JOURNAL OF MATERIALS SCIENCE LETTERS 5 (1986) 203–205

Infrared spectra of aluminium orthophosphate crystals

K. BYRAPPA, S. SRIKANTASWAMY, G. S. GOPALAKRISHNA,
V. VENKATACHALAPATHY
Department of Geology and The Mineralogical Institute, University of Mysore, Manasa Gangotri, Mysore 570 006, India

Aluminium orthophosphate is an important piezoelectric material with greater prospects than the traditional α quartz in electronic industries, because of its large mechanical coupling factors suitable for both bulk and surface wave applications. However, a series of problems connected with the reproducibility, perfection, growth rate and a host of other parameters have yet to be solved. It is only recently that materials scientists have been able to study this material in greater detail [1–3]. As mentioned in an earlier report [4], one still has to study the growth with reference to the presence of various admixtures and selected doping with characterization with reference particularly to the piezoelectric constants. The use of selected dopants may further enhance the piezoelectric effect of aluminium orthophosphate and in some cases new materials of interest may be obtained. In the earlier report [4], the authors reported the influence of admixtures on the crystallization and morphology of aluminium orthophosphate crystals. The present report deals with the influence of admixtures on the internal structure of aluminium orthophosphate crystals.

The experiments were carried out using a hydrothermal technique in Morey-type autoclaves with teflon liners and good quality aluminium orthophosphate crystals were obtained under the following conditions: $AlCl_3$, 3 g; H_3PO_4 (85%), 5 ml; HCl (2 M), 3.5 ml; temperature, 250° C; pressure, 100 atm; duration, 8 days. A detailed report on the crystallization of aluminium orthophosphate has been given in [5]. K^+, Rb^+, Cu^{2+}, Mg^{2+}, Pb^{2+}, Ni^{2+}, Ba^{2+}, Be^{2+}, Fe^{3+}, Cr^{3+}, Bi^{3+}, Co^{3+}, La^{3+}, Ce^{3+}, Nd^{3+}, Gd^{3+}, Zn^{4+}, Zr^{4+} and Ti^{4+} elements have been introduced as admixtures in the form of gels (in some cases as oxides or hydroxides) into the nutrient material. The starting concentrations of these admixtures were kept at either 1.5 or 4 wt %. The characterization of the resultant products revealed the formation of different phases in addition to aluminium orthophosphate in some experiments. In the majority of the experiments where the concentration of admixtures was 1.5 wt %, only one phase – aluminium orthophosphate – was obtained and the quality of the crystals was uniformly good. In the few cases where barium, nickel and zinc were the admixtures, the crystallization of meta- and orthophosphates was observed. Here, the number of aluminium orthophosphate crystals was reduced exponentially, and in some cases only limited grains of aluminium orthophosphate were seen. When the concentration of the admixtures was increased to 4 wt % the formation of the secondary phases (meta- and orthophosphate) increased, and only in a few cases, where bismuth, copper, magnesium, lanthanum and zirconium were the admixtures, did the formation of the main phase, aluminium orthophosphate, persist. Moreover, the formation of orthophosphates of the respective admixtures (isostructural with aluminium orthophosphate) was not observed in all the experiments. This may be due to the fact that the formation of covalent silica-type phosphates, $A^{III}B^{V}O_4$, require the following condition: $r_A + r_B/s < 0.055\,\text{nm}$ [6]. Therefore, in the majority of cases, only the metaphosphates of aluminium and the admixtures are observed. Even the experiments using trivalent elements as admixtures up to 4 wt % did not yield isomorphous series of type $(M_x^{3+}Al_{1-x})PO_4$. This may be due to the lower pressure (< 100 bar) and lower temperature (~ 250° C) conditions of the present experiments. At higher pressure and temperature conditions (> 800° C and > 1 kbar), these trivalent admixtures might easily substitute Al^{3+} to form isomorphous series. Normally, the formation of orthophosphates of various metals takes place under conditions of higher pressure and temperature. In Table I we give the list of metals which can form orthophosphate isostructural with aluminium orthophosphate.

A systematic study of the infrared spectra of the resultant products was carried out in order to study the variation in their internal structures. Since the concentration of these admixtures in the resultant product was at p.p.m. and p.p.b. levels, the variation in the internal structure may not be made easily visible by the routine X-ray technique which gives an image of ideal structure, and it is not possible to fix some molecules, for example (OH) molecules. Contrary to the routine X-ray technique, the infrared spectra give minute structural details about the presence of various molecules in the structure, distortion of $[PO_4]$ tetrahedra due to the presence of admixtures, and so on. The distortion of $[PO_4]$ tetrahedra is very common in phosphates and it results in the wide variation in P–O distances and also in the splitting of the P–O absorption bands in the infrared spectra. From the crystal chemistry of phosphates, it is evident that the variation in P–O distances is quite large and it is difficult to find an analogue to $[PO_4]$ tetrahedra among the inorganic compounds. Thus, one can expect highly complex spectra for these phosphates depending upon the concentration of admixtures, degree of distortion and degree of polymerization. In this respect the study of infrared spectra of phosphates is very important (although it is very difficult because of the complexity of the spectra in some cases) in understanding the internal structures.

0261–8028/86 $03.00 + .12

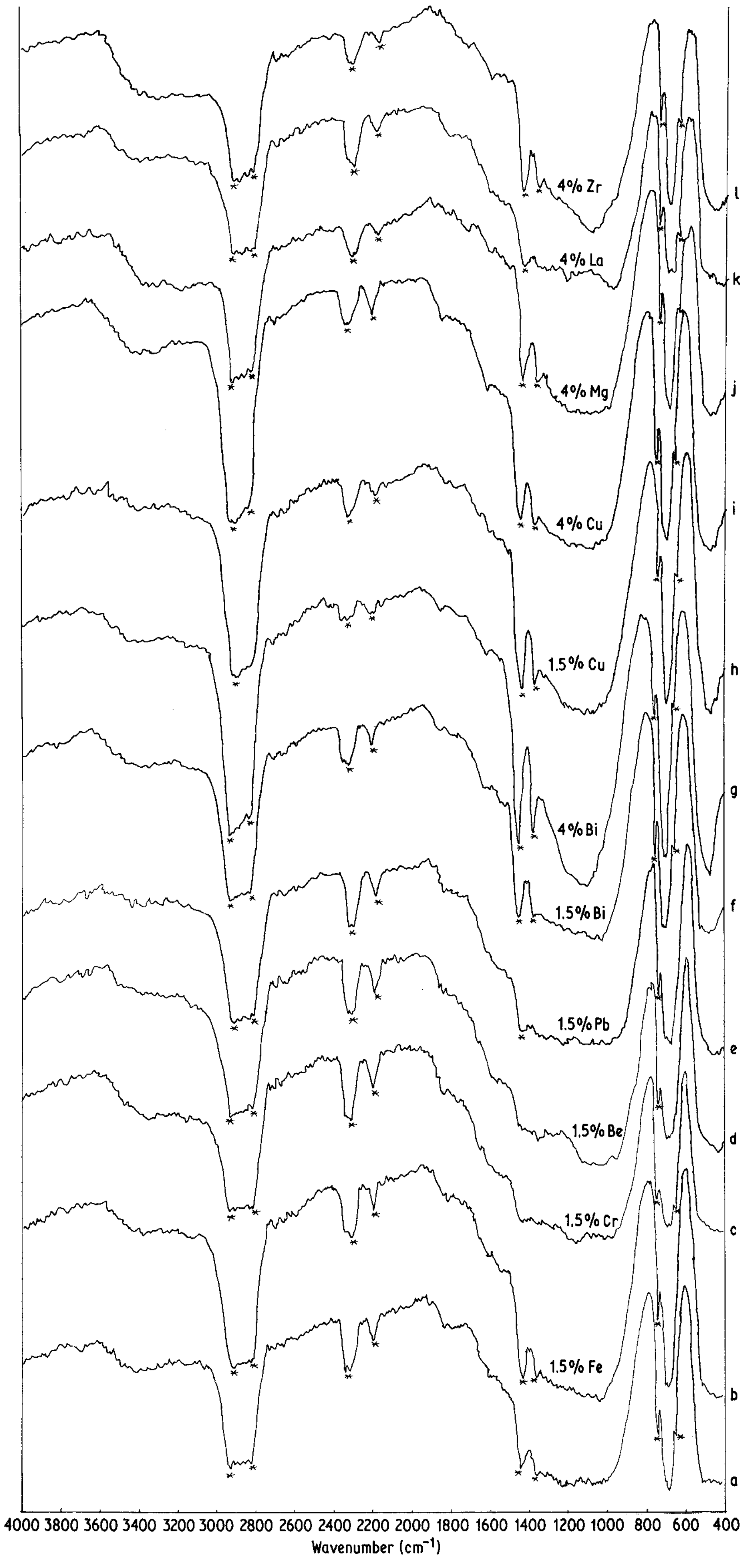

Figure 1 Infrared spectra of $AlPO_4$ crystals containing various admixtures.

The infrared spectra of the resultant products were registered in the range 4000 to 400 cm^{-1} using a Specord 75IR (GDR) spectrophotometer with liquid paraffin. The representative infrared spectra of aluminium orthophosphate crystals containing various admixtures and of metaphosphate are shown in Figs 1 and 2, respectively. It is well known that orthophosphates with a T_d symmetry have four fundamental vibrations: $\nu_1(A_1)$, 980 cm^{-1}; $\nu_2(E)$, 363 cm^{-1}; $\nu_3(F_2)$, 1082 cm^{-1} and $\nu_4(F_2)$, 515 cm^{-1} [7], with two intense

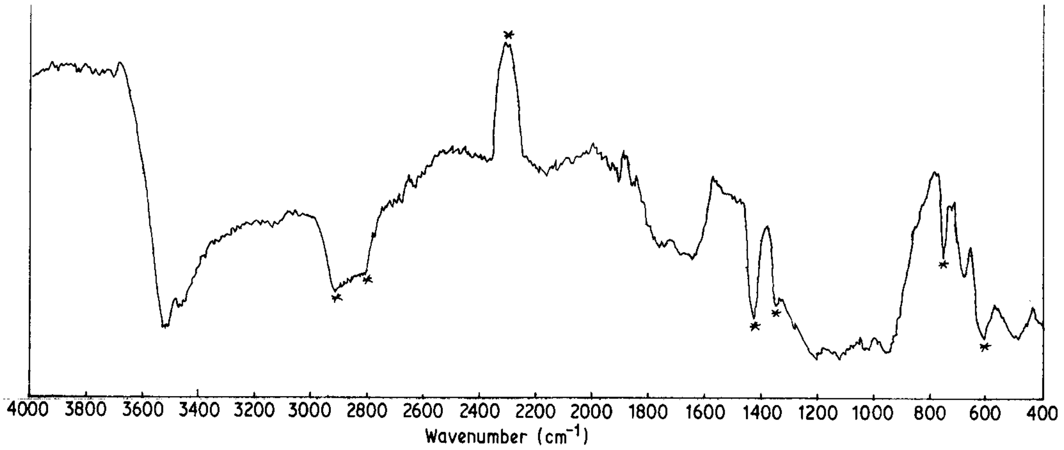

Figure 2 Infrared spectrum of aluminium metaphosphate.

bands for ν_s and ν_l valence vibration in the range 1300 to 950 cm^{-1} and for ν_4 in the range 740 to 400 cm^{-1} (Fig. 1). The spectrum of metaphosphate is more complicated because of the increase in the degree of polymerization of phosphoro-oxygen anions and contains three intense bands in the regions 1315 to 970, 850 to 670 and 600 to 400 cm^{-1} (Fig. 2). The pure aluminium orthophosphate crystals have a very narrow intense absorption peak at 690 cm^{-1} and a broad absorption peak in the range 520 to 400 cm^{-1} (Fig. 1a). With the introduction of admixtures there is a slight change in the spectra of aluminium orthophosphate crystals, particularly with reference to the two above quoted absorption peaks. There is a splitting of the peak at 690 cm^{-1} due to the presence of admixtures and higher O–P–O angles in the structures (Figs 1b to 1). The common feature among all these spectra is the absence of the (OH) band. But the spectra of metaphosphates from all the experiments show large absorption bands for (OH) and the absorption band for liquid paraffin at 2320 cm^{-1} is inverted (Fig. 2). This anomalous absorption of liquid paraffin may be due to the absorption of moisture from the atmosphere, since all the resultant materials were kept exposed to the atmosphere for several days before recording the infrared spectra.

TABLE I Covalent silica-type (A^3PO_4) phosphates

Metal (A)	Ionic radius of A (nm)	$r_A + r_P/2$ (nm)
B	0.021	0.028
Mn	0.070	0.0525
Fe	0.067	0.051
Cr	0.064	0.0495
Ga	0.062	0.0485
Co	0.064	0.0495
Al	0.057	0.046

From the above infrared spectroscopic studies there is not much variation in the internal structure of aluminium orthophosphate with the introduction of admixtures. This may be because even at the higher concentration the admixtures can neither readily diffuse the Al–O and P–O bonds nor form their respective orthophosphates isostructural with aluminium orthophosphate, but form only metaphosphates. Therefore, these admixtures normally enter the lattice only interstitially and not substitutionally, at least under the present experimental conditions.

Acknowledgements

We thank Professor R. Jagadiswara Rao for valuable discussions and CSIR for financial support.

References

1. E. D. KOLB and R. A. LAUDISE, *J. Crystal Growth* **43** (1978) 313.
2. *Idem*, Proceedings of the 35th Annual Frequency Control Symposium. USAERADCOM, Ft Monmouth, New Jersey, May 1981.
3. *Idem*, *J. Crystal Growth* **56** (1982) 83.
4. K. BYRAPPA, S. SRIKANTASWAMY, G. S. GOPALAKRISHNA and V. VENKATACHALAPATHY, *J. Mater. Sci. Lett.* submitted.
5. K. BYRAPPA, V. VENKATACHALAPATHY and B. PUTTARAJ, *J. Mater. Sci.* **19** (1984) 2855.
6. R. G. GREBENSHIKOV, in "Progress in Physics and Chemistry of Silicates" (Nauka, Leningrad, 1978) p. 162.
7. K. NAKAMOTO, "Infrared Spectra of Inorganic and Co-ordination Compounds" (M. Mir, Moscow, 1966).

Received 26 June
and accepted 15 July 1985