
EXPERIMENTAL UNIT FOR MEASURING INFRARED EMISSION SPECTRA OF MOLTEN SALTS

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Study of the structure of molten salts is of great interest from both theoretical and applied standpoints. To obtain data on the structure of polyatomic molecules and the nature of interionic interactions in the molten system, the method of investigating IR spectra of molten salts is used quite successfully together with the method of Raman-spectrum measurement.

The shortcomings and advantages of the known methods for measuring IR spectra of melts have been considered in detail in [1].

The present paper is devoted to an investigation of the thermal emission from "thick layers" (tens of millimeters) of a salt melt.

As was shown in [2], at given wavelength \( \lambda \) and temperature \( T \), the emissivity of a melt \( E(\lambda, T) \) of thickness \( d \) is described by the following equation:

\[
E(\lambda, T) = (1 - r_1) [1 + (r_1 - r_2) \exp(-kd) + (r_2 - 1) \cdot r_1 \exp(-2kd) - r_2 \exp(-2kd)],
\]

where \( k \) is the absorption coefficient of the melt, and \( r_1 \) and \( r_2 \) are reflection coefficients of the melt and the container bottom, respectively.

For \( kd \ll 1 \), the emission spectrum of the melt corresponds to the absorption spectrum, something which was used fruitfully by a number of authors (e.g., [2-5]) for melts of salts containing oxygen anions (mainly nitrates).

The procedure of recording reflection spectra [6-8], requiring considerable adaptation of Soviet equipment [9], is usually used for investigation of complex rare-metal halides. However, from the equation given above, it is evident that for \( kd \gg 1 \), the emissivity of the melt will be expressed as follows: \( E(\lambda, T) = 1 - r_1 \); i.e., in the general case, the emission spectrum should contain intensity decreases at frequencies corresponding to intensity maxima in the reflection spectrum obtained in the usual way.

A high-temperature unit based on a double-beam IKS-22 spectrophotometer, shown schematically in Fig. 1, was assembled for measuring the emissivity of the molten salts. A glassy-carbon or nickel beaker with the melt, 1, was placed in a stainless-steel retort 2, covered with a vacuum seal with a cover 3, equipped with a...
Fig. 1. Diagram of the experimental unit for measuring the thermal emission from the salt melts.

Fig. 2. Infrared emission spectra of melts of potassium fluoride (1), potassium fluoride and 0.1 mole fraction of potassium heptaluorortantalate (2), and potassium fluoride, 0.1 mole fraction of potassium heptafluorotantalate, and 0.01 mole fraction of potassium hydroxide (3).

device for fastening a CsI or KBr optical window 4, and a slide 5, intended for protecting the window during evacuation and melting of the salt. The cover 3 was equipped with a water-cooled jacket and a sleeve for evacuating the retort and filling it with inert gas (not shown in Fig. 1). The retort was placed in a resistance furnace 6 fastened with a device for smooth vertical displacement. A thermocouple was introduced from below, flush with the retort, through a hole 7. The temperature-control system in the furnace was described previously [10]. The furnace and retort were placed under the spectrophotometer. The radiation from the melt was directed to the slot of a monochromator 10 through a hole in the spectrophotometer stand 8, with an aluminum mirror 9 fastened in the cuvette section of the instrument. Heat shielding of the spectrophotometer was accomplished with an asbestos-cement screen 11. A globar was used as the reference source.

The design of the unit also made it possible to measure IR emission spectra of thin layers of the melt by using a platinum crucible with a polished bottom as the container. The unit was tested with melts of alkali-metal nitrates. The obtained spectra of the thin layers (~ 0.1 mm) at the corresponding temperatures agreed satisfactorily with the published data [2, 4-6, 11].

When the melt layer was thickened to 0.5-10 mm, a practically continuous spectrum was observed, something which was also noted in [2]. This was probably due to the particular correlation of the optical parameters of the melt containing oxygen ions.

A different situation was observed for a fluoride melt containing pentavalent tantalum. No characteristic bands were observed in the emission spectra of thin layers of the melt, but when the layer was thickened to 10-20 mm, there were intensity decreases against the background of the continuous spectrum which were due to the selective reflectivity of the melt surface according to the above-presented correlations for thermal emission from the substance.

Figure 2 shows IR spectra of thermal emission from melts of potassium fluoride, a mixture containing potassium fluoride and 0.1 mole fraction of potassium heptafluorotantalate, and this same mixture together with 0.01 mole fraction of potassium hydroxide at 850°C.

For the experiments, we used potassium fluoride with a decreased content of oxygen-containing anions which was obtained by the procedure described previously [12].

Because the maximums of the reflection bands are usually shifted by 5-10 cm⁻¹ toward the shortwave region with respect to the maximums of the corresponding absorption bands [13], it is quite valid to consider the reflection spectra and, therefore, the emission spectra obtained as described without recalculation for the absorption coefficient [1, 13].

The intensity decrease in spectrum 1 (Fig. 2) corresponds to a frequency of 545 cm⁻¹, which should be assigned to bond vibrations of the TaF₇⁻ complex ion. When potassium hydroxide was added, the oxyfluoride complex TaOF₆³⁻ was formed, as indicated by the appearance of an intensity decrease at 910 cm⁻¹.