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A CELL FOR DIELECTRIC MEASUREMENTS IN FLUORINATED ATMOSPHERES

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SUMMARY

A device is described which is suitable for dielectric measurements from 20 to 600°C in various fluorinated atmospheres. The cell has been tested with series of natural and synthetic oxide fluorides and fluorides derived from $(NH_4)_3FeF_6$, chiolite and weberite structural types.

INTRODUCTION

Inorganic ferroelectric materials have been found to be mostly oxides (perovskites, pyrochlores, compounds with the tetragonal tungsten bronze structure for instance) [1]. Although ferroelectric behavior has been recently observed in oxide fluorides [2-4], only one series of fluorides containing transition elements shows this property : the $BaMF_4$ series (M=3d element, Mg, Zn) which derives from the $BaMnF_4$ structural type [5].

Nevertheless, fluorine compounds show obvious advantages in comparison with the corresponding oxides : lower melting points, electronic insulator behavior, transparency in the visible region ; further, numerous series can be synthesized at relatively low temperatures via classical methods of solid state chemistry. The main reason for the lack of dielectric investigations may be attributed probably to the great tendency of these compounds to be sensitive to traces of moisture above 150°C, if special cautions are not taken.

The aim of this work was to set up a cell in which dielectric measurements on oxide fluorides and fluorides could be taken in fluorinated atmospheres (F_2, HF, BF_3, SiF_4).

DESCRIPTION OF THE MEASUREMENT CELL

A cross-section of the cell is shown in Fig. 1. The body (A) is entirely machined from a nickel rod. Three feedthroughs for a thermocouple and electrical wires are set on the top ; these are made of PTFE gaskets (B) tied with brass nuts and ferrules (C). The two parts of the cell are jointed by a PTFE O-ring (D). The electrical contacts on the sample (E) are assured using nickel electrodes (F) firmly set by a device of nickel rods (G) with threaded ends. Heating is provided by an electrical furnace (H). The temperature of the sample is controlled using a nickel-chromel thermocouple (I) and the pressure of the system is measured using a Bourdon manometer (J). The upper part of the apparatus is water-cooled (K) to keep the temperature below 80°C. Air-cooling is nevertheless needed when experi-

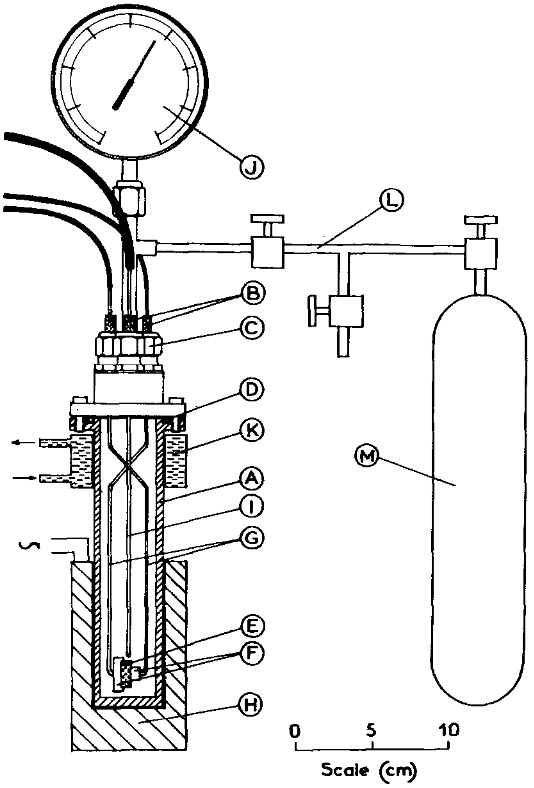

Fig. 1. Cross-section of the experimental cell.

ments are carried out above 400°C. Tubes are made of copper metal (L). The gas cylinder (M) is directly connected to the cell which can be successively evacuated and filled up with inert gas. The fluorinated gases are 98 % F_2, 99.8 % HF, 99.5 % BF_3 and 99.6 % SiF_4 Matheson Gas Products.

Standard ferroelectric samples ($BaTiO_3$, PZT) with well known Curie temperatures have been used to calibrate the temperature.

Before every measurement cycle, the cell is passivated at 150°C with pure fluorine gas in order to obtain a NiF_2 coating. Once inactive, the cell is introduced into a glove box in order to both clean the surface of the Ni electrodes that are in contact with the sample and introduce the pellet. The cell is then evacuated and filled with the fluorinated gas. The pellets are systematically checked after the experiment using X-ray analysis.

The thermal variation of the permittivity ε_r' is measured at a frequency of 1 kHz using an automatic capacitance bridge General Radio 1680.

DIELECTRIC STUDIES IN FLUORINATED MEDIA

The materials tested in the cell have been either oxide fluorides or fluorides. Two synthetic oxyde fluorides $Rb_3MoO_3F_3$ and $Na_5W_3O_9F_5$ were studied, which are related to the $(NH_4)_3FeF_6$ and the chiolite ($Na_5Al_3F_{14}$) structural types respectively. Two classes of fluorides derived from the chiolite and weberite (Na_2MgAlF_7) structures have been investigated, either on minerals from Ivigtut ores (Groenland) ($Na_5Al_3F_{14}$, Na_2MgAlF_7), or on synthetic powders ($Na_5Al_3F_{14}$, Na_2MgAlF_7, Na_2NiMF_7 with M = Al, Fe) and single crystals (Na_2NiAlF_7) prepared by the flux method (6).

Experimental procedure

The compounds are prepared using classical techniques of fluorine solid state chemistry [2, 6-9]. After X-ray diffraction and DTA characterizations, the powders are compressed into pellets of 6 mm diameter and 2 mm thickness. Sintering is achieved 100°C below the melting temperatures and leads to compactnesses of about 0.85. Au film is vaporized on the circular faces of the pellets.

The experiments were carried out from 20 to 550°C in a 20 % SiF_4- 50% N40 argon-30 % N45 oxygen atmosphere for the oxide fluorides, while the fluorides were studied from 20 to 600°C in 20 % HF - 80 % N40 argon gas mixture.

Dielectric studies

The dielectric study of the two well-known oxide fluorides $Rb_3MoO_3F_3$ and $Na_5W_3O_9F_5$ shows in both cases a strong maximum in permittivity at 265 and 525°C respectively. These results are in good agreement with previous studies [2, 7]. It shoud be noticed that the dielectric losses are much lower than those obtained using a classical cell under vacuum or in a dry gas. This improvement can surely be attributed to the total absence of hydrolysis. Fig. 2 shows for example the thermal variation of ε'_r obtained under these conditions for a ceramic of $Rb_3MoO_3F_3$.

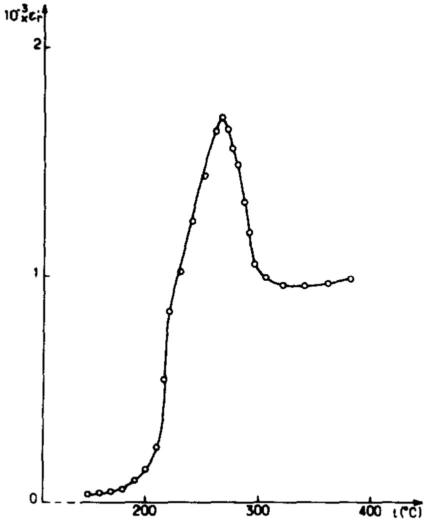

Fig. 2. Thermal variation of ε'_r for a ceramic of $Rb_3MoO_3F_3$ (1 kHz).

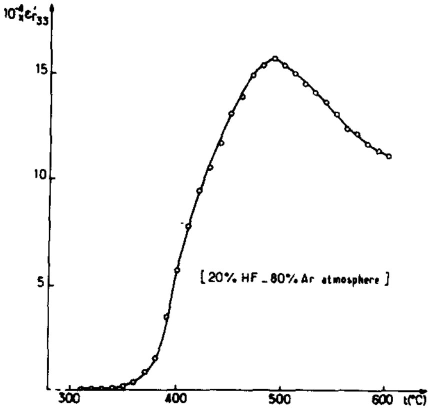

Fig. 3. Thermal variation of ε'_{r33} for a crystal of Na_2NiAlF_7(1 kHz).

Natural chiolite $Na_5Al_3F_{14}$ can be found in the form of large single crystals in cryolite ores. The mineral crystallizes in the tetragonal P4/mnc space group with the cell parameters : a = 7.00 Å, c = 10.39 Å (10). Non-linear optical measurements at room temperature on natural single crystals confirmed the centrosymmetrical space group. The variation of the permittivity with temperature has been investigated from 20 to 500°C. An anomaly in the curve is observed about 460°C and can be correlated with the DTA peak. Due to the anisotropy of the structure which excludes a high temperature cubic form, this transition could be of the 4/mmm → 4/mmm non-ferroic type. Identical results have been obtained with a pellet of $Na_5Al_3F_{14}$ synthesized via solid state reaction.

Minerals of weberite Na_2MgAlF_7 are generally polycrystalline materials. This phase crystallizes in the orthorhombic Immb centrosymmetrical space group (a = 7.05 Å, b = 7.29 Å, c = 9.97 Å) [11] . DTA and permittivity measurements carried out on slices of natural weberite do not show any transition below 650°C.

On the contrary, synthetic weberites Na_2MgAlF_7 and $Na_2NiM^{III}F_7$ (M^{III} = Al, Fe) exhibit a transition above 450°C (Fig. 3). Single crystal studies of Na_2NiFeF_7 [12] and non-linear optical investigations on crystals of Na_2NiAlF_7 show that the low temperature forms are non-symmetrical (Imm2 space group) and accordingly piezoelectric. The crystals generate second harmonics at room temperature. The observed transition could thus be of ferroelectric-paraelectric type (mm2 → mmm).

The studies of transitions in fluorides are still in progress.

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