# Purification of raw material for cesium iodide single crystals and impurity concentration by low-temperature directional crystallization

*L.P.Eksperiandova*

Scientific and Technological Corporation "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

It is shown that the low-temperature directional crystallization of the water-salt eutectics of cesium iodide used as the raw material for single crystals provides its purification (by about 2 orders) from all impurities including the homological ones. In the mentioned crystallization version, the redistribution of impurities is independent of their nature but is defined only by the process realization conditions and depends on the salt concentration and its crystallite size. The low-temperature directional crystallization of CsI solution can be used simultaneously to purify the salt and to concentrate the impurities for analytical purposes in the control of the raw material quality and wastewaters from the single crystal production.

Показано, что низкотемпературная направленная кристаллизация водно-солевой эвтектики на основе иодида цезия, используемого в качестве сырья для монокристаллов, позволяет производить его очистку (на ~2 порядка) от всех примесей, включая гомологические. В указанном варианте кристаллизации перераспределение примесей не зависит от их природы, оно определяется лишь условиями проведения процесса и зависит от концентрации соли-основы и размеров кристаллитов этой соли. Низкотемпературная направленная кристаллизация раствора CsI может быть одновременно использована для очистки и аналитического концентрирования примесей при контроле качества сырья и сточных вод производства монокристаллов.

## 1. Introduction

The microimpurities which are to be controlled in CsI raw material and single crystals include oxygen containing ions ($SO_4^{2-}$, $CrO_4^-$), elementary and organic carbon, isomorphic impurities $Cl^-$, Li (I), Rb (I), heterovalent cations Cu (I, II), Fe (III), U (VI), Th (IV) [1, 2]. The low-temperature directional crystallization (LTDC) is among the techniques suitable to purify the inorganic salts [3]. In the crystallization of water-soluble salts, the LTDC is best applicable to solutions with concentrations corresponding to the water-salt eutectics (WSE). Such systems are solidified integrally, the mother liquor acting as the melt.

We have found before some specific features of the WSE LTDC[4, 5]. The equilibrium coefficients for all the impurities (independent of the nature thereof) have been found to tend to zero, the characteristic coefficients [6] for different impurities in the same matrix $k_L < 1$ and have similar values that are defined by the WSE crystallization conditions and the nature of the main component salt. As the crystallization speed reduces, the eutectics structure becomes more ordered and the $k_L$ values decrease. Basing on the studies of more than 30 salts, the characteristic coefficients of impurity distribution have been found to increase regularly when passing from the eutectics based on fine-crystalline salts to coarse-crystalline ones [1, 3, 4]. At a moderate LTDC speed
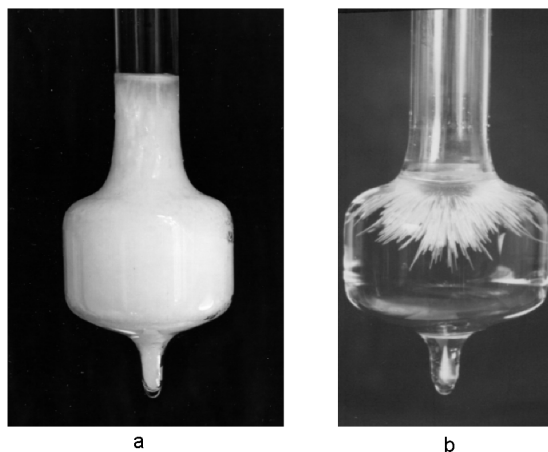
Fig 1. The photograph of containers with crystallized CsI beads eutectic (a) and water with small amounts of a salt and a dye (b).

($f \approx 10$ mm/h), the CsI based eutectics (fine-crystalline structure) shows rather small $k_L$ values (Table 1) even. Such a unique feature provides the effective displacement of the impurity group in the eutectic solution mentioned to the ingot tail.

It is known that for a deep purification of CsI (if the $k_L$ is assumed to be 0.05 and the crystallization front to be concave) the WSE crstallization should be stopped as the crystallized ingot part $g = 0.5$ [7]. This makes it possible to provide the special purity grade CsI (CsI 17-2) to be purified from its homologue Rb(I) (that is very difficult to remove using other methods) by a factor of 250 (the Rb concentration being reduced from $5 \times 10^{-3}$ to $2 \times 10^{-5}$ wt. %). This conclusion is confirmed by our observations on the LTDC of aqueous CsI solutions at different concen-

trations. Fig. 1a shows the photo of the crystallized CsI beads eutectics and Fig. 1b, the appearance of an ice ingot obtained from pure water with CsI addition in a concentration much lower than $C_{eut}$ and containing a model microimpurity convenient to be observed visually (Arsenazo I dye) having $k_L = 0.05$. It is seen in Fig. 1b that the crystallization front is concave. It is seen also that no dendrites are formed at g that confirms the above restriction (g = 0.5) necessary for deep CsI purification. At less stringent requirements to the rubidium content (the purification by a factor of 100), the WSE crystallization can be stopped at $g = 0.8$.

The LTDC for analytical tasks is carried out in the same manner. After the process is over (the solution to be analyzed is solidified completely), the impurity concentrate is separated by pouring a measured amount of hot water onto the upper ingot part, the so formed solution (melt) is weighed and then analyzed. The analysis result, taking into account the concentration, is calculated using the modified Gulliver-Pfann equation [1]

$$C_c = C_0(1 - g)^{k_L - 1}$$

where $g = 1 - m/G$ is the ingot crystallized part; $m$, the concentrate mass; $G$, the weight of the salt to be analyzed; $C_c$ and $C_0$, the impurity concentration in the concentrate and in the initial salt, respectively; $k_L$, the pre-estimated characteristic distribution coefficient. heterogeneous impurities) and similarity of characteristic distribution.

In Table 2, summarized are the characteristics of determination procedures for some impurities after the pre-concentration

Table 1. Characteristic distribution coefficients[*] of different impurities in CsI based eutectics. Crystallization speed $f = 7$ mm/h

| Impurity ($2 \cdot 10^{-4}$–$1 \cdot 10^{-3}$ wt.%) | $k_L$ (g = 0.95) | Impurity ($2 \cdot 10^{-4}$–$1 \cdot 10^{-3}$ wt.%) | $k_L$ (g = 0.95) |
|---|---|---|---|
| Li (I) | 0.04±0.01 | Total heavy metals | 0.04±0.02 |
| Na (I) | 0.10±0.03 | $F^-$ | 0.07±0.01 |
| K (I) | 0.10±0.01 | $Cl^-$ | 0.06±0.02 |
| Rb (I) | 0.03±0.02 | $SO_4^{2-}$ | 0.10±0.03 |
| Cu (I,II) | 0.09±0.02 | $CrO_4^-$ | 0.07±0.01 |
| Fe (III) | 0.06±0.01 | $CO_3^{2-}$ | 0.07±0.02 |
| U (VI) | 0.10±0.01 | Arsenazo I | 0.06±0.01 |
| Th (IV) | 0.08±0.03 | C, C (organic) | 0.04±0.02 |

[*] The $k_L$ values and confidence intervals thereof have been estimated for the number of experiments 3 or 6 at the confidence probability 0.8; $g$ is the crystallized ingot fraction.

Table 2. Parameters of CsI analysis procedures after the crystallization concentration of microimpurities ($g = 0.98$)

| Impurity | Speed, mm/h | $k_L$ | Concentrate analysis method[1] | Sensitivity increase of the direct method (factor) | Determination threshold[2] for procedure with concentration, wt. % |
|---|---|---|---|---|---|
| Li (I) | 8 | 0.08 | FP | 100 | $3 \cdot 10^{-6}$ |
| Rb (I) | 8 | 0.06 | FP | 100 | $3 \cdot 10^{-6}$ |
| Cl⁻ | 7 | 0.06 | PT | 100 | $2 \cdot 10^{-6}$ |
| Cu (I,II) | 7 | 0.09 | SP | 60 | $2 \cdot 10^{-6}$ |
| Fe (III) | 7 | 0.03 | SP | 90 | $1 \cdot 10^{-6}$ |
| U (VI) | 12 | 0.10 | SP | 120 | $5 \cdot 10^{-7}$ |
| Th (IV) | 12 | 0.08 | SP | 120 | $5 \cdot 10^{-7}$ |
| C (org.) | 12 | 0.04 | P | 100 | $2 \cdot 10^{-5}$ |
| $SO_4^{2-}$ | 8 | 0.10 | PT | 100 | $5 \cdot 10^{-6}$ |
| $CrO_4^-$ | 12 | 0.07 | SP | 100 | $2 \cdot 10^{-6}$ |

[1] FP, flame photometry; PT, phototurbidimetry; SP, spectrophotometry; P, potentiometry
[2] The determination threshold is defined as the impurity concentration determined at the trlative error $s_r = 0.3$.

by crystallization and the concentration conditions. The somewhat different $k_L$ values for the same impurities in Tables 1 and 2 are due to the estimation thereof at different $g$ and $f$ values.

Thus, the WSE LTDC is shown to be suitable for the CsI deep purification and for analytical control of the raw material quality used to grow the scintillation single crystals.

### References

1. A.B.Blank, Analysis of Pure Substances Using Crystallization Concentration, Khimia, Moscow (1986) [in Russian].

2. R.A.Laudise, R.L.Parker, The Growth of Single Crystals, Academic Press, New-York, London (1970).

3. L.P.Eksperiandova, A.B.Blank, *J. Analyt. Chem.*, **58**, 658 (2003).

4. L.P.Eksperiandova, I.B.Shcherbakov, *J. Sol. Chem.*, **35**, 1075 (2006).

5. L.P.Eksperiandova, I.I.Fokina, A.B.Blank, Kharkov. Univ. Herald: Chemistry, 2nd Iss., 420, 93 (1998) [in Russian].

6. A.N.Kirgintsev, L.N.Trushnikova, V.T.Lavrentyeva, Water Solubility of Inorganic Substances, Khimia, Leningrad (1972) [in Russian].

7. A.B.Blank, V.G.Chepurnaya, in: Mass Crystallization, 3rd Iss., IREA, Moscow (1977) [in Russian].

## Очищення сировини для монокристалів йодіду цезію і концентрування домішок за допомогою низькотемпературної направленої кристалізації

### *Л.П.Єксперіандова*

Показано, що низькотемпературна направлена кристалізація водної-сольової евтектики на основі йодіду цезію, що використовується як сировина для монокристалів, дозволяє проводити його очищення (на ~2 порядки) від всіх домішок, включаючи гомологічні. У вказаному варіанті кристалізації перерозподіл домішок не залежить від їх природи, він визначається лише умовами проведення процесу і залежить від концентрації солі-основи і розмірів кристалітів цієї солі. Низькотемпературна направлена кристалізація розчину CsI може бути одночасно використана для очищення і аналітичного концентрування домішок при контролі якості сировини і сточних вод виробництва монокристалів.