diffraction pattern of $PbFeO_2F$ at room temperature is shown in Figure 1. The powder X-ray diffraction reveals that the compound has a simple cubic perovskite-type structure with space group $Pm\bar{3}m$, and the lattice parameter was determined to be $a = 0.39991 \pm 0.00001$ nm, the same as reported previously.[6] No additional superstructure peak associated with the atomic ordering and tilting of $Fe(O, F)_6$ octahedra was detected. In the Rietveld refinement, the atoms were first fixed at their special position, e.g. Pb was located at the special position 0, 0, 0 (Wyckoff notation 1*a*). The isotropic atomic displacement parameter of Pb was, then, rather large ($B_{Pb} = 2.64(2)$ Å^2). The calculated bond valence is +1.62 for Pb. These results indicate that Pb ions shift from the ideal 1*a* position and are located in several equivalent positions. Next, we therefore used the models in which Pb atoms shift from the ideal A-site position in the six $\langle 100 \rangle$, twelve $\langle 110 \rangle$, and eight $\langle 111 \rangle$ directions in the refinements. When the Pb atom shifts in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, the shifts are very small and are accompanied by large errors, and the B_{Pb} remains large ($B_{Pb} = 2.6-2.7$ Å^2). In contrast, when the Pb atom shifts in the twelve $\langle 110 \rangle$ direction which is one toward the anions (O and F), B_{Pb} is effectively decreased to 0.28 (21) Å^2 and the reliability factors are slightly decreased: R_{wp} from 9.16 to 9.11% and R_I from 4.46 to 4.29%. For these reasons, this $\langle 110 \rangle$ model was adopted. Though we also tried the disordered splitting models for Fe or O ions, they were not successful. The calculated powder X-ray diffraction pattern of $PbFeO_2F$ is shown in Figure 1. The crystal data from the Rietveld analysis are listed in Tables 1 and 2. The calculated bond valence sums (BV) for constituent ions are listed in Table 3. The value for Fe (BV = +2.91) is relatively consistent with that of the ferric state. In contrast, the value

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Table 1. Structural Parameters in $PbFeO_2F$ at Room Temperature[a]

	site	*g*	*x*	*y*	*z*	*B*/Å^2
Pb	12*i*	1/12	0	0.050(2)	0.050(2)(=*y*)	0.28(21)
Fe	1*b*	1	1/2	1/2	1/2	1.20(5)
O	3*c*	2/3	0	1/2	1/2	0.59(8)
F	3*c*	1/3	0	1/2	1/2	0.59(8)

[a] Space group: $Pm\bar{3}m$ (No. 221), $a = 0.39991$ (1) nm. $R_{wp} = 9.11\%$, $R_p = 7.03\%$, $Re = 5.33\%$, $S = 1.71$, $R_I = 4.29\%$, $R_F = 2.85\%$. O and F are supposed to occupy the 3*c* site statistically.

Table 2. Selected Interatomic Distances (nm) in $PbFeO_2F$ at Room Temperature

Pb−(O,F)		Fe−(O, F)	
0.2544(11)	×1	0.19996(1)	×6
0.2697(5)	×4		
0.2842(1)	×2		
0.2980(6)	×4		
0.3112(11)	×1		

Table 3. Calculated Bond Valence Sums for Constituent Ions in $PbFeO_2F$

		bond valence sum[a]			
atom M	valence assumed	BV (M−O)	BV (M−F)	BV M−($^2/_3$O,$^1/_3$F)	deviation from assumed valence
Pb	2	1.86	1.49	1.74	−13%
Fe	3	3.13	2.46	2.91	−3%
O	−2			−1.66	−16%
F	−1			−1.32	+32%

[a] BV(M−O) and BV(M−F) represent the bond valence sums when Pb and Fe ions are coordinated by only O ions and F ions, respectively. BV(M−($^2/_3$O,$^1/_3$F)) represents the bond valence sum when Pb and Fe ions are statistically coordinated by O and F ions, respectively.

for Pb (BV = +1.74) is underbonded, though the value approaches +2. In addition, it appears that O (BV = −1.66) is underbonded, while F (BV = −1.32) is overbonded. Here, the BVs were calculated assuming that the cations (Pb and Fe) are statistically coordinated by anions (O and F), i.e., the ratio of coordination numbers of O and F is 2:1. These deviations of BV for anions can be attributed primarily to the interatomic distances between the Pb and anions (O, F) since the bond valence sum of the Fe ion is consistent. The Rietveld refinement using powder X-ray diffraction data reveals that the mean structure of this compound is characterized by Pb ions statically shifted in the twelve ⟨110⟩ direction toward the anions (O, F) and Fe ions at a single crystallographic site. On the other hand, the BV results imply that the actual interatomic distances between the Pb and O ions are shorter, while those between the Pb and F ions are longer than the calculated mean interatomic distances. These findings may indicate the possibility of short-range O/F ordering associated with the relaxation of Pb.

The electron diffraction patterns were recorded from some crystallites, and the reconstitution of their reciprocal space always leads to a cubic cell with the parameter $a \approx 0.40$ nm. Typical SAED patterns of different orientations are shown in Figure 2. In the electron diffraction patterns, no peculiar spots and streaks corresponding to O/F ordering or tilting of the Fe(O, F)$_6$ octahedron were observed. These results are in agreement with the results of the X-ray diffraction study. Consequently, no evidence of O/F ordering in $PbFeO_2F$ was detected by TEM experiment in contrast with the situations observed in NbO_2F [7] and FeOF,[8] where structured diffuse scattering arises as a consequence of local O/F ordering.

2. Mössbauer Study. Mössbauer spectra of $PbFeO_2F$ at selected temperatures are shown in Figure 3. All spectra consist of asymmetrical sextets composed of broadened lines, which is in qualitative agreement with that reported by Troyanchuk et al.[6] First, the asymmetry prevents a description of the spectra by means of only a single component, which is not consistent with the presence of one single Fe site, as previously concluded. It is also important to emphasize that the asymmetry from the outermost lines differs above and below 180 K. Different fitting models can be proposed to well describe the hyperfine structure, whatever the temperature. But one can also consider rather narrow distributions of either isomer shifts and/or quadrupolar shifts, correlated with that of the hyperfine field, to describe the asymmetry of the spectra.

The refined values of corresponding hyperfine parameters listed in Table 4 result from a two-sextet fitting model with Lorentzian lines. These two magnetic components originate from cis- and trans-coordination, as suggested by Troyanchuk et al.[6] All the hyperfine parameters were assumed to be free at the beginning of the fitting procedure. Also, because of the lack of resolution of the hyperfine structure, some constraints, particularly on the absorption area, were then considered during the fitting procedure to get relatively temperature-independent proportions, except at the highest temperature, for which the lines are strongly broadened. The values of isomer shift of the two components are almost identical whatever the temperature. The mean values, which are independent of the fitting model, are close to those reported in perovskite-type orthoferrites $LnFeO_3$ (Ln: lanthanide).[14] In addition, these values are consistent with trivalent Fe^{3+} ions coordinated octahedrally in the high-spin state, typically those of FeO_4F_2, which are, indeed, intermediate between those of FeF_6 (0.46 mm/s at 300 K, 0.58 mm/s at 4 K for FeF_3[15]) and FeO_6 (0.37 mm/s at 295 K, 0.49 mm/s at 4 K for hematite α-Fe_2O_3[16]). Consequently, the broadening does originate from the distribution of F and O around Fe atoms, keeping in mind that the octahedral unit has to be FeO_4F_2 to achieve the local electric neutrality, leading thus to a single isomer shift value.

The quadrupolar interactions are responsible for the coordination symmetry of anions, O and F, since all iron ions are trivalent and have a 3d^5 electronic configuration in the high-spin state. The cis- and trans-coordination will give rise to different quadrupolar splittings, with the splitting for trans-coordination being theoretically twice that of cis-coordination in the MA_4B_2-type octahedron.[17] Only pure quadrupolar spectra might provide some information but the decomposition of the compound beyond 500 K prevents such high-temperature experiments. In addition, the quadrupolar shifts observed in addition to the dipolar magnetic interaction are too small and no distinct difference between two

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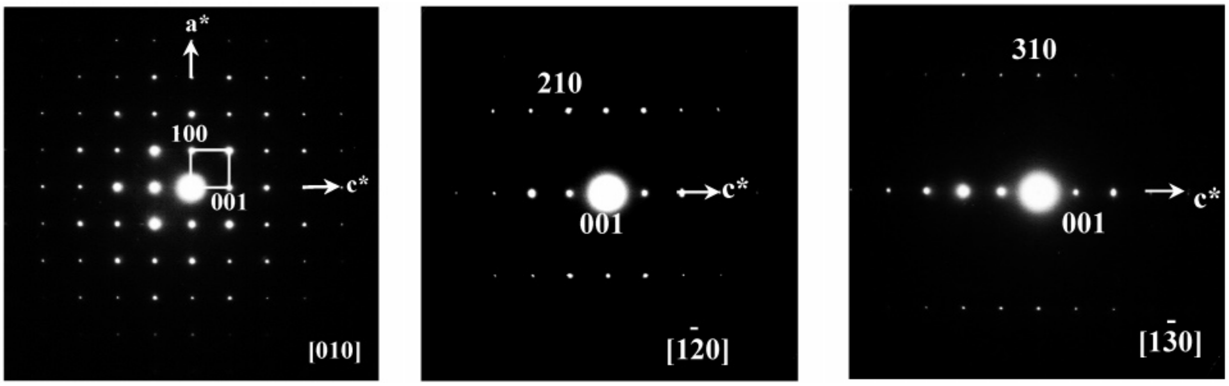

Figure 2. Typical SAED patterns of $PbFeO_2F$ with three different zone axis orientations ([010], [1$\bar{2}$0], and [1$\bar{3}$0]) showing neither additional reflections nor streaks.

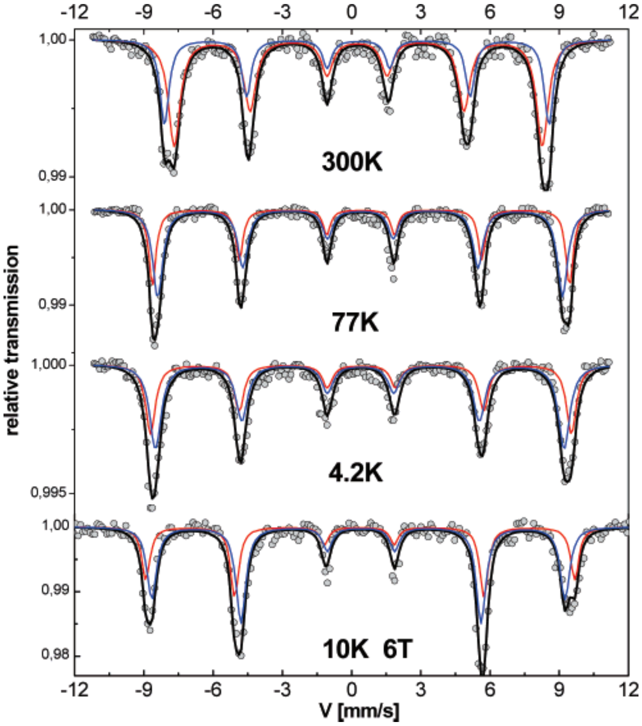

Figure 3. Mössbauer spectra recorded at given temperatures. The spectra are composed of two sextets with Lorentzian lines. These two magnetic components originate from cis- and trans-coordination of F.

components can be observed because the Fe (O, F) octahedron is not distorted, as revealed by X-ray diffraction. In such a way, the local structure induces distributions of quadrupolar electric interactions and of the hyperfine field through the distribution of the superexchange angle.

Table 4. Hyperfine Characteristics of Mössbauer Spectra in $PbFeO_2F$

T (K)	isomer shift[a] (mm/s) ±.01	line width (mm/s) ±.02	quadrupolar shift (mm/s) ±.01	hyperfine field (T) ±.5	proportion % ±2
363	0.41	0.82	−0.07	43.8	53
	0.37	0.57	−0.10	46.7	47
300	0.43	0.63	−0.08	49.3	62
	0.42	0.45	0.05	51.5	38
180	0.51	0.68	−0.08	53.2	61
	0.49	0.49	0.06	54.6	39
77	0.54	0.53	−0.01	54.2	62
	0.56	0.39	0.02	55.9	38
4.2	0.54	0.60	−0.03	54.7	59
	0.57	0.52	−0.02	56.4	41
10 (6 T)[b]	0.55	0.60	−0.11	54.9	61
	0.56	0.54	0.04	56.8	39

[a] Relative to α-Fe metal. [b] Estimated from the effective field obtained from a 6 T applied field experiment at 10 K.

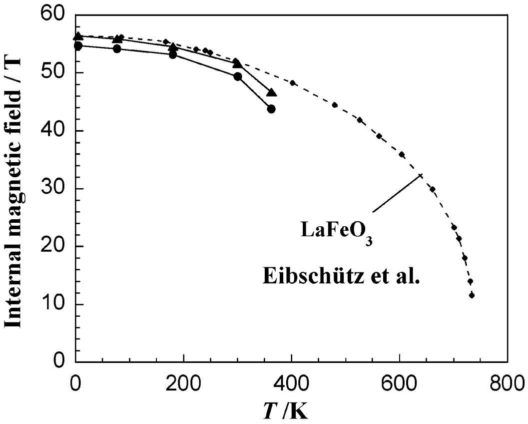

Figure 4. Temperature dependence of the hyperfine field at the iron site in $PbFeO_2F$ compared to that of $LaFeO_3$ (ref 14).

The temperature dependence of hyperfine fields is compared to that of $LaFeO_3$[14] in Figure 4, and related data are provided in Table 2. Slight differences between the Fe sites are observed, while a strong similarity at low temperature with $LaFeO_3$ results from the competition between the following effects: (1) the increase in the superexchange interaction in response to the larger bond angle of Fe−(O, F)−Fe in comparison with those of Fe−O−Fe, 155.7 and 157.3°, in $LaFeO_3$[18] and (2) the decrease in the superexchange interaction which is attributed to the decrease in covalency between Fe and anion by the substitution of F for O. The superexchange interaction between Fe ions in the arrangement −O−Fe−O− is larger than that between Fe ions in the arrangements O−Fe−F and F−Fe−F, resulting in a larger hyperfine field for trans-type coordination and a smaller one for cis-type coordination. Therefore, the component with higher proportion originates from cis-type coordination and that with lower proportion originates from trans-type coordination.

Figure 3 also shows the Mössbauer spectrum at 10 K under an external magnetic field of 6 T. As shown in Figure 3, the

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intermediate peaks corresponding to the nuclear transition from substates $m = {}^1/_2$ to ${}^1/_2$ and $-{}^1/_2$ to $-{}^1/_2$ show higher intensity than those observed on zero-magnetic field Mössbauer spectra, while the positions of the outermost lines remain quite unchanged. The intensity ratio of the six lines is close to 3:4:1:1:4:3, indicating that the angle between the γ-ray and the internal magnetic field at the nucleus is close to 90°. Thus, the effective field is oriented perpendicular to the external magnetic field and is rather similar to that of the hyperfine field. It can be concluded that the magnetic configuration behaves as a regular antiferromagnet. This result is in good agreement with the lack of spontaneous magnetization at 5 K. The internal magnetic field decreases with increasing temperature, as seen in Figure 4. The temperature dependence predicts that the Néel temperature would be above 500 K, though the sample would be decomposed around this temperature.[6]

The probabilities of cis- and trans-type coordination are estimated to be 0.8 and 0.2, respectively, if both 4O and 2F statistically coordinate each Fe ion. The proportion ratio for the two Mössbauer components is approximately 0.6:0.4, as seen in Table 4. This result implies that trans-type coordination preferably occurs in this compound, though medium- or long-range O/F ordering is not observed in this perovskite.

Conclusion

A cubic cell with twelve equivalent crystallographic Pb sites and a single crystallographic Fe site characterizes the mean structure of the present oxyfluoride perovskite, while the Mössbauer spectra suggest Fe sites with different atomic surroundings. The hyperfine characteristics are consistent with the presence of HS Fe^{3+} ions located in FeO_4F_2 octahedral units where O and F are randomly distributed, giving rise to cis- and trans-type coordinations. $PbFeO_2F$ behaves as an antiferromagnet, but its decomposition at approximately 500 K prevents us from estimating the Néel temperature. No apparent evidence of O/F ordering in $PbFeO_2F$ was detected in this study.

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