Semiconductor Physics, Quantum Electronics & Optoelectronics. 2001. V. 4, N 2. P. 139-141.

PACS: 78.20.C, 82.80.C, 78.30

IR spectroscopy of KBr salt and crystals

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Abstract. The IR absorption spectra of the KBr salt pellets of different purity and crystals grown of them were investigated in the region of 400…4000 cm^{-1}. It was found that by the IR spectra of the KBr salt pellets suitable for growing optically pure crystals one can evaluate the KBr salt quality. Revealed in the IR spectra are not only the impurity oxygen-containing molecular anions and the adsorption water but also, indirectly through them, the most dominating cations of sodium, barium and calcium. Determined was the concentration, beginning from which sodium ions are observed in the IR spectra of the KBr salt pellets. The coefficient of proportionality between the concentration of sulfates in the KBr salt and the absorption coefficient of SO_4^{2-} ions at the frequency of deformation vibration ν_4 was found. The latter allows to estimate quantitatively the sulfates in the KBr salt.

Keywords: IR spectroscopy, express control, salt quality, absorption coefficient.

Paper received 04.11.00; revised manuscript received 05.01.01; accepted for publication 16.02.01.

1. Introduction

It is known that no absorption bands should be present in the IR spectra of KBr crystals. This is primarily achieved by a high degree of the KBr salt purity with respect to oxygen-containing molecular anions: SO_4^{2-}, NO_3^-, NO_2^- etc. apart from this, the impurity polyvalent cations M^{2+} (where M = Ca, Ba, Mg, Pb) may form complexes $M^{2+}SO_4^{2-}$ which are also revealed in the IR spectra of KBr pellets and crystals. Presence of large amounts of Na^+ ions worsens structural quality of KBr crystals.

Unlike nitrates and nitrites that can be eliminated by the overheating melt prior to crystal growth (Figs 1–2, 2–2) SO_4^{2-} ions enter the crystal and, therefore, are considered to be the most harmful impurity. An attempt to evaluate the KBr salt quality by the IR spectra of KBr pellets (the salt suitable for obtaining optically pure crystals) was made in the present paper.

2. Experimental

The IR spectra of KBr pellets and crystals were measured on the spectrophotometers UR-20 and Specord M-82. KBr pellets of different purity grade were prepared by pressing the preliminarily ground salt at a pressure of 6000 kgf/cm^2. KBr crystals were grown by an open Kyropulos method. The observed in the IR spectra absorption bands were interpreted by the deformation and valence vibrations of molecular anions and their complexes with the polyvalent cations [1-4]. Concentration of Na^+ ions in the KBr salt was measured by the IR spectra of KBr pellets prepared in a humid atmosphere. Concentration of Na^+ ions in the model samples was determined by the method of flame photometry. For the determination of SO_4^{2-} ion concentration in the KBr salt by the experimental data the authors calculated the coefficient of proportionality between concentration and absorption coefficient of SO_4^{2-} ions at 615 cm^{-1} [5]. Concentration of sulfate-ions in the KBr salt was determined by the turbidimetry method [6].

3. Results and discussion

The results of the measurements of the IR spectra of KBr pellets and crystals are given in Figs 1-3. They confirm that the anionic impurities in the KBr salt are directly manifested in the IR spectra of pellets. The cations Na^+, Ba^{2+} and Ca^{2+} which dominate among other impurity cations can be revealed indirectly as well, e.g. by structure variation of the absorption bands of H_2O and SO_4^{2-} ions.

Table. Crystallohydrates of alkali halide salts.

Metal \ Halogen	F	Cl	Br	J
Cs	–	–	–	–
K	$KF\cdot 2H_2O$	–	–	–
Li	–	$LiCl\cdot 2H_2O$	–	–
Na	–	–	$NaBr\cdot 2H_2O$	$NaI\cdot 2H_2O$ ($NaI\cdot 5H_2O$)

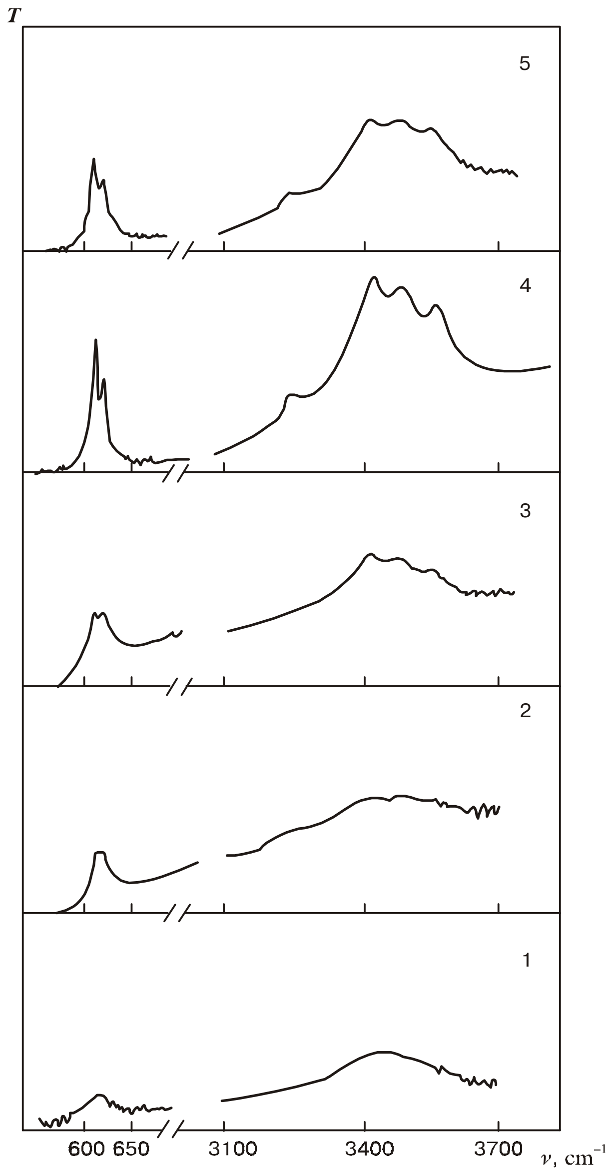

Fig. 1. IR spectra of different grade KBr pellets: 1 – ultra pure, 2, 3 – chemical pure, 4 – pure, 5 – salt after durable storage. Content of M^{2+} ions: 1. Ba^{2+}– $2\cdot 10^{-4}$, Ca^{2+}–$1\cdot 10^{-4}$, Mg^{2+}–$3\cdot 10^{-5}$, $Pb^{2+}1\cdot 10^{-5}$mass%; 3. Ba^{2+}–$1\cdot 10^{-3}$, Ca^{2+}–$2\cdot 10^{-4}$, Mg^{2+}–$5\cdot 10^{-5}$, Pb^{2+}–$2\cdot 10^{-5}$ mass%.

As it is seen from Fig. 3 and the Table, sodium in the KBr salt can be rather clearly revealed at a concentration ~$9\cdot 10^{-2}$ mass% by the IR spectra of KBr pellets ~0.1 cm thick, the latter being prepared by grinding the salt in a humid atmosphere. This was promoted by the crystallohydrate $NaBr\cdot 2H_2O$ formation, its water giving two splitted absorption bands of valence and deformation vibrations ν_2 and ν_3 at 1630 and 3400 cm^{-1}. Sulfate-ions in the IR spectra of the salt are observed by the absorption bands of $\nu_3(F_2)$ and $\nu_4(F_2)$ and at the presence of complexes $M^{2+}\,SO_4^{2-}$, when the local symmetry of SO_4^{2-} ions is lowered from T_d to C_{2v}, which leads to a splitting of $\nu_3(F_2)$ and $\nu_4(F_2)$ vibrations into three components and to the appearance of $\nu_1(A_1)$ vibration in the IR spectrum. Clear manifestation of the resolved structure of the absorption bands of sulfates depends on a quantitative ratio between SO_4^{2-} and M^{2+} ions in KBr crystals (Figs 1, 2) and allows to interpret their availability. The coefficient of proportionality between SO_4^{2-} ion concentration in the KBr salt and absorption coefficient of SO_4^{2-} ions at the frequency of deformation vibrations at 615 cm^{-1} for a number of salts turned out to be 0.005 mol.%·cm (Fig. 4). This enables to evaluate concentration of SO_4^{2-} ions the most harmful impurity in the KBr salt. The minimal concentration of SO_4^{2-} ions determined by this method depends on the error of readings of the IR spectrophotometer transmission level and maximum possible pellet thickness. In this case, for the pellet thickness 0.25 cm it

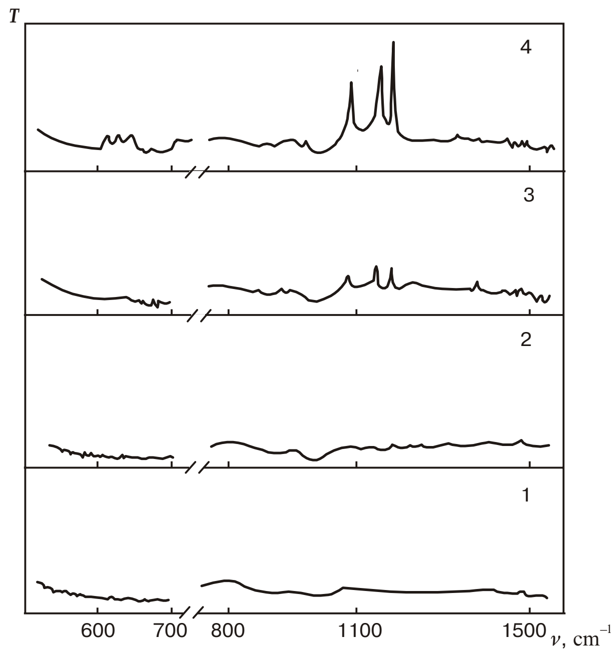

Fig. 2. IR spectra with different structure of SO_4^{2-} absorption bands of KBr crystals grown from the salts shown in Fig. 1 (curves 1-4, respectively). Content of M^{2+}–ions: 4. Ba^{2+}–$1\cdot 10^{-3}$, Ca^{2+}–$5\cdot 10^{-5}$, Mg^{2+}<$1\cdot 10^{-5}$, Pb^{2+}– $1\cdot 10^{-5}$ mass%.

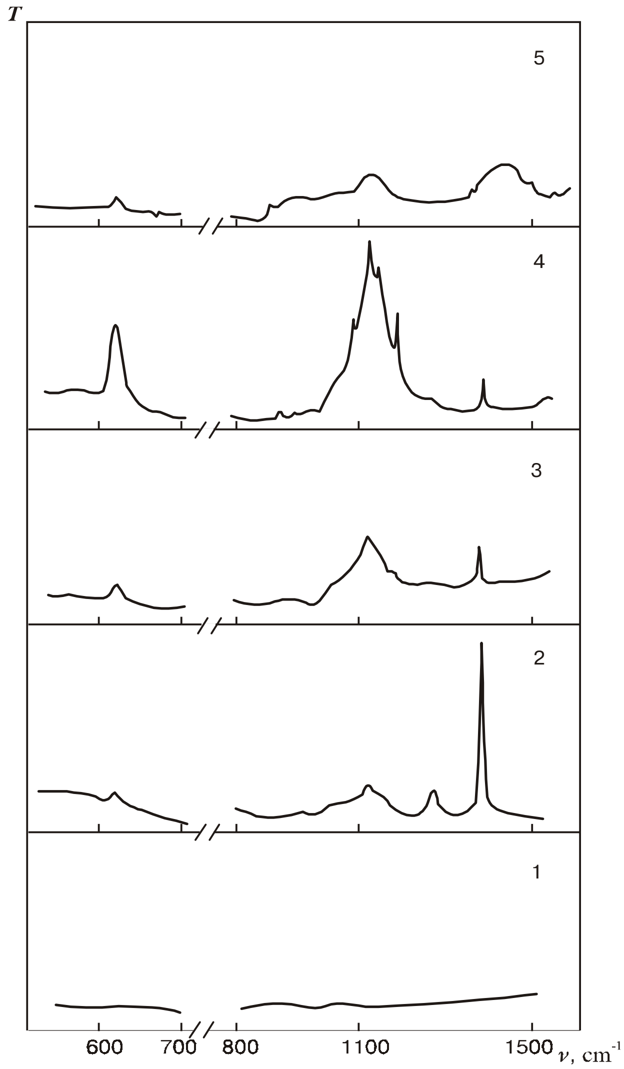

Fig. 3. Absorption bands of water (ν_2 and ν_3) in the IR spectra of samles with different content of sodium: 1 – $2.6{\cdot}10^{-2}$mass%, *d* = 0.105 cm; 2 – $6{\cdot}10^{-2}$ mass%, *d* = 0.11 cm; 3 – $9{\cdot}10^{-2}$ mass%, *d* = 0.10 cm; 4 – $3.2{\cdot}10^{-2}$ mass%, *d* = 0.35 cm; 5 – $NaBr{\cdot}2H_2O$, *d* = 0.12 cm.

is $5{\cdot}10^{-4}$ mol.%. Our experience showed that if in the IR spectrum of the KBr pellets apart from the unresolved bands of the adsorption water ν_2 and ν_3 there are no absorption bands of other molecular ions (Fig. 1-1), then such salt is suitable for growing optical KBr crystals.

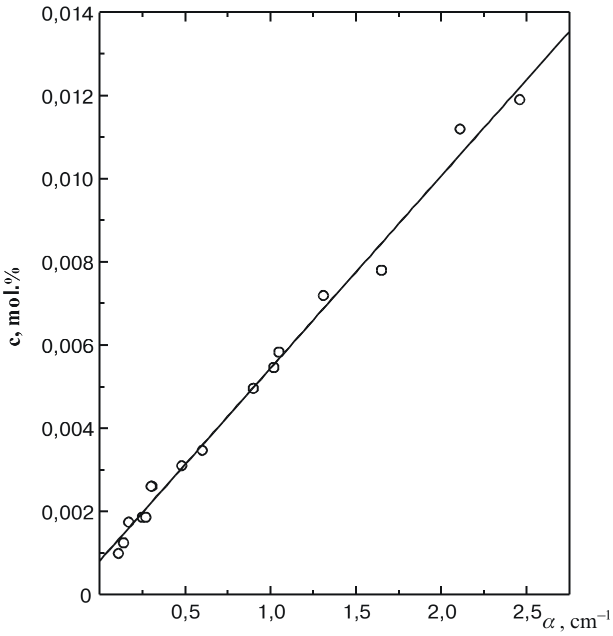

Fig. 4. A linear dependence between the absorption coefficient of SO_4^{2-}–ions at 615 cm^{-1} (k_1) and their concentration (c) in KBr pellets.
Leveling of the straight line $c = ak_1 + b$, where a = 0.005 mol.%·cm, b = 0.0008.

Conclusions

A possibility of an express-control of KBr salt quality (for growing optical crystals) using the analysis of the IR spectra of these salt pellets has been proved in this paper. The speed, absence of a chemical part of sample preparation and small necessary amounts of the sample are the main advantages of this method of analysis as compared to other physical-and-chemical methods [7].

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