

THE RELATIVE PERMITTIVITY CHANGE OF $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ AND $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ BETWEEN 193—353 K

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Recently many articles were published on the structure of cerium(III)-nitrate and yttrium(III)-nitrate supplied by Merck. Some of the investigations proved that the bound water is the same in these compounds. Our investigations support the bound water differences indicated by Merck, as well as the first bound water release temperature, which had been found to be (341—343) K cerium(III)-nitrate and (331—333) K in the case of yttrium(III)-nitrate.

Introduction

During our experiments regarding the dielectric behaviour of these substances, we have examined the relative permittivity change of cerium(III)-nitrate and yttrium(III)-nitrate. The temperature range was between 193—353 K at $\omega = 10^4$ 1/s constant angular frequency. Both substances are known to contain bound water, although this amount of water varies, depending on temperature.

We tried to find discrete temperatures at which an unambiguous phase transition or change in structure could be detected, due to change in the amount of absorbed water. For this purpose, we have examined the relative permittivity temperature dependence of the above mentioned substances, assuming that the changes in structure are followed by a sudden change of permittivity.

We have kept the tested, highly hygroscopic substances at 40 °C for few days, then they were dried in a desiccator at ambient temperature for two months. The conductivity of the substances prepared in such a manner was an order of nS, while their conductivity was an order of mS prior to drying.

The tested substances have not been purified. According to the data of the producer (Merck) the quality of yttrium(III)-nitrate was laboratory pure, while the cerium(III)-nitrate contained 1.5% of other rare-earth metals.

Measuring equipment

We determined the permittivity by measuring the capacitance of a measuring condenser (Fig. 1). This capacitance was measured by means of an a.c. bridge. As a basic instrument we used a $\omega \sim 10^4$ 1/s angular frequency (1591.5 Hz) bridge, type B331 MK from WAYNE KERR, while a signal generator type 3310 A from HEW-

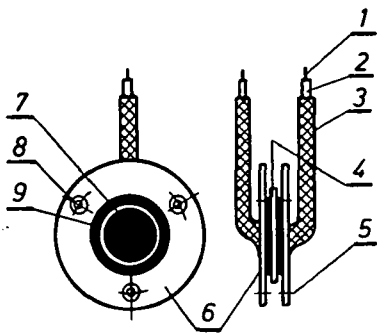


Fig. 1. 1 — copper wire, 2 — teflon insulation, 3 — shielding, 4 — sample, 5 and 8 — coupling bolt holes, 6 — insulation material, 7 and 9 — shielding harness and measuring armature

LETT PACKARD served as an external source. As a signal detector we used an ORTHOLOCSCTM-9505 TWO PHASE LOCK-IN ANALYSER from EGG BODKREAL. Its output signal was transmitted to a HP 7046 A X—Y recorder.

In such a manner we obtained the plot of the capacitance of the measuring condenser and the thermo-voltage on the output. At the same time we could also measure the conductivity using the equipment (Fig. 2). The measuring condenser together with the thermostat was placed in the internal part of a VÖTSCH VMT II test chamber, where the temperature could be varied continuously between 193—353 K.

We measured the temperature with a thermocouple and its hot spot was directly at the measuring condenser while its cold junction was

at water freezing point. From the capacitance of the measuring condenser, filled with the substance to be tested, the permittivity can be determined by means of a calibration curve. For recording the calibration curve a substance of known permittivity was placed in the measuring condenser.

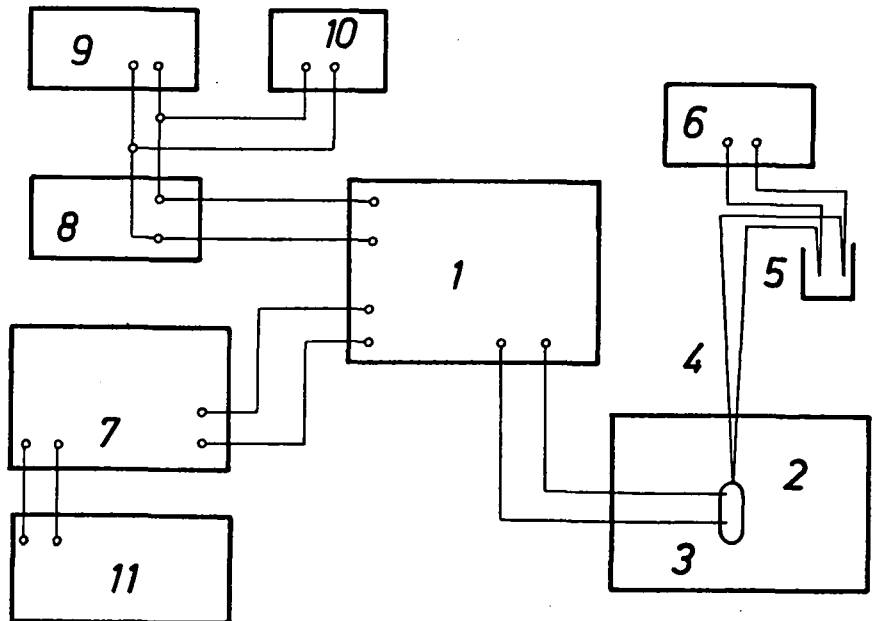


Fig. 2. 1 — WK, 2 — test chamber, 3 — thermostat, 4 — thermocouple, 5 — cold junction, 6 — multimeter, 7 — lock-in analyser, 8 — multimeter, 9 — signal generator, 10 — frequency meter, 11 — X—Y recorder

The curve obtained in such a manner properly agreed with the curve, which was drawn on the basis of a theoretically derived formula [1,2] for this type of condenser. The difference was below 1%.

For the substance tested, pellets have been pressed under 15 MPa pressure. The results of the measurements have been affected by the parallelism of the sample surfaces, their roughness and changes in the solidity by each specimen. If the sample surfaces were not parallel and the circumference of the surfaces was rough an air gap could appear between the measuring condenser and the circumference of the sample. The existence of such an air gap could be an important source of errors during the permittivity measurements, so we made measurements for the evaluation of errors. The known permittivity for the pellet dispersion of substances having various thicknesses was 1.5% at 95% reliability.

Results of measurements

The results of the tested substances are shown in Fig. 3. For the temperature dependence of the relative permittivity of cerium(III)-nitrate we have shown two

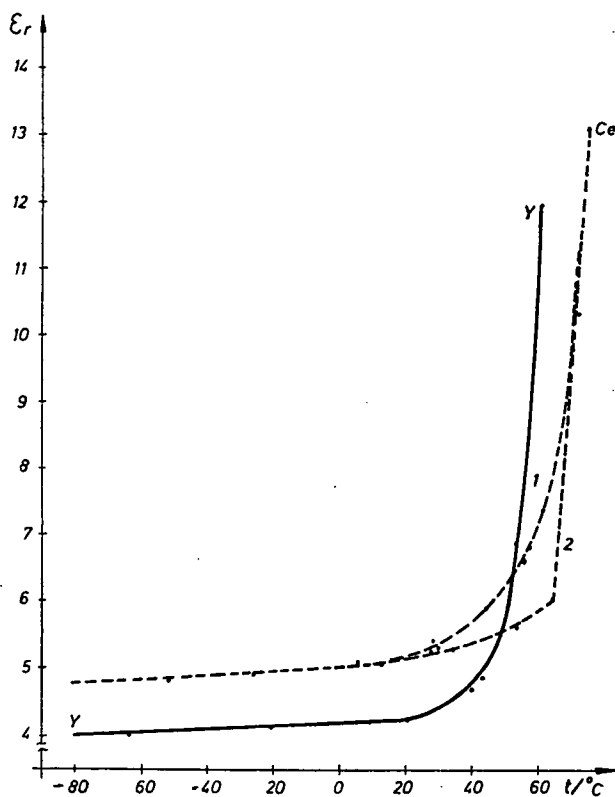


Fig. 3.

curves heated in two different ways. In the case of curve 1 the temperature change was about $1^{\circ}\text{K}/\text{min.}$, while in the case of curve 2 the the temperature change was so slow, that the reading has practically happened at a complete thermal equilibrium. In the case of yttrium(III)-nitrate the heating rate was the same as at curve 1 of the previous sample.

Analysis of results

The relative permeability of yttrium(III)- and cerium(III)-nitrates shows a slight change in the low temperature range which proves that there is a dominant induced polarization.

The relative permittivity of cerium(III)-nitrate at such temperatures is higher at about 20% than that of yttrium(III)-nitrate. This difference is due to the fact, that there are more water molecules near the cerium ion than near the yttrium ion. This assumption is supported by the sample-structure test results [3, 4].

The relative permittivity of yttrium(III)-nitrate shows a jump at about 323 K which is followed by a sudden increase in conductivity. The same phenomenon happens in the case of cerium(III)-nitrate at about 333 K. The increase of permittivity can be explained by the orientation polarization of the releasing water molecules. Neither does this method provide any information regarding the release of water quantity nor does it give details of the occurring change in structure. The structural change of the cerium(III)-nitrate is supported by the crystallographic tests [5] while there is no indication in literature about the structural changes of yttrium(III)-nitrate at 333 K. Another change of structure at higher temperature (361 K) has already been reported [6].

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ИЗМЕНЕНИЯ ДИЭЛЕКТРИЧЕСКОЙ ПРОНИЦАЕМОСТИ В $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ И $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ В ИНТЕРВАЛЕ ТЕМПЕРАТУР 133—353 К

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Измерены изменения диэлектрической проницаемости в $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ и $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ в интервале температур 193—353 К. Полученные результаты подтверждают различное количество и различие в характере связывания кристаллизационной воды, предположенное фирмой изготовителем препаратов (Мерк).