Structural transformations in the system lanthanum bromide – water – electrical field

S A Vinokurov, N V Klassen, A D Orlov
Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Russia
E-mail: sergvin@issp.ac.ru

Abstract. We found several manifestations of severe influence of relatively week direct electrical fields on interactions of water with lanthanum bromide. The rate of dissolution of these crystals in water at the negative electrode exceeds this value at the positive electrode by several times. Pulse-like growth of solid micro-rods at the negative electrode from the solution of lanthanum bromide subjected to direct electrical field was observed. Auto-oscillations between the contents of water bound in hydrated lanthanum bromide and free water were found. These oscillations are attributed to severe difference of the electrical polarizabilities of free and bound water.

1. Introduction
The actuality of studies presented in this paper is determined by several reasons. Single crystals of lanthanum bromide belong to the best scintillators required for medical diagnostics, radiation monitoring etc. [1-3]. They are highly hydroscopic and inclusions of water deteriorate their technical parameters significantly. On the other hand lanthanum bromide belongs to highly brittle materials. This property induces severe problems for the processes of preparation of scintillators from this crystal. Penetration of water produces structural non-homogeneities and internal stresses between the hydrated and non-hydrated regions and can be one of the reasons of this brittleness. Lanthanum bromide has ionic interatomic bonds. So its structural non-homogeneities can create local electrical fields. Due to high electrical moment of water molecules these fields are capable to rearrange their distribution enhancing the internal stresses. So studies of behavior of various combinations from lanthanum bromide, water and electrical field are important for practical applications. E.g., developments of any ways of protection of these crystals against penetration of water molecules or of their removal are actual. On the other hand these studies will give new information about details of structure of water which is vague up to now [4, 5]. The spatial distribution of molecules in liquid water is not chaotic. They form well arranged clusters including several tens or even hundreds of elementary water. Generally speaking the interaction of water with other substances should be dependent strongly on structures of these clusters. So systematical studies of these interactions with materials having well known atomic structures can give important information about arrangements of water clusters. Anyway more than 70% of living bio-systems including humans consist from water solutions. So collecting detailed information of behavior of these solutions in various situations is necessary for deeper understanding of functional activities of human organisms.

Water solutions of salts of inorganic metals and electrical fields play important roles in these...
functions, so our work can be interesting for biologists. Earlier we published a paper about particularities of interactions of water with micro-capillaries of plants in weak electrical fields [6]. Comparison of results of the former paper and of this one can be useful for deeper understanding of interactions of water with inorganic and organic systems [4, 5].

2. Experimental techniques and materials
We used pieces of lanthanum bromide with irregular initial forms obtained from cracked single crystals grown from the melt [7]. They were kept in hermetic vessel but nevertheless were hydrated partially with molecules of water [8 - 12]. For studies of transformations of these samples in water they were placed at the glass slide of the optical microscope between two aluminum electrodes made from parallel plates having 1 mm thickness and fixed to the glass hermetically with 3 mm distance between them. Drops of distilled water were poured between the electrodes. The transformations were registered with the video-camera via the microscope. Direct electrical field was applied to the electrodes with the values varied from zero to 22 volts.

3. Experimental results and discussion
Generation of significant asymmetry of the dissolution rates of lanthanum bromide samples in water was found during application of the direct electrical field which was rather weak (not more than 100 V/cm) – Figs. 1, 2. It turns out that the dissolution rate in the region of the solution close to the negative electrode exceeds the rate in the region close to the positive electrode by several times (the ration of these rates can achieve even 10 times). Fig. 1 (a,b,c,d) demonstrates the sequence of the states of the lanthanum bromide crystals at various moments of time with the temporal intervals between them of about 20 seconds.

The negative electrode is place at the right side, the positive one – at the left. It is seen clearly that the extreme right piece is dissolved faster significantly than the pieces with more left positions.

Fig. 2 demonstrates two stages of dissolution of the pair of LaBr$_3$ pieces. The left piece is placed at the positive electrode whereas the right one – at the negative. The time interval between the photos is 20 seconds. The comparison of the changes of the samples manifests the difference in the dissolution rates being not less than 10 times.

Fig. 3 reveal the distinct difference of the chemical compositions of the solution at the left and the right sides of the sample of lanthanum bromide. The solution at the left side is much more red than the solution at the right side. It is well known that bromide agglomerations in water have red coloration [13]. During the dissolution of lanthanum bromide in the direct electrical field the negative ions of bromine should be transported preferentially to the positive electrode whereas the positive ions of lanthanum should be attracted in the opposite direction. The bromine ions are coagulated in the red agglomerations. These agglomerations deteriorate the removal of the dissolution products by diffusion. Hence the dissolution at the left side of the sample should be retarded. This explanation is in good correspondence with the experimental results.

One more “geometrical” experimental particularities of the dissolution processes of lanthanum bromide is not connected immediately with the external electrical field. Some pieces demonstrated significant anisotropy of the dissolution rate (Fig.4). This means that this rate in a certain direction was bigger than the rate in perpendicular direction by several times. Optical microscopy of the dissolution of the samples with this kind of anisotropy revealed quasi-periodical superstructure of parallel lines with the distances between these lines being several tens of micrometers. The maximal dissolution rate was observed in the direction perpendicular to these lines. This fact is confirmed by the Figs. 1 and 4. Fig. 5 shows one more particularity of the dissolution induced by the direct electrical field. As it was emphasized earlier the dissolution rate at the right side of the solution (close to the negative electrode) was higher significantly
Figure 1. a,b,c, d. Severe asymmetry of the dissolution of lanthanum bromide crystals in the direct electrical field. The negative electrode is at the right side.

Figure 2. The asymmetry of the dissolution rates of lanthanum bromide crystals at the left (positive) and the right (negative) electrodes. The temporal interval between the photos is 20 seconds.
Figure 3. The asymmetry of the coloration of the water solution of lanthanum bromide in the direct electrical field. The negative electrode is at the right.

than at the left side. This asymmetry at Fig. 5 was observed when the field was 10 V/cm. But when the external field has been increased abruptly to 100 V/cm, the dissolution has been changed by local growth of several rod-like ledges, starting from the negative electrode and separated from each other by distances about 0.5 millimeters. Figs. 5a, 5b and 5c were made with the time intervals of 1 second. So the growth rate of the upper ledge is about 0.5 mm/sec. When this growing ledge achieved almost the middle of the inter-electrode space the longitudinal growth has been changed by the transverse dissolution (Fig. 5c). The thickness of the ledge was decreased by about 3 times in one second. The analogous change from the longitudinal growth to the transverse dissolution was observed at the lower ledge.

Fig. 6 shows one more version of the anisotropy of the dissolution induced by the combined influence of external electrical field and water. The initial state of a piece of lanthanum bromide in the direct field of 100 V/cm but without water is presented at Fig.6a. The sample has an oval geometry and does not demonstrate internal anisotropy. The next Fig.6b shows the same piece after pouring water between the electrodes. In the regions contacting with neighbor pieces of lanthanum bromide some features of anisotropy appeared (e.g., a beak-like ledge at the left side of the upper part of the sample). The next photos are made with the time intervals of one second. Fig.6c shows slight rotation of the sample counterclockwise. Fig. 6d demonstrates further rotation and the formation of a triangle at the left side and a thin horizontal line going from the sharp left end of the triangle towards the negative electrode. The creation of the beak-like ledge and the subsequent triangle geometry resulted from the anisotropy of the dissolution is induced by combined action of water, electrical field and point-like contacts with the neighbors. For example relatively sharp angle between the edges of the sample under consideration and its upper neighbor produces significant local enhancement of the electrical field due to anomalously high electrical permittivity of water [9]. This enhanced electrical field induces modification of internal structure of the crystals and subsequent anisotropic acceleration of the dissolution. This anisotropy produced a thin ledge at the left side of the sample (Fig.6e).
Figure 4. The anisotropy of the dissolution of lanthanum bromide crystals. The time of the photos is shown at the left of the bottom line.
Figure 5. The asymmetry of lanthanum bromide grains in water solution at the right (negative) and the left (positive) electrodes.
Figure 6. a,b,c,d,e. Dissolution anisotropy caused by the combined action of the external electrical field and water

The counterclockwise rotation of the sample (Fig.6c, 6d) and the final fixation of the thin needle-like ledge of the sample in the direction parallel to the external electrical field make us to assume that the initial vertex of the triangle and the resulting ledge are charged negatively. So they are repelled by the negative electrode. The creation of this negative charge can be attributed to accelerated dissolution of the sample surface and fast removal of positive ions of lanthanum.

One more manifestation of the influence of the electrical field on the system lanthanum - water was found when the direct filed was applied to the thin polycrystalline layer of lanthanum.
Figure 7. Auto-oscillating appearances and disappearances of water drops at the surface of the polycrystalline lanthanum bromide precipitation layer subjected to the direct electrical field bromide precipitated from water solution on the glass slide of the microscope (Fig. 7). The first photo presents this layer at the initial moment (17.00). The transverse dimensions of the photo are 0.5 mm. After 20 seconds of observations two small drops of water appeared at the left half of the top region (17.20). In the next 30 seconds one more drop appeared in the middle of the sample (17.50). Then the drops at the left part disappeared whereas the middle drops was growing during 20 seconds (18.00 and 18.10). At the next stage the middle drop began to disappear whereas at the top region of the sample a small drop appeared once more (18.20). The photos at 18.30 and 18.40 demonstrate creation of two more drops at the top left part and subsequent connection of these two drops (19.00). Then the upper drop disappeared (19.10). During the next intervals of 30 seconds two new drops appeared in the middle part (20.00) and disappeared (20.30). During the next 120 seconds two new drops appeared, grew significantly achieving the biggest dimensions and disappeared again in the middle region.
Figure 8. Auto-oscillations of the water meniscus level at the negative electrode in the direct electrical field. The interval between the photos is about 10 seconds

The experimental observations presented at Fig. 7 reveal oscillating behavior in the system water – lanthanum bromide induced by the external electrical field. These oscillations manifest themselves in the appearance of water drops at a certain place of polycrystalline lanthanum bromide, subsequent their disappearance, next appearance in another point, etc. The typical time intervals of these oscillations are of the order of 10-20 seconds.

Fig 8 presents another manifestation of the oscillating extraction of water from polycrystalline lanthanum bromide precipitation induced by the direct electrical field of the amplitude about 100 V/cm. Here the modifications of the meniscus of water adjusted to the negative electrode from aluminum is presented. The spatial amplitude of the oscillations of the edge of the water meniscus is about 100 micrometers. The time intervals between the neighbor photos are about 10 second. The sequence of the positions of the meniscus corresponds to oscillations of the amount of free water extracted from the hydrated lanthanum bromide when the electrical field is applied.

Conclusions
• Interaction of water with crystals of lanthanum bromide is regulated in a wide range by relatively low electrical field either increasing or decreasing significantly the rate of dissolving of these crystals by water.
• Essential asymmetry of dissolving of lanthanum bromide grains has been found in direct electrical field: at the negative electrode the rate of the dissolving exceeds the rate at the positive electrode by several times. This is explained by significant difference in the mobilities of the lanthanum and bromine ions dissolved in water.
• Oscillations of hygroscopicity of lanthanum bromide crystals in weak direct electrical field with periods of several seconds has been found. This phenomenon was expressed in abrupt extraction of micro-drops of water at the surface of solid polycrystalline lanthanum bromide precipitated at glass slide of the and subsequent their disappearance. These oscillations are explained by strong difference of the electrical polarizabilities of free and bound water molecules resulting in local variations of the internal electrical fields and the mechanical stresses induced by hydration and dehydration of lanthanum bromide.
• Pulse forming of needle – like microcrystals in water solutions subjected to pulses of direct electrical field has been found. These pulsed forming is explained by high electrical polarizability of water-less lanthanum compounds in comparison with the hydrated compounds.
• Strong anisotropy of the dissolution rate of some grains of lanthanum bromide in water has been found even without the external electrical field. The grains differ from others by the presence of microscopic systems of periodical parallel rows. The dissolution rate was bigger significantly in the direction perpendicular to these rows. The resulting forms of such grains before their complete dissolution became needle-like.

• The facts of asymmetry and anisotropy of dissolution of lanthanum bromide in water, auto-oscillations of local content of water and presence of layer-like superstructures are important for the development of optimized techniques of processing of as-grown lanthanum bromide crystals.

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