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Synthesis and characterization of Na_2GdOPO_4 and Na_2LaOPO_4

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Abstract

A new orthorhombic phase of previously reported orthorhombic Na_2GdOPO_4, sodium gadolinium oxyphosphate, was synthesized by solid state reactions starting with four different sets of chemicals at 1000°C. The unit cell dimensions were calculated using its powder X-ray diffraction data and were found to be $a=14.709(6)$, $b=10.661(4)$ and $c=13.081(6)$ Å and the space group is probably $Pmm2$ (No: 25). Its monoclinic form was also obtained by further heating the orthorhombic phase at 1000°C. The unit cell dimensions of the monoclinic form was found to be $a=14.719(5)$, $b=10.669(3)$, $c=13.091(5)$ Å and $\beta=92.274°(2)$. Using the same procedure Na_2LaOPO_4 was also prepared the first time in this work through three sets of starting materials at 1000°C. Na_2LaOPO_4 also crystallizes in the orthorhombic system with $a=13.657(5)$, $b=11.076(5)$, $c=6.730(3)$ Å which seems to be isostructural with Na_2GdOPO_4 prepared before in our laboratory. The IR data of both Gd and La compounds agreed with the literature values.

Keywords: Oxyphosphates; X-ray diffraction; Rare earths; Na_2GdOPO_4; Na_2LaOPO_4

1. Introduction

Oxyphosphates of the type $MOPO_4$, $MM'OPO_4$ have gained great importance in the last two decades in the field of communication and laser technology [1]. $MOPO_4$ type materials possess properties that make them potentially useful for catalytic, electronic and ion exchange applications. Therefore, the structures of series of compounds with M in an octahedrally and P in a tetrahedrally coordinated sites have been reported. Monoclinic form of $TaOPO_4$ have been first reported by Hahn [2], Heider [3] and Rakhmalutin et al. [4] and the unit cell dimensions are given by Levin and Roth [5]. Its tetragonal form was also synthesized [6] under 25 to 60 kbar pressure and 500 to 1500°C temperature interval. Single crystal methods [7] were used to synthesize orthorhombic $NbOPO_4$. Above 1250°C tetragonal $NbOPO_4$ was also prepared which is isostructural with $MoOPO_4$ [8] where each tetrahedron via its four vertices links four chains of corner sharing octahedra. Another oxyphosphate, in this structure, is $WOPO_4$ which has both monoclinic and tetragonal forms [9]. However $SbOPO_4$ belongs to another structure type in which octahedra and PO_4 tetrahedra form a network [10]. Two crystalline forms are known for $VOPO_4$, one of them is orthorhombic, β-$VOPO_4$ which has a network structure and the other one is α-$VOPO_4$ possessing a layered structure [11–16].

One of the most important oxyphosphates of the type $MM'OPO_4$ is $KTiOPO_4$ (KTP). It is unique in its overall qualifications for second-order nonlinear and electrooptic processes [17]. The crystal structure of $KTiOPO_4$ was first reported in 1974 by Tordjman et al. [18], since then many researchers have studied the preparation of KTP and its isostructural analogues. Solid state synthesis of $MTiOPO_4$ (M=K, Rb, Tl) was carried out at 1000°C [19] and to improve the crystal quality Kanno [20] prepared KTP via mechanical mixing route.

The qualities and the potential applications of KTP arose great interest in the mixed analogues which have partial or complete substitution on K, Ti and P sites [21,22]. For example, K is replaced by Rb, Na, Ag, Cs, Tl; Ti by Sb, Sn and P is replaced by Si and As.

The first study related to oxyphosphates of rare earths and alkaline metals of the type M_2LnOPO_4 (Na_2GdOPO_4) was carried out by Uztetik-Amour and Kizilyalli [23] by the solid state reaction of:

$$Na_4P_2O_7 + Gd_2O_3 \rightarrow 2Na_2GdOPO_4$$

Therefore, in the present work, preparation of Na_2GdOPO_4 and Na_2LaOPO_4 was carried out by using different phosphating agents in the following solid state reactions at different temperatures and time intervals:

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$$Gd_2O_3 + 2(NH_4)_2HPO_4 + 2Na_2CO_3 \rightarrow 2Na_2GdOPO_4 + 4NH_3 + 2CO_2 + 3H_2O$$

$$Gd_2O_3 + 2NH_4H_2PO_4 + 2Na_2CO_3 \rightarrow 2Na_2GdOPO_4 + 2NH_3 + 2CO_2 + 3H_2O$$

$$Gd_2O_3 + 2NaH_2PO_4 \cdot 2H_2O + Na_2CO_3 \rightarrow 2Na_2GdOPO_4 + CO_2 + 6H_2O$$

$$Gd_2O_3 + 2Na_2HPO_4 \rightarrow 2Na_2GdOPO_4 + H_2O$$

$$La_2O_3 + 2(NH_4)_2HPO_4 + 2Na_2CO_3 \rightarrow 2Na_2LaOPO_4 + 4NH_3 + 2CO_2 + 3H_2O$$

$$La_2O_3 + 2NH_4H_2PO_4 + 2Na_2CO_3 \rightarrow 2Na_2LaOPO_4 + 2NH_3 + 2CO_2 + 3H_2O$$

$$La_2O_3 + 2NaH_2PO_4 \cdot 2H_2O + Na_2CO_3 \rightarrow 2Na_2LaOPO_4 + CO_2 + 6H_2O$$

2. Experimental details

The chemicals used were commercial Gd_2O_3 (99.9% pure, obtained from Fluka); Na_2CO_3, $(NH_4)_2HPO_4$, $NH_4H_2PO_4$ (Merck); $NaH_2PO_4 \cdot 2H_2O$ (Fisher); Na_2HPO_4 (Aldrich). X-ray powder diffraction patterns were taken by using Phillips diffractometer with PW 1050/25 goniometer and Fe Kα (30–40 kV,10–20 mA, $\lambda = 1.93728$ Å) radiation. Nicolet 510 FT-IR spectrophotometer was used to obtain infrared absorption spectra. Spectra of solid samples were obtained from KBr pellets with 3:100 product to KBr ratio. The experimental XRD data were refined using least squares and computer indexing techniques supplied from Huber Company (Germany).

In all experiments stoichiometric amounts of reactants were weighed separately and crushed well in an agate mortar. Then the mixture was transferred into a porcelain crucible and put into a furnace for heating. After each heating period samples were taken for XRD and IR analysis. The chemical analysis for rare earths and phosphorus were done through oxalate and magnesium ammonium phosphate method respectively [24]. In the density measurement picnometer method was used.

3. Results and discussion

In the synthesis of Na_2GdOPO_4 the XRD patterns of the products were about the same for all experiments performed at 900°C for different time intervals. Unreacted Gd_2O_3 was observed together with α-$Na_3Gd(PO_4)_2$ [25]. Therefore, it was concluded that the solid-state reactions at this stage did not give the expected product. But the experimental and theoretical weight losses agreed quite well.

The IR spectra of the products have supported the presence of $Na_3Gd(PO_4)_2$ [26] and Gd_2O_3 [27]. In some samples Gd_3PO_7 [28,29] was also present.

Prolonged heating of the products at 1000°C (two 6-h periods and grinding in between) resulted in one phase product which is Na_2GdOPO_4. However the obtained XRD patterns were different from the pattern we presented before [23]. The indexing of the data showed that the new product is also orthorhombic with the refined unit cell parameters of $a = 14.709(6)$, $b = 10.661$ (4) and $c = 13.081$ (6) Å and the probable space group is *Pmm*2 (No: 25). These parameters are different from the unit cell parameters given by Uztetik et al. [23], which were $a = 13.074(6)$, $b = 10.637(5)$ and $c = 6.469(3)$ Å. As it is seen two of them (10.661 and 10.637, 13.081 and 13.094) are similar but the third one 'a' is nearly equal to $2^{1/2} \times 10.63$. In our previous study, the obtained Na_2GdOPO_4 was not pure but together with β-$Na_3Gd(PO_4)_2$. In the present investigation although there were some matching peaks which belong to $Na_3Gd(PO_4)_2$ it was considered that the product was Na_2GdOPO_4, since all the peaks could be indexed with the new parameters and two of the unit cell parameters were similar but the third one was different ($c \cong 2 \times 6.469$). We concluded that the obtained product in our study is a new form of Na_2GdOPO_4. Table 1 shows the X-ray powder data of this new phase.

In the IR spectra of the compounds the bands due to Gd_2O_3 have disappeared completely. The present bands were due to Na_2GdOPO_4 which agreed with the IR data given in literature [23,30] where the IR band locations of Na_2GdOPO_4 were given as: 1136, 1099, 1034, 982, 965, 945, 926, 909, 604, 579, 560, 548, 523, 470, 406, 381 and 367 cm^{-1} (Fig. 1).

The density of Na_2GdOPO_4 is measured as 4.13 g cm^{-3} experimentally and the number of molecules per unit cell (Z) was calculated as 16. The analysis of the amounts of Gd and P in the sample was in good agreement with the empirical formula.

This new phase of Na_2GdOPO_4 was also observed previously by Kizilyalli and Welch [25], then Sungur and Kizilyalli [31,32]. However they decided that in the XRD pattern there were more than one phase, one of them was designated as 'x-phase' and the others are $Na_3Gd(PO_4)_2$ and Gd_3PO_7. In these studies excluding the $Na_3Gd(PO_4)_2$ and Gd_3PO_7 lines x-phase was first indexed in the cubic system with unit cell parameter of 14.547 Å then with an orthorhombic system where $a \cong b \cong c \cong 14$ [32] which is the parameter a of Na_2GdOPO_4 in our study. They stated that the appearance of x-phase depends on the composition of the reaction mixture but not the temperature. This phenomena was also observed in our studies.

Further heating the mixture, $Gd_2O_3 + NH_4H_2PO_4 + Na_2CO_3$, at 1000°C resulted in a product which was indexed in the monoclinic system with the refined cell

Table 1
X-ray powder diffraction data of orthorhombic Na_2GdOPO_4

d_{obs}(Å)	d_{calc} (Å)	I/I_0	$h\ k\ l$
14.6929	14.7088	30	100
13.3049[a]	13.0811	5	001
10.7390[a]	10.6611	10	010
9.6682	9.7748	10	101
8.6227	8.6321	8	110
8.2411[a]	8.2641	11	011
7.3480	7.3544	20	200
7.1373	7.2048	10	111
6.4964[a]	6.5405	60	002
6.0422	6.0537	5	210
5.5100	5.4940	5	211
5.1812	5.2131	6	112
5.0313	5.0116	6	120
4.9112	4.8874	6	202
4.5837[a]	4.5911	25	301
4.4231	4.4428	8	212
4.3060	4.3160	6	220
4.2261[a]	4.2167	6	311
4.1194[a]	4.0987	17	221
3.9692	3.9781	5	122
3.8687	3.8920	17	113
3.6826	3.6772	20	400
3.5466[a]	3.5381	25	213
3.4719[a]	3.4762	23	410
3.3273	3.3398	24	131
3.2437[a]	3.2583	8	303
3.1686[a]	3.1596	28	322
3.1178[a]	3.1081	43	231
3.0290	3.0269	10	420
2.9752	2.9882	5	204
2.9417	2.9418	45	500
2.8376[a]	2.8358	10	510
2.7821[a]	2.7800	100	323
2.7215	2.7182	25	413
2.7029[a]	2.7076	22	133
2.6547[a]	2.6658	50	040
2.6140[a]	2.6116	13	041
2.5719	2.5714	13	141
2.4588	2.4610	12	241
2.4099[a]	2.4064	5	034
2.3745	2.3748	5	134
2.3437	2.3399	5	242
2.3006[a]	2.3050	11	341
2.2687	2.2661	6	530
2.2296	2.2272	10	620
2.2236	2.2214	9	424
2.1862[a]	2.1871	7	504
2.1446	2.1412	8	532
2.1227	2.1293	10	441
2.1102[a]	2.1069	21	035
2.0797[a]	2.0832	5	151
2.0565	2.0616	8	710
2.0295	2.0272	4	052
2.0011	1.9992	14	126
1.9625	1.9615	10	604
1.9521	1.9530	15	541
1.9446	1.9460	30	226
1.9170	1.9155	29	053
1.9113[a]	1.9155	28	053
1.8699	1.8670	7	045
1.8512[a]	1.8522	8	145
1.8266	1.8264	9	117
1.8215	1.8207	9	801
1.8016	1.7992	6	543
1.7767	1.7768	6	060
1.7585	1.7607	7	061
1.7435	1.7433	11	732
1.7390[a]	1.7381	12	820
1.7178	1.7173	9	634
1.7123	1.7116	9	551
1.7032	1.7032	11	162
1.6898	1.6875	6	046
1.6867[a]	1.6875	7	046
1.6650[a]	1.6641	13	526
1.6539[a]	1.6528	12	055
1.6489	1.6501	14	740
1.6323[a]	1.6330	19	830
1.6275	1.6291	16	606
1.6114	1.6104	10	616
1.5948	1.5957	8	346
1.5903	1.5901	8	427
1.5831	1.5828	14	734
1.5733	1.5764	9	545
1.5716	1.5711	8	536
1.5577	1.5580	11	626
1.5543	1.5526	15	164
1.5309	1.5304	11	903

[a] Matching peaks with the previous data [23].

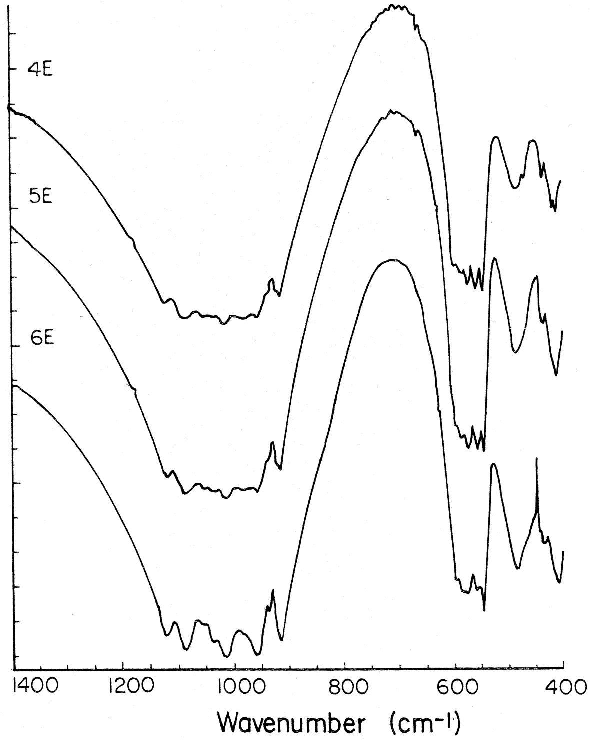

Fig. 1. IR Spectra of new orthorhombic form of Na_2GdOPO_4.

parameters of $a=14.719(5)$, $b=10.669(3)$, $c=13.091$ (5) Å and $\beta=92.74°(2)$. This monoclinic phase is slightly different from the orthorhombic phase of Na_2GdOPO_4

presented in this study. But the disappearance of some peaks and changes in the relative intensities showed the presence of a phase transition. X-ray powder data of monoclinic Na_2GdOPO_4 [33] will be published later.

Table 2
X-ray powder diffraction data of the orthorhombic Na_2LaOPO_4

d_{obs}(Å)	d_{calc}(Å)	I/I_0	*h k l*	Remarks
13.466	13.651	9	100	
11.114	11.063	15	010	
8.6898	8.5949	12	110	
6.8746	6.8255	6	200	
6.7302	6.7283	6	001	
6.5153	–	12	–	$Na_3La(PO_4)_2$
6.0585	6.0351	6	101	
5.7785	5.7486	9	011	
5.5507	5.5316	9	020	
5.3279	5.2980	9	111	
5.1576	5.1266	9	120	
5.0313	–	6	–	$Na_3La(PO_4)_2$
4.8172	4.7916	6	201	
4.6494	–	12	–	$Na_3La(PO_4)_2$
4.3975	4.3969	10	211	
4.2979	4.2729	9	021	$Na_3La(PO_4)_2$
4.2183	4.2082	15	310	
4.1343	–	12	–	$Na_3La(PO_4)_2$
3.8687	–	9	–	$Na_3La(PO_4)_2$
3.7733	3.7693	13	301	
3.6895	3.6877	6	030	
3.6246	3.6217	9	221	
3.5685	3.5601	9	130	
3.5357	–	17	–	$Na_3La(PO_4)_2$
3.5142	3.5141	18	320	
3.4667	–	10	–	$Na_3La(PO_4)_2$
3.4307	–	9	–	$Na_3La(PO_4)_2$
3.3708	3.3642	9	002	
3.2665	3.2611	93	102	
3.2347	3.2338	100	031	
3.1430	3.1327	12	112	$Na_3La(PO_a)_2$
3.0647	–	16	–	$Na_3La(PO_4)_2$
3.0408	3.0436	6	401	
2.9828	–	21	–	$Na_3La(PO_4)_2$
2.9344	2.9346	21	411	
2.9054	2.9044	5	420	
2.8119	2.8126	48	122	$Na_3La(PO_4)_2$
2.7627	2.7658	9	040	
2.7153	2.7107	15	140	
2.6999	–	21	–	$Na_3La(PO_4)_2$
2.6313	2.6277	9	312	
2.4816	2.4853	12	032	$Na_3La(PO_4)_2$
2.4219	–	9	–	$Na_3La(PO_4)_2$
2.3493	2.3474	6	431	$Na_3La(PO_4)_2$
2.2985	2.3007	9	521	
2.2687	2.2752	15	600	
2.2636	–	12	–	$Na_3La(PO_4)_2$
2.2418	2.2428	7	003	
2.1978	2.1943	6	530	
2.1671	2.1701	12	113	$Na_3La(PO_4)_2$
2.1373	2.1365	12	042	$Na_3La(PO_4)_2$
2.1209	2.1155	12	611	
2.0316	–	36	–	$Na_3La(PO_4)_2$
2.0139	–	12	–	$Na_3La(PO_4)_2$
1.9886	1.9883	36	223	
1.9521	1.9501	6	700	
1.9461	–	18	–	$Na_3La(PO_4)_2$
1.9099	1.9082	9	351	
1.8835	1.8846	9	602	$Na_3La(PO_4)_2$
1.8685	1.8667	12	541	
1.8565	1.8566	12	450	
1.7954	–	10	–	$Na_3La(PO_4)_2$
1.7749	1.7741	9	721	
1.7561	1.7571	21	640	
1.7527	–	24	–	$Na_3La(PO_4)_2$
1.7255	1.7239	6	730	
1.7058	1.7064	6	800	$Na_3La(PO_4)_2$
1.6825	1.6821	9	004	
1.6680	1.6655	9	551	
1.6640	1.6630	12	014	$Na_3La(PO_4)_2$
1.6489	1.6508	15	114	$Na_3La(PO_4)_2$

IR spectrum of monoclinic Na_2GdOPO_4 is the same as orthorhombic phase obtained in this study.

3.1. Preparation of Na_2LaOPO_4

Using the procedure given in experimental section the solid state reaction was performed at 900°C for three 6-h successive periods. In the X-ray powder pattern, lines due to $NaPO_3$, La_3PO_7 and $Na_3La(PO_4)_2$ were observed which showed the difficulty of obtaining the expected product at this temperature.

In the IR spectra of the products besides the lines due to double phosphates [31] and La_3PO_7 [30], P–O–P bands were also observed which confirmed the presence of $NaPO_3$ [34]. Therefore to obtain Na_2LaOPO_4 the temperature was increased.

Two successive heatings were carried out at 1000°C (6-h periods). It was seen that lines due to $NaPO_3$ and La_3PO_7 disappeared for all the obtained products, instead new lines formed in the X-ray pattern.

Examinations revealed that the obtained pattern resembles the XRD pattern presented by Uztetik-Amour and Kizilyalli [23] for Na_2GdOPO_4. The splitting of peak at $d=3.12$ Å to $d=3.12$ and 3.16 Å in the pattern of Na_2GdOPO_4 was present at $d=3.23$ and 3.27 Å in the pattern of lanthanum compound. Adopting the unit cell parameters of Na_2GdOPO_4, Na_2LaOPO_4 was indexed in the orthorhombic system with the refined unit cell parameters of $a=13.657(5)$, $b=11.076(5)$ and $c=6.7295(3)$ Å. The calculated *hkl* values and that of Na_2GdOPO_4 were the same except some additional values in this case. Since the radius of La^{3+} is greater than the radius of Gd^{3+}, the unit cell parameters of Na_2LaOPO_4 is greater than that of Na_2GdOPO_4. Therefore, it can be concluded that Na_2LaOPO_4 has the same structure as Na_2GdOPO_4. The *d*-spacings and *hkl* values of the new compound Na_2LaOPO_4 are presented in Table 2. The unidentified lines were due to $Na_3La(PO_4)_2$.

Examination of the unit cell parameters showed that there are some resemblances between the Na_2LaOPO_4 and $MTiOPO_4$ type of orthorhombic compounds (M=K,Rb, Tl) [19].

In the IR spectra of the products (Fig. 2) P–O–P bands were not present showing the absence of $NaPO_3$. The experimental density of the compound was not determined since the product contained $Na_3La(PO_4)_2$ as impurity.

4. Conclusion

Na_2GdOPO_4, sodium gadolinium oxyphosphate, was synthesized previously together with β-$Na_3Gd(PO_4)_2$ from the solid state reaction of Gd_2O_3 and $Na_4P_2O_7$ at 1200°C [23]. In the present study pure Na_2GdOPO_4 was synthesized using four different sets of reaction mixtures at

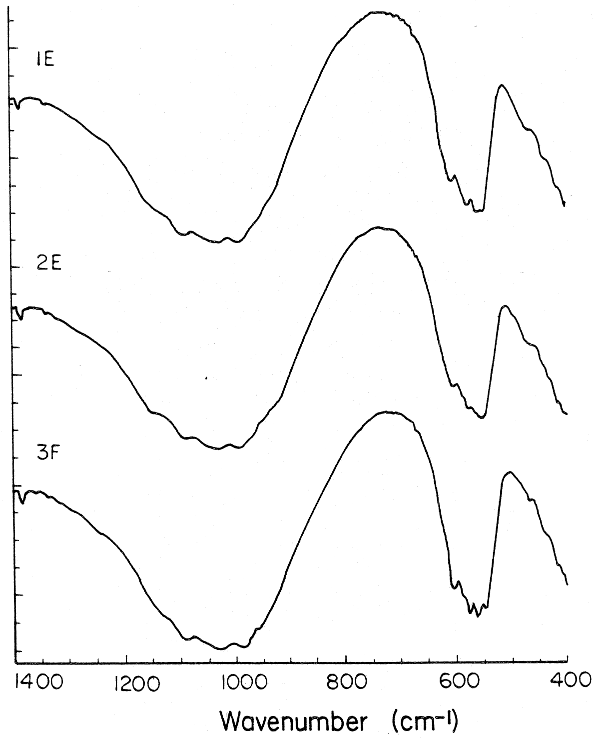

Fig. 2. IR spectra of orthorhombic form of Na_2LaOPO_4.

lower temperature (1000°C). A new orthorhombic phase of Na_2GdOPO_4 was obtained with the unit cell parameters of $a=14.709(6)$, $b=10.661(4)$ and $c=13.081(6)$ Å. The *x*-phase which was obtained by Sungur and Kizilyalli [31,32] was identified as the new form of Na_2GdOPO_4 by indexing the X-ray pattern with the new unit cell dimensions. Density of Na_2GdOPO_4 was measured as 4.13 g cm^{-3} where $Z=16$ and the space group was probably *Pmm*2. Further heating of the new orthorhombic Na_2GdOPO_4 at 1000°C resulted in the monoclinic form of this compound. The unit cell parameters were calculated to be $a=14.719(5)$, $b=10.669(3)$, $c=13.091(5)$ Å and $\beta=92.274°(2)$.

Furthermore using the same procedure orthorhombic Na_2LaOPO_4 was also synthesized using three sets of starting materials at 1000°C. However the compound was not pure, some lines due to $Na_3La(PO_4)_2$ was also observed. The unit cell dimensions of this compound are $a=13.657(3)$, $b=11.076(5)$, $c=6.730(3)$ Å. These unit cell dimensions were found to be similar to Na_2GdOPO_4 prepared previously and $MTiOPO_4$ type of orthorhombic compounds [17–19,35–39]. Further heating of orthorhombic Na_2LaOPO_4 at 1200°C showed that this compound was not very stable at this temperature and the main product was $Na_3La(PO_4)_2$.

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