

## Granulation as a method for preparation of alkali halide salts for the growth of scintillation single crystals

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Described is a granulation method for high-purity alkali halide salts by spraying the melt into liquid nitrogen, as well as the design of the apparatus for realization of this process. Thermochemical treatment of the melt carried out directly in the apparatus allows to process the wastes of the manufacture of scintillation detectors (crystal cuttings and fragments or chips) for obtaining products suitable for repeated utilization as a starting material for crystal growth.

Описан метод гранулирования щелочногалогенидных солей особой чистоты путем распыливания расплава в жидкий азот, а также конструкция аппарата для осуществления процесса. Термохимическая обработка расплава непосредственно в аппарате позволяет перерабатывать отходы производства сцинтилляционных детекторов (обрезков, осколков кристаллов и стружку) в продукт, пригодный для повторного использования в качестве сырья для выращивания кристаллов.

Pulling of large-size doped crystals with homogeneous composition is possible only with replenishment of the growth zone by the starting material of a preset composition. As is known, at pulling of semiconductor silicon and germanium crystals granulated starting material is utilized. While pulling alkali halide scintillation single crystals, replenishment by fine crystalline powder [1] or by the melt [2] is employed. The former technique requires additional (and expensive) preparation of the starting material which comprises high-temperature drying, purification from organic impurities and homogenization of the powder containing the activator. The procedure of homogenization is not easily producible, it is laborious and at the same time significant, since the degree of homogenization of the powder and activator influences homogeneity of the scintillation characteristics of the grown crystals. Replenishment by the melt

provides the highest degree of homogenization, however, this technique has a drawback: a limited volume of the feeder sets a limit on the dimensions of the pulled crystals.

One of the problems characteristic of the manufacture of alkali halide scintillation single crystals and detectors on their base is processing of the technological wastes which exceed 30 % of the total production of the detectors. The present paper describes the method and equipment for alkali halide salt granulation. The latter, being a method for preparation of the starting material for crystal growth, is also an economical technique of waste processing which provides return of the wastes to the growth process. Granules practically do not consolidate, they have larger bulk weight in comparison with fine-grain powders and higher looseness, and this is greatly important for operation of the replenishment sys-

tem used in automated methods of crystal pulling from the melt.

*Essence of melt dispersion method.* Granulation is a technological process which results in aggregation of the substance into particles of certain shape and preset dimensions (of the same granulometric composition). Depending on the method of obtaining, granules may have different shape and dimensions (tablets, cylindrical or spherical particles). There exist several methods of granulation described in detail in the monographs [3] and [4]. The choice of granule obtaining method depends on the chemical nature of the substance and future application of granules. In the present paper we consider the method of melt dispersion which consists in spraying of the melt followed by fast crystallization of drops in a gaseous medium on a cooled surface or directly in a liquid cooling agent inert with respect to the substance to be granulated. For dispersion, there are used different methods, such as centrifugal or ultrasonic spraying of liquids and spraying of streams.

Spraying of a melt and subsequent fast crystallization of drops in a liquid cooling agent seems to be the most suitable for preparation of high-purity starting material for the obtaining of single crystals or processing of the wastes which provides their repeated utilization in the technological process. First of all, melts can be additionally purified by chemical treatment using different reagents. Secondly, the said method is technically simple, and when certain regulations of the production hygiene are observed, the granules obtained do not contact with atmosphere, and this is very significant for granulation of highly hygroscopic salts such as sodium iodide. Thirdly, prior to the process of granulation preset quantities of activator and other components can be introduced into the melt for making, e.g. CsI(Tl, Na) granules, to obtain a perfectly homogenized material suitable for utilization in any crystal growth method. Finally, for the growth of complex-composition single crystals such as CsI(Tl, Na, Br) by the method of pulling from the melt with replenishment by unmelted material, preparation of the starting material by melt granulation method seems to be the most suitable.

*"Grad" apparatus for granulation of alkali halide salts.* The apparatus works on the principle of spraying melted salt stream into drops followed by their freezing in liq-

uid nitrogen. To spray liquids, there are used different types of atomizers which design and characteristics are described in detail in [5]. Stream-type atomizers have the simplest design. They are suitable for the cases when medium-size granules (measuring 1.5–0.5 mm) are required and the granulometric composition may vary within wide limits. A simplest stream atomizer is a cylindrical capillary which inside diameter defines granule dimensions. While flowing out of the capillary, streams of liquid break down into drops at a certain distance, at low outflow rates the drop size being approximately equal. When the outflow rate increases, e.g. under hydrostatic pressure of the melt column in the crucible, the stream flow becomes turbulent, break-down into drops takes place closer to the edge of the capillary and the stream itself acquires the shape of flare. The drop diameter diminishes and the difference in the drop dimensions increases. The mechanism of stream breaking into drops is investigated in detail in [5–7].

While flowing out of the capillary the melt stream is perturbed and deformed under the influence of defects and roughness of the capillary edge. Under the action of surface tension forces and external factors the stream starts vibrating and breaking into parts. Due to surface tension forces, the stream parts acquire a shape with a minimum surface energy, and the stream parts are transformed into small spheres of different diameters. In [3] the following dependence of the drop diameter on the stream diameter is established:

$$d_k/d_c = (3/2 \cdot \lambda/d_c)^{1/3}, \quad (1)$$

where  $d_k$  and  $d_c$  are the drop and stream diameters, respectively,  $\lambda$  is the wavelength of stream instability (the parameter depending on the stream rate, the chemical nature of the liquid, its surface tension and other factors [6]).

The schematic diagram of the apparatus "Grad" is shown in Fig. 1. Its main unit (component) is platinum crucible (1) shaped as a ring-like reservoir of cylindrical shape. The crucible capacity is 150 l. The crucible bottom holds four atomizers (2). To reduce the duration of granulation, each of the atomizers has four capillaries with a diameter of 1.2 mm. All the atomizers are supplied with removable filters (3) made of fine multi-layer pressed platinum mesh. Melting of salts or crystal wastes in the crucible is

realized by the side (4), central (5) and bottom (6) heaters. When its power is increased, the bottom heater also serves for melting solidified salt clusters in the capillaries before starting the process of granulation. The heating unit which comprises the side, central, bottom heaters, the heat insulating lining (7), as well as the crucible with the starting material are located in the upper part of the hermetically sealed steel chamber (8). Located in the lower part of the chamber (9) is the container (10) with liquid nitrogen. The container is a collector and accumulator of granules. Both parts of the chamber are joined together by means of a horizontal flange joint supplied with sealing rubber spacer. Liquid nitrogen (tank) enters the container from the reservoir (tank) through the pipe connection (11). The chamber cover (12) has the peephole windows (13) for observing the process of starting material melting, the pipe connection (14) for vacuum pumping and the pipe connection (15) for introduction of the activator and other additions into the melt. The valve (16) is meant for release of gaseous nitrogen in the case when its pressure exceeds a preset value. The chamber casing has a water-cooled jacket.

**Granulation process.** Granulation may be realized not only for the initial salts but also for the wastes of single crystal production which are crystalline fragments, cutting remnants and chips resulting from mechanical treatment of single crystals. After placing the starting material into the crucible and sealing the chamber, the latter is subjected to vacuum pumping, and the material is being dried in the process of pumping. The temperature conditions depend on the quantity of salt or the type and composition of the charged wastes and their humidity. In particular, in the process of sodium iodide granulation the temperature of the salt at the initial stage of drying is raised up to 70–80°C, and drying is realized for 6–7 h to remove crystallization water and suppress the reaction of hydrolysis. While drying cesium iodide which does not form crystalhydrate this stage is shorter and lasts for 3–4 h. Afterwards the temperature of the heaters is raised up to 300–400°C. The duration of drying at this temperature depends on the content of moisture in the starting material and on its dispersity. If the initial salt contains organic impurities, they can be burned directly in the granulator using the technique described in [8]. For this purpose the salt is heated up to

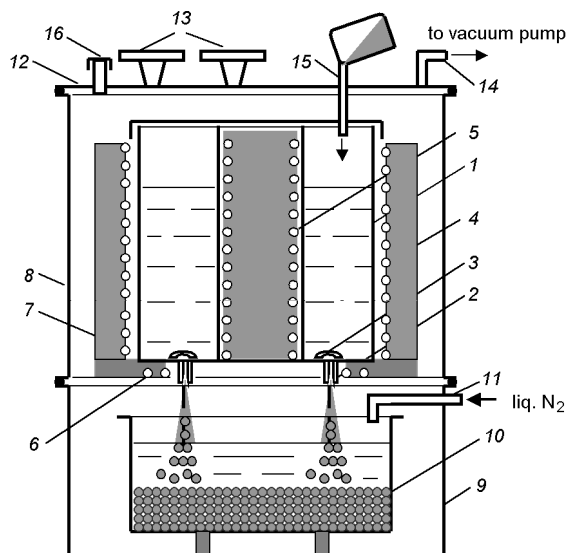


Fig. 1. Schematic diagram of "Grad" apparatus for granulation of alkali halide salts: 1 – crucible; 2 – atomizers, 3 – filters; 4 – side heater; 5 – central heater; 6 – bottom heater; 7 – insulating lining; 8 – upper chamber part; 9 – lower chamber part; 10 – container for granules; 11 – pipe connection for nitrogen feed; 12 – cover; 13 – peephole windows; 14 – pipe connection for vacuum pumping; 15 – pipe connection for introduction of additions; 16 – valve

a temperature of 550–580°C, then a dry mixture of inert gas and oxygen is injected. After being held for certain time in the chamber, the gas and the products of combustion are pumped out. Then the heaters are set to provide the conditions of salt melting. When the salt is melted, the required activator weight is introduced by means of the pipe connection (15). Uniform distribution of the activator is provided due to short-duration holding of the melt in the chamber and to natural convection in the melt. After settling of the melt, liquid nitrogen is pumped into the container (10), and the temperature of the bottom heater is raised. When solidified salt clusters are melted, melt streams flow out of the capillaries, spontaneously break down into drops and reach liquid nitrogen where they transform into spherical granules with small shrinkage cavities as a result of fast crystallization. Intense evaporation of liquid nitrogen raises the pressure in the chamber which is released into atmosphere using the valve (16). In the process of this evaporation, nitrogen is periodically pumped into the container to maintain its level and to provide the presence of 80–100 mm high

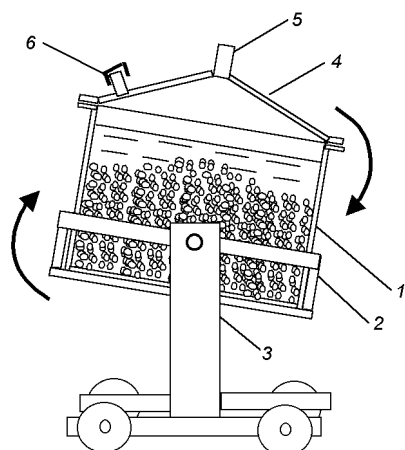


Fig. 2. Platform for discharge of granules. 1 – container with granules; 2 – rotary platform; 3 – trolley; 4 – cover; 5 – branch pipe; 6 – valve.

nitrogen column over the granules. The four atomizers each having four capillaries provide fast and complete outflow of the melt from the crucible even in the case when any of the filters is choked by insoluble impurities. Experiments show that the consumption of liquid nitrogen is approximately 5 l per a kilogram of sodium or cesium iodide, and this is in agreement with the calculated data on thermal balance.

It is very significant for the obtained granules to acquire room temperature without access of air. For this purpose, the container with the granules is held in the granulator till nitrogen completely evaporates and the granules are heated up to room temperature. However, if it is necessary to immediately granulate another portion of the starting material, the following is to be done. After complete outflow of the melt, the container with the obtained granules and a layer of liquid nitrogen over them is placed onto a special rotary platform (Fig. 2), then covered by air-tight cap with a valve for release of evaporating nitrogen and kept there till the granules are heated up to room temperature. In most cases the granules acquire room temperature in 18–24 h. The cap has a conical shape and in its vertex there is located a tube for drawing the obtained granules from the granulation apparatus into air-tight ampoules where the product is stored before its utilization. Out of the ampoules the granules are placed into a tank or the growth apparatus feeder without access of air. If the above-said requirements are not fulfilled and the granules are drawn at ni-

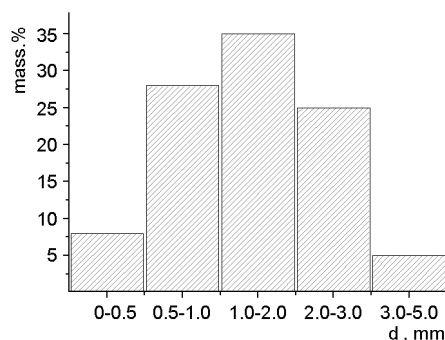


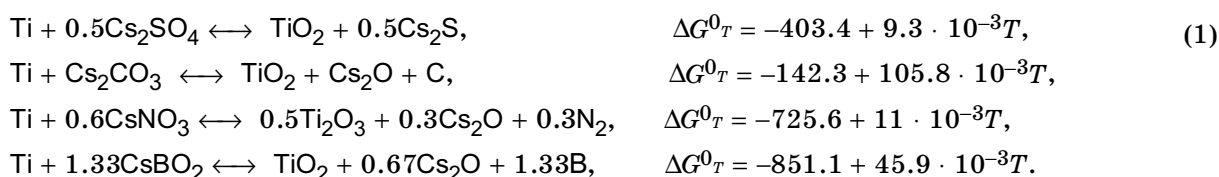
Fig. 3. Distribution of granules in size.

trogen temperature ( $-195^{\circ}\text{C}$ ), then fast condensation is initiated on their surface, and this is inadmissible for water-soluble substances. Fig. 3 presents the histogram of granule size distribution.

If the storage regulations are observed, granulated salts are more convenient for growing crystals both by the Stockbarger method and by the method of pulling from the melt on the seed with replenishment. Large bulk weight and looseness make granules preferred for utilization in automated methods of crystal growth with replenishment, especially in the case of multi-component systems. Granulation seems to be the most economical method for processing scintillator production wastes, in particular, for  $\text{CsI}(\text{Tl})$  and  $\text{CsI}(\text{Na})$ . Besides crystal fragments, cutting remnants and chips, there can be also subjected to procession the scintillators rejected as defective (coloration in light, the presence of cracks, foreign-phase inclusions). In this case, the processed material is to be preliminarily washed out of production contamination and abrasives which may be present on the surface, by means of distilled water. Then it is dried in vacuum cabinet. The process of waste granulation is distinguished from starting salt granulation only by the fact that the melt is subjected to chemical purification from oxygen-containing impurities by treatment with metallic titanium. For this purpose, little quantities of small-size pieces of pure titanium or ground titanium sponge are added to the wastes before charging the crucible. After melting the salt or wastes, the melt is kept in the crucible for an hour or so. Being a very active element, titanium decomposes oxygen-containing anions at high temperatures, and there are formed titanium oxides (mainly,  $\text{TiO}_2$  and  $\text{Ti}_2\text{O}_3$ ) slightly soluble in the melt. Presented below are examples of the reactions and their isobar-isothermal potentials ( $\Delta G^0_T$ ) for the

Table. Impurities content in granules produced from wastes.

Impurities	Impurities content., mass. %					
	Standard	Conditional number of granules pieces.				
		1-88	3-88	7-88	21-88	33-88
Fe	$3 \times 10^{-5}$	$< 3 \times 10^{-5}$	$3 \times 10^{-5}$	$3 \times 10^{-5}$	$3 \times 10^{-5}$	$< 3 \times 10^{-5}$
Ca	$3 \times 10^{-4}$	$< 3 \times 10^{-4}$	$< 3 \times 10^{-4}$	$3 \times 10^{-5}$	$< 3 \times 10^{-4}$	$< 3 \times 10^{-4}$
Al	$5 \times 10^{-5}$	$< 5 \times 10^{-5}$	$< 5 \times 10^{-5}$	$5 \times 10^{-5}$	$< 5 \times 10^{-5}$	$< 5 \times 10^{-5}$
Cu	$5 \times 10^{-6}$	$< 5 \times 10^{-6}$	$5 \times 10^{-6}$	$7 \times 10^{-6}$	$< 5 \times 10^{-6}$	$5 \times 10^{-6}$
Ni	$5 \times 10^{-6}$	$< 5 \times 10^{-6}$	$7 \times 10^{-6}$	$< 5 \times 10^{-6}$	$< 5 \times 10^{-6}$	$< 5 \times 10^{-6}$
Pl	$5 \times 10^{-6}$	$< 5 \times 10^{-6}$	$< 5 \times 10^{-6}$	$< 5 \times 10^{-6}$	$< 5 \times 10^{-6}$	$< 5 \times 10^{-6}$
Tl	no norm	$5 \times 10^{-4}$	$2 \times 10^{-3}$	$5 \times 10^{-4}$	$3 \times 10^{-3}$	$3 \times 10^{-3}$
pH	5 — 7	6.2	6.0	6.0	5.2	6.0



most frequently occurring impurities  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{BO}_2^-$  (see Eq. 1).

Further the process of waste granulation does not differ from the one described above.

The method of granulation was used for industrial processing of more than 14000 kg of wastes and of the scintillators rejected as defective at testing. As a rule, one melting procedure yielded approximately 250 kg of granules. Table contains the results of the analysis of several batches of CsI granules for the content of cationic impurities compared with the requirements of the standard TU-6-09-4083-85. The presented data show that the content of controlled impurities corresponds to the standard requirements. The presence of the uncontrolled Tl impurity on the level of  $5 \cdot 10^{-4} - 2 \cdot 10^{-3}$  mass. % is explained by its presence in the initial material (pieces and cutting remnants of CsI(Tl) crystals). However, since the granules are meant for the growth of CsI(Tl) crystals in which the content of Tl must be on the level of  $5 \cdot 10^{-2} - 1 \cdot 10^{-1}$  mass.%, such a fact does not worsen their quality.

Large-size crystals with a diameter exceeding 420 mm and a length of 400 mm were grown using the apparatus "Kristall-500" [2]. The scintillators made from these crystals had high spectrometric charac-

teristics which did not differ from those of analogous samples obtained from extra-pure salts. Many of these scintillators shaped as truncated pyramid with a length exceeding 300 mm were used while creating calorimeters for experiments in high-energy physics in the scope of the programs KEK and SLAC, as well as for the astrophysical spectrometer SLAC.

### References

1. L.G.Eidelman, V.I.Goriletsky, V.G.Protsenko et al., *J. Cryst. Growth*, **128**, 1059 (1993).
2. B.G.Zaslavsky, *J. Cryst. Growth*, **200**, 476 (1999).
3. P.V.Klassen, J.G.Grishaev, Foundations of Granulation Technology, "Khimia", publ., Moscow, (1982), [in Russian].
4. A.I.Kolpashnikov, A.E.Efremov, Granulated Materials, "Metallurgia" publ., Moscow, (1977), [in Russian].
5. V.A.Borodin, Ju.G. Dityakin, L.A.Klyachko, V.I.Yagodkin, Destruction of Liquids, "Mashinostroenie" publ., Moscow, 1967, [in Russian].
6. A.S. Lishevsky, Processes of Fuel Spraying Diesel Nozzles, "Mashgiz", publ. Moscow, (1963), [in Russian].
7. D.V.Reley, Theory of Sound, "Gostehizdat", publ. Moscow, (1962), [in Russian].
8. V.I.Bobyry, S.I.Vasetsky, E.V.Danilenko, B.G.Zaslavsky, Pat.1039253 RF, (1993).

## **Гранулювання, як метод підготовки лужногалоїдних солей для вирощування сцинтиляційних монокристалів**

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Описано метод гранулювання лужногалоїдних солей особливої чистоти шляхом розпилювання розплаву у рідкий азот, а також конструкція апарату для здійснення процесу. Термохімічна обробка розплава безпосередньо в апараті дозволяє переробляти відходи виробництва сцинтиляційних детекторів (обрізків, осколків кристалів і стружку) у продукт, придатний для повторного використання як сировину для вирощування кристалів.