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STUDY OF "PURE" KTaO₃ AND KTN SINGLE CRYSTALS BY THERMAL CONDUCTIVITY MEASUREMENTS DOWN TO 50 mK

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<u>ABSTRACT</u> - We have measured the thermal conductivity of pure and doped (Nb, Na, Li, Co, Ag, etc...) KTaO₃ single crystals to investigate the induced ferroelectric phase transition mechanisms. The strong phonon scattering observed in the "purest" KTaO₃ is tentatively explained as well as the enhancement of this scattering by substituing Nb in the crystals. Results of preliminary numerical analysis of the curves are given.

In recent years, a substantial amount of work has been undertaken to understand the mechanisms by which a ferroelectric phase transition (FPT) can be induced by adding impurities in "incipient ferroelectrics" such as KTaO3 (1). Several authors have shown that the mixed crystals KTa $_{1-x}$ Nb_x O₃ (KTN) can undergo a FPT at a temperature Tc depending on x for x > xc = 0.8 %, but a number of questions of interest about nucleation and dynamic of FPT are not answered yet (2). Also the origin of the disorder induced Raman scattering observed in pure KTaO₃ is not well understood (3). Experimental - We have studied single crystals of KTaO₃ (pure or doped with different ions) and KTN crystals (0 < x < 3 %) by measuring the thermal conductivity K(T) in the temperature range from 50 mK to 200 K, as this property has been shown suitable to investigate samples with both isolated ions and extended defects.

All crystals were grown by a flux technique and preliminary results on KTaO₃, pure or doped with Ag or Cu, and KTN crystals, have been previously reported (3). In the present work, other crystals doped with Co, Ni, Fe, Na and Li have been measured, and the effect of heat treatments on pure KTaO₃ has also been studied. The results are illustrated in figures 1 and 2 and can be summarized as follows :

- (a) The strong phonon scattering observed in "pure" KTaO₃ is not significantly changed by (i) adding paramagnetic impurities such as Co, Ni, Ag or Cu at concentrations lower than .5 % (ii) annealing in air or vacuum (iii) applying a magnetic field up to 7 Teslas (fig.2; note the enlarged scale compared to fig.1).
- (b) This scattering is slightly increased, together with a change of shape, by adding 1.5 % iron or 0.3 % Li ; the curves are similar to that of a semiconducting sample (fig.2).

(c) A strong enhancement of the scattering depending of the concentration of the dopant, and without change in shape, is observed in KTN and K_{1-x} Na_x TaO₃ (fig.1)
One crystal, namely 1 % lithium-doped KTaO₃, cannot fit in this scheme : its behaviour around 7 K is quite the same than the .3 % Li doped crystal, but below .7 K



Figure 1

it exhibits a K(T) \sim T^2 law which implies additional phonon scattering in this temperature range similar to that observed in glasses.

Discussion - From these results, it is clear that scattering in "pure" KTaO3 cannot be due to isolated defects such as paramagnetic impurities or oxygen vacancies or hydrogen. The other point is that Nb and Na doping lead to qualitatively comparable effects ; this is not the case for Li, confirming the pecularity of this system (especially at concentrations around 1%), which has been claimed by several authors (5)(6). Therefore we suggest that phonon scattering in "pure" KTaO3 arises from very small quantities of electric dipoles induced by residual and unavoidable Nb or Na (namely \sim 10 ppm, from the more accurate available analysis). These dipoles can locally polarize the lattice over several atomic distances via long range interaction. It can be expected that these extended defects are strongly coupled with phonons. This scattering must be nearly concentration independent as long as no overlap between the perturbed regions takes place. From the less concentrated Nb-doped crystals measured (.15% and .3%) we can roughly estimate at \sim 1000 ppm the mean concentration to achieve overlap so that the radius of one perturbed region would be 5-10 atomic distances. Increasing the Nb concentration results in an extension of the "ordered" part of crystal, until $x = x_c$ where the whole sample becomes ferroelectric over this

critical concentration. Supplementary Nb do not play any role otherwise acting as ponctual defects at high temperature. Although the measurements on $K_{1-x}Na_xTa0_3$ crystals are not so comprehensive and that the determination of reliable Na concentration is still a major problem, it can be expected that a quite similar interpretation holds for this system.

Preliminary computer calculations have been done within the Callaway model. All the Nb and Na-doped crystals can be fitted using a total relaxation time

 $\tau^{-1}(\omega,T) = v/\alpha L + A\omega^{4} + \tau^{-1}_{R}(\omega,T) + \tau^{-1}_{U} + \tau^{-1}_{N}$

where $v/\alpha L$ is the boundary scattering term calculated from the size of the samples, $A\omega^4$ the point defect scattering and τ^{-1}_{P} is given by the phenomenological expression:

$$\tau^{-1}_{R}(\omega,T) = D_{(x)} \cdot \omega^{2} \cdot f(T) \text{ with } f(T) = \begin{cases} \exp \left[-\alpha \left[(T-To(x))/To(x)\right]^{2} \text{ if } T < To(x) \\ \exp \left[-\beta \left[T - To(x)\right]\right] \text{ if } T > To(x) \end{cases}$$

The parameters needed to fit the adjustements shown in figure 1 are listed in the table 1.

	"Pure"	.15 % Nb	.3 % Nb	3 % Nb	Na
$D_{(x)}(s^{-1})$	3.106	107	3 x 10 ⁷	2.5 x 10^8	2 x 10 ⁷
a	2.6	2.6	2.2	1.3	3.2
ß	. 15	. 3	. 22	. 18	. 22
Т _О (К)	8	7.2	6	. 35	8

<u>Table 1</u>

It can be seen that, although x is changing by a factor 20 for the KTN samples, α and β are nearly constant within a factor of 2. The parameter T₀ decreases continously down to \approx OK as x increases. If we suppose that T₀ defines very crudely the wavelength of the most strongly scattered phonons, this wavelength increases with x and can be related to the extension of the "ordered" part of the crystal. Also the value T₀ = 8 K for pure KTa03 leads to a perturbed volume of about 8 unit cells, in agreement with the qualitative estimation given above.

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