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Introduction

An attractive feature of ^{6}Li containing fluorescence materials that determines their potential application in radiation detection is the capture reaction with slow (~<100 keV) neutrons: $^{6}Li + n = {}^{4}He + {}^{3}H + 4.8MeV$.[1] The use of ^{6}Li-salicylate (LiSal, $LiC_6H_5O_3$) for thermal neutron detection was previously studied in liquid[2,3] and polycrystalline[4,5] scintillators. The studies showed that both liquid and polycrystalline LiSal scintillators could be utilized in pulse shape discrimination (PSD) techniques that enable separation of neutrons from the background gamma radiation. However, it was found[3] that the efficiency of neutron detection using LiSal in liquid solutions was severely limited by its low solubility in commonly used organic solvents like, for example, toluene or xylene. Better results[4] were obtained with neutron detectors containing the compound in its crystalline form, such as pressed pellets, or microscopic-scale (7-14 micron) crystals dispersed in various media. The expectation drown from these studies was that further improvement of pulse height, PSD, and efficiency characteristics could be reached with larger and more transparent LiSal crystals, growth of which has not been reported so far.

In this paper, we present the first results on growth and characterization of relatively large, a cm-scale size, single crystals of LiSal with good optical quality. The crystals were grown both from aqueous and anhydrous (methanol) media, mainly for neutron detection studies. However, the results on growth and structural characterization may be interesting for other fields where LiSal, together with other alkali metal salicylates, is used for biological, medical, and chemical (as catalyst) applications.[6-8]

1. Experimental section

The row material for crystal growth was purchased from Sigma-Aldrich (LiSal, 99.99%). The initial powder was freely dissolved in water, ethanol, and methanol, enabling the use of solution technique which is the only option for LiSal decomposing below its melting point. Water and anhydrous methanol (MeOH) were used for crystal growth. A few mm size seeds were obtained by spontaneous precipitation from such solutions. Further crystal growth was performed on these seeds using slow evaporation technique.

X-ray diffraction method was used to examine the structure of LiSal crystals. The experiments were carried out using the vertical Philips goniometer utilizing cooper Kα radiation. Photoluminescence (PL) spectra were measured using a commercial Fluoromax-2 spectrometer. The scintillation light yield was evaluated from the emission spectra acquired under beta excitation using a $^{90}Sr/^{90}Y$ source, in comparison with two standard inorganic crystals: BGO and BaF_2. Detection of MeOH separated from single crystals was performed by gas chromatography-mass spectrometry (GC-MS) using a Hewlett Packard (HP) 6890 GC coupled to a HP5973 mass selective detector with the injection temperature set at 250 C. Methanol was identified by MS=31 and authenticated with both a methanol standard and a NIST library search.

The pulse shape discrimination measurements were performed using a polyethylene moderated ^{252}Cf source to irradiate crystals coupled to a H3378-50 Hamamastu photomultiplier tube (PMT). The signals collected at the PMT anode were recorded using a high resolution waveform CompuScope 14200 digitizer with a sampling rate of 200MS/s, for offline analysis. The ability of an organic crystal to discriminate between the neutrons and gamma rays emitted from the ^{252}Cf source was evaluated with the charge comparison method based on the consideration that, for a defined amplitude value, the signal produced by a neutron has a larger slow component with respect to the signal produced by a gamma ray.[9-11] In the offline analysis, the recorded waveforms were numerically integrated over two different time intervals: Δt_S and Δt_F, corresponding to the slow and the fast component of the signal respectively. The value of the ratio of charge $R=Q_S/Q_F$ over these two time intervals indicated whether the considered event was due to a neutron (high R value) or a gamma ray (small R value).

2. Results and discussion

The room-temperature solubility of LiSal was measured as 132.1 g in 100 g of water and 162.3 g in 100g of methanol. At this extremely high solubility of LiSal, the initially colorless saturated solutions prepared for growth had the consistency of dense sugar “syrup” that very quickly became brown producing similarly colored crystals. However, when solutions were prepared with pH 2 by addition of the small amounts of salicylic acid, formation of color was much slower giving enough time for growth of completely colorless crystals. Since growth was performed by the simple evaporation technique without the reversible rotation required for rapid growth of large defect-free crystals[12], crystals were grown at slow growth rate not exceeding 1-2 mm/day in any direction.

Relatively large single crystals, similar to those shown in Figure 1, could be grown using both from water and methanol solutions. Both types of crystals remained clear and transparent as long as they were immerged in the growth solutions, even under the condition that the solutions were open to the atmosphere for the free evaporation.

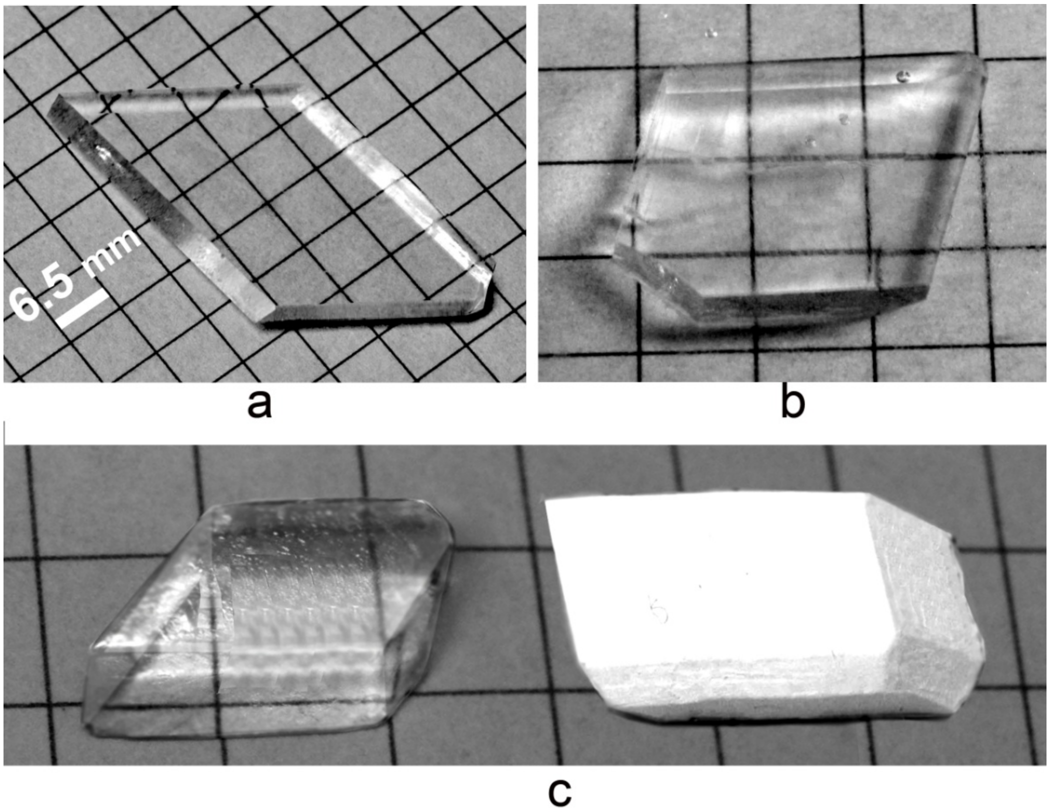

Fig.1. LiSal single crystals: (a) – Grown from water; (b) – Grown from methanol; crystal surface is covered with paraffin oil to prevent fast degradation in air; (c) - Crystals grown from water (left) and methanol (right) after 1 day exposure to air with no paraffin oil on the surface.

However, their behavior was different after removal from the growth solutions. Crystals grown from water (Figure 1a) remained unchanged being exposed to air during indefinite periods of time. No precautions were needed to preserve them in the course of measurements. On the contrary, crystals grown from MeOH (Figure 1b) immediately started degrading becoming completely opaque (Figure 1c) in the entire volume after few hours upon their removal from solution. To prevent this kind of degradation, crystals grown from MeOH had to be preserved in the paraffin oil, so that some measurements were made with the crystals having a thick oil layers on the surface (as in Figure 1b), or placed in quartz containers filled with the oil.

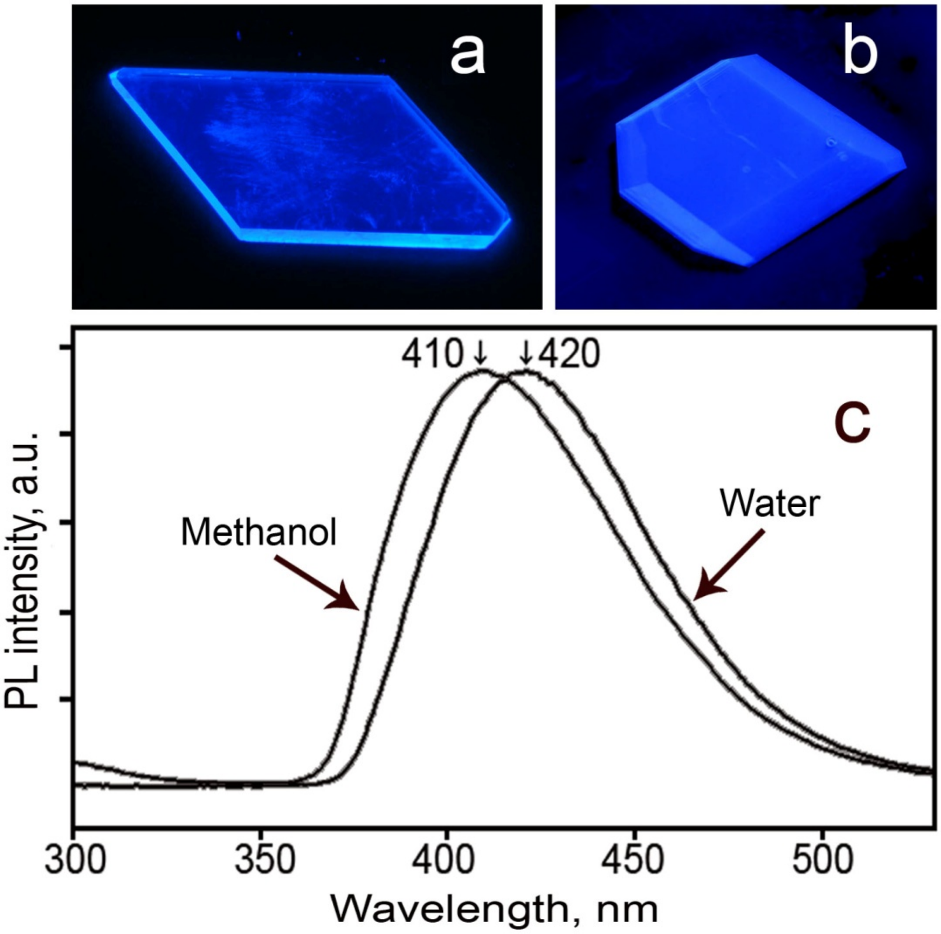

Fig. 2. Photoluminescence images of LiSal crystals grown from water (a) and methanol (b) solutions with the corresponding photoluminescence spectra (c).

Both kinds of crystals were highly fluorescent (Fig. 2, a and b), yielding approximately same scintillation light yield (LY) of about 7000 photon/MeV. Crystals grown from water consistently had longer-wave-length peak energy of the PL spectra (Fig. 2, c) showing, together with the different air-sensitivity, possible formation of compositional or polymorphic modifications of LiSal in different solvents. Existence of such modifications was confirmed by the X- ray diffraction (XRD) analysis. The different peak positions of the XRD patterns

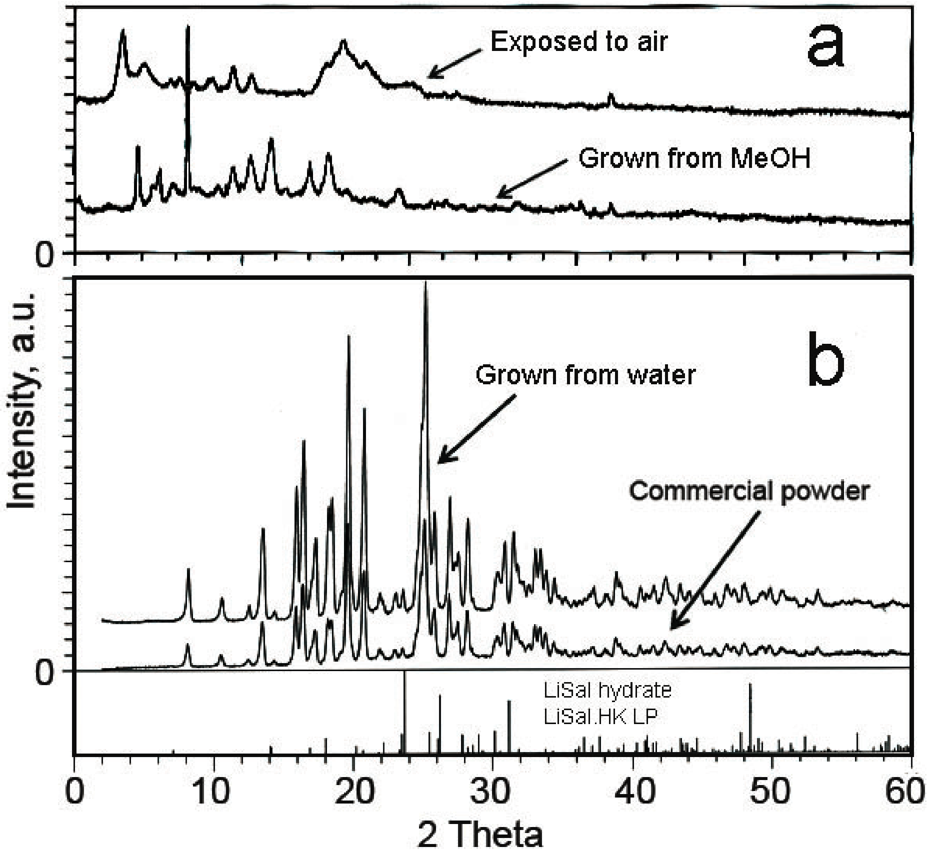

Fig. 3. XRD patterns of Lisal samples: (a) - crystals grown from methanol solution; lower pattern corresponds to as grown crystals protected by paraffin oil; upper pattern was obtained with methanol-grown crystals exposed to air for two days;. (b) - commercial (Aldrich) LiSal powder and crystals grown from water solutions. Reflection lines for LiSal monohydrate calculated from Ref.13 are given for comparison.

presented in Figure 3, a and b, clearly indicates different crystallographic structures for LiSal: unstable phase grown from methanol, with the XRD pattern changing in time (Fig. 3, a), and the stable modification formed in water solutions (Fig. 3, b).

Detailed structural and compositional investigation of LiSal polymorphs is beyond the scope of this work. Nevertheless, some interesting conclusions can be made on the basis of simple observation and measurements made with the grown crystals. Considering the differences between crystals grown from water and methanol, it would be logical to assume that, similarly to a previous work,[13] crystals of a hydrated LiSal form in water solutions, while pure anhydrous LiSal grows from water-free MeOH. However, the experimental results do not support such an assumption. The lack of coincidence between the XRD peaks of water-grown LiSal and reflection lines calculated using LAZY-PULVERIX computer simulation software

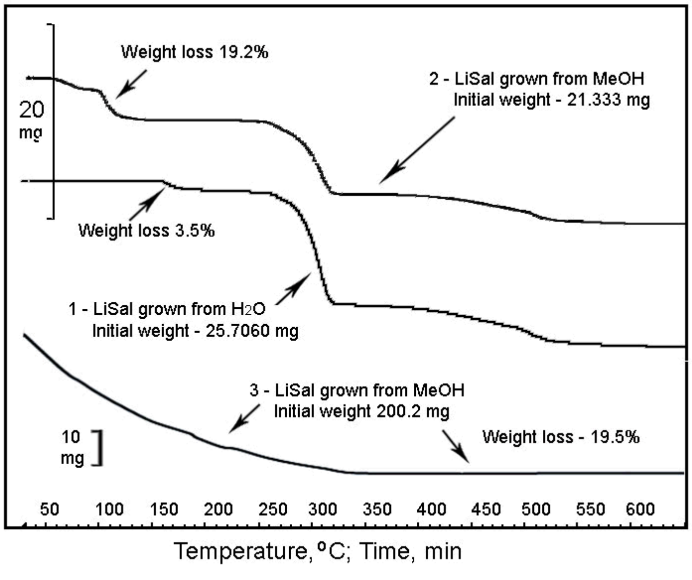

Fig. 4. Weight loss in LiSal single crystals grown from water and methanol: 1 and 2 – thermogravimetric curves obtained by heating under inert gas atmosphere; large weight loss in both types of crystals around 300 °C corresponds to the previously studied decomposition of LiSal molecules [Ref. 14]; 3 – kinetic of the weight loss measured at room temperature.

from Ref.13, indicates that crystals grown from water in our experiments are not LiSal monohydrate. Thermogravimetric analysis (TGA) made with the water-grown LiSal showed that a piece of a single crystal looses only 3.5% of its weight at the temperature around 150^{o}C (Fig. 4, Curve 1). This fraction, which is about three times smaller than that expected for the dehydration of the LiSal·H_2O (11.1%), also indicates the absence of LiSal with larger numbers of water molecules. From these results, it seems much more likely that crystals grown from water in our experiments do not contain molecular water in their composition. An additional proof that these crystals correspond to a pure, non-hydrated form of LiSal is provided by the full coincidence of the two XRD patterns in Figure 3 b showing identical structures for water-grown LiSal crystals and high purity commercial crystalline powder not listed as a hydrate by the vendor.

Formation of the non-hydrated form in our experiments in comparison to the LiSal monohydrate obtained in previous studies can probably be explained by the difference in the initial material preparation. Reaction between lithium hydroxide and salicylic acid in aqueous media was used to synthesize LiSal in Ref.13. Additional factors could be introduced by the difference in the pH or other conditions. For example, in our experiments crystal growth started immediately after the preparation of the saturated solutions, while in the previous work LiSal molecules were exposed to water for few months until the solution reached saturation.

It is interesting that crystals grown from MeOH also lose weight (Curve 2 in Fig. 4) instead of gaining expected from the hydration process. The weight-loss fraction in this case is much higher, 19.2%, which is close to 18.2 %, the theoretical loss of the methanol weight calculated for decomposition of a LiSal·MeOH molecule. The fact that this weight loss is almost precisely the same, whether crystals were heated in the inert gas atmosphere or exposed to open air at room temperature (Curve 3 in Fig. 4), indicates that the transformation in the LiSal crystals removed from methanol growth solution is caused not by the hydration in air but, more likely, by the liberation of MeOH from the molecules of LiSal·MeOH adducts. Such conclusion was fully confirmed by the compositional analysis of the weight fraction releasing during the degradation. For the analysis, inclusion-free single crystals dried and sealed under nitrogen were left in glass vials for more than 24 hours. Large amounts of MeOH detected by gas chromatography-mass spectrometry were found only in the vials containing methanol-grown samples.

More precise quantitative analysis of the PSD studies made with LiSal single crystals, as well as their comparison to Li-loaded glass and plastic scintillators, will be a subject of a separate publication. Fortunately for the application, first PSD tests showed that the unstable

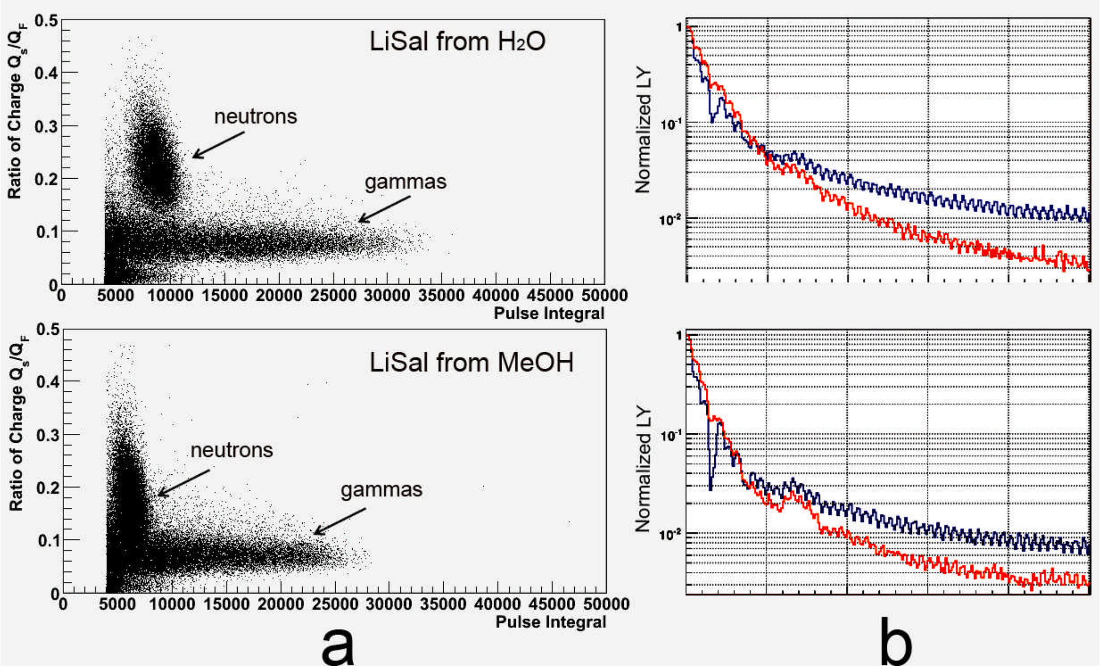

Fig. 5. (a)- Pulse Shape Discrimination obtained with LiSal single crystals. The results show noticeably better neutron/gamma separation in LiSal crystals grown from water solutions. (b)- Average waveforms corresponding to the neutrons (blue) and gammas (red) for each of the scintillators. ^{252}*Cf source with 4”plastic moderator.*

methanol-grown crystals did not exhibit any superior properties in comparison with the stable modification produced from water solutions. Initial, perfectly transparent, single crystal samples of both types, having approximately same size and no visible defects, were used for these tests. To avoid the degradation of the methanol-grown sample and to conduct the measurements under the same conditions, both crystals had a thin layer of paraffin oil on the surface. As clearly shown in Figure 5, better separation between the gamma and neutron events was obtained in the water-grown material. To understand the variation of the performance, the peak-normalized waveforms were averaged for each of the gamma and neutron capture regions and compared. The average light curves of gammas are approximately the same for both samples, but the methanol-grown crystal yields approximately 30% less light 250 ns after the peak light yield consistent with the observed poorer separation. For the practical use, this result is important because it enables to concentrate further studies on the stable crystals that can be produced at larger sizes by simple and inexpensive growth from water solutions. It also can be helpful in dealing with small, microscopic crystals, in which the degradation cannot be easily seen. For example, it can explain the lower PSD performance of the LiSal polycrystalline samples obtained from MeOH in comparison to similar samples produced from water solutions.[3]

Conclusion

Lithium salicylate (LiSal) single crystals have been grown from water and methanol solutions for thermal neutron detection studies. The results of observations and structural studies showed that LiSal crystallizes from water as a stable modification different from the monohydrate LiSal·H2O reported previously. Growth from methanol results in the formation of unstable crystals of LiSal·MeOH that quickly degrade in air. First radiation detection tests showed a good neutron/gamma separation in water-grown modification making LiSal in its single crystals form a potential material for thermal neutron detection.

Acknowledgements

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