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Synthesis and crystal structure study of $RbLaP_4O_{12}$

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Abstract

An X-ray diffraction single crystal study of the monoclinic phase of $RbLaP_4O_{12}$, which occurs at room temperature, has been performed with the aim of determining the atomic structure. This compound crystallizes in the space group C2/c with unit cell dimensions a= 7.946(6)Å, b= 12.835(6)Å, c= 10.769(10)Å, β= 110.624(7)°, Z= 4 and V= 1027.9(13)Å^3.

The refinement converged to R= 0.019 and wR= 0.019 using 6412 independent reflections ($I > 2\sigma(I)$). The P_4O_{12} anion has a twofold symmetry, the La atom is eightfold coordinated. The main characteristic of this atomic arrangement is a stacking of three dimensionally framework delimiting intersecting tunnels in which the Rb^+ cations are inserted, linked LaO_8 layers parallel to (001) planes connected together by P_4O_{12} groups lying in (010) planes. Infrared and Raman spectrum was investigated at room temperature in the frequencies range, 400–1600 cm^{-1}, showing some characteristic vibration bands of infinite chain structure of PO_4 tetrahedra linked by bridging oxygen.

Keywords

Crystal study; X-ray diffraction; Infrared spectrum; Raman spectrum.

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INTRODUCTION

Many recent studies have been devoted to the cyclophosphates materials, first because they have many interesting properties. For example, luminescence and spectroscopic properties $CsPrP_4O_{12}$ and $RbPrP_4O_{12}$[1,2], $LiErP_4O_{12}$[3], have been carefully studied and because they can be used in a large number of technological applications such as mini LASER[4-9].

These cyclophosphates contain rings of up to 12 tetrahedrons, but those with three, four (cyclotetraphosphate), and six units are most common and have stoichiometries $P_nO_{3n}^{-n}$. The cyclotetraphosphate compounds crystallize generally at room temperature in two space groups, in the monoclinic system C2/c and the cubic system I - 43d.

The present work is to report new results of crystal growth and refinement of the structure of $RbLaP_4O_{12}$ phosphate having the space group C2/c. This compound is isostructural to $NH_4CeP_4O_{12}$[10], $NH_4PrP_4O_{12}$[11], $NH_4NdP_4O_{12}$[11], $RbNdP_4O_{12}$[12], $RbSmP_4O_{12}$[13], $KSmP_4O_{12}$[14], $KEuP_4O_{12}$[15], $KHoP_4O_{12}$[15], KYP_4O_{12}[16] and $KDyP_4O_{12}$[17]. To grow such compounds in the form of monocrystals requires the investigation of relation amoung reacting component and the dependance of the phase formation on the temperature and pressure. In this context, our research program consists to study the solid solution $RbLaP_4O_{12}$ obtained from the XRD data, and the energies of the vibrational modes obtained from the infrared and Raman spectra.

EXPERIMENTAL

Synthesis

Small Single crystals of $RbLaP_4O_{12}$ were prepared by flux method. A mixture of La_2O_3 and Rb_2CO_3 was slowly added to phosphoric acid H_3PO_4 (85%). The mixture was placed in a platinum crucible and fired at 400°C. Evaporation of the solvent at this temperature brings the desired monocrystals at 20 x 6 x 0.2 mm in size start crystallizing in the melt.

X-ray diffraction

The composition of the obtained crystals was determined by the crystal-structure refinement.

The unit-cell dimensions were measured and refined using indexation of diffraction markings collected with a Kappa CCD Enraf Nonius using Mo Kα radiation. The structure $RbLaP_4O_{14}$was analyzed with the crystallographic CRYSTALS[18] program. The structural graphics were created by DIAMOND[19] program. The structure was solved by conventional Patterson and difference-Fourier techniques. The chemical crystal data, the parameters used for the X-ray diffraction data collection and strategy used for the crystal structure determination and their results are listed in TABLE 1. The final positions and equivalent isotropic thermal parameters are given in TABLE 2.

TABLE 1 : Crystal and experimental data

Chemical formula	$RbLaP_4O_{12}$
Formula weight	540.26 $gmol^{-1}$
Crystal system	monoclinic
Space group	C2/c
a	7.946 (6)Å
b	12.835 (10)Å
c	10.769 (10)Å
β	110.624 (7)°
V ($Å^3$)	1027.9 (15)
Z	4
Dx	3.491 g/m^3
θmax	41.8°
Θmin	5.1°
T	298k
Δρmax	1.69 $eÅ^{-3}$
Δρmin	–2.02$eÅ^{-3}$
Data collection instrument	Kappa CCD
Radiation, graphite monochromator λ	0.71073Å
Measured reflections	12222
Unique reflections	6412
R	0.019
R_w	0.019
CCDC deposition number	423039

TABLE 2 : Atomic coordinates and equivalent thermal parameters of atoms

Atoms	X	Y	Z	Ueq
La	0.5000	0.6223 (9)	0.2500	0.0059
Rb	0.5000	0.3137 (2)	0.2500	0.0258
P1	0.2147 (5)	0.5221 (3)	0.4421 (4)	0.0073
P2	0.9619 (5)	0.6657 (3)	0.5057 (4)	0.0075
O1	0.2787 (18)	0.5294 (11)	0.3292 (13)	0.0137
O2	0.0931 (17)	0.6221 (10)	0.4339 (13)	0.0134
O3	0.0694 (17)	0.4302 (10)	0.4117 (12)	0.0120
O4	0.7959 (16)	0.6972 (10)	0.3956 (12)	0.0119
O5	0.3450 (18)	0.4892 (10)	0.0797 (12)	0.0139
O6	0.4356 (17)	0.7542 (10)	0.3974 (14)	0.0139

Infrared spectroscopy

The infrared absorption spectra of the pure dried KBr pressed pellets of the powdered samples were studied in the range of 4000–400 cm^{-1} with the use of Perkin-Elmer spectrometers, IR783 and FT-IR spectrum 1000.

Raman spectroscopy

The Raman spectrum was recorded, at room temperature, with a Raman microprobe combined with Dilor XY spectrometer and an argon ion laser where the 514.5 nm radiation coming from the laser served as the excitation beam. A microscope attached to the system allowed for a selection of a region of good optical quality in the crystalline sample.

RESULTS AND DISCUSSION

Crystal structure description

The projection of the structure along the C axis on to the (001) plane, shows that it can be described as a three-dimensional $RbLaP_4O_{12}$ framework forming cavities where the Rubidium ions are located. The $RbLaP_4O_{12}$ array is built up from PO_4 tetrahedra and LaO_8 octahedra.

The anionic layers formed by $[P_4O_{12}]^{4-}$ groups are centered by the planes z= 0 and 1/2, whereas the cationic layers made by Rb^+ and La^{3+} cations are centered by the planes z = 1/4 and 3/4 (Figure 1).

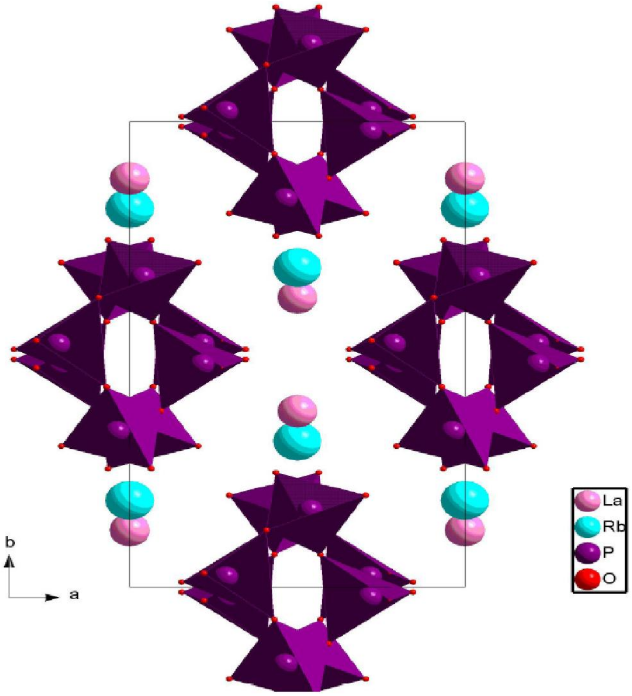

Figure 1 : Projection of $RbLaP_4O_{12}$, crystal structure on the ab plane.

The crystal structure of the title compound is related to that of monoclinic $RbSmP_4O_{12}$[13]. In fact, these two structures have similar typical layered organization of anionic $[P_4O_{12}]^{4-}$groups and cations, Rb^+ and ln = (La^{3+} or Sm^{3+}). Comparison of the structure of $RbLaP_4O_{12}$ with that of cubic $CsNdP_4O_{12}$[20] shows different atomic arrangement in the compounds. Indeed, the crystal structure of $CsNdP_4O_{12}$[20] is built from NdO_8 polyhedra and P_4O_{12} groups linked by Nd–O–P mixed bridges to form a three-dimensional framework delimiting tunnels in which the Cs^+ cations are inserted. Moreover, the atomic arrangement of $CsNdP_4O_{12}$ has not typical layered organization observed in the structure of $RbLaP_4O_{12}$.

The geometry of the different polyhedral has been studied. The anionic ring $[P_4O_{12}]^{4-}$, is built by two crystallographic independent tetrahedra, $P(1)O_4$ and $P(2)O_4$, and their symmetrical obtained by symmetry plane situated at x= 1/2, which are linked by oxygen b ridges P(1)–O4–P(2).

The PO_4 tetrahedra which correspond to P(2) are quite regular, O–O distances ranging from 2.481 to 2.562 Å; the P–O distances ranging from 1.4856(14)Å to 1.6011(15)Å and O–P–O angles ranging from 104.82(10)° to 118.97(9)° show that P(2) is located at the center of gravity of its tetrahedron. In the $P(1)O_4$ tetrahedra the O–O distances, ranging from 2.495 to 2.527Å, show that the O4 tetrahedra are almost regular. However the P(l)–O distances range from 1.4764(17) to 1.6012(14)Å and O–P–O angles ranging from 101.72(9)° to 120.37(10)°. Moreover, the P–O–P angle (134.49(8)°) is rather far from 180°. These results are very similar to those observed for the $RbNdP_4O_{12}$[12] and $RbSmP_4O_{12}$[13].

The lantanium ion is surrounded by eight oxygen atoms (Figure 2) located at distances ranging from 2.4915(17) to 2.513(18)Å, with O–La–O angles very different from 90 and 180°. The O_8 octahedron surrounding La, characterized by O–O distances ranging from 2.714 to 2.891 Å, is almost regular.

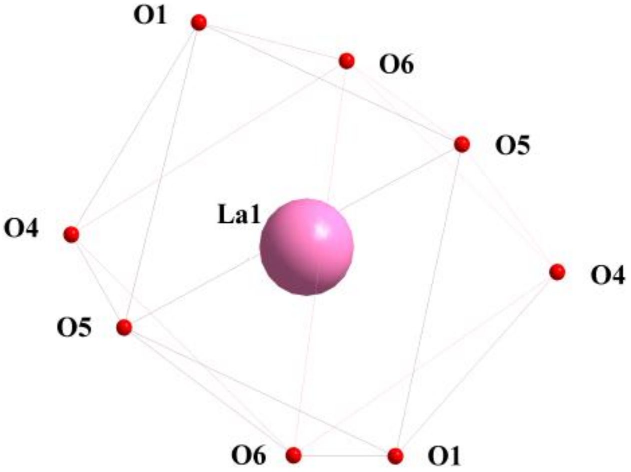

Figure 2 : Coordination of Lanthanium.

The average La–O bond length of 2.502 Å is higher than the similar average value of 2.358 Å in KYP_4O_{12} and is shorter than the similar averages of 2.408Å in $KGdP_4O_{12}$ and 2.420Å in $KSmP_4O_{12}$. This is due to the difference of the ionic radii between the trivalent cations La^{3+}, Y^{3+}, Gd^{3+} and Sm^{3+}.

In spite of the absence of a composition range which would correspond to the possibility of a rubidium nonstoichiometry, this oxide can be considered to have a tunnel structure, a large tunnels running along [001] are indeed observed which are comparable to those reported in to others rare earth cyclotetraphosphates[10-13]. The rubidium

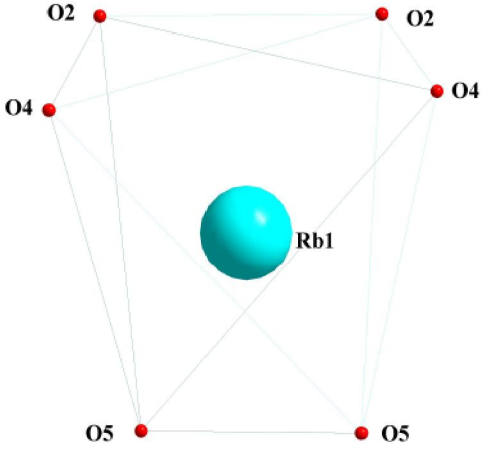

Figure 3 : Coordination of Rubidium.

atoms have a 6-fold coordination of oxygen atoms (Figure 3). This coordination is quite irregular, as can be seen in other cyclotetraphosphates. In fact, the Rb–O distances range from 2.892(2) to 3.079(2) Å, The average Rb–O bond length of 2.99 Å.

Spectroscopic analysis

The IR and Raman spectra are, respectively, shown in Figure 4 and 5. The band (IR) or line (Ra) number is in almost agreement with that of the theoretical prediction as TABLE 4. The bands and lines observed in the regions 1136–1328 and 581–1120 cm^{-1} can be, respectively, attributed to the antisymmetric and the symmetric stretching vibrations (ν_{as} and ν_s) of $(PO_2)^-$ species and of POP bridges[21,22]. It is generally admitted that the symmetric stretching vibrations (ν_s POP) in chain cyclophosphates occur in the range close to 552 cm^{-1} as strong Raman lines and weak infrared bands. The antisymmetric modes (ν_{as} POP) are located around 1067 cm^{-1} and give rise to strong infrared bands and weak Raman lines. In the low frequency region below 539 cm^{-1}, it is very difficult to distin-

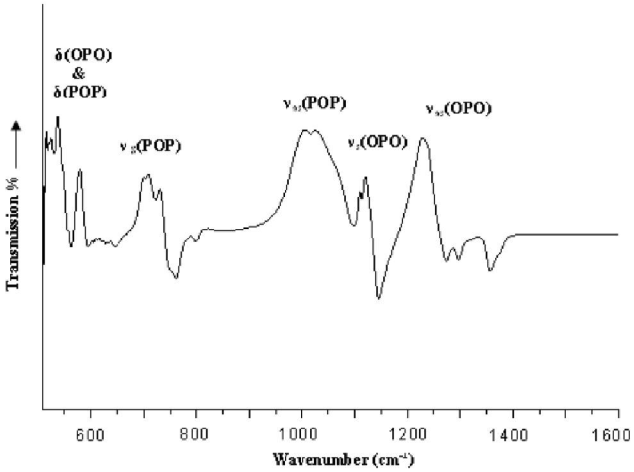

Figure 4 : IR spectrum of monoclinic $C2_1/c$ $RbLaP_4O_{12}$, powder.

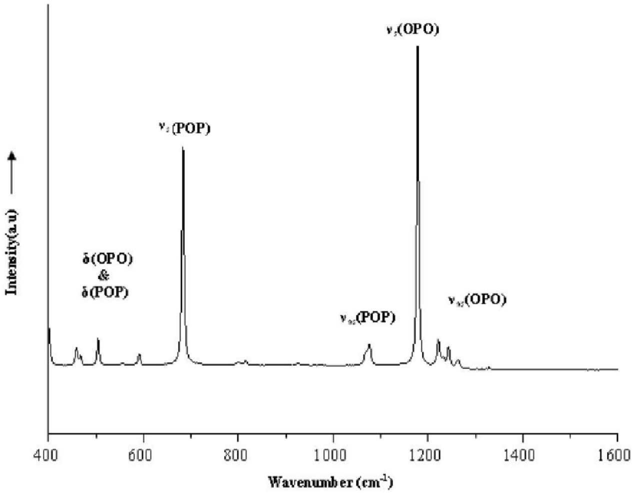

Figure 5 : Raman spectrum of monoclinic (C2/c) $RbLaP_4O_{12}$, powder.

TABLE 3 : Selected bond lengths (Å) and bond angles (°)

Tetrahedron $P(1)O_4$			
P1–O5ii	1.4862 (17)	O5ii–P1–O1	120.37 (10)
P1–O1	1.4764 (17)	O5ii–P1–O2	109.29 (10)
P1–O2	1.5910 (16)	O1–P1–O2	106.36 (9)
P1–O3	1.6012 (15)	O5ii–P1–O3	109.30 (8)
		O1–P1–O3	108.17 (10)
		O2–P1–O3	101.72 (9)
Tetrahedron $P(2)O_4$			
P2–O2iii	1.6011 (15)	O2iii–P2–O3iv	104.86 (8)
P2–O3iv	1.5886 (15)	O2iii–P2–O6v	106.94 (10)
P2–O6v	1.4856 (15)	O3iv–P2–O6v	107.38 (10)
P2–O4	1.4862 (15)	O2iii–P2–O4	104.82 (10)
		O3iv–P2–O4	112.79 (8)
		O6v–P2–O4	118.97 (9)
Polyhedron LaO_8			
La1–O4i	2.5131 (18)	O4i–La1–O1i	125.67 (7)
La1–O1i	2.5098 (18)	O4i–La1–O6i	72.52 (8)
La1–O6i	2.4943 (19)	O1i–La1–O6i	77.33 (6)
La1–O5i	2.4916 (18)	O4i–La1–O5i	146.40 (5)
La1–O1	2.5098 (18)	O1i–La1–O5i	72.58 (7)
La1–O4	2.5131 (18)	O6i–La1–O5i	140.81 (6)
La1–O5	2.4915 (18)	O4i–La1–O1	77.32 (7)
La1–O6	2.4943 (19)	O1i–La1–O1	123.26 (8)
		O6i–La1–O1	149.81 (4)
		O5i–La1–O1	69.36 (5)
		O4i–La1–O4	134.99 (7)
Polyhedron RbO_6			
Rb1–O5i	2.892 (2)		
Rb1–O5	2.892 (2)		
Rb1–O4ii	3.019 (2)		
Rb1–O4iii	3.019 (2)		
Rb1–O2iv	3.079 (2)		

Symmetry codes : (i) –x+1, y, –z+1/2; (ii) x, –y+1, z+1/2; (iii) x+1, y, z; (iv) –x+1, –y+1, –z+1; (v) –x+3/2, –y+3/2, –z+1; (vi) x–1, y, z; (vii) x, –y+1, z–1/2.

TABLE 4 : Mode frequencies cm^{-1} in $RbLaP_4O_{12}$

IR	Raman	Assignement
1328 w	1261 vw	ν_{as}OPO
1281 w	1239 vw	
1224 w	1218 vw	
1136 vs	1175 vs	ν_sOPO
1120 w		
1087 s		ν_{as}POP
803 s	1067 vw	
733 s		ν_sPOP
711 s	684 s	
581 vs	552 vw	
539 vs	495 vw	δPOP and δOPO
527 vs		

Note: vs - Very Strong; s - Strong; vw - Very Week.

guish the antisymmetric (δ_{as}) and symmetric (δ_s) bending modes of $(PO_2)^-$ species and (δPOP) bending. Moreover, these modes overlay with external modes.

The observation of this vibrational mode is a good criterion to differentiate cyclotraphosphates from chain structure polyphosphates.

CONCLUSION

Synthesis and crystal structure were described for rubidium lanthanium cyclophosphate $RbLaP_4O_{12}$. The structure was determined by a single crystal X-ray analysis, and it was shown that this compound crystallized in a monoclinic system C2/c. In this structure, Lanthanium atoms were in eight fold coordination. The PO_4 chains were joined to each other by LaO_8 dodecahedra, giving a three-dimensional framework structure. The energies of the vibrational modes of the crystal were assigned on the basis of the characteristic vibrations of the P–O–P bridge and PO_2 groups.

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REFERENCES

[1] K.Horchani, J.C.Gacon, M.Ferid, M.Trabelsi-Ayedi, O.Krachni, G.K.Liu; J.Lumin., **24**, 169 **(2003)**.

[2] Y.C.Zhang, W.D.Cheng, D.S.Wu, H.Zhang, D.G.Chen, Y.J.Gong, Z.G.Kan; J.Solid State Chem., **177**, 2610 **(2004)**.

[3] B.M.Angelov; J.Alloy Compd., **48**, 395 **(2005)**.

[4] W.Wolinski, M.Malinowski, R.Wolski, in: Proceedings of Ninth International Congress, Laser 89 Optoelectronic., **(1990)**.

[5] M.Malinowski, W.Strek; J.Phys.C Solid State, **20**, 2595 **(1987)**.

[6] K.Horchani, M.Ferid, J.C.Gacon, C.Dujardin, N.Garnier, C.Garapon, M.Trabelsi-Ayedi; J.Lumin., **69**, 94 **(2001)**.

[7] H.G.Danielmeyer, H.P.Weber; IEEE J.Quantum Elect., **8**, 805 **(1972)**.

[8] S.R.Chinn, H.Y.-P.Hong; Appl.Phys.Lett., **26**, 649 **(1975)**.

[9] M.Malinowski; J.Phys.–Condens.Mat., **1**, 4673 **(1989)**.

[10] M.Rzaigui, N.K.Ariguib; J.Solid State Chem., **49**, 391 **(1983)**.

[11] R.Masse, J.C.Guitel et, A.Durif; Acta Cryst.B, **33**, 630 **(1977)**.

[12] H.Koizumi, J.Nakano; Acta Cryst.B, **33**, 2680 **(1977)**.

[13] K.K.Palkina, S.I.Maksimova, N.T.Chibiskova; Izv.Akad.Nauk SSSR Neorg.Mater., **17**, 1248 **(1981)**.

[14] M.Ferid, N.K.Ariguib, M.Trabelsi; J.Solid State Chem., **69**, 1 **(1987)**.

[15] K.K.Palkina, V.G.Kusnetsov, N.N.Chudinova, N.T.Chibiskova; Izv.Akad.Nauk SSSR Neorg.Mater., **12**, 730 **(1978)**.

[16] A.Hamady, T.Jouini, A.Driss; Acta Cryst.C, **51**, 1970 **(1995)**.

[17] K.Horchani, M.Ferid, J.C.Gacon, S.Lecocq, M.Trabelsi, I.Gregora; Mater.Res.Bull., **37**, 1259 **(2002)**.

[18] P.W.Betteridge, J.R.Carruthers, R.I.Cooper, K.Prout, D.Watkin; J.Appl.Cryst., **1487**, 36 **(2003)**.

[19] K.Brandenburg, M.Berndt; DIAMOND. Crystal Impact Gb R, Bonn, Germany. Version 2.1.b, **(1999)**.

[20] K.K.Palkina, S.I.Maksimova, N.T.Chibiskova; Dokl.Akad.Nauk SSSR., **257**, 357 **(1981)**.

[21] R.K.Brow, D.R.Tallant, J.J.Hudgens, S.W.Martin, A.D.Irwin; J.Non-Cryst.Solids, **177**, 221 **(1994)**.

[22] K.Meyer; J.Non-Cryst.Solids, **209**, 227 **(1997)**.