Syntheses, Crystal Structure and Optical Properties of the Polymorphs of Potassium Ferrisilicate (KFeSiO₄) & Effect of Calcium Doping on the Phase Stability

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By

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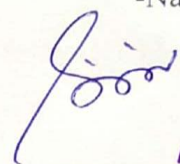
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Approval Sheet

This thesis entitled as "Syntheses, Crystal Structure, and Electronic Properties of the Polymorphs of Potassium Ferrisilicate (KFeSiO$_4$) & Effect of Calcium Doping on the Phase Stability" is approved for the degree of Master of Science.
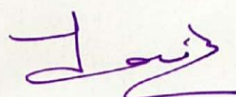
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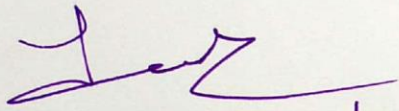Dr. Jai Prakash
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Declaration

I declare that this thesis is an original report of my research, has been written by me and has not been submitted for any previous degree. The experimental work is almost entirely done by me with the help of my supervisor Dr. Jai Prakash. The collaborative contributions have been indicated clearly and acknowledged. Due references have been provided on all supporting literature and resources.

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Acknowledgments

Abstract

The two polymorphs of KFeSiO$_4$ namely α-KFeSiO$_4$ and β-KFeSiO$_4$ have been synthesized using solid-state methods at 1000ºC and 830ºC, respectively. The low temperature polymorph, β-KFeSiO$_4$ crystalizes in the $P6_322$ space group of the hexagonal crystal system (a = 5.260(1) Å, b = 5.260(1) Å, c = 8.801(1) Å) whereas the high temperature α-KFeSiO$_4$ phase adopts orthorhombic crystal structure (a = 5.470(1) Å, b = 9.190(1) Å, c = 8.580(1) Å). The Fe and Si atoms are statistically disordered at the same site in the β-KFeSiO$_4$ structure. Each Fe/Si atom in this structure is coordinated to four oxygen atoms in a tetrahedral fashion. The red colored β-KFeSiO$_4$ phase starts transforming to yellowish colored α-KFeSiO$_4$ phase on heating in the air above 910ºC. Yellow colored crystals of α-KFeSiO$_4$ have been prepared by the flux method using KI as the molten flux.

The stability of hexagonal β-KFeSiO$_4$ phase on the substitution of calcium cations at the potassium sites has been investigated in detail. Our studies show that the β-phase could be stabilized even at 1000ºC by Ca-doping. Five different compounds having formula K$_{1-x}$Ca$_x$FeSiO$_4$ with different "x" were synthesized. From optical measurement, the band gap of β-KFeSiO$_4$ and α-KFeSiO$_4$ are 1.9(1) eV and 2.2(1) eV, respectively. The melting point of the α-KFeSiO$_4$ phase has been determined by heating the sample in an alumina crucible at various temperatures. It has been found that the melting point of the alpha phase is above 1090ºC. The disordered distribution of Fe/Si in β-KFeSiO$_4$ is also supported by the FTIR data. The Si—O—Si symmetric stretching frequency and Fe—O—Fe symmetric stretching frequencies in FTIR data of α-KFeSiO$_4$ suggest the possibility of ordered Fe and Si sites in the orthorhombic crystal structure. However, crystallographic studies are required to support this conjecture.

Content

1. Introduction

The system $K_2O\text{-}Fe_2O_3\text{-}SiO_2$ was partly investigated[1] to know the existence and nature of a ternary compound. Two ternary compounds of this systems are iron-leucite and iron-feldspar. Later it was found that iron-leucite $(KFeSi_2O_6)$[1] shows analogous polymorphism with its aluminum analogue $KAlSi_2O_6$ and iron-feldspar $(KFeSi_3O_8)$[1,2,3] is with $KAlSi_3O_8$. So iron can appear instead of aluminum in some compounds maintaining the same crystal system. Another ternary compound of the $K_2O\text{-}Fe_2O_3\text{-}SiO_2$ was $KFeSiO_4$ which had two polymorphs[4]. There were few experimental data of these compounds. In 1983, Bentzen published a paper[5] containing the synthesis and characterization of the polymorphs of $KFeSiO_4$ by glass devitrification process. Three polymorphs of $KFeSiO_4$ were low-temperature β-form, high-temperature α-form and metastable γ-form. β- and γ-$KFeSiO_4$ are isomorphous with the two analogues of $KAlSiO_4$[6], kalsite and synthetic kaliophilite. Also, a phase of $KFeO_2\text{-}SiO_2$ was published[7]. Suitable sized crystals of β-$KFeSiO_4$ and γ-$KFeSiO_4$ could not be prepared for single crystal studies. Diffraction patterns of these phases showed remarkable similarities of with $KAlSiO_4$[4,6] structure ($P6_3$). Both crystalizes in hexagonal crystal systems. Bentzen described γ-$KFeSiO_4$ as Fe/Si disordered structure and β-$KFeSiO_4$ as Fe/Si ordered structure[5]. Weissenberg photographs of an α-$KFeSiO_4$ sample revealed an orthorhombic unit cell. But the space group could not be determined due to the presence of more than one crystal in the sample. Above 910ºC the low-temperature polymorph (β-$KFeSiO_4$) begins to transform into high-temperature polymorph (α-$KFeSiO_4$). In 1999, the crystal structure of β-$KFeSiO_4$ was published[8]. Single crystals of the low-temperature β form of KFeSiO4 were grown from a KVO_3:K_2MoO_4 flux. It was melted at 900°C in a covered platinum crucible for five days and cooled down to 800ºC at a rate of 0.01ºC per minute. The crystals formed as elongated hexagonal prisms which were separated from the flux by applying hot water. Electron microprobe analysis of one crystal did not detect any molybdenum or vanadium and yielded a composition slightly enriched in silicon, *viz.*, $Fe_{0.97}K_{0.97}O_4Si_{1.03}$ corresponding to the substitution $Si^{4+} = K^+ + Fe^{3+}$. This composition was used for the structural refinement.

β-$KFeSiO_4$ crystallizes with a kalsilite-type unit-cell with $P6_322$ symmetry[8]. The tetrahedral framework, $[FeSiO_4]^-$ is built of staggered six-membered rings forming nine-coordinated sites around the K^+ ions. The apical oxygen atoms are also shifted off the threefold axes and split over three equivalent positions in order to eliminate linear M—O—M

linkages. Fe/Si distribution in β-KFeSiO$_4$ is completely disordered and the structure is well described in the P6$_3$22 space group with a single tetrahedral site. The average tetrahedral bond length (<M—O> = 1.72 Å) is intermediate between the Si—O and Fe—O bond lengths (1.62 and 1.87 Å, respectively).
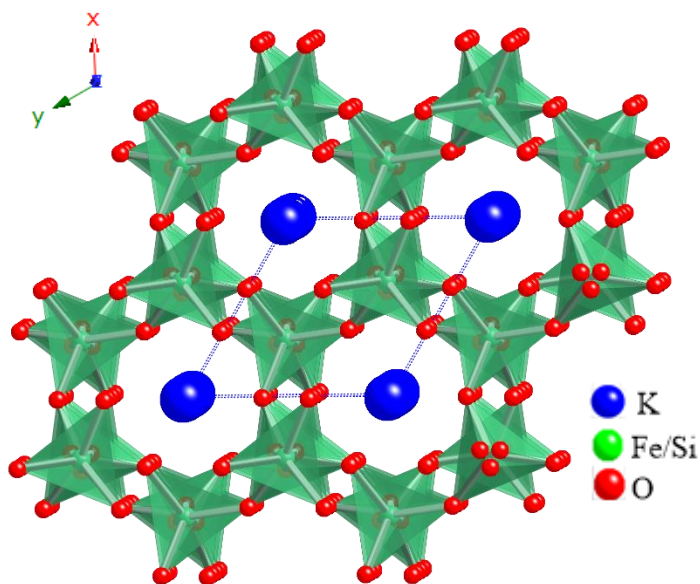
Single-crystal grown from a KVO$_3$:K$_2$MoO$_4$ flux. Ag-Kα radiation (λ = 0.56086Å) was used.

Fe$_{0.97}$K$_{0.97}$O$_4$Si$_{1.03}$

Space Group: P6$_3$22

Crystal system: Hexagonal

a = 5.2600 Å	α = 90°
b = 5.2600 Å	β = 90°
c = 8.801 Å	γ = 120°

Here we are going to reproduce the results i.e. synthesis of the polymorphs of KFeSiO$_4$ using direct heating solid-state synthesis approach. Single crystal preparation using flux method, band gap determination of the polymorphs and effect of calcium doping to check the phase stability of the low-temperature polymorph.

Before going to the synthesis part, some topics need to be discussed to get a better understanding of the project work.

1.1. Direct Heating or Ceramic Method- Probably the most widely used method for the preparation of a polycrystalline solid is the direct reaction of a mixture of solid reactants at an elevated temperature. Solids do not usually react at room temperature. So to make it react it is necessary to heat the mixture of reactants to much higher temperatures often above 1000°C. And the reactions are not instantaneous. The heating should be for a considerable time. This means that in solid state synthesis thermodynamic factor and kinetic factor both are important. Here K$_2$CO$_3$, Fe$_2$O$_3$, and SiO$_2$ are reacting to form KFeSiO$_4$. After an appropriate heat-treatment, the starting materials partially react to form KFeSiO$_4$. This nucleation is difficult because it needs structural

reorganization of reactants i.e. bonds must be broken and reformed and atoms must migrate from its lattice. So only high temperature can supply the thermal energy needed to jump out from their lattices and diffuse through the crystal. With time the reaction rate slows down. This is because to grow the $KFeSiO_4$ layer thicker, counter diffusion of K^+, Fe^{3+} and Si^{4+} ions are necessary through the formed $KFeSiO_4$ layer. As the diffusion rates slow down the reaction rate also falls. So sufficient time should be allowed for the completion of the reaction.

1.2. Use of Mortar-Pastel and Pellet Formation of the Sample- The reaction rate of this type of reaction varies enormously with the surface area of the reactants. The surface area of a solid depends on particle size. Using a mortar and pastel for grinding, particle size can be reduced and surface area can be increased to allow more exposure to heat. The total area of contact between the grains of reacting solids depends approximately on the total surface area of the grains. The area of contact can be maximized by pressing the reacting powder into a pellet. It is done by pressing the sample to high pressure e.g. 1500-2000 psi. The effect of pressure causes the reacting particles to fit together better.

1.3. Flux Method for Single Crystal **Growth**- Flux method is a method for crystal growing of desired substance in a suitable solvent. A solvent is chosen which has a melting point lower than the substance. It is taken as three to five times in quantity compared to the sample to. The mixture of sample and flux are heated in a crucible which is unreactive to both the solvent and the solute until both the components melt giving rise a complete solution. Then very slow cooling is done. Slow cooling allows proper nucleation of crystal seeds. As material precipitates out from the solution, the amount of sample in the flux decreases and the temperature at which the solution is saturated lowers. One disadvantage of this process is that not very large crystals can be grown.

1.4. Optical band gap determination: The UV-Visible spectrum can be used to calculate the band gap of a semiconducting material. Band gap is the energy difference between the valence band and the conduction band. For an electron to jump from valence band to conduction band it requires a specific amount of energy which is called the band gap energy (Figure 1.a). For insulators, the band gap is more than 4 eV and for semiconductors, it is less than 3 eV. All semiconductors can be divided into direct band gap and indirect band gap. In the first case position

of valence band and conduction band coincide in the *k*-vector space (Figure 1.b) where in the second case they don't (Figure 1.c). Photon absorption is only necessary for the electronic transition from valence band to conduction band for direct-gap semiconductors. For indirect-gap semiconductors, the participation of additional particle which would change the momentum of the electron is necessary.
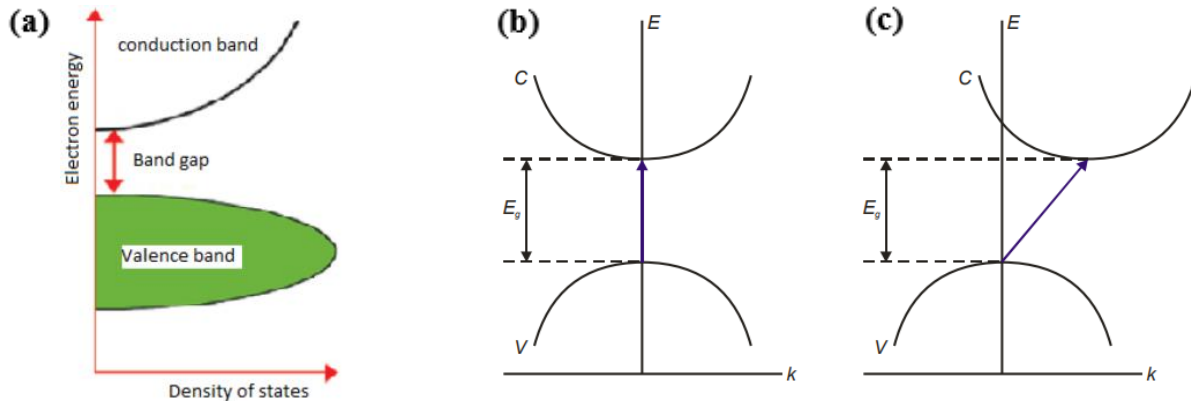
Figure 1: (a) Explanation of band gap. Orientation of valence band and conduction band for (b) Direct bandgap semiconductors, (c) Indirect band gap semiconductors.

The UV-Visible spectrometer records the intensity of transmitted light (I) from the sample and compares it to the incident intensity (I_0). The absorbance "**A**" is defined as, **A = - Log (I/I$_0$).** By plotting the graph between $\alpha^{(1/n)}$ versus photon energy (**hν**). Where "**α**" is the optical absorption coefficient which can be calculated from the equation, **α = 2.303A/t**; where **t**= thickness of the sample. Photon energy can be calculated using the equation, **hν = 1240/wavelength (nm),** in eV. The factor "**n**" takes the values 0.5, 2, 1.5, 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. Plotting the graph between $\alpha^{(1/n)}$ versus photon energy (hν) we get a vertical segment when the vertical segment is extrapolated it cuts the X-axis at a particular point. The value of that point is the band gap energy (**E$_g$**).

2. Experimental

2.1. Materials and Reagents: K_2CO_3 (Alfa, 99%), Fe_2O_3 (Alfa, 98%), and SiO_2 (SRL, Silica gel for TLC), SiO_2 (Alfa, wide pore 150 Å), KCl (SRL, extra pure), KBr (SRL, extra pure), KI (SRL, extra pure), $CaCO_3$ (SRL, extra pure).

2.2. Synthesis

(a) Synthesis of polycrystalline β-KFeSiO$_4$ – The synthesis of β-KFeSiO$_4$ was attempted using the high-temperature solid-state method. The starting materials K_2CO_3 (4.29 mmol), Fe_2O_3 (4.16 mmol), and SiO_2 (8.32 mmol) were dried at 150-200ºC in the air for 2 hours in an oven to remove any moisture present in the reactants. Stoichiometric amount of Fe_2O_3 and SiO_2 and 5% excess of K_2CO_3 were weighed and homogenized properly using an agate mortar & pastel. An excess of K_2CO_3 was used to compensate for the loss of potassium at high temperature due to vaporization. The homogenized reaction mixture was then transferred to an alumina boat for heat treatment using a high-temperature furnace. The temperature of the furnace containing the reaction mixture was then slowly raised to 830ºC (in 6 hours) and the reactants were allowed to react at the same temperature for two days in the air. The same procedure was followed using SiO_2 (Alfa, wide pore 150 Å) instead of SiO_2 (SRL, Silica gel for TLC).

(b) Synthesis of polycrystalline α-KFeSiO$_4$ – The synthesis of α-KFeSiO$_4$ was attempted using the high-temperature solid-state method. The starting materials K_2CO_3 4.29 mmol), Fe_2O_3 (4.16 mmol), and SiO_2 (8.32 mmol) were dried at 150-200 in the air for 2 hours in an oven. The reactants were weighed and ground using an agate mortar & pastel to produce a homogenous mixture of reactants. The mixture was then transferred to an alumina boat and kept inside a high-temperature furnace for heat treatment in the air. The temperature of the furnace was slowly increased to 1000ºC (10 hours) and the reaction mixture was allowed to anneal for two days before switching off the furnace. The same procedure was followed using SiO_2 (Alfa, wide pore 150 Å) instead of SiO_2 (SRL, Silica gel for TLC).

(c) Synthesis of single crystals of α-KFeSiO$_4$ – The molten flux method was employed for the synthesis of α-KFeSiO$_4$. Potassium chloride (KCl, melting point = 770°C) was used as a molten flux. The flux (KCl) was taken three times to that of the α-KFeSiO$_4$ in weight. The flux and the polycrystalline α-KFeSiO$_4$ compounds were mixed and ground properly using an agate mortar & pastel. The mixture was then Transferring to an alumina crucible and placed in a high-temperature chamber furnace. The temperature of the reaction mixture was slowly ramped up to 1200 $^\circ$C (16 hours) and held constant at this temperature for 24 hours. The reaction mixture was then allowed to slowly cool down to 1100°C at a rate of 5°C /hour followed by annealing at the same temperature for 6 hours. Finally, the reaction mixture was cooled to room temperature at a rate of 20°C / hour. The same procedure was followed using KBr and KI as molten fluxes.

In another experiment, KCl was used as both molten flux and reactant. An excess of KCl (8.42 mmol) was mixed with stoichiometric amounts of Fe$_2$O$_3$ 4.01 mmol) and SiO$_2$ (8.02 mmol). The reactants were homogenized using an agate mortar and pestle before subjecting to same reaction condition as discussed above to grow the single crystals of α-KFeSiO$_4$ phase.

(d) Calcium substituted polycrystalline β-K$_{1-x}$Ca$_x$FeSiO$_4$ phases– A series of six calcium-substituted β-K$_{1-x}$Ca$_x$FeSiO$_4$ phases (x = 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5) were synthesized by the high temperature solid-state method. The stoichiometric amounts of dried CaCO$_3$, Fe$_2$O$_3$, SiO$_2$, and an excess of K$_2$CO$_3$ were homogenized and heated at 1000°C temperature for 1 days in the air. The reaction product was then ground into fine powder by using an agate mortar and pestle. The ground product was then reheated at 1000°C temperature for 2 days in the air.

2.3. Characterizations:

(a) Powder X-ray diffraction (PXRD)- The phase purity of the as-synthesized compounds was evaluated by the powder X-ray diffraction studies. The Cu tube was used as an X-ray radiation source in the diffractometer (Model name -X Pert Pro-PAN analytical) and data were recorded with the help of X Pert High Score software. The polycrystalline sample was fixed at a flat sample stage. Scan angle and scan rates were 10°-70° and 0.0167 $^\circ$ per second, respectively. 'X' celerator detector was used to collect the reflections. The powder patterns thus obtained was analyzed using Match3 software suit (version 3.6.1).

(b) Ultra Violet-Visible Diffuse Reflectance Spectroscopy (UVDSR) - The optical properties of the α- & β-KFeSiO$_4$ phases were characterized using a UV-visible diffuse reflectance spectrophotometer (Shimadzu-3600) with BaSO$_4$ as a standard reference. The wavelength of the radiation was varied from 200 nm to 800 nm.

(c) Fourier Transform Infrared Spectroscopy (FTIR)- Alpha Bruker instrument was used to collect the IR data. The scan range was from 500 cm^{-1} to 3800 cm^{-1}. Data was recorded in transmittance mode. The samples were placed at the tip of the probe of the instrument and within few seconds data was recorded.

(d) Thermal gravimetric analysis (TGA)- TGA was done in a PerkinElmer STA-8000 instrument. 29.379 mg sample was analyzed. The sample was heated from 100$^{\text{o}}$C to 1200$^{\text{o}}$C at 10$^{\text{o}}$C /minute ramp rate in a nitrogen atmosphere with a purge rate of 20 mL/minute.

3. Results and Discussion:

3.1. Powder X-ray Diffraction (PXRD) Data-

(a) Synthesis of polycrystalline β-KFeSiO₄: The beta phase is the low-temperature polymorph of the potassium ferrisilicate. The heating the ($K_2CO_3 + Fe_2O_3 + SiO_2$) mixture using pure silica at relatively lower temperature produced the brown colored product which was identified as β-KFeSiO₄ with a small amount of secondary phase from the PXRD studies. The relative percentage of the secondary phase was very less as compared to the beta phase synthesized using impure silica (Figure 2).
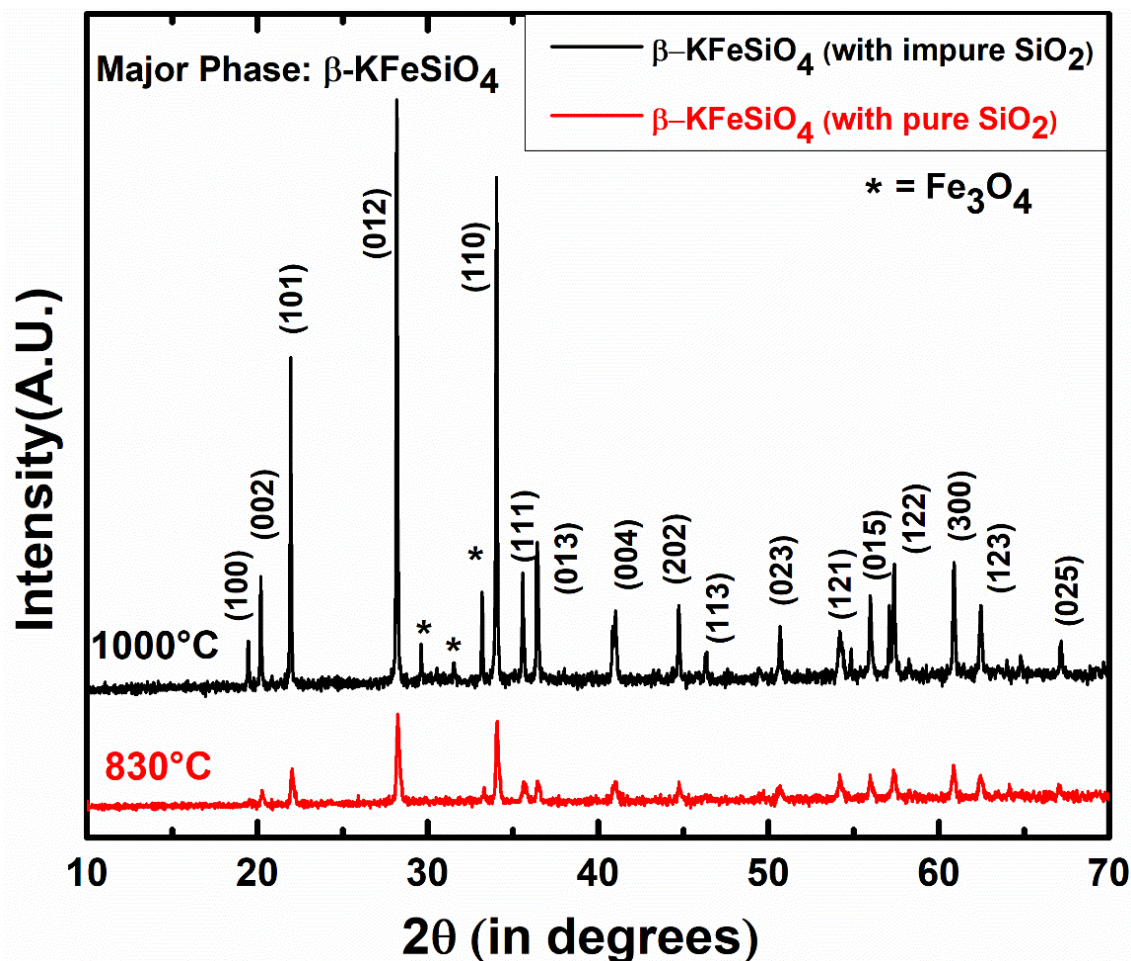

Figure2: *PXRD patterns for the synthesis of β-KFeSiO₄ using pure and impure silica.*

(b) Synthesis of Polycrystalline α-KFeSiO$_4$: The PXRD pattern of the reaction product obtained by the heating the reactants (K$_2$CO$_3$, SiO$_2$, and Fe$_2$O$_3$) at 960$^{\text{o}}$C using impure silica and 3% excess K$_2$CO$_3$ is shown in figure 3.
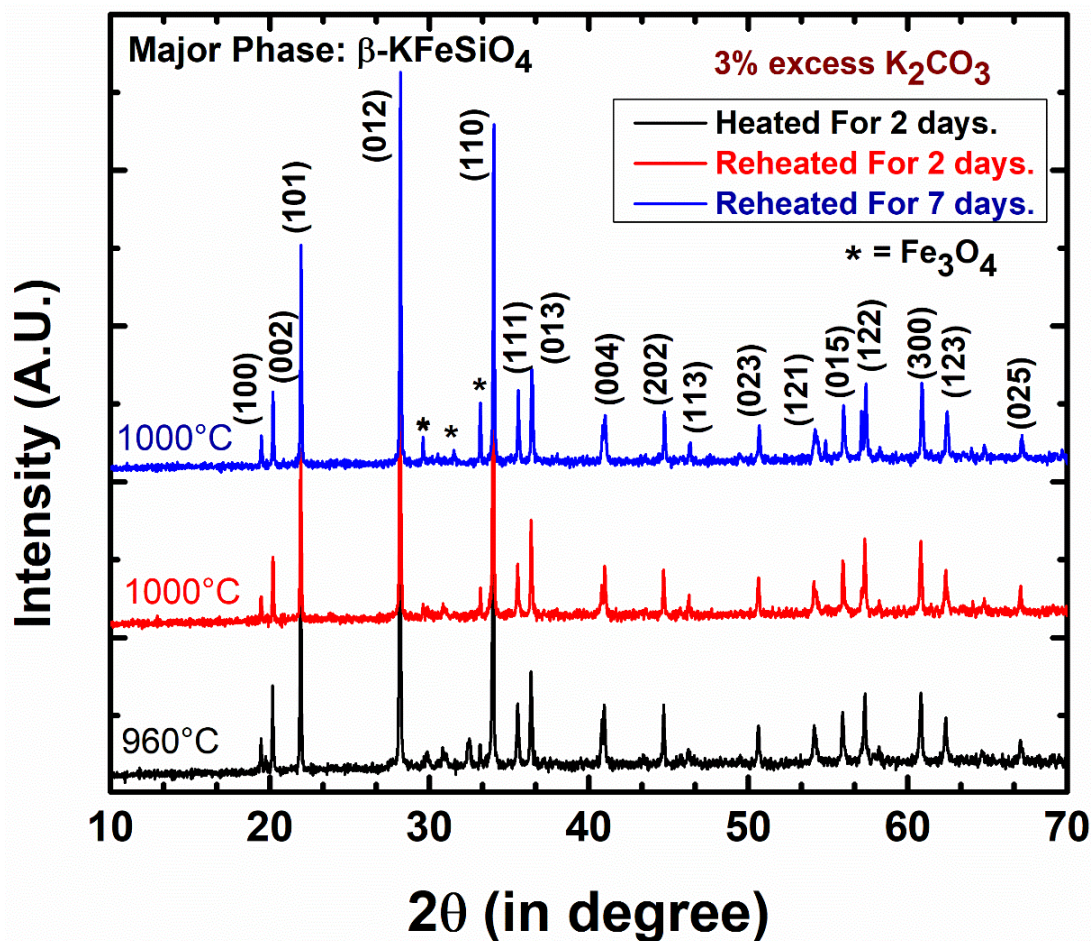

Figure 3: PXRD pattern of β-KFeSiO$_4$ showing the variation of time and temperature on it.

The PXRD pattern shows the formation of β-KFeSiO$_4$ along with a small amount of Fe$_3$O$_4$ phase as a secondary phase. It should be noted that the source of iron used was Fe$_2$O$_3$, and the secondary phase is the Fe$_3$O$_4$ phase. This indicates the reduction of iron in Fe$_2$O$_3$ to Fe$_3$O$_4$ at high temperature in the air. It is a well-known fact that the partial pressure of oxygen decreases on increasing the temperature, and hence Fe$_3$O$_4$ phase was stabilized at high temperature. The presence of Fe$_3$O$_4$ also indicates that the reaction did not complete. The alpha form of KFeSiO$_4$ is the high-

temperature form (thermodynamic product) but the reaction at 960°C only yielded low-temperature beta form. Hence, the reaction product was reheated at 1000°C for 2 days and 7 days, respectively to stabilize α-KFeSiO$_4$ but again β-KFeSiO$_4$ was observed (Figure1) as the major phase with increased amount Fe$_3$O$_4$ secondary phase. The increase of the secondary phase (Fe$_3$O$_4$) is attributed to the loss of potassium at high temperature due to sublimation of potassium with time. Finally, the reaction product was heated at 1000°C using 5% excess potassium carbonate for two days. However, the only β-KFeSiO$_4$ phase was observed along with the Fe$_3$O$_4$ phase as shown in figure 4.
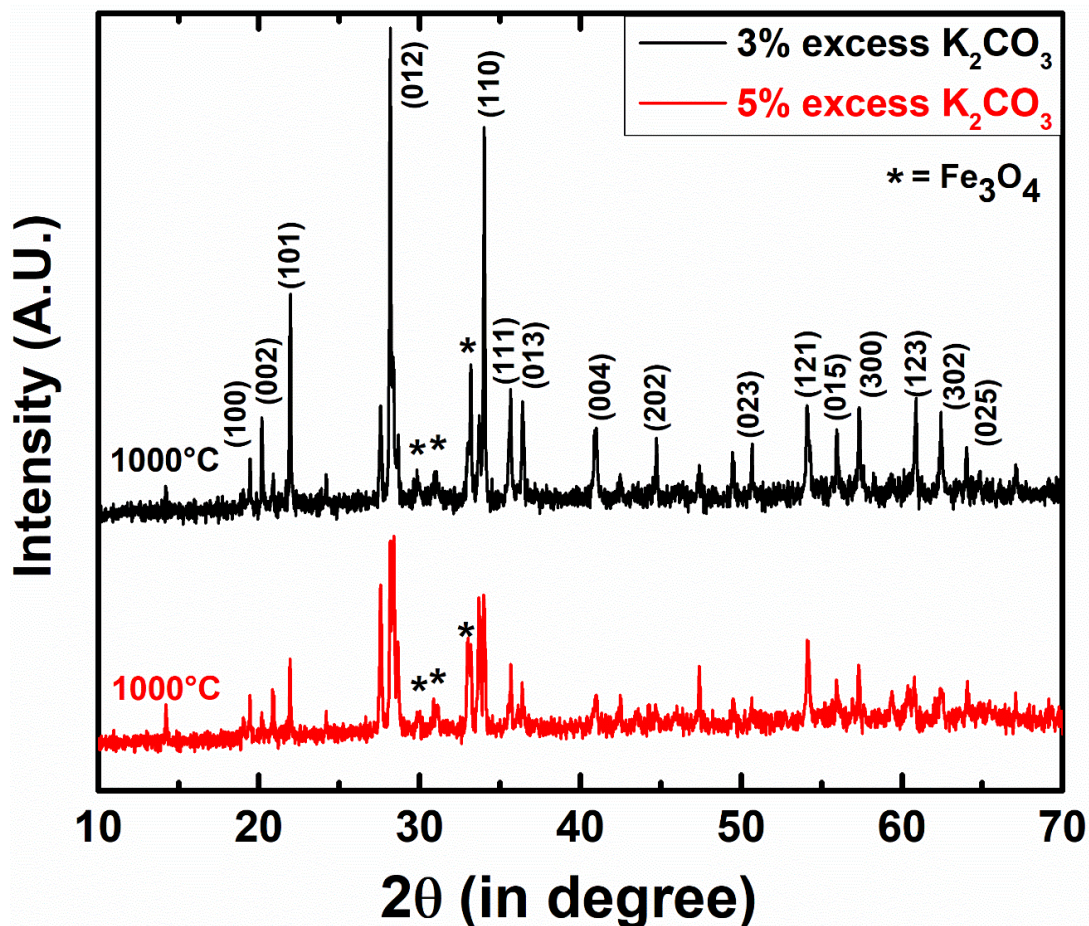

Figure 4: *PXRD patterns of β-KFeSiO₄ showing the effect of excess potassium addition on it.*

As discussed earlier, the Alpha form is the high-temperature phase of KFeSiO$_4$, so heating the reaction mixture above 1000°C is expected to only produce α-KFeSiO$_4$. So, the reaction product was then heated at 1100°C for 24 hours, and the PXRD pattern of the product shows the formation

of the desired α-KFeSiO$_4$ (Figure 5). This happened as expected when we heated the mixture at 1100ºC. This is surprising since the earlier studies have indicated that the beta form will start transforming to alpha form above 910ºC.
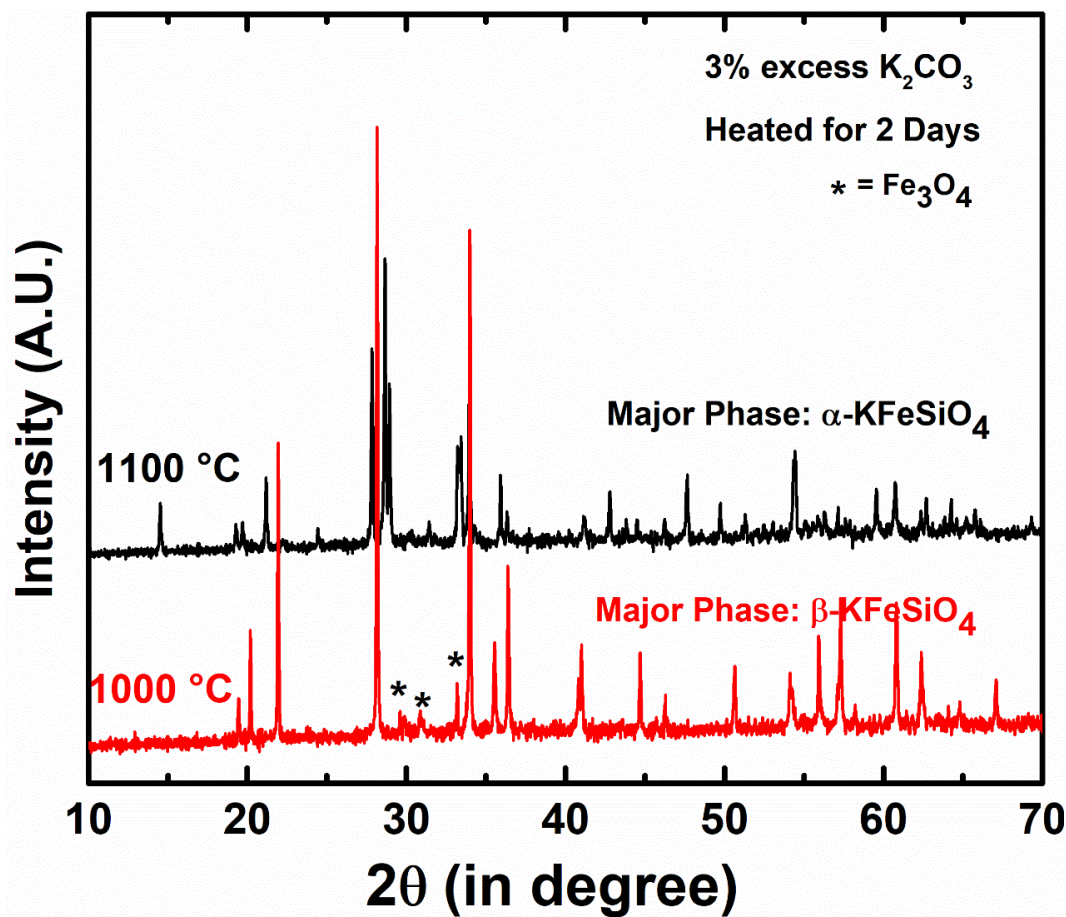

Figure 5: *PXRD patterns of the sample (K$_2$CO$_3$ + Fe$_2$O$_3$ + SiO$_2$) heated at 1000ºC and 1100ºC causes the formation of β and α phases.*

The reaction for the synthesis of alpha form is repeated using pure SiO$_2$, and it was observed that the pale yellow colored alpha phase could be stabilized at 1000ºC by heating the reactants for 1 day in the air. The TLC silica used in earlier reactions contains some impurities like CaSO$_4$, Zn etc. which might be responsible for the stabilization of the β-phase even at higher temperatures where only α-phase supposed to exist (Figure 6).
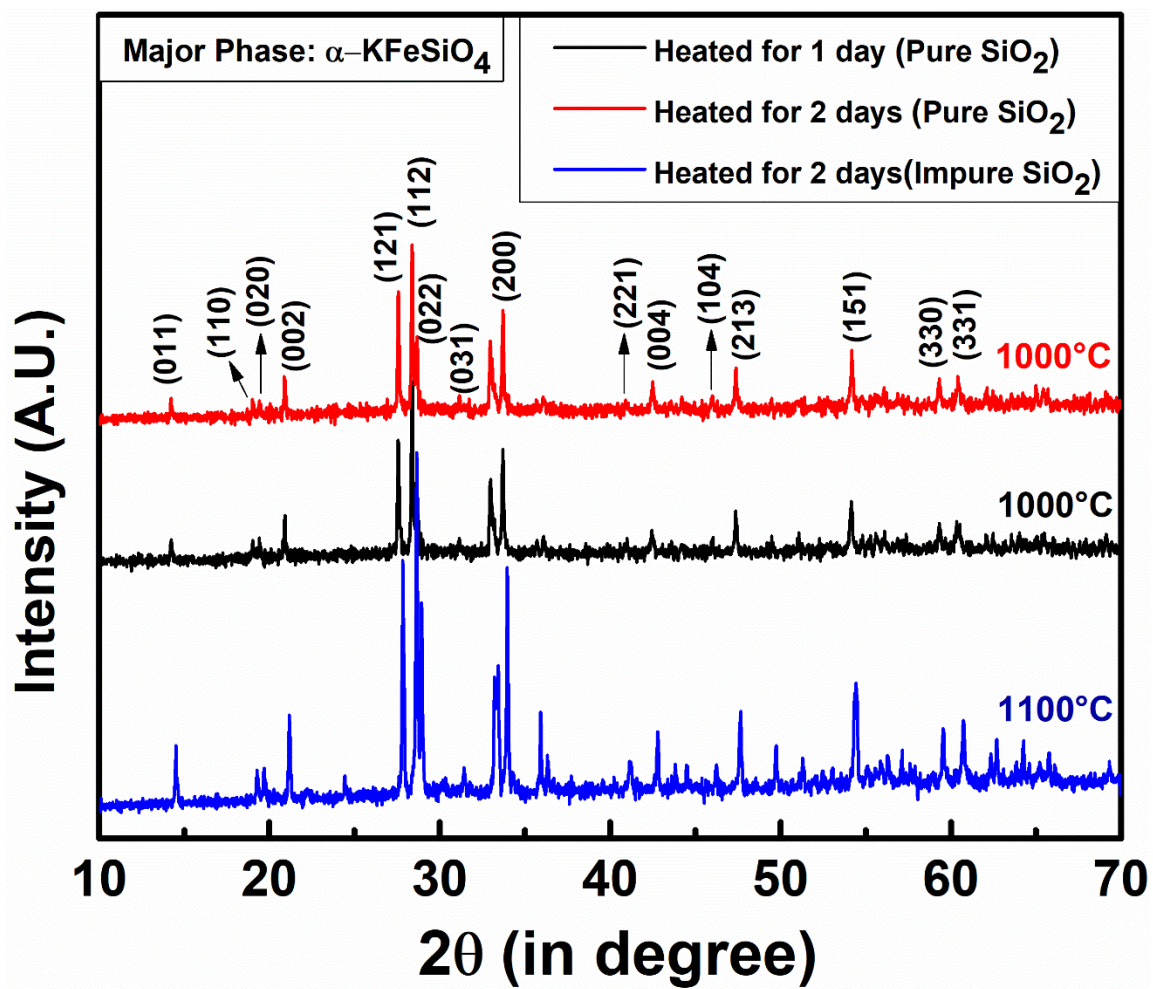
Figure 6: *PXRD patterns of α-KFeSiO₄ showing the variation of silica on it.*

(c) Synthesis of the single crystal of α-KFeSiO₄: The crystal structure of the alpha phase is unknown, and only cell constants were determined in the earlier published report[8]. In order to determine the structure using the single crystal *X*-ray diffraction technique, synthesis of good quality crystals is necessary. Hence, the crystal growth of the alpha form was attempted using the molten flux method. In a typical molten flux method, the polycrystalline alpha form was mixed with excess K*X* flux, and heated at 1200°C. It is expected that at such a high temperature, the K*X* salts are present as the molten liquid, and the solid polycrystalline alpha form starts to dissolve in the flux. A very slow cooling of the mixture leads to crystallization of the alpha form, and it should lead to the formation of single crystals. In the case where K*X* (*X* = Cl, Br, I) was used solely as flux small crystals were found at the end of the reaction. Among the three fluxes, comparatively larger yellow-colored crystals developed in KI medium (Figure 7.a). In the second case where KCl was used as both flux and reactant, larger greenish colored crystals were found (Figure 7.b) in contrast to the molten flux reactions using K*X* salts.
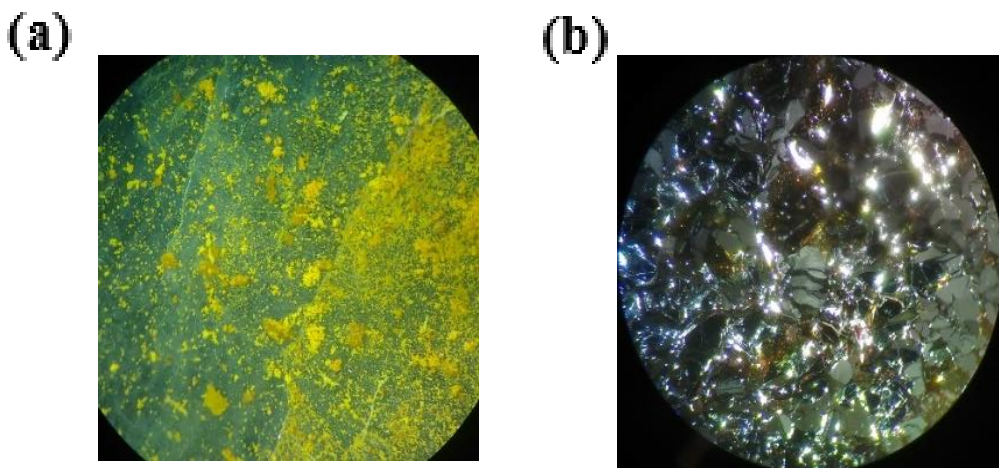

Figure 7: *Single crystals of α-KFeSiO₄, (a) KI used as flux (b) KCl used as a reactant and flux.*
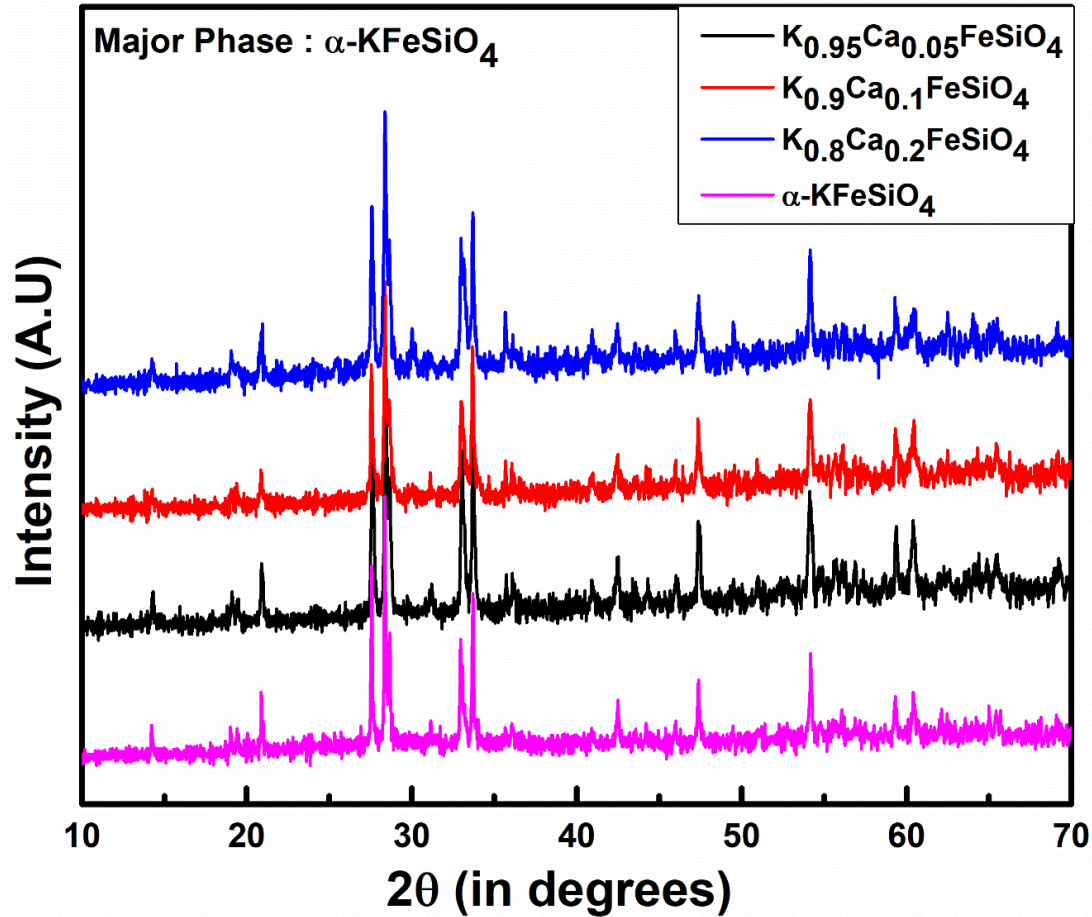
Figure 8: *PXRD patterns showing the effect of calcium doping on (K₂CO₃ + Fe₂O₃ + SiO₂) mixture.*

(d) Calcium substitution at the potassium site in *β*-KFeSiO₄: To our surprise, the only beta form was obtained at temperatures $\leq 1000^{\circ}$C in our earlier attempts to synthesize polycrystalline alpha KFeSiO₄ using the impure source of SiO₂ i.e. silica gel (impurities like CaSO₄, Zn etc.). This suggests that the stabilization of the beta phase is possibly due to the unintentional incorporation of calcium at potassium sites. The replacement of Fe^{3+} with Zn^{2+} is less likely due to overall charge imbalance of the final composition. Hence, we have systematically investigated the effect of Ca-substitution on the stability of beta phase of KFeSiO₄.
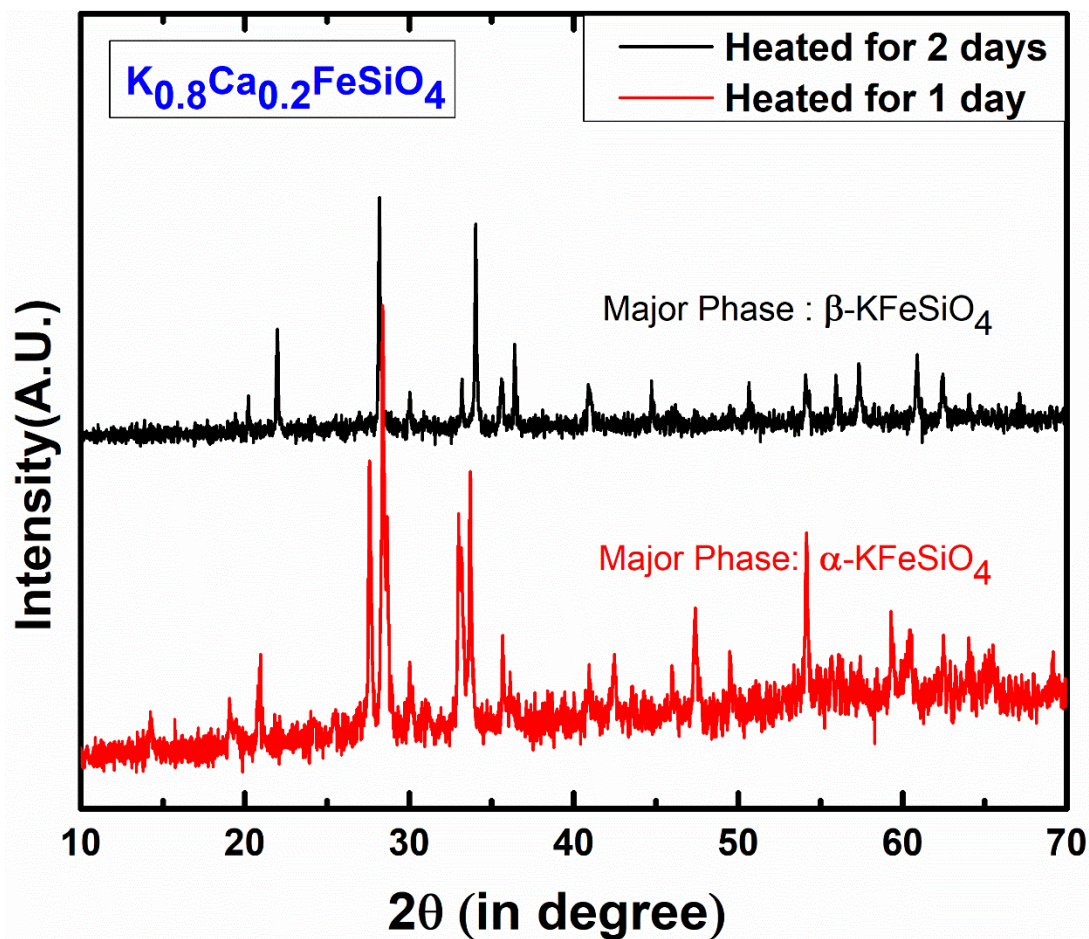
Figure 9: *PXRD patterns of $K_{0.8}Ca_{0.2}FeSiO_4$, heated at 1000ºC for 1 & 2 days caused to form α- & β-phases respectively.*

Five compositions of $K_{1-x}Ca_xFeSiO_4$ with different amount of calcium substitution were synthesized to determine the homogeneity limit of calcium atoms at the K-sites. In first three cases ($x = 0$ .05, 0.1, 0.2), when the reaction mixture was initially heated for one day at 1000ºC, mainly alpha phase was formed as can be seen in the powder X-ray diffraction patterns (Figure 8). The reaction products (main phase alpha form) of these three reactions were then compacted under pressure to form circular disks which were again reheated at 1000ºC for two days in the air. The PXRD patterns of the products of these reactions show the formation of mainly beta phase (Figure 9) in all three cases. This indicates the successful incorporation of calcium cations at the potassium sites leading to the stabilization of beta phase as per our hypothesis.
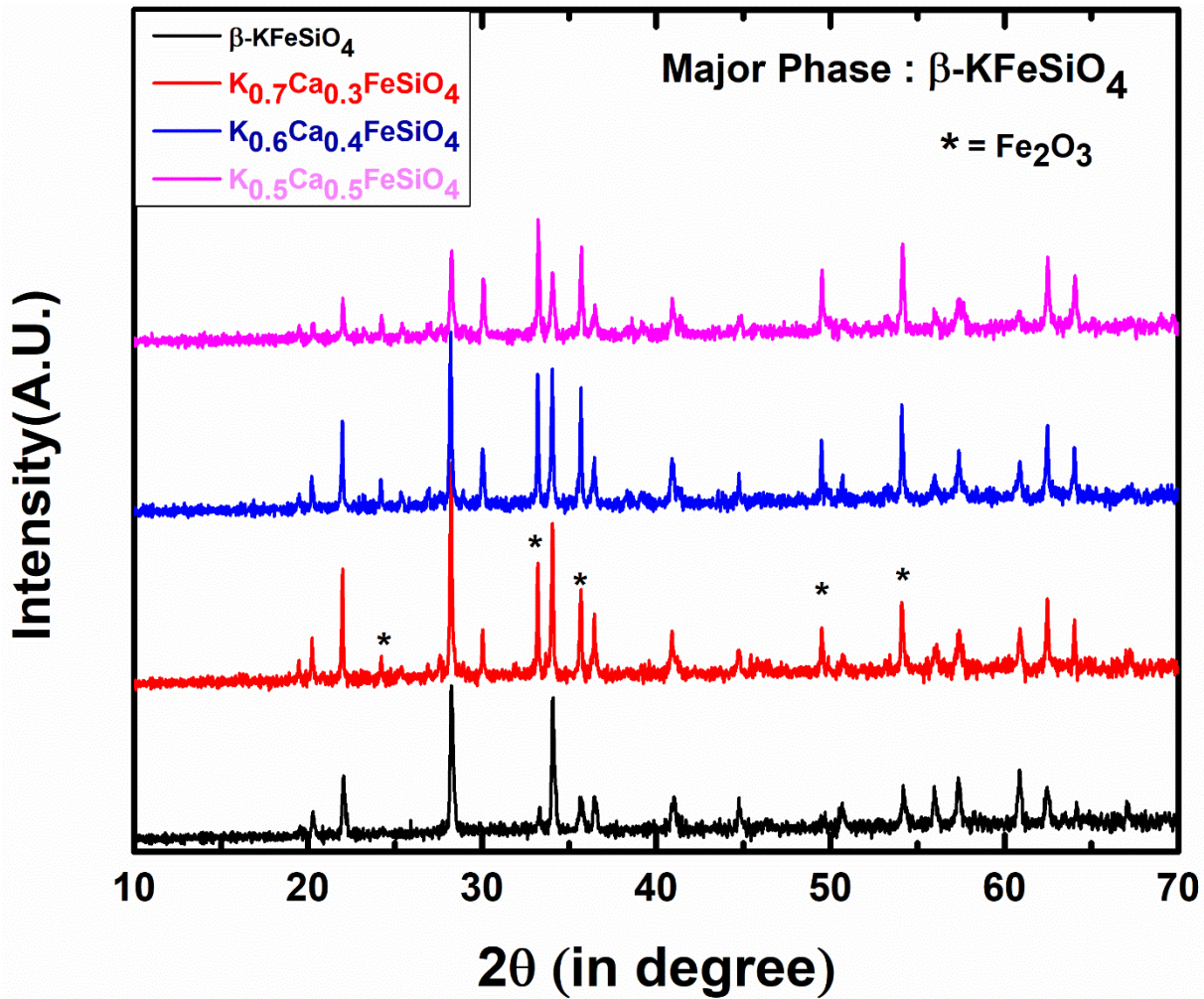
Figure 10: *PXRD patterns of $K_{0.7}Ca_{0.3}FeSiO_4$, $K_{0.6}Ca_{0.4}FeSiO_4$, $K_{0.5}Ca_{0.5}FeSiO_4$ showing the formation of β-phase after 1day heating.*

Similarly, for '*x*' = 0.3, 0.4, and 0.5 compositions, the beta form was obtained by heating the reaction mixture at 1000°C for one day. The PXRD patterns did not show any peak corresponding to the calcium carbonate of any other calcium-based secondary phase (Figure 8 & Figure 10). Hence, it is safe to conclude that the calcium is replacing the potassium cations in the lattice of *β*-KFeSiO$_4$.
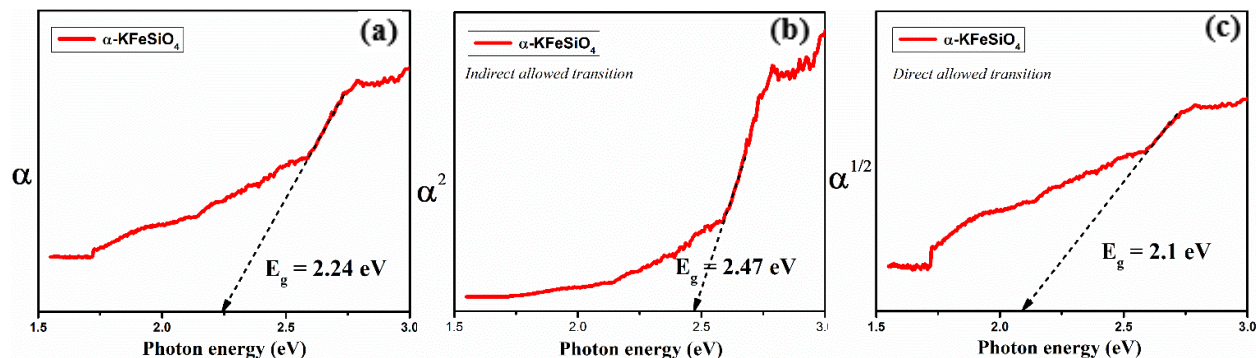
3.2. Optical band gap determination of α- & β-KFeSiO$_4$:

Figure 11: *(**a**) Optical absorptivity (α) of α-KFeSiO$_4$ with a band gap of 2.24 eV, plots of (**b**) α^2 vs energy and (**c**) $\alpha^{1/2}$ vs energy.*

The optical absorbance data were collected at 298 K on a thin single crystal film. α-KFeSiO$_4$ shows a band gap transition at 2.24 eV (Figure 11.a) which is consistent with its pale yellow color. When square and the square root of absorptivity (α) were plotted against energy (in eV) it gives an indirect band gap at 2.47 (Figure 11.b) eV and a direct band gap at 2.1 eV (Figure 11.c).
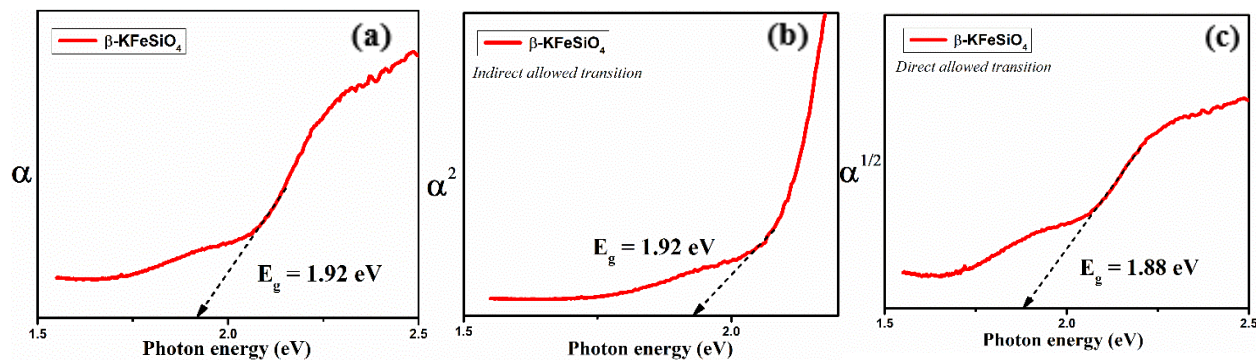
Figure 12: *(**a**) Optical absorptivity (α) of β-KFeSiO$_4$ with a band gap of 1.92 eV, plots of (**b**) α^2 vs energy and (**c**) $\alpha^{1/2}$ vs energy.*

The brown color of β-KFeSiO$_4$ is consistent with a band gap of 1.92 eV (Figure 12.a). Indirect and direct band gaps are 1.92 eV (Figure 12.b) and 1.88 eV (Figure 12.c) respectively in this case.

3.3. IR Spectrum of α-KFeSiO$_4$ & β-KFeSiO$_4$:

In the case of α-KFeSiO$_4$ (Figure 14.a), the Si—O—Si symmetric stretching frequency (785 cm^{-1}) and Fe—O—Fe symmetric stretching (711 cm^{-1}) frequencies are quite separate. So, in the crystal, there would be a properly ordered linkage of Si—O—Si and Fe—O—Fe. A strong band at 888 cm^{-1} indicates Si-O-Si antisymmetric stretching. At 567 cm^{-1}, a medium strong band appears due to Fe—O bending vibration. A small hump on this peak is seen due to Fe—O—Si bending vibration.
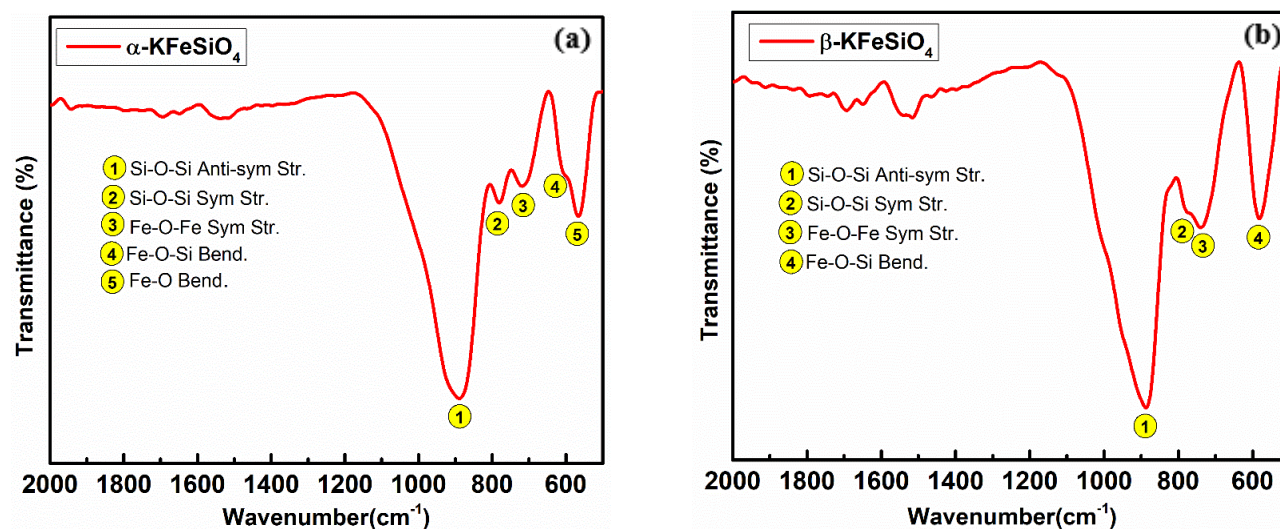
Figure 14: *FTIR data of (**a**) α-KFeSiO$_4$, (**b**) β-KFeSiO$_4$.*

In β-KFeSiO$_4$ (Figure 14.b), the Si—O—Si symmetric stretching frequency and Fe—O—Fe symmetric stretching frequencies are quite close. This is due to the disordered arrangement of Fe and Si in the crystal. Fe or Si can share the same tetrahedra surrounded by four O atoms. It is clearly indicated by a strong band of Fe—O—Si bending (581.74 cm^{-1}).

4. Conclusion

The low and high-temperature polymorphs of $KFeSiO_4$ were synthesized using the ceramic method. The $\beta \rightarrow \alpha$ transformation occurs above 910°C and transformation completes near 1000°C. Heating the reaction mixture (K_2CO_3 + Fe_2O_3 + SiO_2) at 1000°C for 2 days ensures the formation of α-$KFeSiO_4$. KI should be used as a flux to grow single crystals of α-$KFeSiO_4$ compared to KCl or KBr as a flux. When KCl is used both as reactant and flux to form single crystals of α-$KFeSiO_4$, large sized crystals were obtained compared to the case where KI is solely used as a flux. By calcium substitution in place of some potassium in β-$KFeSiO_4$, the phase gets stabilized even at high temperatures. The greater charge density of Ca^{2+} compared to K^+ causes a strong ionic bonding interaction with the oxygen anions. When the quantity of calcium is less it needs more time to get incorporated into the system and make it stable. It is convenient to the fact that when the composition of Ca, "x" was 0.05, 0.1, 0.2 it takes 2 days to stabilize β-$KFeSiO_4$ to 1000°C. Previously after 1day heating α-$KFeSiO_4$ was obtained. Increasing the Ca quantity (x= 0.3, 0.4, 0.5), the rate of incorporation of Ca in the place of K increases and we get β-$KFeSiO_4$ at 1000°C even after 1day heating. The band gap of β- and α-polymorph are 1.92 eV and 2.24 eV respectively. Which is quite consistent with the colors of brown β-$KFeSiO_4$ and yellow α-$KFeSiO_4$. Strong band of Fe—O—Si bending (581.74 cm^{-1}) indicates the Fe/Si disordered structure in β-phase and quite separate Si—O—Si symmetric stretching frequency (785 cm^{-1}) and Fe—O—Fe symmetric stretching (711 cm^{-1}) frequencies are indicative of an ordered crystal structure of the α-phase.

5. Future work

The crystal structure of α-$KFeSiO_4$ is yet unknown. We have synthesized yellow single crystals of α-$KFeSiO_4$ phase which could be used to collect single crystal X-ray diffraction data to determine its structure in the future. We have also synthesized five samples of Ca-doped β-$K_{1-x}Ca_xFeSiO_4$ samples (x = 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5). The structural aspects of these Ca-doped compounds will be studied by Rietveld refinement of the powder X-ray diffraction data. Also, the Fe^{2+} state of iron in β-$KFeSiO_4$ should get oxidized to Fe^{3+} due to the substitution of divalent calcium cations at the potassium sites. Hence, it will be interesting to study the magnetic behavior of these compounds. We also expect a change in the band gap of β-$KFeSiO_4$ phase in response to calcium substitution. The optical studies of these compounds will shed more light on the trend of change

of optical band gaps. A low-temperature ion-exchange method could be used to exchange potassium with lithium in the β-KFeSiO$_4$ phase that has open tunnels in its crystal structure. These materials will have potential applications in the field of Li-ion battery.

6. References

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