Crystal structure and vibrational properties of $RFe_3(BO_3)_4$ (R = Ce – Lu) ferroborate crystal: *ab initio* calculations

V.P. Petrov[1,*], V.A. Chernyshev[1], and A.E. Nikiforov[1]

[1]Ural Federal University, 620002 Ekaterinburg, Russia

Abstract. The *ab initio* calculations of the crystal structure and lattice dynamics of ferroborate crystal family $R Fe_3(BO_3)_4$ (R = Ce, Pm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), S.G. $R32$, has been carried out within the framework of the MO LCAO approach by using density functional theory and effective 4*f*-in-core pseudopotential for rare earth element. The fully optimized geometry as well as vibrational frequencies has been calculated.

We calculated the crystal structure of $RFe_3(BO_3)_4$ (S.G. R32), and afterward the phonon spectrum was calculated. The calculations were performed in the framework of the density functional theory by using hybrid functional B3LYP. The program CRYSTAL14 [1] intended for periodic calculations in the MO LCAO approach was used. ECP ("effective 4*f*-in-core pseudopotential") was used for the rare earth ions [2]. This approach has shown good results and the agreement with experiment for the crystals $RFe_3(BO_3)_4$ (R = Pr, Nd, Sm) [3]. In this work we carried out similar calculations for the remaining ions of the rare earth row. The results of calculations of the crystal structure are given in Table 1. Axis z is directed along C_3 and x along C_2. The crystal structure consist of a spiral chains of "octahedral" FeO_6 placed around the trigonal C_3 axis and straight chains of RO_6 prisms strung on the trigonal axis. The structure contains two types of BO_3 triangles also. One type is equilateral triangles BO_3 strung on the trigonal axis between RO_6 prisms; another type is isosceles triangles that are placed aside of the trigonal axis and connect chains RO_6 and FeO_6. The calculations predict that in the middle of the row (R=Dy, Ho) the isoscele triangle $B2O_3$ becomes almost equilateral. The lattice parameters a and c decrease in the row La-Lu that corresponds to the lanthanide contraction. The distorted octahedron FeO_6 in the end of the series (R=Lu) is closer to the ideal octahedron.

Table 1. Lattice parameters (a, c) and bond lengths (Å) of structure-forming units of $RFe_3(BO_3)_4$

R	a	c	RO_6 prism	FeO_6 "octahedron"			$B1O_3$ equilateral triangle	$B2O_3$ isosceles triangle	
Ce	9.6986	7.7512	2.467	1.972	2.064	2.091	1.388	1.371	1.386
Pm	9.6682	7.7026	2.431	1.980	2.055	2.077	1.385	1.373	1.383
Eu	9.6500	7.6778	2.410	1.984	2.050	2.070	1.383	1.374	1.380
Gd	9.6409	7.6674	2.401	1.986	2.048	2.066	1.382	1.374	1.379
Tb	9.6306	7.6551	2.389	1.989	2.045	2.063	1.381	1.375	1.378
Dy	9.6223	7.6454	2.380	1.991	2.043	2.060	1.380	1.376	1.377
Ho	9.6142	7.6361	2.371	1.993	2.041	2.056	1.379	1.376	1.377
Er	9.6059	7.6270	2.363	1.995	2.039	2.054	1.378	1.375	1.377

* Corresponding author: lancervlad@gmail.com

Tm	9.5985	7.6191	2.355	1.996	2.037	2.051	1.377	1.374	1.378
Yb	9.5908	7.6116	2.347	1.998	2.035	2.048	1.377	1.373	1.378
Lu	9.5843	7.6047	2.340	2.000	2.034	2.046	1.376	1.372	1.379

Table 2. Vibrational frequencies, cm^{-1} of $RFe_3(BO_3)_4$ (R = Ce–Lu).

Irrep.	Ce	Pm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
A_1	181	182	182	183	183	184	184	184	184	184	185
	291	299	302	305	307	309	312	314	316	318	319
	463	465	463	466	467	468	469	469	470	471	472
	644	648	649	649	650	651	652	652	652	653	653
	941	950	955	957	959	960	961	962	962	962	962
	990	989	988	988	987	988	988	989	991	992	993
	1202	1212	1219	1223	1227	1230	1234	1237	1241	1244	1247
A_2	34	43	46	50	53	55	59	60	62	67	65
	155	159	160	161	161	161	162	162	162	161	163
	191	195	193	194	193	191	190	187	185	183	181
	206	204	202	203	204	205	207	208	209	209	211
	258	258	256	257	256	256	255	255	255	252	254
	310	300	289	288	282	279	276	273	270	267	265
	337	339	341	341	343	344	345	347	348	352	350
	370	376	380	382	384	385	387	388	390	392	393
	620	621	621	621	622	622	622	623	623	623	623
	694	690	690	691	691	691	691	690	690	690	690
	755	751	749	747	746	745	744	743	743	759	741
	1268	1265	1262	1261	1258	1257	1256	1254	1253	1251	1250
E	86	87	87	87	87	87	87	87	87	87	88
	160	161	161	162	161	161	161	161	161	161	161
	192	196	198	199	200	201	203	204	204	205	206
	239	238	234	236	235	235	235	234	234	233	233
	265	269	269	271	271	272	272	272	272	272	272
	273	275	276	278	280	280	282	283	283	283	283
	316	316	316	317	317	317	317	318	318	318	319
	350	351	346	345	342	339	337	336	334	331	330
	363	366	368	371	372	374	375	377	378	379	380
	377	379	379	382	383	384	386	387	389	390	391
	430	431	432	433	434	435	437	438	439	440	441
	577	580	581	581	581	582	582	583	583	583	583
	619	623	625	626	627	628	630	631	632	633	634
	662	665	667	668	668	669	670	671	672	672	673
	754	751	752	752	752	752	752	753	753	753	753
	968	969	968	968	968	967	967	967	966	966	965
	1159	1174	1183	1187	1192	1195	1198	1203	1206	1209	1212
	1195	1203	1209	1213	1217	1220	1222	1226	1229	1232	1234
	1293	1289	1286	1284	1281	1280	1279	1278	1277	1276	1275

The frequencies of normal optical vibrations $\Gamma = 7A_1 + 12A_2 + 19E$ are given in Table 2. According to the calculations, by replacement of the rare earth ion, the lowest A_2 mode has the most significant changes. In this mode, the translations of the rare earth ion [3] are the most significant. High-frequency phonons, which are caused by BO_3 groups, react less along the Ce-Lu row. These are modes: A_1 in range 640-1200, A_2 in range 620-1270, E in range 570-1290 cm^{-1}. The degree of participation of the ions in the modes was analyzed in the previous study [3]. It should be noted that the using of *ab initio* approach allows us to describe the structure and lattice dynamics of $RFe_3(BO_3)_4$ for the all R=Ce-Lu.

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References

1. R. Dovesi et al., Int. J. Quantum Chem. **114**, 1287 (2014)
2. http://www.tc.unikoeln.de/PP/clickpse.en.html
3. V.A. Chernyshev et al., Phys. of the Solid State **58**, 1642 (2016)