

# CRYSTALLOGRAPHIC AND MAGNETIC PROPERTIES OF $\text{KFeO}_2$

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## 1. Introduction

The compounds of the alkali and iron materials [ $\text{AFeO}_2$ : A= Li, Na, K] have been studied because of the possibility as low-cost substitutes for cathode materials in rechargeable lithium batteries [1-5]. Though potassium iron oxide was known as the material with the highest Néel temperatures among iron-oxide compounds [6-7], there have been very few reports on the  $\text{KFeO}_2$ . Since this material is of very unstable nature due to hygroscopic property of potassium, it is very difficult to get single phase  $\text{KFeO}_2$ .

In this work, we have successfully synthesized single phase of  $\text{KFeO}_2$ , and then studied the magnetic and crystallographic properties.

## 2. Methods and Results

$\text{KFeO}_2$  powders were fabricated by the ball-mill method. Potassium carbonate ( $\text{K}_2\text{CO}_3$ ) and iron oxide ( $\text{Fe}_2\text{O}_3$ ) were used as starting materials. Weighted potassium carbonate and iron oxide [ $\text{K}_2\text{CO}_3:\text{Fe}_2\text{O}_3=1.2:1$  at.%] were mixed for 48 h by planetary ball-mill. The rotation speed was 350 rpm and the charge ratio (powder-to-zirconium ball) were 1:3. Milling time was 48 h and afterward the compounds were calcined at 1173 K for 10 h. In order to obtain homogeneous material, it was necessary to grind the samples after first firing and press the powder into pellets before secondary heat treatment at same temperature for 20 h. Finally, single phase  $\text{KFeO}_2$  was successfully obtained, and the all sample preparation for measurements were taken in glove-box (Ar gas based) because of hygroscopic property of potassium.

The crystal structure of the sample was characterized by x-ray diffraction with Cu-K $\alpha$  radiation and neutron diffraction at Korea Atomic Energy Research Institute Reactor HANARO HRPD (high resolution powder diffractometer,  $\lambda=1.8348$  Å). Magnetic properties were measured using a vibrating sample magnetometer (VSM) and Mössbauer spectroscopy with a 40 mCi  $^{57}\text{Co}$  source in a Rh matrix.

The x-ray diffraction patterns for  $\text{KFeO}_2$  sample show a single phase, without any segregation of second phase within the instrumental resolution limit. In Fig. 1, we represent the observed and calculated peak profile, and Bragg position of the patterns for  $\text{KFeO}_2$ . Crystal structure of the sample at room temperature is determined to be an orthorhombic structure of space group  $Pbca$  with its lattice constants  $a_0=5.557$ ,  $b_0=11.227$ , and  $c_0=15.890$  Å, respectively, by Rietveld

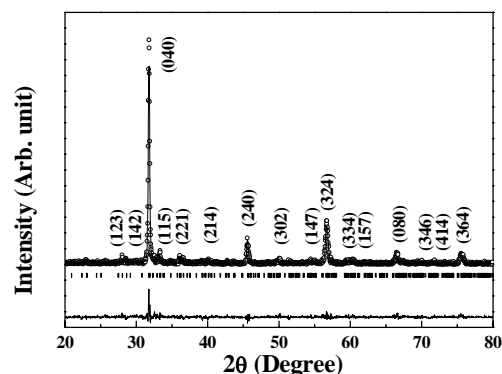


Fig. 1. Refined XRD patterns of  $\text{KFeO}_2$  at room temperature. Open circles represent the observed patterns, and continuous lines represent calculated and difference (obs-cal) patterns. Tick marks correspond to the position of the allowed Bragg reflections.

refinement and then the final Bragg factors  $R_B$  was under 5 %.

We were able to know that there are two kinds of K atoms, two kinds of Fe atoms, and four kinds of O behaviors and have magnetization of 0.11, 0.12 emu/g. Each Fe atom has four Fe neighbours with antiparallel moments coupled to it through the oxygen atoms.

Fig. 2 shows Mössbauer spectra at various temperature. Mössbauer spectra are composed of one six-line hyperfine pattern in which the  $\text{Fe}^{3+}$  ions are one kind of tetrahedral site in ordered phase. Using a least-squares computer program, one set of six Lorentzian lines were fitted to the Mössbauer spectrum below the magnetic ordering temperature, under the well-known restraints which are valid when the quadrupole interaction is much weaker than the magnetic hyperfine interaction. Table.1 presents the magnetic hyperfine fields, electric quadrupole splitting, and isomer shifts at some typical temperatures. The isomer shift at room temperature is found to be 0.09 mm/s corresponding to highly covalent ferric state. This analysis result is in agreement with the assumption that the magnetic moments of two kinds of Fe atoms are equal.

Fig. 3 shows neutron diffraction patterns of  $\text{KFeO}_2$  at 4.2 K. We cannot find any other different position magnetic peak and structure peaks, aside from  $\text{KFeO}_2$ . Neutron diffraction refinement at 4.2 K revealed the orthorhombic structure of antiferromagnetic ordering in which each Fe atom has four Fe neighbours having antiparallel moments coupled to it through the oxygen atoms.

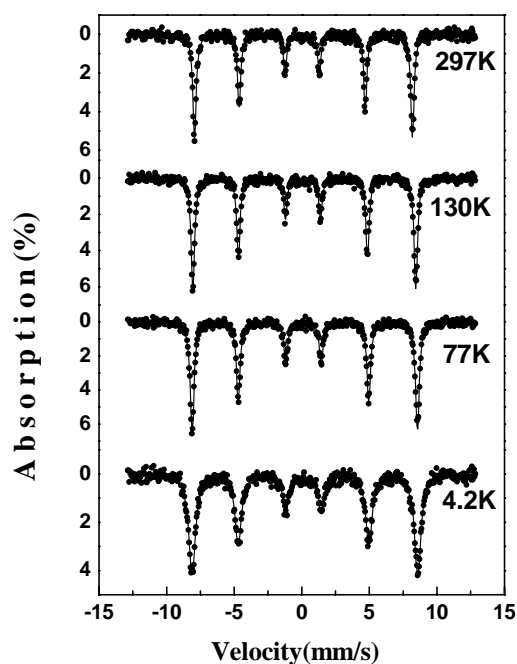


Fig. 2. Mössbauer spectra of  $\text{KFeO}_2$  at various temperatures.

TABLE I  
MÖSSBAUER PARAMETERS VARIOUS TEMPERATURE

Temperature (K)	$H_{\text{Hf}}$ (kOe)	$E_Q$ (mm/s)	$\delta$ (mm/s)
4.2	519	0.046	0.19
77	516	0.045	0.17
180	512	0.046	0.14
297	495	0.040	0.09

### 3. Conclusion

Well-crystallized ordered  $\text{KFeO}_2$  powders have been successfully prepared by ball-method. The isomer shift values at 4.2 K, 77 K, 130 K and 297 K for one sextet patterns are 0.19, 0.17, 0.14 and 0.09 mm/s relative to the Fe metal, respectively, which are consistent with the high-spin  $\text{Fe}^{3+}$  charge states.

### References

- [1] K. Edstrom, S. Ito, R. G. Delaplane, The crystal magnetic structure of nonstoichiometric  $\text{K}^+$   $\beta$ -ferrite, *Journal of Magnetic and Magnetism Materials*, Vol. 212, p. 347, 2000.
- [2] S. Ito, et al, Crystal structure and electric conductivity of  $\beta$ -ferrite with ideal composition  $\text{KFe}_{11}\text{O}_{17}$ , *Solid State Ionics* Vol. 86-88, p. 745, 1996.
- [3] M. Tabuchi. Et al. Preparation of  $\text{AFeO}_2$  (A=Li,Na) by hydrothermal method, *Solid State Ionics*, Vol. 79, p. 220-226, 1995.
- [4] Mitsuharu Tabuchi. et al,  $\text{Li}^+/\text{Na}^+$  exchange from  $\alpha$ - $\text{NaFeO}_2$  using hydrothermal reaction, *Solid State Ionics*, Vol. 90, p. 129-132, 1996.

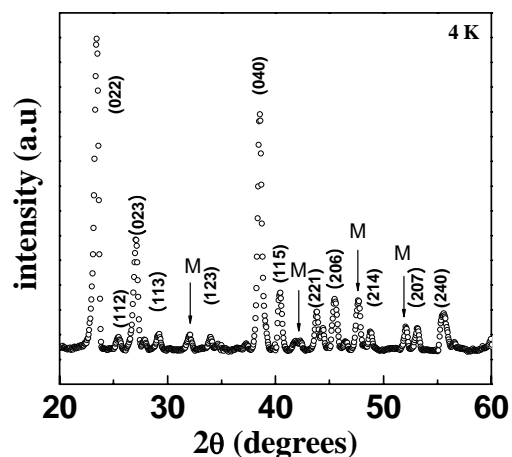


Fig. 5 . Neutron diffraction patterns for  $\text{KFeO}_2$  at 4 K. M indicate magnetic phase.

[5] Shigeru Ito, Takahiro, Kazuo Akashi, Preparation and properties of Lithium inserted  $\text{K}^+$ - $\beta$ -ferrite, *Solid State Ionics*, Vol. 113-115, p. 23-27, 1998

[6] Klis T, Bando Y, and TaKada, Mössbauer study of  $\text{KFeO}_2$ , *J. Phys. Soc. Japan*, Vol. 29, 1970.

[7] Z. Tomkowicz and A. Szytua, Crystal and magnetic structure of  $\text{KFeO}_2$ , *Journal of Physics and Chemistry of Solids*, Vol.38, p.1117, 1976.