

MS35-P3 **Crystal structures and stability of trigonal KLnF_4 fluorides (Ln = Y, Ho, Er, Tm, and Yb).** Karen Friese,^a Nicholas Khaidukov,^b Andrzej Grzechnik,^c ^aJülich Centre for Neutron Science, Germany, ^bKurnakov Institute of General and Inorganic Chemistry, Moscow, Russia ^cInstitute of Crystallography, RWTH Aachen University, Germany
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Trigonal KYF_4 doped with optically active rare earth ions is an efficient phosphor and a promising host for solid state lasers and thermoluminescent dosimeters [1-3]. Its multisite structure, with several crystallographic sites for rare earth ions, enhances the efficiency of up-conversion luminescence due to the interactions of ions located at various lattice sites. According to earlier studies on doped KYF_4 , the luminescence data cannot be exclusively interpreted on the basis of a fully ordered K-Y distribution in the lattice [4].

Undoped and doped trigonal KLnF_4 fluorides (Ln = Y, Ho, Er, Tm, Yb) were synthesized hydrothermally and studied with synchrotron single-crystal and powder diffraction as a function of temperature and pressure. At atmospheric conditions, KHoF_4 and KErF_4 crystallize in space group $P3_1$, while KTmF_4 , Er:KYbF_4 , and KYF_4 crystallize in space group $P3_2$. In both enantiomorphic structures, the K^+ and Ln^{3+} cations are completely ordered. All these structures are related to the structure of CaF_2 fluorite (space group Fmm). No phase transition is detected in KYF_4 at low temperatures down to 100 K at ambient conditions.

Er:KYbF_4 and KYF_4 undergo irreversible pressure-induced phase transitions at about 4 GPa. In each case, the single-crystals become fragmented into several crystallites indicating a possible first-order character of the transformations. The data for KYF_4 collected at 4.12 GPa could tentatively be indexed with the primitive hexagonal lattice $a \approx 16.1 \text{ \AA}$ and $c \approx 19.6 \text{ \AA}$. Up to the phase transitions, Er:KYbF_4 and KYF_4 are more compressible along the c axis and their bulk compressibility predominantly results from the contraction of the KF_8 polyhedra.

According to Abrahams [5], KYF_4 fulfils all the criteria to be a potential ferroelectric and our analysis of the pseudo-symmetry shows that the same is true for all the KLnF_4 compounds studied here at atmospheric conditions. An analysis of the pseudo-symmetry with respect to the minimal supergroups $P3_112$ and $P3_212$, ($t = 2$) shows that the pseudo-symmetry increases with decreasing radius of the Ln^{3+} ion. It is also reflected in the fact that all the investigated crystals are twinned with the additional 2-fold axis as a twinning operation. In addition, pseudo-symmetry with respect to the minimal supergroups $P3_1$ and $P3_2$ ($k = 3$) gives rise to a pseudo-centering $X = (0,0,0), (1/3, 2/3, 0), (2/3, 1/3, 0)$. Pseudo-symmetry with respect to this minimal k -supergroup also increases with decreasing radius of Ln^{3+} .

At high pressures, the pseudo-symmetry in Er:KYbF_4 and KYF_4 is decreased and larger displacements of the atoms are necessary to reach the higher symmetrical space groups.

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MS35-P4 **Kamiokite: A new multiferroic mineral**
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In recent years, the coupling between magnetic and dielectric properties in transition metal oxides gave rise to a significant research effort [1–3]. This effort is governed by the emergence of new fundamental physics and potential technological applications [2–4]. Multiferroic materials exhibit simultaneously (ferro/antiferro)magnetic, ferroelectric and ferroelastic properties. Contrary to multiferroic materials, magnetoelectric materials show an induced electrical polarization by a magnetic field. A proper understanding of the interplay between the various physical properties of these two types of materials relies heavily on the knowledge of the detailed crystal and magnetic structures.

The search for new materials presenting strong interplay between dielectric and magnetic properties has been concentrating mostly on perovskite related materials [2-4]. In order to further investigate the richness of this physics, it is of interest to search for new candidates. In this perspective, several minerals have been shown to be good candidates for multiferroic and/or magnetoelectric properties. Lately, minerals belonging to the melilite family [5] and the pyroxene family have shown some interesting properties [6].

We present here our results on the kamiokite mineral of ideal formula $\text{Fe}_2\text{Mo}_3\text{O}_8$. This mineral crystallizes in the pyroelectric symmetry $P6_3mc$ and orders antiferromagnetically at low temperature. We have investigated it by SQUID magnetometry, single crystal neutron diffraction and dielectric spectroscopy. These results show that Kamiokite is a new multiferroic mineral.

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