

Mössbauer and XRD studies on the effect of doping iron in $\text{KCaY}(\text{PO}_4)_2$

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Abstract. The effect of doping iron at the yttrium site in hexagonal $\text{KCaY}(\text{PO}_4)_2$ is studied for various concentrations of x ($0 \leq x \leq 1$), of iron using Mössbauer and X-ray diffraction methods. For low iron concentrations, very little changes in structure are seen but at $x \approx 0.1$, onset of new peaks in the XRD pattern is observed. The Mössbauer study of the doped samples reveals that iron has a solubility of up to 2.5% in the parent phase with any excess iron precipitating out to form a new and unknown phase. From a detailed analysis of the X-ray diffraction pattern (corresponding to $x = 1$) of the latter phase, it is found that this phase is rhombohedral with the possible space group $R\bar{3}$.

Keywords. Mössbauer spectroscopy; X-ray powder analysis; crystal structure; Fe-substitution.

1. Introduction

Interest in double phosphates, with the general formula $\text{ABLn}(\text{PO}_4)_2$ (A = alkali, B = alkaline earths and Ln = rare earths), is increasing in recent times owing to their applications as phosphors and laser materials, when doped with active centres. These phosphates which are known to exist in three structures viz. hexagonal, tetragonal and monoclinic (Et-Tabirou and Daoudi 1980; Arthus *et al* 1991; Tie *et al* 1995a), are found to be structural analogues of the corresponding orthophosphates: LnPO_4 . Recently Tie *et al* (1995b) have reported the synthesis of a new hexagonal double phosphate, $\text{KCaY}(\text{PO}_4)_2$ which is isostructural with hexagonal $\text{KNd}(\text{PO}_4)_2$. Its space group is reported to be $P6_222$ (Vlasse *et al* 1982). The structure is a three-dimensional network consisting of $\text{Ln-PO}_4\text{-Ln}$ chains parallel to the c axis. These chains are interconnected leaving large open channels, lined with oxygen atoms, running parallel to the c axis. As early as in 1950, Mooney (1950) had pointed out that the open channels in the hexagonal LnPO_4 could accommodate a neutral molecule of water. In the case of $\text{KCaY}(\text{PO}_4)_2$, the potassium atoms are found to occupy these channels instead of the zeolitic water. The calcium atoms, on the other hand, occupy the same sites as the rare earth ions which are eight-fold coordinated to oxygen atoms. As a result, Tie *et al* (1995b) expect disorders in the K^+ and Ca^{2+} distributions leading to deviations in the site symmetries of the PO_4 and YO_8 polyhedra from D_2 to C_2 . Using infrared and Raman spectral data of this compound they have been able to see this deviation in the symmetry.

They have also investigated (Tie *et al* 1995c) the luminescent properties of Eu^{3+} -, Gd^{3+} - and Dy^{3+} -doped $\text{KCaY}(\text{PO}_4)_2$.

Since yttrium in $\text{KCaY}(\text{PO}_4)_2$ is eight-fold coordinated to oxygens, substitution of iron for yttrium is expected to bring about changes in structure as this high a coordination is somewhat unusual for iron, leading to a possible new phase. Hence we have doped various concentrations of iron and studied them using powder X-ray diffraction and Mössbauer spectroscopy. In this paper we report the results of the study on $\text{KCaY}_{1-x}\text{Fe}_x(\text{PO}_4)_2$ for $x = 0.01, 0.05, 0.10, 0.50$ and 1.

2. Experimental

Both the doped and undoped samples of potassium calcium yttrium diphosphate were prepared by first mixing and grinding stoichiometric amounts of di-ammonium hydrogen phosphate, calcium carbonate, potassium carbonate and yttrium oxide along with ammonium chloride, which was used as a flux. This mixture was filled in a boat and heat treated at 573 K, 953 K and finally at 1293 K for a duration of 6 h each, with intermittent grinding of the reactants. The final product obtained was whitish, pale yellowish or dark reddish depending on whether the sample was undoped, partly doped or completely doped with iron. They were characterized by powder X-ray diffraction (XRD) technique. A Siemens D-500 powder diffractometer employing $\text{CuK}\alpha$ radiation was used for this purpose. The room temperature Mössbauer measurements were made on a home-made spectrometer (Chittaranjan *et al* 1993), working in the transmission geometry. The Mössbauer source was a 18 mCi ^{57}Co isotope

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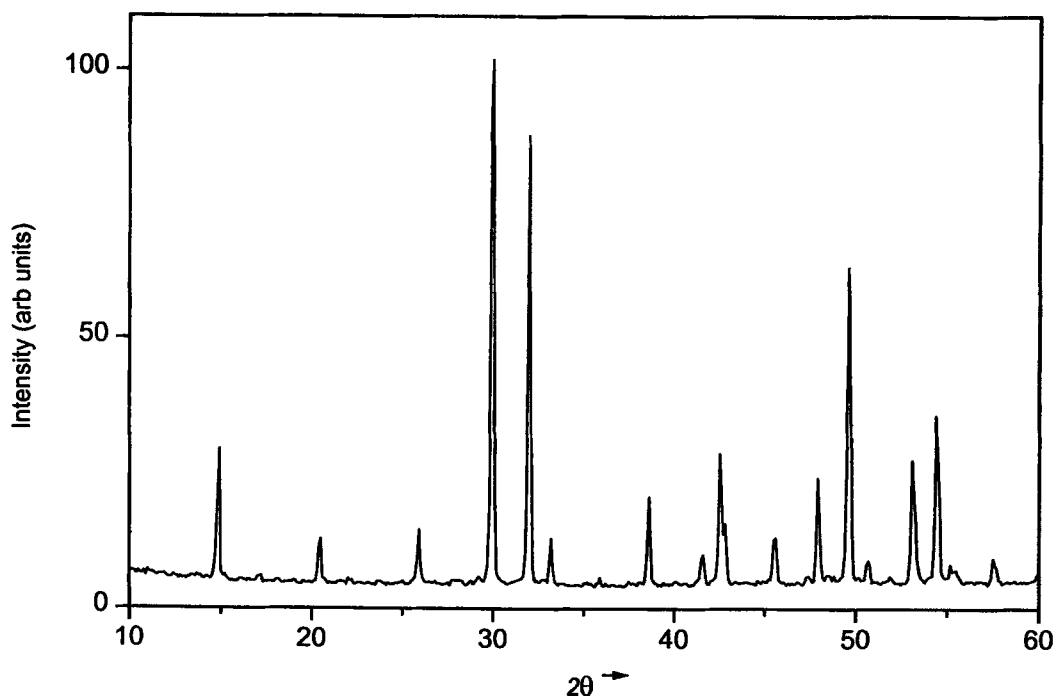


Figure 1. Powder X-ray diffraction pattern of as-prepared $\text{KCaY}(\text{PO}_4)_2$.

embedded in rhodium matrix. The spectrometer had an inherent linewidth of 0.23 mm/sec. Data analysis was done using a nonlinear least squares program based on the Levenberg–Marquardt method (Press *et al* 1988). The isomer shift values were reported with respect to α -iron. Particle size distribution was determined with the help of ‘Malvern Instruments’ particle size analyzer.

3. Results and discussion

The X-ray diffraction pattern of the as-prepared $\text{KCaY}(\text{PO}_4)_2$ powder sample is shown in figure 1. The pattern is found to match well with the reported one (Tie *et al* 1995b). The lattice constants as determined from the experimental pattern are found to be $a = 0.6886$ nm and $c = 0.6339$ nm. An interesting observation regarding the as-prepared doped samples was that they were found to be more compacted than the virgin sample which was powder-like. A preliminary check on the particle size indicated that for the 5% iron-substituted sample, about 18% of the particles are having a size of $< 2 \mu$ and for the case of 10% iron, about 35% of the particles are below 2μ size. The particle size distribution in the case of 5% and 10% iron-doped samples are tabulated in table 1.

In figure 2 are shown the XRD patterns of 1%, 5%, 10%, 50% and 100% (figures 2b–2f, respectively) Fe-substituted samples of $\text{KCaY}(\text{PO}_4)_2$ along with that of the undoped sample (figure 2a). A comparison of these reveals the following interesting features: the XRD patterns of the 1% and 5% Fe-doped $\text{KCaY}(\text{PO}_4)_2$ show

Table 1. Particle size distribution in as-prepared $\text{KCaY}_{1-x}\text{Fe}_x(\text{PO}_4)_2$.

$x = 0.05$		$x = 0.10$	
Size ($\leq \mu\text{m}$)	(%)	Size ($\leq \mu\text{m}$)	(%)
188.0	100	13.2	100
77.5	90	9.8	92
13.2	73	7.3	74
7.3	47.5	4.7	49
1.9	17.6	1.9	35

little changes (figures 2b and 2c) as compared to the undoped sample (figure 2a) case. However, new peaks are seen to emerge at $\approx 11^\circ$, 14° , 26° , 28° , 31° , 35° , etc in the pattern for $x = 0.1$. These peaks are seen to grow in intensity for higher iron content (figures 2e and 2f). However, for $x = 1$ case (figure 2f) only the peaks corresponding to the newly formed phase are present. In order to find out whether the appearance of the new peaks is due to a structural phase transition possibly induced by doping of iron or not, a comparison of the peak positions in figure 2a with those of the corresponding peaks in figures 2d and 2e was done. Very little shifts (maximum increase of about 0.05° in 2θ) were observed in the original peak positions which means that the appearance of the second phase is not due to any phase transformation. Thus it appears that the diffraction patterns of all the partially-doped samples reflect mixed phase with peaks of both the parent and the new phase being present. The diffraction pattern corresponding to figure 2f does not fit to any of

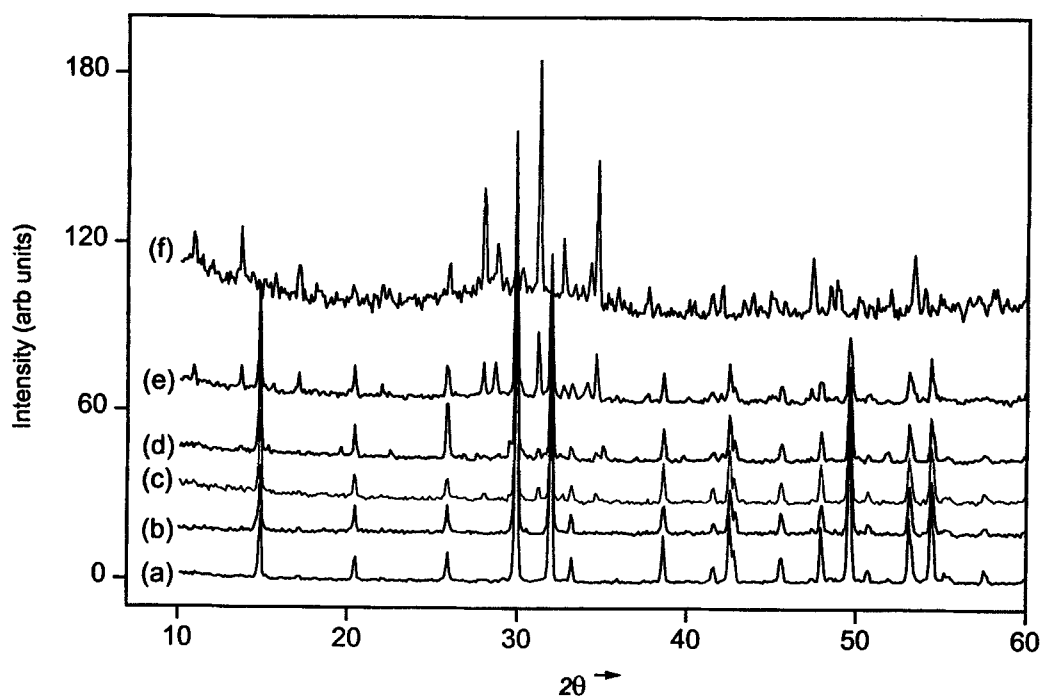


Figure 2. Powder X-ray diffraction patterns of as-prepared $\text{KCaY}(\text{PO}_4)_2$ doped with (a) 0%, (b) 1%, (c) 5%, (d) 10%, (e) 50% and (f) 100% iron.

the known patterns but closely resembles that for $\text{Ca}_7\text{Mg}_2\text{P}_6\text{O}_{24}$ (JCPDS/ICDD Pattern No. 200348) (Ito 1968).

The pattern in figure 2f was initially fitted using TREOR (Werner 1964), a trial-and-error program for finding the approximate crystal system. The best fit obtained was for the hexagonal system having the following cell constants: $a = 1.034$ nm and $c = 1.856$ nm with a figure-of-merit of about 16. With this information as a reference, the XRD pattern in figure 2f was next fitted systematically to each of the hexagonal and rhombohedral space groups, using the NBS-AIDS*83 least-square refinement program based on a routine by Appleman and Evans (1973). The best fit obtained was for the rhombohedral space group, $R3$, with a fairly high figure-of-merit, $F = 31$ with all the 44 lines getting indexed. The refined cell constants are: $a = 1.0344 \pm 0.0001$ nm and $c = 1.8578 \pm 0.0004$ nm. Table 2 shows the fitted XRD data.

Figure 3 shows the Mössbauer spectra corresponding to the 5%, 10%, 50% and 100% Fe-doped samples of $\text{KCaY}(\text{PO}_4)_2$. Since the spectra are due to a mixture of the parent phase and a phase whose structure is not known, they were initially fitted with one doublet and later with two doublets, three doublets, etc. Of all the fits, only the two-doublet fit showed consistency in relation to the Mössbauer parameters (table 3). Another noteworthy feature was the observation of the following systematics: doublet 1 was common only to all the partially-doped samples while doublet 2 was common to all the spectra. As the magnitude of the peak shift in the XRD patterns of

Table 2. Fitted XRD data of the new phase.

Space group: $R3$							
$a = 1.034$ nm				$c = 1.856$ nm			
d_{obs} (Å)	hkl	$ I_0$	d_{calc} (Å)	d_{obs} (Å)	hkl	$ I_0$	d_{calc} (Å)
8.096	101	39	8.070	2.858	205	100	2.860
6.462	012	40	6.448	2.738	214	37	2.736
5.187	110	25	5.172	2.685	303	20	2.689
4.370	021	18	4.354	2.652	116	20	2.657
4.126	104	15	4.123	2.585	220	64	2.586
4.032	202	20	4.034	2.542	107	17	2.545
3.970	113	18	3.970	2.502	125	19	2.503
3.433	015	29	3.432	2.400	312	13	2.398
3.329	211	20	3.331	2.386	223	19	2.386
3.227	024	23	3.224	2.148	306	21	2.149
3.183	122	56	3.181	1.918	045	30	1.918
3.097	006	35	3.096	1.879	324	21	1.879
2.988	300	29	2.986	1.865	413	24	1.864

the partially-doped samples is not significant, and since a quadrupolar doublet is seen in all the Mössbauer spectra of the partially-doped samples, we infer that Fe has a slight solubility of less than 5% in $\text{KCaY}(\text{PO}_4)_2$ and that further addition of the dopant results in the precipitation of a second phase. These observations show that Mössbauer results are in agreement with the XRD results. The relative areas of doublets 1 and 2 of the partially-doped samples are plotted in figure 4. Since the ratio of the relative areas of doublet 1 to doublet 2 for $x = 0.05$ is almost 50 : 50, we can immediately see that 2.5% of Fe

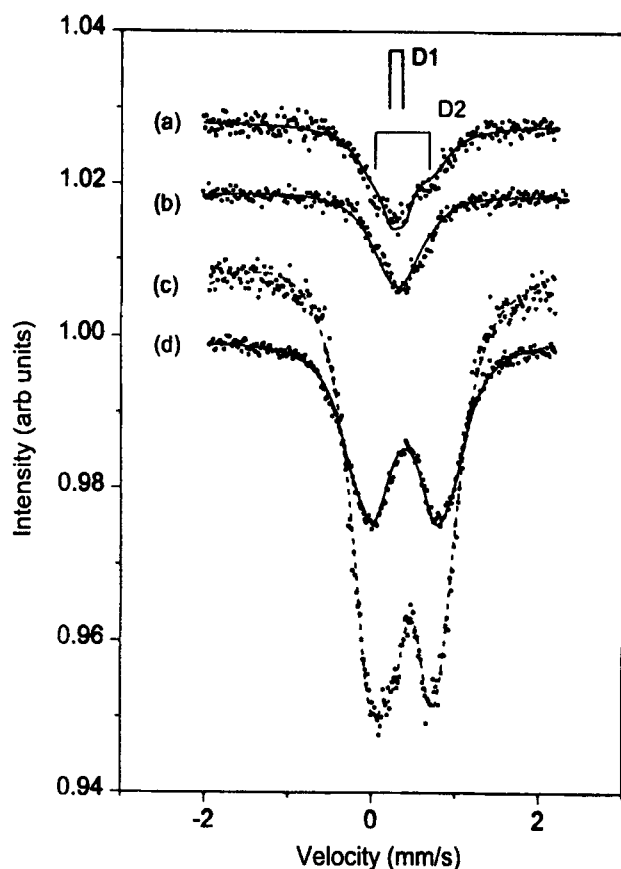


Figure 3. Mössbauer spectra at room temperature of as-prepared $\text{KCaY}(\text{PO}_4)_2$ doped with (a) 5%, (b) 10%, (c) 50% and (d) 100% iron.

Table 3. Room temperature Mössbauer parameters of as-prepared $\text{KCaY}(\text{PO}_4)_2$ doped with (a) 5%, (b) 10%, (c) 50% and (d) 100% iron.

x	Parameters	Doublet 1	Doublet 2
0.05	Γ	0.24(1)	0.55(2)
	C	0.31(2)	0.37(2)
	Q	0.14(2)	0.70(4)
	A	0.48	0.52
0.1	Γ	0.23(1)	0.56(2)
	C	0.35(3)	0.38(2)
	Q	0.15(2)	0.68(2)
	A	0.32	0.68
0.5	Γ	0.22(1)	0.55(2)
	C	0.32(2)	0.39(2)
	Q	0.16(2)	0.68(2)
	A	0.04	0.96
1.0	Γ	0.42(2)	0.54(3)
	C	0.37(2)	0.39(2)
	Q	1.24(2)	0.69(2)
	A	0.20	0.80

Γ : FWHM, C: Isomer shift (wrt α -iron) in mm/s, Q: Quadrupolar splitting (mm/s), A: Area.

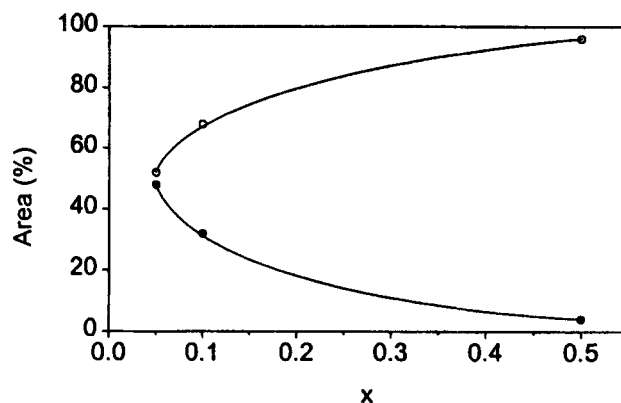


Figure 4. Relative areas of the doublet 1 (\bullet) and doublet 2 (\circ) for various concentrations of Fe in the Mössbauer spectra of the partially-doped samples of $\text{KCaY}(\text{PO}_4)_2$.

has substituted in the parent phase and the rest has formed the second phase. If this is indeed the case we should expect for the $x=0.1$ and 0.5 , relative area ratios of 25 : 75 and 5 : 95, respectively. From figure 4 we see that the area ratios for these two concentrations are close to what is expected. This close agreement in the area ratios between what is expected and what is observed substantiates the aforementioned picture.

From the isomer shift values of the two doublets it is seen that Fe exists in the 3+ oxidation state in both the parent and the new phases. The small value of the quadrupolar splitting for doublet 1 means that the Fe environment in the parent compound is nearly cubic. Doublet 2 has a large quadrupolar splitting indicative of an asymmetric site for Fe with a distorted local structure in the new phase. The other doublet for $x=1$ sample is quite broad and we attribute it to the presence of an amorphous phase that may be due to some unreacted phases still being present. This corresponds to the slightly broad background seen in the XRD pattern in figure 2f.

From table 3 it is seen that the linewidth for doublet 2 corresponding to the new phase is fairly large. This broadening may be due to inhomogeneity of iron environments over the sample leading to a distribution of quadrupolar splittings. This seems unlikely in the present case as the XRD patterns in figures 2c, 2d and 2e do not show any broad background. The other reasons for line broadening are slow relaxation rates, low frequency thermal vibrations (Fluck 1966) and the presence of other cations in the second coordination sphere leading to differing environments around the iron atom, also called the next-nearest-neighbour effect (Russo *et al* 1996). Large linewidths, for instance, have been observed for Fe spectrum in the case of spinels (Russo *et al* 1996) and in $\text{LnSr}_2\text{Cu}_2\text{Ga}_{(1-x)}\text{Fe}_x\text{O}_7$ (Rykov *et al* 1994) where thermal vibrations of the Fe atom situated in a tetrahedral site are the cause. Since we do not know the complete crystal structure of this phase, it is difficult, at this stage, to pinpoint with definiteness the reason for the large linewidth.

4. Conclusions

We have investigated a recently reported novel compound, $\text{KCaY}(\text{PO}_4)_2$ upon doping iron at the yttrium site to study its stability and local atomic structure by powder X-ray diffraction and Mössbauer spectroscopy.

From our results we have found that iron has a solubility of up to 2.5% in the hexagonal $\text{KCaY}(\text{PO}_4)_2$ but additional doping results in the precipitation of a second phase as shown by the Mössbauer and XRD results. Detailed analysis of the XRD data of this unknown phase has shown that it is rhombohedral with $R\bar{3}$ as its space group. Our Mössbauer data on this phase indicate that Fe occupies unique sites that are chemically equivalent.

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