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SUBSTITUTION FLUORINE-OXYGEN IN SOME FERROELECTRIC COMPOUNDS WITH OXYGEN OCTAHEDRA

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The substitution of oxygen by fluorine in some ferroelectric phases with a tetragonal tungsten bronze type structure has shown that the Curie temperature and the permittivity decrease with increasing fluorine content.

The $ABCNb_5O_{15}$ phases ($A = Ca, Sr, Ba$; $B = Ca, Sr, Ba$; $C = Na, K$), with tetragonal tungsten bronze structure have ferroelectric properties.¹⁻⁵ It seemed interesting to prepare derivated phases in which oxygen will be partially replaced by fluorine.

A certain number of $ACDNb_5O_{14}F$ compounds ($A = Ca, Sr, Ba$; $C = Na, K$; $D = Na, K$) have been obtained: $CaK_2Nb_5O_{14}F$, $SrK_2Nb_5O_{14}F$, $SrNaKNb_5O_{14}F$, $BaNa_2Nb_5O_{14}F$, $BaK_2Nb_5O_{14}F$ and $BaNaKNb_5O_{14}F$.⁶ However, it is possible to prepare phases with more fluorine, for example $K_3(Nb_4Ti)O_{12}F_3$ and even $K_3Fe_5F_{15}$.⁷

We propose to study the crystallographic and dielectric properties of the systems: $Sr_2KNb_5O_{15}-SrK_2Nb_5O_{14}F$, $Sr_2KNb_5O_{15}-Sr_2K(Nb_4Ti)O_{14}F$ and $Ba_2NaNb_5O_{15}-BaNa_2Nb_5O_{14}F$, $Ba_2NaNb_5O_{15}-Ba_2Na(Nb_4Ti)O_{14}F$. The electric neutrality is realized in two different ways. This is to make sure that the obtained results are independent of the

various types of cationic substitutions, and depend only on the introduction of fluorine ions. Four solid solutions have been obtained.

Sintered samples have been prepared at 1200°C in platinum tubes sealed under dry oxygen. The dielectric measurements have demonstrated the existence of permittivity maxima. Figure 1 shows, for example, the obtained results in the case of the solid solution $Sr_{2-x}K_{1+x}Nb_5O_{15-x}F_x$. We remark here that the temperature at which the maxima appear decreases, and also that the dielectric constant increases for a small amount of substitution.

Dielectric measurements at variable frequencies,

FIGURE 1 Variation of the permittivity with the temperature for the solid solution $Sr_{2-x}K_{1+x}Nb_5O_{15-x}F_x$.

FIGURE 2 Variation of the Curie temperature with the composition.

FIGURE 3 Variation of the Curie temperature with the composition.

as well as the appearance of hysteresis loops lead us to believe that we have a case of a ferroelectric-paraelectric transition. The variation of Curie temperatures is represented in Figure 2. We observe in all cases a strong decrease of T_c for small fluorine compositions.

When fluorine is substituted for oxygen, the Nb—X (X = O, F) bonds become less covalents, and the anisotropy of the bonds decreases. Therefore the temperature required to give isotropic bonds (paraelectric phase) decreases.

We then proceeded to explain the increasing of the permittivity of sintered samples by studying the influence of the replacement of oxygen by fluorine

simultaneously in the sintered samples as well as single crystals of $\text{Ba}_{0.725}\text{Sr}_{1.775}\text{Nb}_5\text{O}_{15}$ composition. The single crystals of the oxyfluoride were prepared by solid state diffusion from oxide crystals.

All the phases show a ferroelectric-paraelectric transition and a decrease of T_c with the amount of fluorine (Figure 3). The sintering behaviour is favourably influenced by the presence of fluorine.

Similar results have also been found in other structural types: perovskite and pyrochlore.^{8,9}

In other words the replacement of oxygen by fluorine in ferroelectric sintered samples has been used to obtain dielectric materials with high performances.¹⁰

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