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Crystallization and characterization of $Na_2(La, Me)Zr(PO_4)_3$

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$Na_2(La, Me)Zr[PO_4]_3$ (where Me = Co, Al, Cr) crystals have been grown by three methods: by chemical reaction; from highly concentrated phosphoric acid solutions; and by a hydrothermal technique. The advantages and disadvantages of each method to obtain these crystals have been discussed. Morphological, X-ray, chemical analysis and IR-spectral studies were performed on these crystals.

1. Introduction

There is a growing interest in the growth and characterization of various phosphates with the beginning of their applications in opto-electronics and in the construction of solid electrolytes. However, attention was confined only to their luminescent properties. Only in the late seventies, an interest in the investigations of various other physical properties such as ionic conductivity and piezoelectricity in these phosphates developed. The ionic conductivity was first reported in "Nasicon" and later on in "Lisicon" types of phosphates [1–3]. These materials are important solid electrolytes with high values of ionic conductivity, which are almost equivalent to Naβ-alumina [4]. Since then a lot of reports have appeared on ionic conductivity in various other phosphates ($Na_3Sc_2P_3O_{12}$ [5], $NaScP_4O_{12}$ [6], $CsNdP_4O_{12}$ [7] and $RbNdP_4O_{12}$ [7]) and similarly in mixed alkaline rare earth silicates ($Na_5GdSi_4O_{12}$ [8], $Na_5YSi_4O_{12}$ [9] and $Na_5RSi_4O_{12}$ [10] etc.).

In all these materials, the ionic conductivity and the optical properties depend mainly on the type of rare earth cation and the crystalline structure. However, the structures of many new solid electrolytes have yet to be studied because of the nonavailability of the materials in the form of single crystals. It is well known that the phosphates of mixed alkaline and rare earth elements exhibit island, ribbon, layered ring and framework types of structures. They have highly distorted structures with a very wide variation in P–O bond lengths and the ideal $[PO_4]$-tetrahedron has a lower symmetry. The $[PO_4]$-tetrahedra share all the corners to form a three-dimensional network. The inter-isolation of the rare earth polyhedra and the distortion of the overall structure are mainly responsible for the presence of luminescence and ionic conduction in these materials. The activation energy depends mainly on the radii of the rare earth cation [10]. The ionic conductivity depends upon the crystallographic orientation. The study of ionic conductivity in condensed phosphates needs a thorough knowledge of crystalline structure. Hence, the growth of these materials in the form of single crystals is highly desirable to understand various physical characteristics.

The present paper describes the crystallization of complex triorthophosphates (by various techniques) containing alkaline rare earth and transitional elements as their cations and also their characterization using X-rays, chemical analysis, morphology and IR-spectroscopy.

2. Experimental methods

Phosphates containing various elements like alkaline earth, transitional and rare earth are being grown by various techniques. The most important ones are: (a) from the evaporation of phosphoric acid solutions, (b) from the melt, (c) from flux, (d) by chemical reactions, and (e) hydrothermal growth. The latter one is less popular due to the lack of growth technology in phosphorus media. The authors have grown $Na_2(La, Me)Zr[PO_4]_3$ crys-

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TABLE I Stiochiometric ratio of the starting materials used in the crystallization of $Na_2(La, Me)Zr(PO_4)_3$

Number	Na_2O	La_2O_3	ZrO_2	P_2O_5
1	1.8	1	0.7	6.2
2	4.6	1	0.7	25.6
3	4.6	1	0.4	18.8
4	4.6	1	0.35	15.3
5	3.5	1	0.3	12.5
6	2.0	1	0.5	9.4

tals by chemical reaction, from aqueous solutions and by the hydrothermal method with a special emphasis on the latter one. We have studied the advantages and disadvantages of each technique. It is found that the quality and size of the crystals vary distinctly with respect to the growth technique adopted. The use of phosphates in optoelectronics requires the development of perfect and high quality crystals with a definite morphology [11]. Therefore, in the present paper we have paid more attention to the quality and morphology of the crystals obtained by each method.

(a) By chemical reactions: a mixture of starting components Na_2CO_3, La_2O_3, $ZrOCl_2$, and $NH_4H_2PO_4$ were taken in a specified proportion in a platinum crucible and held at 200° C for several hours and later on the mixture was fired up to 900° C and held for 24 to 40 h, followed by a slow cooling at the rate of $5^\circ\,C\,h^{-1}$ up to 700° C; then at the rate of $10^\circ\,C\,h^{-1}$ up to 600° C; and finally at the rate of 20 to $30^\circ\,C\,h^{-1}$ up to 250° C. The mixture was then quenched to room temperature. The resultant material was washed in water to remove the remaining phosphorus media. Table I gives the ratios of the starting materials used. The morphology and the quality of the crystals grown by this method will be discussed later. In this method crystals were obtained under the conditions of supersaturation which is the result of the following chemical reaction:

$$m\,Na_2O + n\,La_2O_3 + p\,Me_2O_3 + q\,ZrO_2 + r\,P_2O_5 \rightarrow Na_{2m}La_{2n}Me_{2p}Zr_qP_{2r}O_{(m+3n+3p+2q+5r)}$$

The main drawback of this method is the problem connected with control over spontaneous crystallization.

(b) From aqueous solutions: this is a popular method of growing various types of phosphates. A mixture of 85% orthophosphoric acid and Na_2CO_3 was placed in a platinum crucible and it was held at room temperature until the evolution of CO_2 was complete. Later the required oxides of La, Zr, Co or Cr or Al or Ga were added to this mixture and the crucible was kept inside the furnace. These oxides dissolve completely in 85% H_3PO_4 to form a homogeneous solution. It is well known that the phosphates containing alkaline, rare earth and transitional elements show a negative temperature coefficient of solubility. Moreover, the transitional metals substitute the rare earth elements in the structure. Therefore, this solution was held at 250 to 300° C for 1 or 2 days until the desired equilibrium between vapour and solution had been established. Then the temperature of the reactor was slowly increased to a predetermined level (500 to 600° C) at a rate of $5^\circ\,C\,h^{-1}$ and held for 6 to 7 days. The resultant material was cleaned thoroughly in warm water to remove the excess of H_3PO_4. The $Na_2(La, Me)Zr(PO_4)_3$ (where Me = Al, CO, Cr) crystals were obtained using different proportions of the starting materials (Table I). The main drawback of this method is the use of platinum crucibles at higher temperatures (> 600° C) for a long time. This allows the entry of platinum into the growing crystals. However, this problem can be overcome by using vitreous carbon crucibles. The crystals were produced by homogeneous nucleation and range in size from 0.5 to 3 mm. It was observed that variation in the ratio of the starting components did not influence the size and morphology of the crystals. It was only the temperature of growth which influenced the size of the crystals.

(c) Hydrothermal method: the growth of phosphates by the hydrothermal technique is relatively new. In general there are very few reports on the growth of phosphates by this method [12–14]. Therefore, the authors have made an attempt to grow complex triorthophosphates by the hydrothermal technique and discussed the advantages and disadvantages of the method in detail. On the whole the method corresponds to the one given in [14, 15]. The experiments were carried out in Morey type autoclaves with Teflon liners within a temperature range of 200 to 300° C and in the pressure range 6 to 10 atms. It has been reported earlier that experiments carried out under hydrothermal conditions show that in the system where $P_{H_2O} \geqslant 6$ atm, the crystallization of polyphosphates or ultraphosphates ceases and only simple orthophosphates crystallize irrespective of the temperature of the system. Similarly an increase in the concentration of alkalis in the system leads to decondensation and in the products of crystallization, ultraphosphates having either a highly condensed state or a complex anionic structure (P_5O_{14}) disappear. In the place of this, polyphosphates with radicals $(PO_3)_4$, $(PO_3)_3$, (P_4O_{12}) and finally (PO_4) start crystallizing [16]. Therefore, in our experiments the temperature of growth was mainly varied within the range 200 to 600° C. Platinum liners were used in experiments carried out at higher temperatures ($> 300°$ C). From the experimental results it was found that to grow single crystals of $Na_2(La, Me)Zr(PO_4)_3$ (where Me = CO, Al, Cr) a temperature range of 200 to 300° C is quite sufficient using a hydrothermal technique. The crystals range in size from 0.5 to 3 mm. At higher temperatures it was found that the crystal size increased distinctly because of the higher rate of growth produced by the higher ionic mobility, low viscosity and higher concentration of solute ions. In all the experiments carried out by hydrothermal techniques the crystals resulted through spontaneous nucleation. The seeding technique was not used. The starting materials such as oxides of Me, La, Zr were taken in a teflon liner (for temperatures $< 300°$ C) or in a platinum liner (for temperatures $> 300°$ C) and 85% orthophosphoric acid was poured into it. The alkaline component of the starting materials was taken in the form of a molar solution with a definite molarity and this solution acts as a mineralizer. Since the crystallization was carried out by spontaneous nucleation, the temperature of the furnace was slowly raised to control the rate of nucleation. The quality of crystals obtained by the hydrothermal technique was much better than the ones obtained by the other two methods. Here the rate of heating was the main parameter to reduce the number of crystals and increase the size of the crystals. The crystals exhibit good morphology. The use of other alkalis leads to the formation of respective alkaline, rare earth and transitional metal triorthophosphates.

Shannon *et al.* [17] have shown that an increase in the concentration of sodium increases the ionic conductivity. Similarly, it has been reported [18] that an increase in the concentration of alkalis leads to an increase in the values of fluorescent lifetime in $CsNdP_4O_{12}$ crystals and glasses. However, an attempt to increase the concentration of Na beyond 10 wt% in the present compounds yielded crystals that were mostly massive and poor in quality.

3. Results

3.1. Morphology

The morphology of $Na_2(La, Me)Zr(PO_4)_3$ crystals is very interesting, beacuse of their wide diversity (Fig. 1). The study of morphology is quite important due to its device potential. It was found that the morphology of $Na_2(La, Me)Zr(PO_4)_3$ crystals vary according to the growth technique, the physico-chemical conditions and the composition of the starting materials. On the whole the crystals obtained by the hydrothermal technique were very good in quality and exhibited an excellent morphology. The crystals varied in size from 1 to 3 mm, and the crystal surfaces were very smooth and vitreous in lustre. Irregular crystals with indistinct morphology were almost absent. The colour varied with the trivalent cation used. For example, in case of the chromium compound it was green, in case of the cobaltic compound it was light purple to dark pink; in case of the aluminium compound it was pure white. The crystals obtained by the hydrothermal technique are prismatic, tabular, rhombohedral and also occasionally rod-shaped (in the case of the aluminium compounds). Twinning was very common in these crystals obtained by all three methods. In the case of cobalt bearing compounds it was quite common in some experiments. The crystals obtained by chemical reactions were usually rhombohedral, plate like, rod-shaped, prismatic, fibrous, massive and also equi-dimensional depending upon the physico-chemical conditions and compositions. The crystal size varied from 0.5 to 7 mm. When the rate of cooling was high the crystals were large in size. Plate and rhombohedral crystals were common for chromium compounds. Fibrous and rod-shaped crystals were common for aluminium compounds. Finally rhombohedral and prismatic shaped crystals were common for cobaltic compounds. In contrast to the smooth surfaces of the crystals obtained by the hydrothermal technique, the crystals obtained by chemical reaction exhibited highly rough surfaces with numerous striations, growth spirals and growth steps (Fig. 1j). However, the vitreous lustre remains the same in both. All the crystals were normally elongated along the c-axis. The elongation of the crystals increases with an increase in the concentration of alkalis in the composition.

The crystals grown from aqueous solutions were almost uniform in morphology with rhombohedral, tabular and prismatic habits. The size of

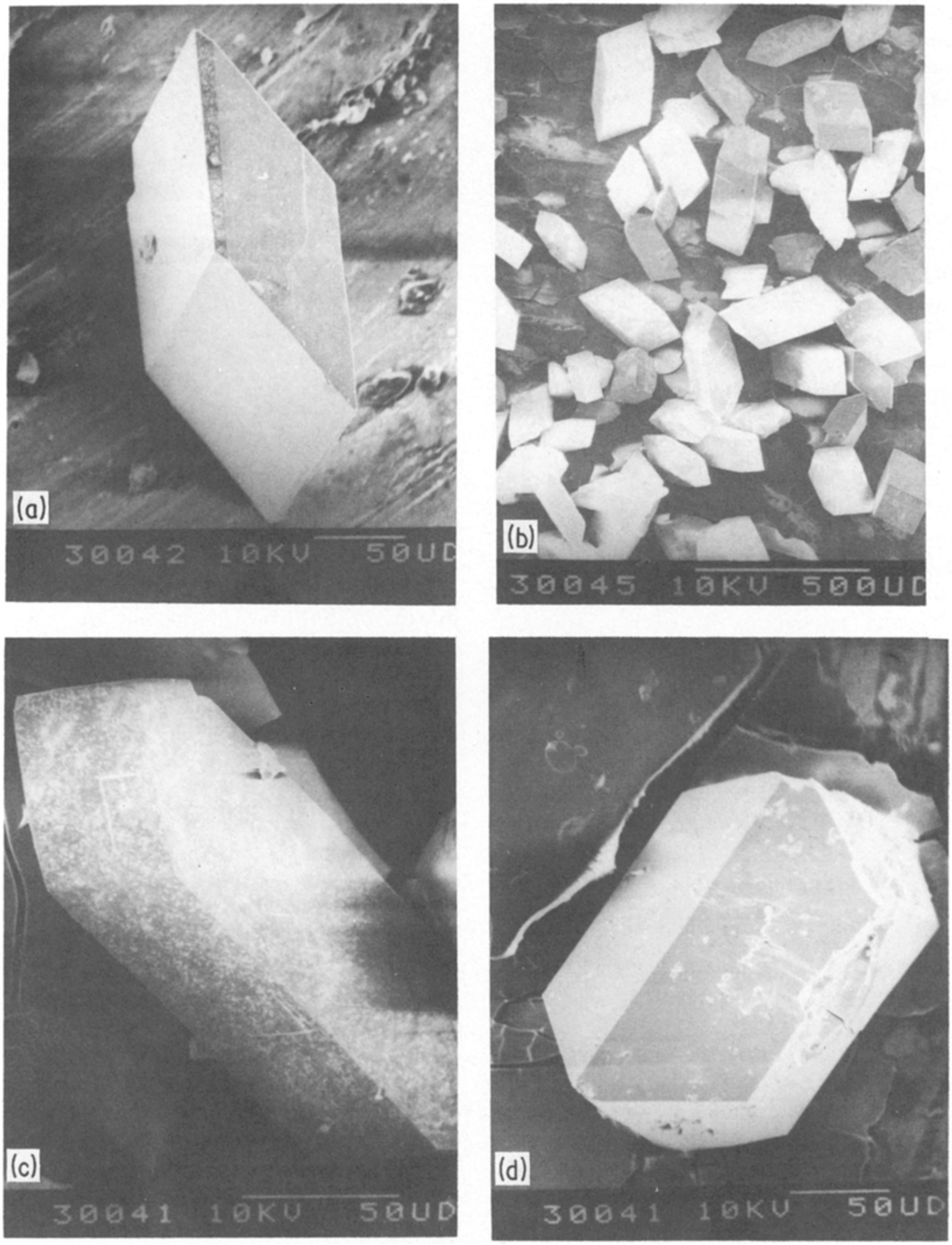


Figure 1 Representative photographs of $Na_2(La, Me)Zr(PO_4)_3$ (where Me = Co, Al, Cr) crystals: (a, b, c) $Na_2(La, Co)Zr(PO_4)_3$; (d, e) $Na_2(La, Al)Zr(PO_4)_3$; (f, g, h) $Na_2(La, Cr)Zr(PO_4)_3$; and (i, j) $Na_2LaZr(PO_4)_3$.

the crystals varied from 1 to 3 mm. Higher concentrations of alkalis ($>$ 10 wt %) and also trivalent elements La_2O_3($>$ 20 wt %), Al_2O_3 or Cr_2O_3 or Co_2O_3($>$ 15 wt %) causes crystallization to be too rapid and results in the development of poor quality crystals.

3.2. Characterization

The crystals obtained were subjected to various studies like X-rays, chemical analysis, and IR-spectroscopy. From the X-ray study it was found that these materials crystallize in the lower symmetry group (monoclinic and triclinic). Complete

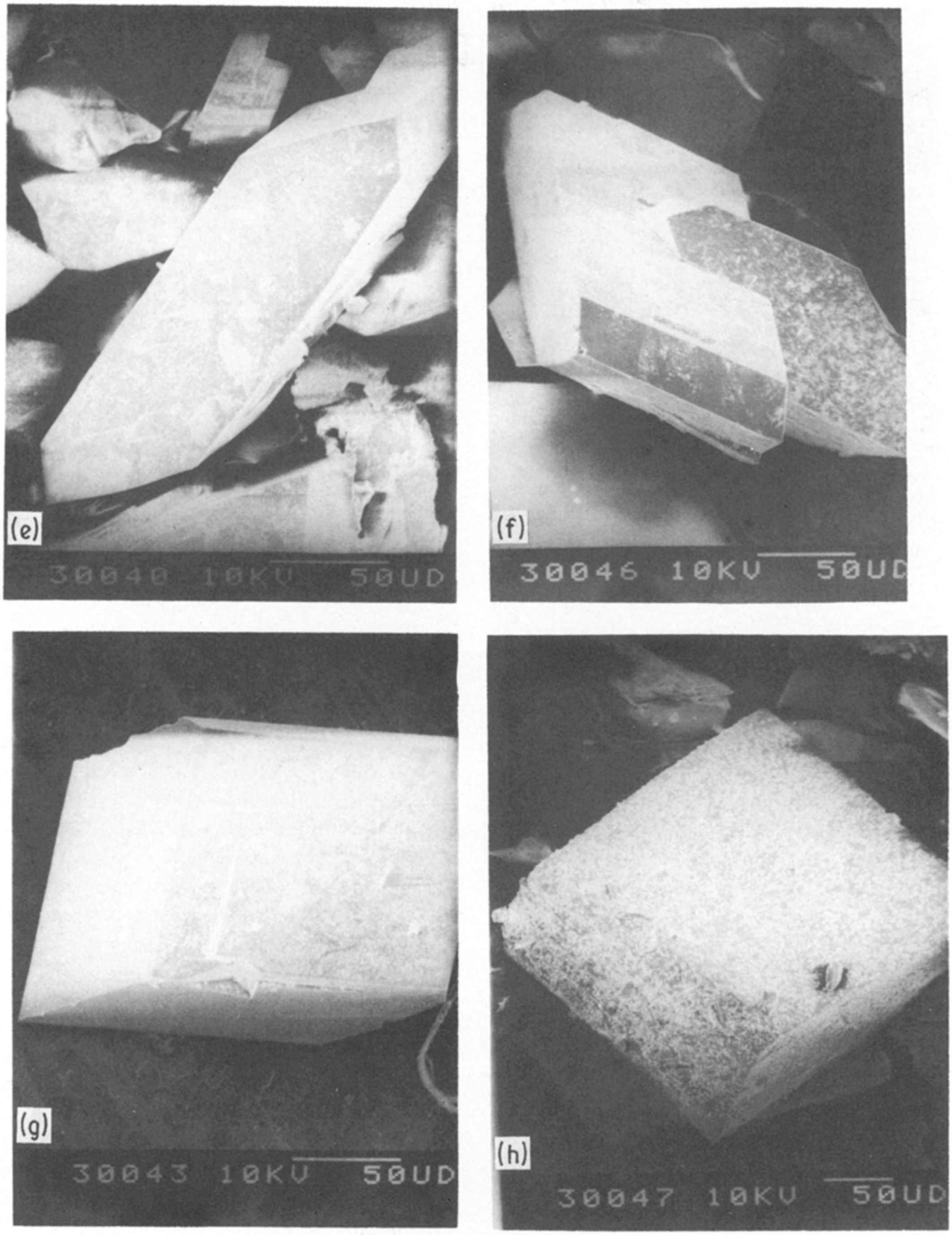


Figure 1 continued.

crystal data for these compounds will be published elsewhere. The authors carried out chemical analysis for some representative crystal samples and the results are given in Table II.

A systematic study of IR-spectra for $Na_2(La, Me)Zr(PO_4)_3$ (where Me = Co, Al, Cr, Ga) crystals was carried out by using a Specord 75 IR spectrophotometer with liquid paraffin. The spectra were taken in the range 400 to 4000 cm^{-1} (Fig. 2). The study of IR-spectra for these compounds revealed many structural details, particularly with reference to (PO_4)-tetrahedra. The multiplication of the

Figure 1 continued.

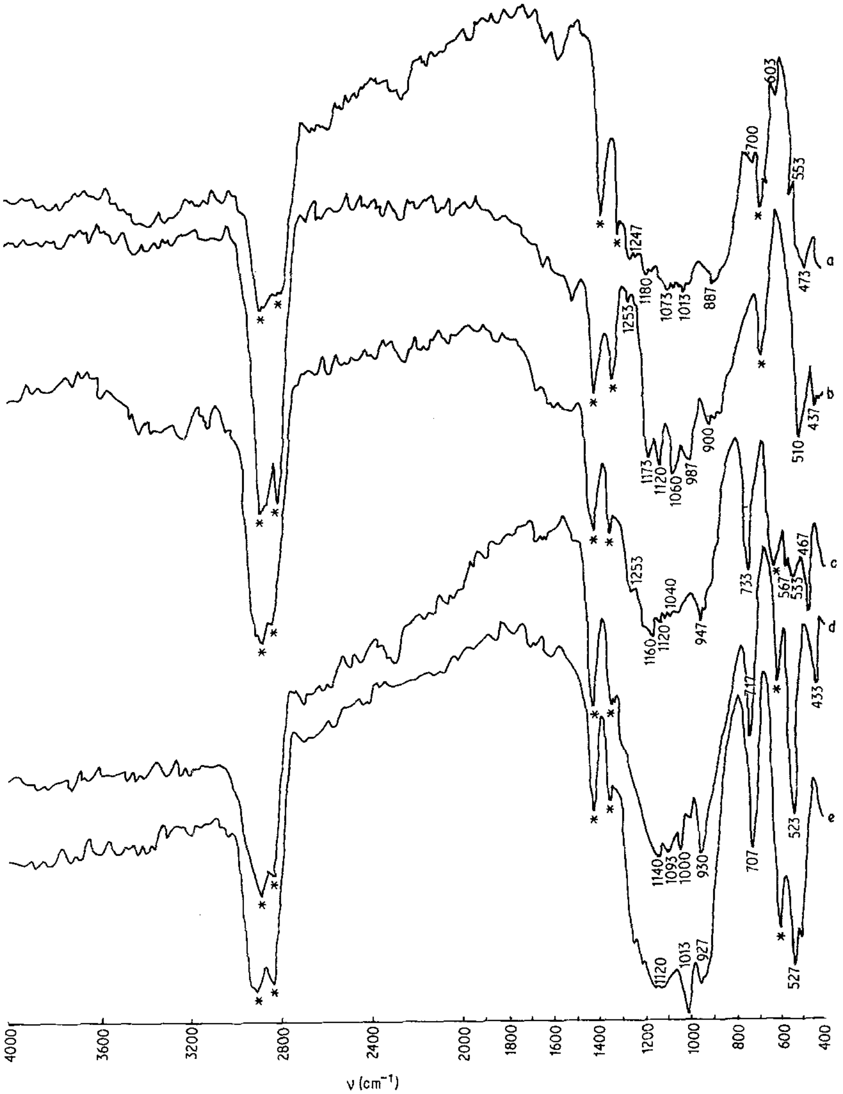
absorption bands in the spectra indicates the distortion of (PO_4)-tetrahedra. Fig. 2 shows that the triorthophosphates have three groups of absorption bands (intense bands in the range 900 to 1200 cm^{-1} and medium intense bands at 740 cm^{-1} and 600 to 450 cm^{-1}) unlike the condensed phosphates which have four to five groups of absorption bands (1340 to 1260, 1180 to 1080, 870 to 680 and 620 to 420 cm^{-1}) [19, 20]. In comparison with IR-spectra for condensed phosphates (Fig. 3), the spectra for triorthophosphates look very simple. The absorption bands in the range 1300 to 1260 cm^{-1} is missing in triorthophosphates. Similarly, the multiplication of the spectra in the medium intense bands have less splitting. The multiplication and fine structure of the spectra in these two ranges always give a clue to the complexity of the internal crystalline structure. With an increase in the degree of condensation of the anionic group, there occurs an increase in the number of absorption bands of phosphoro–oxygen anions in the spectra. From Fig. 2, it is found that the concentration of $(OH)^{-1}$ is extremely meagre. Hence it can be predicted that the crystals will have better physical properties like luminescence and ionic conduction (to be published separately).

TABLE II Results of the chemical analysis for $Na_2(La, Me)Zr(PO_4)_3$ crystals

Crystal type	Compound	wt %
(1) $Na_2(La, Al)Zr(PO_4)_3$	(a) Na_2O	7.57
	La_2O_3	17.13
	Al_2O_3	12.94
	ZrO_2	15.98
	P_2O_5	46.38
	(b) Na_2O	5.96
	La_2O_3	30.88
	Al_2O_3	12.72
	ZrO_2	10.61
	P_2O_5	40.00
(2) $Na_2(La, Co)Zr(PO_4)_3$	Na_2O	7.99
	La_2O_3	6.48
	Co_2O_3	27.90
	ZrO_2	19.70
	P_2O_5	37.93
(3) $Na_2(La, Cr)Zr(PO_4)_3$	Na_2O	2.27
	La_2O_3	33.22
	Cr_2O_3	29.06
	ZrO_2	2.20
	P_2O_5	33.35

4. Conclusions

1. $Na_2(La, Me)Zr(PO_4)_3$ (where Me = Co, Al, Cr) crystals can be grown successfully by chemical reactions, from aqueous solutions and by hydro-



Fgure 2 IR-spectra of $Na_2(La, Me)Zr(PO_4)_3$ crystals: (a) $Na_2LaZr(PO_4)_3$; (b) $Na_2(La, Co)Zr(PO_4)_3$; (c) $Na_2(La, Al)Zr(PO_4)_3$; (d) $Na_2(La, Cr)Zr(PO_4)_3$; and (e) $Na_2(La, Ga)Zr(PO_4)_3$.

thermal techniques within a wide range of physico-chemical conditions.

2. The morphology of the crystals varies depending upon the growth techniques, physico-chemical conditions and the starting materials.

3. Surplus amounts of alkalis and trivalent cations in the starting material do not produce good quality crystals.

4. The crystals grown by the hydrothermal technique are better in quality than the crystals

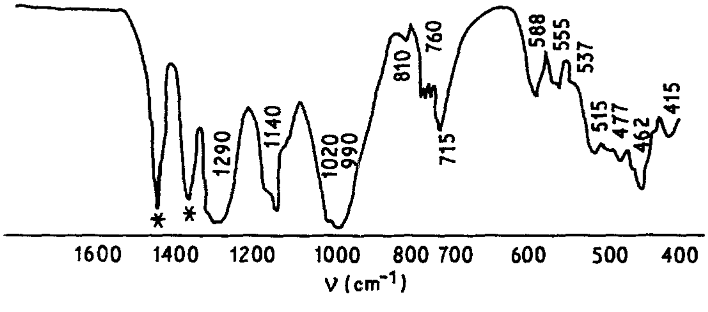


Figure 3 IR-specta of BiP_5O_{14} crystals [19].

grown by chemical reactions and from aqueous solutions.

5. IR-spectra of $Na_2(La, Me)Zr(PO_4)_3$ crystals reveal a complicated and fine crystalline structure for these compounds.

6. The present study shows that $Na_2(La, Me)Zr(PO_4)_3$ crystals are prospective materials for ionic conduction and luminophores.

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