

Mechanism of light scattering defects formation in NaI:Tl during crystal growth

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Nature of growth light scattering defects in NaI:Tl crystal has been studied by optical and electron microscopy technique. The heterogeneous mechanism of inclusion formation has been proposed. This mechanism consists in three stages. At first stage, sodium oxide diffuses to the internal surfaces of gas bubbles or channels. The oxide then reacts with carbon dioxide and converts into sodium carbonate. At the third stage, a new phase is formed inside the gas-filled channels. Finally carbonates covered internal surface of gas channels due to the shape of inclusion becomes morphologically stable.

Key words: growth defects, inclusion of new phase, heterogeneous decay of solid solution.

Методами оптичної та електронної мікроскопії вивчено природу ростових дефектів, що призводять до розсіювання світла, у кристалах NaI:Tl. Запропоновано гетерогенний механізм утворення виділень нової фази, що складається з трьох етапів. Спочатку окис натрію дифундує до внутрішніх поверхонь газонаповнених каналів. Далі оксид реагує з вуглекислим газом і перетворюється в карбонат натрію. На третьому етапі фаза, що утворилася, вистилає внутрішню поверхню газового каналу, внаслідок чого його форма набуває морфологічну стабільність.

Ключові слова: ростовые дефекты, выделения новой фазы, гетерогенный распад твердого раствора.

Методами оптической и электронной микроскопии изучена природа ростовых светорассеивающих дефектов в кристаллах NaI:Tl. Предложен гетерогенный механизм образования выделений, включающий три этапа. Вначале окись натрия диффундирует к внутренним поверхностям газонаполненных каналов. Затем оксид реагирует с углекислым газом и превращается в карбонат натрия. На третьем этапе образовавшаяся фаза выстилает внутреннюю поверхность газового канала, вследствие чего его форма приобретает морфологическую устойчивость.

Ключевые слова: ростовые дефекты, выделения новой фазы, гетерогенный распад твердого раствора.

Introduction

First of all, the authors would like to note that their views on the nature of defects in crystals and their evolution were formed under the influence of two monographs by Ya.E. Geguzin: "Macroscopic defects in metals" [1] and "Motion of macroscopic inclusions in solids" [2]. Since all authors are more or less related to the Chair of crystal physics of Kharkiv National University, they fully share conviction of professor Geguzin that a defective structure decisively determines the functional parameters of ready products from single crystals.

In this paper, the nature and mechanism of the regular formation of growth defects in a NaI:Tl crystal is considered. Detectors made from this material are most widely used in science and technology as effective scintillators [3, 4]. For a number of applications needed scintillation detectors of very large size. For example, in nuclear medicine (Anger camera) or in spectrometric portals (control of the spread of radioactive and fission materials), sensitive elements are large-area plates or long cylinders. For these purposes, ingots with a diameter of 500 mm and more are grown by modified Kyropulos technique with feeding by initial salt or melt [5]. The actual problem of the growth of large-sized crystals is the problem of light scattering which is associated with growth light-scattering inclusions (LSD – light-scattering defects). This LSDs are usually concentrated in bands of entrapping.

The photograph presented in Fig. 1 shows the longitudinal cross section of a single crystal in the upper part of a cylindrical ingot. This part of ingot corresponds to the beginning of growth in height. Usually at this transient moment the rate of crystallization is maximal. As it seen on photograph the light-scattering centers surround a front of crystallization and resemble a cloud.

Despite years of efforts to study the LSD in these crystals, the existing views on their nature were contradictory and even mutually exclusive. Nature of LSD was attributed to either gas bubbles, 100-500 nm in size, or inclusion of Na_2CO_3 phase [6]. The second model assumes a homogeneous decay of the impurity solution in the crystal lattice.

Two mutually exclusive viewpoints can be reconciled in the assumption of a heterogeneous decay of a solid solution [7]. As nucleation centers in this case, one should consider gas bubbles. Further studies questioned the last assumption, it turned out that LSDs are formed even at low concentration of CO_3^{2-} ions in the crystal lattice, which is clearly insufficient for effective separation of the second phase.

The present paper is devoted to a consistent presentation of the concepts of the nature of LSD and consideration of the heterogeneous mechanism for the formation of three-dimensional defects, which is not associated with the diffusion of carbonate ions.

Experimental

NaI:Tl crystals have been grown by modified Kyropoulos technique with feeding by melt, detailed description of equipment and process has been done in [5, 8]. A typical diameter of ingots was 250 mm while a height was ~350 mm. Ingots were grown in an argon atmosphere [8]. Several experiments have been made in mixed Ar+CO₂ gaseous medium [9] according to recommendations of [10]. The composition of the gaseous medium in the furnace was analyzed using an omegatron-type mass spectrometer, which was connected to a pressure sensor through a leak.

Gas sampling was performed every day throughout the growth process. For example, In Tab. 1 are presented the typical results of gas atmosphere analysis at furnace during the growth of crystal.

Table 1. Concentration of Ar, CO₂ and H₂O in atmosphere of furnace during the crystal growth

Atmosphere	#	Gas concentration		
		Ar	CO ₂	H ₂ O
Ar	1	92.1	0.3	–
	3	91.2	0.4	–
	5	89.8	0.54	–
Ar+ CO ₂	1	81	6.0	4.9
	2	82	6.7	3.4
	3	88	5.3	3.4
	4	82.4	6.6	4.0
	5	86	6.5	4.0
	6	84	6.8	5.0

It can be seen that in the case of Ar medium, water is not detected in furnace volume, contrary to second case when water is recorded throughout the entire growth process. This result is in good agreement with our data obtained earlier in [9]. In cited paper the pulsed injection of CO₂ into the furnace containing only Ar leads to the appearance of water vapours above the melt.

For a deliberate obtaining of LSD in growing crystal, a short pumping of furnace volume was carried out. In this case a large muddy zone was observed. Sometimes the ingot contained a large amount of LSD and even a gas bubbles visible to the naked eye. The advantage of this experiment is that it allows to model the cloudy zone quite simply. Below we will show that in zones of different nature (spontaneous or created intentionally) defects of predominantly one sort are detected.

The form of gas bubble was studied using an optical microscope in a dry room. Electron-microscopic studies were carried out on a transmission microscope EM-250 using the technique of coal replicas. Samples measuring 5×5×15 mm³ were cleavage along the growth axis from different parts of ingot. The transverse cleavage of the samples was carried out in vacuum. Replicas have been deposited on fresh surface of sample using VUP-5 installation. Shading of replicas has been made by gold.

Model of the band of entrapping

Let's consider the situation, when the gas pressure over the melt is abruptly reduced. Well known that gas

solubility in the melt sharply depends on pressure in furnace. Decrease of gas pressure results in appearance of gas bubbles in melt. Some of these bubbles enter to the crystallization front. So, gas bubbles can be incorporated into crystal lattice and form here a gas filled cavities. The zone of ingot containing entrapment of such gas inclusions is schematically depicted in Fig. 2 and is designated as a cloudy or muddy area.

In [6], we showed that the gas filled inclusions obtained in this manner are characterized by the presence of cavities in the form of prolonged channels. A gas bubble, often faceted, has a continuation in the form of a gradually disappearing "tail", elongated along the growth axis. The boundary between the upper transparent part of the crystal and the cloudy zone is quite sharp. As the equilibrium between the gas pressure over the melt and its concentration in the liquid phase is reached, the release of large bubbles ceases. Below the bubble area there is a zone where the LSDs are gradually disappearing. This is due to the fact that gas bubbles have a small size and are not visible in optical microscope [6]. They are detected by the increased scattering of light (in the laser beam), by the deterioration of transmission and by the significant dispersion of the extinction coefficient.

Despite the fact that gas bubbles are not distinguishable here the electron microscopic studies have revealed a huge number of "hollow rods", the skeleton of which is formed by carbonates of sodium and/or thallium [6, 7]. As an example, Fig. 3 shows a photograph of replica, which correspond to the turbid zone of ingot. It can be seen (Fig. 3a) that a large number of rods that stick out from the replica. Presence of the rods on photo means that their solubility in water is small. A separate rod in enlarged form is shown in Fig. 3 b. It is clearly seen that the rod is hollow inside. This fact, like the approximately cylindrical symmetry of the defect, clearly indicates that hollow rod is directly related to gas channel inherently. The electron diffraction pattern obtained from an individual inclusion (like a rod presented in Fig. 3b) shows that the rod has an amorphous structure (the insert in Fig. 3). It should be noted that defects in the form of hollow rods are characteristic for all studied NaI crystals containing such entrapment of inclusions.

Gradually, without a sharp boundary between zones, the entrapment area turns again into a clear ingot. Gas bubbles of "classical form" (spherical or ellipsoidal) are also found here, but their concentration in clear zone is too small for appreciable scattering of light.

Impurity composition of large crystals

Well known that contamination of large NaI:Tl ingot connected mainly with the presence in crystal lattice the anion impurities like OH⁻; CO₃²⁻ and O²⁻. Activator is the desired impurity in crystal, its concentration (C_{Tl}) in grown ingot is determined by chemical analysis on thallium [11]. The value of C_{Tl} well corresponds to optimum: (4-6)·10⁻² mole % [12]. Data on the C_{Tl} are presented in Table 2 as concentration in *ppm*, number of Tl⁺ in cubic centimeter (cm⁻³), and as an average distance between activator centers.

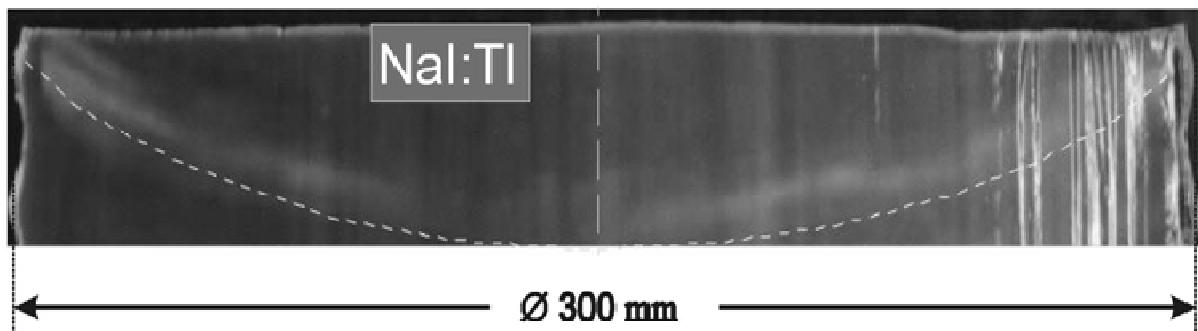


Fig. 1. Photograph of longitudinal section of ingot. The dashed line shows the crystallization front. The position of front corresponds to the beginning of growth with constant diameter. The cloud of LSD is located just above the dashed line

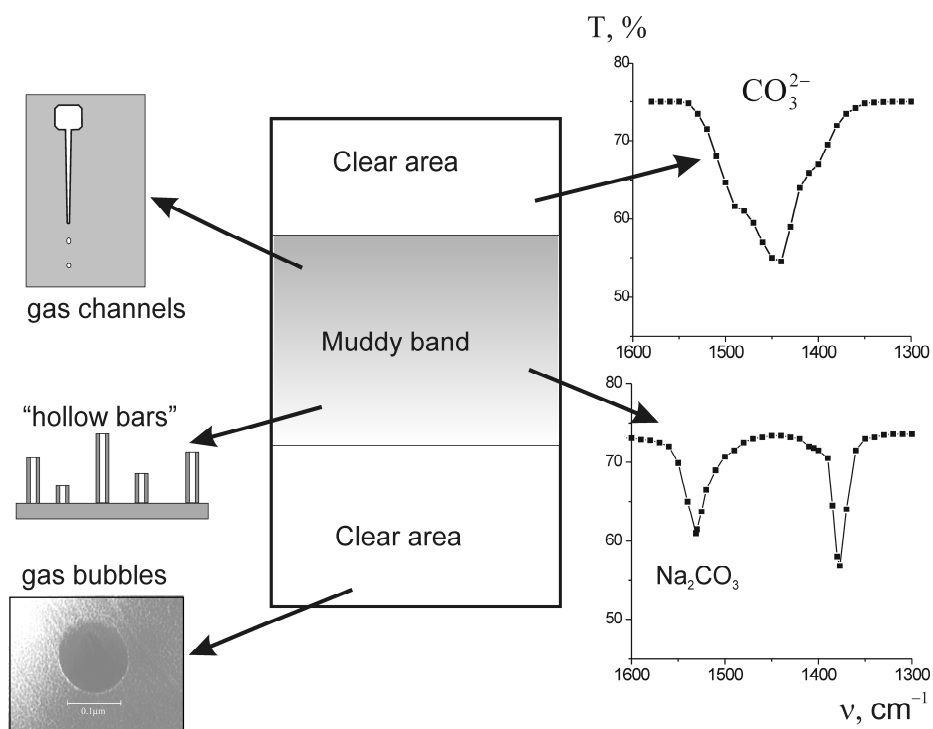


Fig. 2. Schematic imaging of band of entrapping. Explanations are given in the text

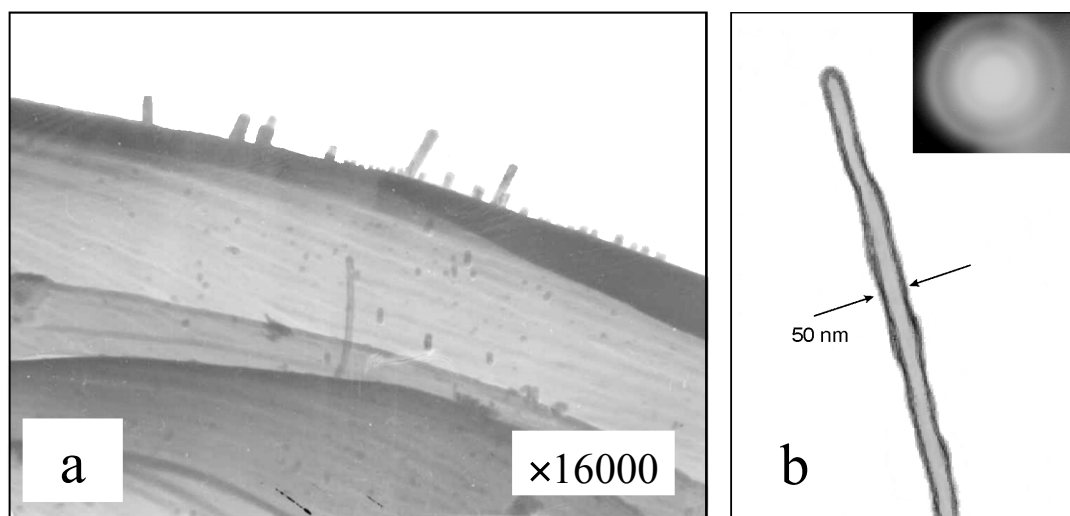


Fig. 3. Replica with hollow rods protruding from it (a). Electron-microscopic imaging of separated rod (b), in insert electron diffraction pattern is shown.

The information on the oxide compounds and its concentration is obtained from the analysis of thermally stimulated luminescence (TSL) curves [13, 14]. The setup for TSL measurements is described in [15]. Data on oxide concentration are also given in Table 2 as a number of $O^{2-} - V_A^+$ dipoles.

The concentration of carbonate ions (C_K) is determined from the spectra of IR absorption using a UR-20 spectrophotometer. We shall discuss the IR spectra itself and the changes in them a little later. Here, we note that according to the known Smakula formula, the absorption coefficient (k_{880}) at the maximum of the band 880 cm^{-1} (a deformation vibration ν_1 in CO_3^{2-} ion) is proportional to the number of the absorbing centers: $C_K = b \cdot k_{880}$, where b is the transition coefficient. For NaI crystals, its value is known: $b = 8 \cdot 10^{-2}\text{ cm}^2$. A vibration ν_1 band is chosen for the reason that its intensity depends little on the local environment of impurity anion. Contrary an intensity of the 1440 cm^{-1} band (valence ν_3 -vibration) depends on the environment, therefore, by k_{1440} , the number of non-associated $CO_3^{2-} - V_A^+$ dipoles can be judged. The data on the value of C_K in the transparent part of ingot are given in Tab. 2.

Table 2. Concentration of impurities and the average distance between similar centers

Cation / anion	Content, ppm	Content, cm^{-3}	Distance, lattice constant
Tl^+	500	$5 \cdot 10^{18}$	9
CO_3^{2-}	1	$1 \cdot 10^{16}$	464
O^{2-}	900	$9 \cdot 10^{18}$	7

An unexpected result was the fact that the value of C_K turned out to be practically the same in different parts of the crystal, and intensity of 1440 cm^{-1} band does not decrease in the turbid zone, i.e. the formed LSD are not associated with the decay of carbonate solid solution. Moreover, the formation of LSD is observed in crystals with a rather small C_K , when the average distance between identical ions is hundreds of lattice parameters (see column 4 in Table 2). In this situation the diffusion mechanism is not effective to precipitate formation from $CO_3^{2-} - V_A^+$ dipoles.

From the data of Table 2, it is possible to draw a completely definite conclusion that $O^{2-} - V_A^+$ dipoles at annealing should diffuse to the center of nucleation first of all. An internal (like a bubble or channel) or external free surfaces will be enriched by sodium oxide.

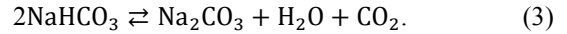
Mechanism of LSD formation

The proposed mechanism for the LSD formation is based on the processes of gas evolution at the crystallization front. The solubility of gases in the melt depends on many factors and varies from the nature of the gas. It is known [16] that the solubility of carbon dioxide exceeds that of argon by two or three orders of magnitude. Therefore, the formation of bubbles at the front is more likely when the growth process is carried out not in Ar, but in CO_2 atmosphere.

Gas evolution at the crystallization front leads to the formation of babbles and gas channels. Such cavity

as is known [2] are unstable during annealing and are transformed into a chain of pores of round shape. This slow process is impeded by another, faster process, which takes place simultaneously with the first during the growing process. It is, as shown above, the diffusion of sodium oxide. The $O^{2-} - V_A^+$ dipoles at annealing 450° effectively reach the outer or inner surface of the crystal, as will be shown below, at foreseeable intervals. The formation of an oxide coating on the inner surface just prevents the transformation of gas channels into a chain of bubbles.

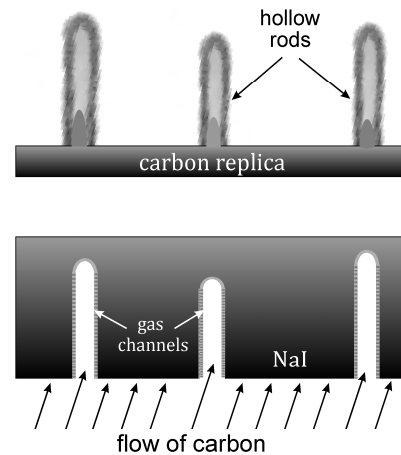
Since the babbles have been filled by CO_2 and H_2O , following chemical reactions occur on their internal surface:



Analysis of reactions (1-3) shows that carbon dioxide is spent while the amount of water does not decrease during annealing. Water can be transformed to $NaHCO_3$ when crystal is cooled.

Diffusion processes lead to the formation of a peculiar framework within the channel. The solubility of Na_2CO_3 ; $NaHCO_3$ and Tl_2CO_3 compounds in water is much less [7] than the solubility of NaI. For this reason, after dissolution of NaI, almost insoluble inclusions remain on the replica, which are observed in the electron microscope as protruding elongated rods. So, the proposed mechanism explains the origin of the hollow rods, but the way of attaching the protruding rods to the replica is still incomprehensible. An answer is given in scheme on Fig.4. During the replica making carbon atoms can penetrate into gas channel (if the rod is hollow) and create a spike to attach the rod to replica.

Fig. 4. Process of replica deposition and structure of created carbon replica with attached hollow rods



The mechanism of LSD formation is heterogeneous. This circumstance allows us to reconcile two seemingly opposite viewpoints on the origin of inclusions. As it turned out, their nature is closely related to both gas bubbles and Na_2CO_3 phase. A feature of proposed mechanism is the fact that the second phase formation occurs at crystal-gas interface. Inclusions of new phase are not directly related to decay of the solid solution of

sodium carbonate in the NaI lattice. Initially the decay of sodium oxide solid solution occurs, and the final product is formed as a result of chemical reactions with water and CO₂ at the interface. This feature makes it possible to explain the incomprehensible fact that concentration of carbonate in form of CO₃²⁻ – V_A⁺ dipoles is the same in clear area of ingot and in the muddy zone. The striation theory [17] predicts a sharp decrease in the amount of impurity in the region below the entrapping zone. It is clear that in our case, the muddy zone is associated with gas bubbles and channels not with carbonate.

Moreover, proposed mechanism can explain other, at first sight, unrelated experimental fact. The point is that repeated annealing often reveals the entrapping zone in initially transparent part of ingot. Consider the lower part of the growing crystal, which was least annealed in the growth furnace. If gas bubbles are present in this region but their inner surface has not yet been covered with the new phase, then repeated prolonged annealing will lead to the LSD formation according to mechanism described above. Reflectivity of the "rods" is much higher than just gas bubbles, and for this reason the hidden capture region becomes observable visually.

The nature of the LSD formed by the trapping mechanism of gas bubbles on the crystallization front is well known and described in many works, for example, in the already mentioned monograph [2], also for CsI crystals in [18]. Professor Geguzin touched upon this problem in [19]. The mechanisms of LSD formation associated with the homogeneous decay of the activator subsystem also well known in CsI:Tl crystal [20] and in CsI:Na [21]. The rather complicated mechanism for the formation of the LSD, which includes the trapping of bubbles, the heterogeneous decay of a solid solution and chemical reactions at the interface, as we know, was first discovered in this section.

Experimental confirmations of mechanism

Gas bubble composition. The proposed mechanism is based on the assumption that H₂O and CO₂ enter to a bubble, in contrast to the results of [22], where water was not detected. Generally speaking it is clear that the composition of the gas above the melt is qualitatively identical to that in the bubble. Quantitative differences are associated with solubility of individual gas in the melt. It turned out (see an experimental) that H₂O vapors above the melt is always recorded when growth takes place in CO₂ atmosphere. If crystal grows in Ar atmosphere, water is not detected above the melt. However it is known that CO₂ injection causes immediate release of water from the melt [9] in accordance with reaction (3). H₂O molecules are formed in the melt and evaporates through the free surface into the furnace volume. On the front of crystallization water evaporates into the gas bubbles.

So, the gas bubbles have to contain water vapors. To check this conclusion, mechanical destruction of the samples carried out in a manner similar to experiments [22]. In accordance with [22] mass-spectra do not show water evaporation from bubbles even for samples made from muddy zone. It is known that at room temperature

water interacts with Na₂CO₃ and CO₂. As a result of interaction baker soda NaHCO₃ is formed. For this reason mass-spectra were measured during heating and melting of sample. Melting of this crystal leads to release of water and carbon dioxide, 30-50 times more intense than when melting transparent samples.

IR spectra. According to Panova and Mustafina [23], the local environment of CO₃²⁻ ions should differ in the transparent part of the crystal in comparison with the muddy zone. In Fig.5 the corresponding IR absorption spectra are presented. For the transparent part of the crystal (regardless of its position relative to the turbid part), a standard set of absorption bands is observed with maxima at 1440 cm⁻¹ and 880 cm⁻¹. These bands are most intense and are well manifested even at small CO₃²⁻ concentration, their position is in good agreement with recent our [14, 24] and literature data [23].

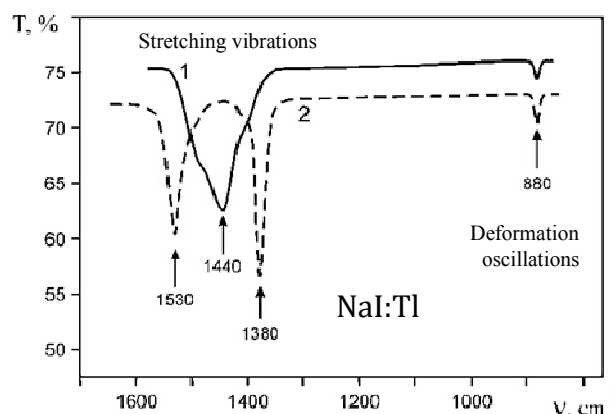


Fig. 5. Spectra of IR absorption in different areas of ingot. 1 – the clear zone, 2 – muddy band.

Another picture is observed in the muddy zone. The local environment only slightly distorts the deformation vibrations, so the maximum of the ν₁-band is still located at 880 cm⁻¹, while the stretching vibration split into two bands: 1380 and 1530 cm⁻¹. Well known that the first band is also characteristic for CO₃²⁻ ions, but it is observed in CsI crystals with volume centered lattice [24, 25]. As for the additional band at 1530 cm⁻¹, the authors of [23] observed it in crystals with the LSD at a high concentration of carbonate ions and attributed to the precipitates of Na₂CO₃ phase.

Usually, the IR absorption spectrum corresponding to the muddy zone consists of overlapping bands at 1380; 1410; 1440 and 1530 cm⁻¹. If the carbonate-ion concentration is low, a band of 1480 cm⁻¹, which is characteristic for an interacted pairs of Me²⁺CO₃²⁻ [23]. In any case, we can conclude that the local environment of a big part of CO₃²⁻ ions in muddy zone does not correspond to that in regular lattice. Therefore we believe that the 1530 cm⁻¹ band is characteristic for the skeleton of hollow bar. A feature of turbid samples is the fact that prolonged annealing at 450°C leads to an increase of absorption bands intensity at 1380 and 1530 cm⁻¹, but practically does not affect the intensity of the 1440 cm⁻¹ band.

Second phase manifestation on the free surface of sample after annealing. The next point concerns the experimental verification of the diffusion mechanism of

the LSD formation. If internal surface of the gas-filled channels are covered over time by new phase, then almost the same can be observed on the outer surface of the sample. To this end, NaI:Tl crystals with a chipped surface were annealed in inert (Ar) and reactive (CO₂) atmosphere. The annealing time (60 hours) approximately is matched the duration of growth process.

A rather intensive course of diffusion processes could be judged visually by the formation of a yellow coating of TII on the cold parts of ampoule. It could be expected that less volatile compounds, such as Na₂O; Na₂CO₃ and NaOH at temperature of 550°C will remain on the surface.

The study of annealed samples using a scanning electron microscope revealed the following. On the surface of samples oval precipitates were observed in large numbers, which, judging from the contrast of the image, had a smaller effective atomic number than the matrix, see photograph on Fig. 6. At the same time, crystals grown in vacuum and not containing oxygen

impurities were characterized by the absence of such precipitates on the surface. To establish the composition of precipitates, an analysis of characteristic X-ray emission was carried out. Emission has been excited separately in the matrix or in islands with a smaller atomic number. The size of the precipitates (~ 5-7 μm) did not prevent such microanalysis, since the electron beam can be focused on a site with diameter of ~ 1 μm. Spectra of characteristic X-ray emission are shown in parts A and B of Fig. 6.

From obtained results it can be concluded that the main elements of the new phase are sodium, oxygen and carbon. The emission spectrum in the main features corresponds to the spectrum of caustic soda Na₂CO₃ or sodium bicarbonate NaHCO₃, which was checked separately. It can be concluded that the mechanism for precipitate formation on the free surface of NaI:Tl crystal is analogous to that in the gas channels.

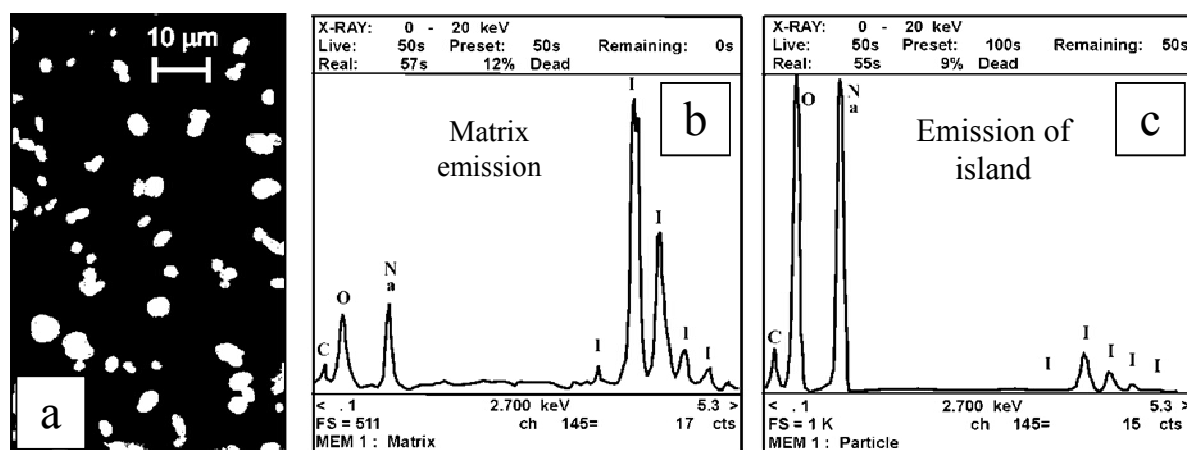


Fig. 6. Photograph of second phase inclusions on free surface of NaI:Tl crystal after annealing (a). Scanning electron microscopy. Characteristic X-ray spectra excited in matrix (b) and new phase inclusion (c)

Conclusion

The existing viewpoints on the nature of the light scattering centers in NaI:Tl crystals are analyzed. It has been shown that contradictory representations can be combined under the assumption of heterogeneous decomposition of the solid solution. The nature of light scattering defects was studied by optical and electron microscopy. It is shown that the primary type of three-dimensional defects in the capture regions is the release of a new phase in the form of hollow rods, which are oriented along the growth axis.

On the basis of the fact that the solubility of the second phase in water is much less than that of the basic substance, it is concluded that the release is associated with sodium and thallium carbonates. This conclusion agrees with the data of IR spectrometry that the local environment of carbonate ions in the capture regions does not correspond to their environment in the regular NaI lattice. The conclusion is made about the heterogeneous mechanism of LSD formation, according to which the focus of decomposition are gas-filled cavities elongated along the growth axis. Mass spectrometric

analysis showed that the gas bubbles are filled with carbon dioxide, argon and water.

The conditions for the appearance of centers of light scattering in NaI:Tl crystals are studied. It was found that the formation of carbonate precipitates inside gas bubbles occurs independently of the concentration of carbonate ions in these crystals. By chemical analysis, IR spectroscopy, and thermally stimulated luminescence, it was shown that all light scattering samples contain sodium oxide in comparable amounts ($5 \cdot 10^{-2}$ mol%) with an activator concentration. It was found that the decomposition of the solid solution with the formation of second phase precipitates inside gas bubbles occurs in crystals containing carbonate ions in small amounts ($\leq 1 \cdot 10^{-4}$ mol%). A mechanism is proposed for the formation of precipitates, which includes three stages. At the first stage, sodium oxide diffuses to the outer and inner surfaces of the crystal. On the second, a chemical reaction occurs between the conversion of oxide to carbonate. On the third - the formed phase lays the internal surface of the gas-filled channel. The resulting skeleton gives morphological stability to the gas channels.

Literature

1. Ya.E. Geguzin. Macroscopic defects in metals, Metallurgizdat, Moscow (1962), 252 p.
2. Ya.E. Geguzin, M.A. Krivoglaz. Motion of macroscopic inclusions in solids, Metallurgiya, Moscow (1971), 344 p.
3. P. Lecoq, A. Gektin, M. Korzhik. Inorganic Scintillators for Detector Systems, Springer (2017), 408 p.
4. Grupen C., Shwartz B.A. Particle Detectors, Cambridge University Press (2008), 651 p.
5. A.V. Gektin, B.G. Zaslavsky. Crystal Growth Technology, John Wiley & Sons, Ltd, Chichester, 511 (2003).
6. K.A. Kudin, V.I. Glushko, V.V. Shlyakhturov, A.Yu. Voloshko A.M. Kudin, Physical Surface Engineering, 9, 395 (2011).
7. A.V. Kolesnikov, K.A. Kudin, V.P. Seminozhenko, P.V. Mateychenko. In: Functional materials for scintillation technique and biomedicine, Kharkov, ISMA, 72 (2012).
8. B.G. Zaslavsky, S.I. Vasetsky, A.M. Kudin, A.I. Mitichkin, J. Crystal Growth, 198/199, 856 (1999).
9. B.G.Zaslavsky, S.I.Vasetsky, A.V. Kolesnikov, B.V. Grinyov, A.I.Mitichkin, K.A. Kudin, Functional Materials, 12, 147 (2005).
10. A.N. Panova, V.I. Goriletsky, T.B. Grinyova, K.V. Shakhova, J. Crystal Growth, 198/199, 865 (1999).
11. E.P.Kisil, L.I. Philippovich, V.V. Varchenko, K.N. Belikov. Methods and objects of chemical analysis, 9, 125 (2014).
12. L.N. Trefilova, A.M. Kudin, L.V. Kovaleva, B.G. Zaslavsky, D.I. Zosim. NIMA, A486, 474 (2002).
13. A.N. Panova, A.M. Kudin, A.V. Dolgopolova. Optics and Spectroscopy, 63, 444 (1987).
14. K.A. Kudin, A.V. Kolesnikov, B.G. Zaslavsky, A.I. Mitichkin. S.I. Vasetsky, A.Yu. Voloshko, D.S. Sofronov, Functional Materials, 18, 254 (2011).
15. A.V. Dolgopolova, E.N. Kovaleva. A.M. Kudin, A.N. Panova. Single crystal materials, Kharkov, VNII monokristallov, 11, 125 (1983).
16. L.E. Ivanovsky, V.N. Nekrasov. Gases and ions melts, Nauka, Moscow (1979), 371p.
17. Handbook of crystal growth. Bulk crystal growth: Basic Techniques, and Growth Mechanisms and Dynamics, 2-nd ed. Ed. P. Rudolph, Elsevier (2015), 1381 p.
18. L.M. Shamovsky. Crystal-phosphors and scintillators in geology, Nedra, Moscow (1985), 239 p.
19. Ya.E. Geguzin. Bubbles, Nauka, Moscow (1985), 174 p.
20. G.Kh. Rosenberg, G.V. Ptitsyn, L.V. Kovaleva, Solid State Physics, 21, 2970 (1979).
21. G.Kh. Rosenberg, G.V. Ptitsyn, E.F. Tchaikovsky, Yu.T. Vyday. Solid State Physics, 16, 3336 (1974).
22. E.F. Tchaikovsky, N.I. Davydenko, Yu.F. Derkach, E.V. Kovtun. Methods of obtaining and investigation of single crystals, Kharkov, VNII monokristallov, 5, 44 (1980).
23. A.N. Panova, R.Kh. Mustafina. Single crystals and scintillators, Kharkov: VNII monokristallov, 5, 1, 239 (1969).
24. B.V. Grinev, L.N. Shpilinskaya, L.V. Kovaleva, A.M. Kudin, A.I. Mitichkin, T.A. Charkina, Optics & Spectroscopy, 89, 50 (2000).
25. L.N. Shpilinskaya, S.I. Vasetsky, L.V. Kovaleva, A.M. Kudin, A.I. Mitichkin, T.A. Charkina, Functional materials, 6, 364 (1999)