

## 21. STRUCTURAL RESULTS FROM METHODS OTHER THAN DIFFRACTION

## 21.1-1 STUDYING REAL STRUCTURE OF CRYSTALS BY DIELECTRIC SPECTROSCOPY.

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Data on real structure of crystals obtained by universally accepted techniques (EPR, optical spectroscopy, combinational dissipation etc) may be far more numerous and complete if dielectric spectroscopy is used as a further-aid. It is especially important when point defects of the studied crystals are non paramagnetic, optically inactive though electrically active in non-excited state.

Quartz is a good example of these crystals. Electrically active point defects in quartz are known to be alkali metal ions that dominate there as the type.

We have compared experimental temperature/frequency dependencies  $\epsilon''$  at temperatures of 300-800 K with Debye theoretical curve and presented Cole-Cole and Scafe diagrams. As a result we state a presence of a broad energy spectrum of impurity alkali ions. Energy distribution is not Gaussian, the observed asymmetry of normalized  $\epsilon''(\omega\tau)$  function proving it. The distribution parameter of relaxation time ( $\alpha$ ) increases with crystallization temperature and with lower rates of growth.

We have postulated presence of  $H_2O$  molecules in structure voids of cancrinite crystals using energy parameters of relaxation polarization in a temperature range of 350-500 K.

We have calculated the  $\alpha$  value to change from 0.05 to 0.40 at temperatures of 350-500 K. This change may result from multiple structure positions of  $H_2O$  molecules and their reorientations at various temperatures (Kolodieva et al., Sintez miner. i exper. isled., Moskva (1981) 41).

Dielectric spectroscopy approach to non-relaxation maxima  $\epsilon''(T)$  should be very careful. In interpreting of the experimental results special attention should be paid to reversibility of the observed change of the dielectric characteristics and to their correlation to other physical properties.

For example, we can state that the non-relaxation maximum  $\epsilon''$  in the region of 650-800 K in cancrinite is not reproducible at repeated heating. This fact may result from irreversible changes of cancrinite structure further corroborated by substantial weakening of its piezo effect after heating to 800 K.

Similar maxima of  $\epsilon''(T)$  obtained during heating of fluorphlogopite (up to 900 K) are reproducible though after certain intervals of time. This is a case of reversible processes with great relaxation time of the crystal to the initial state. General phenomenology may describe this process as a recombination of defects that determine dielectric losses with acceptor centers thermally activated in this temperature range to form metastable pairs (or complexes) that dissociate later on (Kolodiev et al., Vses. nauchn. konfer. "Fizika dielektrikov". Sektsiya "Protssy elektroporenosa". Thes. dokladov, Baku (1982) 63).

## 21.1-2 NMR AND EPR SPECTROSCOPY OF ALKALI SELENITES. By I.S. Vinogradova, L.V. Kirensky Institute of Physics, Academy of Sciences, Siberian Branch, Krasnoyarsk, USSR.

The results of the study of single crystals of  $MeHSO_3$  ( $Me = Li, Na, K, Rb, Cs$ ) by  $^1H, ^2D, ^7Li, ^{23}Na, ^{87}Rb, ^{133}Cs$  and  $^{77}Se$  nuclear magnetic resonance spectroscopy are reported. In addition, the electron paramagnetic resonance spectra of  $SeO_2$  radicals were investigated. Special attention was paid to the study of hydrogen bond networks and proton dynamics. The structural data for some crystals were first obtained by the spectroscopic methods. The present study has shown that the substitution of alkali ion leads to a change of crystal symmetry. The rubidium and potassium salts are triclinic and isostructural, the sodium salt is monoclinic, the lithium and caesium salts are orthorhombic. The  $^7Li, ^{87}Rb$  and  $^{133}Cs$  NMR spectra were measured over a wide temperature range with the aim of searching for phase transitions. No phase transitions have been discovered in any of the  $MeHSO_3$  crystals investigated.

The structural parameters of hydrogen bonds were determined from deuteron magnetic resonance spectra. The lengths of hydrogen bonds are in the range 2.5-2.6 Å. The deuterons are ordered in single-minimum potential wells. Only in  $NaDSeO_3$  crystals did we find disorder of deuterons in a two-minimum potential well without a transition into an ordered state up to 77K.

Unusual proton magnetic resonance spectra have been found in  $KHSeO_3$  single crystals. The spectra are doublets in many orientations of crystals relative to  $H_0$ . A recent ND structure investigation of  $KHSeO_3$  (B.A. Sarin, N.N. Bydanov, I.S. Vinogradova, E.E. Rider, S.P. Solovjev, *Sov. Phys. Crystallogr.* (1984) 29) permits the observed spectra to be connected with a distinctive feature of the proton system, namely chains with p-p distances 2.6 Å and 2.8 Å. In the other crystals of the  $MeHSO_3$  family, as well as in  $MeH_3(SeO_3)_2$  crystals, the PMR spectra are single lines.

$KHSeO_3$  and  $RbHSO_3$  have shown unusual EPR spectra of  $SeO_2$  radicals. Besides components of spectra typical for  $SeO_2$  radicals we found additional lines. The nature of these is not understood. Comparisons of spectral and structural characteristics and physical properties of  $MeH_3(SeO_3)_2$  and  $MeHSO_3$  crystals have also been made.