

CRYSTAL GROWTH OF PURE AND LEAD DOPED BARIUM-LITHIUM FLUORIDE

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ABSTRACT

We determined the conditions of preparation and growth of pure and lead doped BaLiF₃ crystals for a simple pulling equipment without diameter control. We utilized an empirical step temperature program which is compared with a theoretical non-linear program proposed to BaLiF₃ crystals growth. To improve the optical quality of crystals obtained we realized a study of the macroscopic shape of the growing interface and growth direction. The distribution coefficient of Pb in BaLiF₃ was estimated as 0.05.

MATERIALS INDEX: perovskite, fluorides, barium, lithium, lead.

Introduction

In the last few years, a lot of work has been done in the search of new laser host materials. Recent investigations showed that cubic perovskite type crystals are interesting matrix to these type of applications: Cr³⁺ doped KZnF₃, results in a "vibronic" laser, broadly tunable over several nanometers at room temperature (1); Ni²⁺ in KMgF₃, shows laser emission at 1.591 μm at 77 K (2), and Pb²⁺ centers in KMgF₃ also results in a tunable laser media working at 77K (3,4).

BaLiF₃ is an "inverse" perovskite with cubic structure (space group O_h¹ - Pm3m), where the monovalent ion Li⁺ is at the center of a F₆^h octahedron whereas the Ba²⁺ divalent ions are in the 12-fold environment site, resulting in a different crystal field interaction from classic perovskite structure (5). The compound BaLiF₃ melts incongruently and a single crystal must be

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grown from a non-stoichiometric melt to avoid other phase precipitations. Neuhaus *et al* (6) and Leckebusch *et al* (7) proposed that crystal growth can be achieved by a programmed non-linear temperature decrease of the melt considering the liquidus line (A - B) from the phase diagram of LiF - BaF₂ system (figure 1). Experimentally they have applied a linear program of temperature (arithmetic mean) for the BaLiF₃ growth. In this work the preparation and crystal growth conditions of pure and lead doped BaLiF₃ with good optical quality are presented. We used a non-linear program with 3 different temperature rates. The segregation coefficient of Pb²⁺ in BaLiF₃ was estimated.

Theoretical temperature program

A study of figure 1 shows that BaLiF₃ melts incongruently and any single crystal must be grown from a melt containing an excess of LiF to avoid the precipitation of BaF₂. This excess of LiF must be maintained throughout the growth period. Neuhaus proposed that a temperature decrease of the melt considering the liquidus line A-B from the phase diagram of LiF - BaF₂ system, would assure a constant supersaturation of the melt and consequently would provide a homogeneous crystal growth. Leckebusch presented a theoretical non-linear temperature

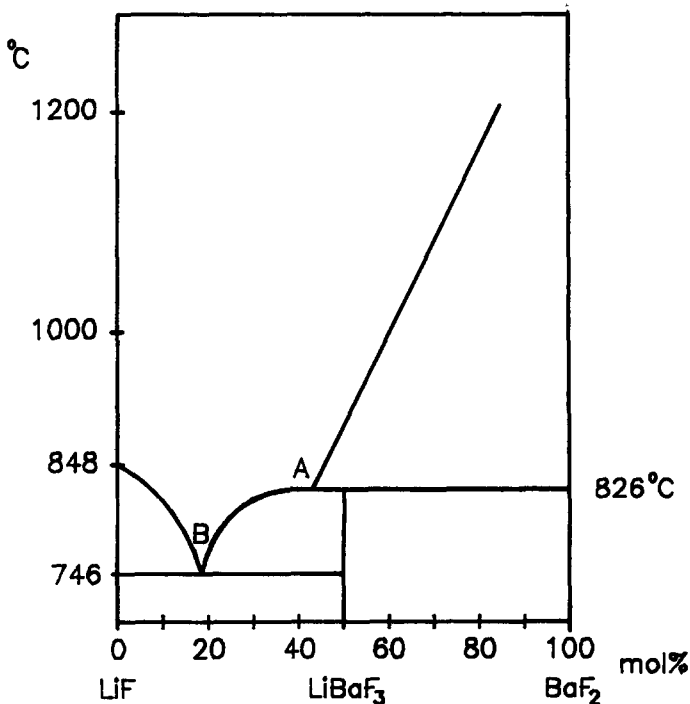


FIG. 1
Phase diagram of LiF - BaF₂ system (6,7).

program for BaLiF₃ described by:

$$\frac{dT_x}{dt} = \frac{F \rho_c}{M} V_{lin} \frac{L_a R T^2 \left(\frac{1}{n_a + n_b - n_x} - \frac{1}{n_a - n_x} \right)}{\left[R T \ln \left(\frac{n_a - n_x}{n_a + n_b - n_x} \right) - L_a \right]^2} \quad [1]$$

This equation was computed from the cryoscopic relation,

$$\ln x_a = \frac{L_a}{R} \left(\frac{1}{T_x} - \frac{1}{T} \right) \quad [2]$$

where L_a is the heat of fusion, R the gas constant, T_x the melt temperature, T the melting temperature of BaLiF₃ and x_a the molar ratio, defined as:

$$x_a = \left(\frac{n_a - n_x}{n_a + n_b - n_x} \right) \quad [3]$$

where n_a , n_b are the initial molar concentration of BaLiF₃ and LiF, respectively and n_x the molar concentration of crystallized BaLiF₃ growing with uniform cross section area (F) and constant linear velocity (V_{lin}), defined by:

$$n_x = \rho_c F V_{lin} t / M \quad [4]$$

where ρ_c is the density in the solid phase, M is the atomic weight and t the time of growth. Leckebusch reported the growth of BaLiF₃ crystals with 40-45 g, with no cylindrical morphology, applying a constant temperature rate calculated from an arithmetic average of this theoretical non-linear program. In this work we determined an empirical step temperature program to the growth of cylindrical and homogeneous BaLiF₃ crystals with 160-180g. This empirical program is compared with the theoretical program above mentioned.

Crystal growth experiments

a) BaLiF₃ preparation

The starting materials used are BaF₂ and LiF obtained from Rhone-Poulenc (99,99%). Lithium Fluoride was first purified by crystallization. The two fluorides were weighted and mixed with non-stoichiometric ratio (43% BaF₂ and 57% LiF) in a vitreous carbon crucible. The mixed charge was pre-heated at 700°C at a 10⁻³ mmHg pressure to eliminate water trace contamination. To avoid oxyfluoride impurities, reactive atmosphere processing

(RAP) (8) was used for compound fusion. Pure CF_4 was introduced up to 1.2 bar prior to materials fusion. The melt was then allowed to soak for several hours. After treatment the material was maintained in a dry box to avoid contamination before crystal growth.

In the first experiments ammonium bifluoride (NH_4HF_2) was mixed with starting materials, but the most successful synthesis was obtained only with CF_4 as RAP agent.

The same synthesis process was used for lead doped materials except that pre-treatment was made at 500°C to provide low evaporation rate of lead fluoride. We have worked with 5, 10 and 20 mole% concentration of PbF_2 (Merck - optipur) in BaF_2 -LiF mixture.

The basic fluorides - LiF and BaF_2 - and the compound prepared by using the conditions described earlier, were analyzed by atomic emission spectroscopy (table I). Important concentrations of metallic impurities are not evident. The same was observed for single crystals obtained from this materials.

TABLE I
Atomic Emission Spectrographic Analysis

	LiF (%)	BaF_2 (%)	BaLiF_3 - CF_4 treated (%)	BaLiF_3 crystal (%)
B		0.003	0.003	< 0.003
P		< 0.15	< 0.15	< 0.15
Fe	0.002	0.025	0.025	0.025
Cr		< 0.0045	< 0.0045	< 0.0045
Ni	0.002	< 0.0045	< 0.0045	< 0.0045
Zn		< 0.15	< 0.15	< 0.15
Si	0.005	< 0.006	0.006	0.006
Al	0.0018	0.06	0.002	0.002
Mn	0.0002	0.0015	<0.0045	<0.0045
Mg	0.0025	< 0.0045	0.0045	0.0045
Pb	< 0.001	< 0.0045	<0.0045	< 0.0045
Sn		< 0.003	< 0.003	< 0.003
Bi		< 0.0015	< 0.0015	< 0.0015
V		0.003	0.01	0.003
Cu	0.0035	0.0015	0.0015	0.0015
Co		< 0.0045	< 0.0045	< 0.0045
Ca		0.25	0.25	0.025
Ba	0.0075	-	-	-
Sb		< 0.0045	<0.0045	< 0.0045

b) Crystal growth

A modified NRC model 2085 Czochralski pulling system was used for crystals growth, under a mixed atmosphere of CF_4 and Ar to produce a partial HF pressure to react with traces of water and/or oxygen impurities which may be still present in prepared BaLiF_3 compound. A Platinum crucible was used for pure BaLiF_3 melts, but for BaLiF_3 :Pb, it was necessary to use a vitreous carbon crucible to avoid Pt/Pb alloy formation. The charge of one run was 250 - 270 g. The pulling rate was 1 mm/h and the

rotation rate ranged from 10 to 80 rpm. The temperature rate program will be discussed below. Undoped crystals were grown along $\langle 001 \rangle$, $\langle 011 \rangle$ and $\langle 111 \rangle$ directions. Pb-doped crystals were grown only at $\langle 111 \rangle$ direction. The size of the boules were generally 25 - 30 mm diameter X 60 - 70 mm long. After growth the crystals were annealed in Ar atmosphere at 700°C and cooled at 10°C/h to room temperature.

Results and discussion

a) Temperature program

The first runs were performed with $\langle 001 \rangle$ seeds and constant rotation rate of 10 rpm. We started the pulling with a temperature rate of -0.5°C/h . The crystal diameter grew gradually reaching a final constant value of 30 mm. The diameter was kept constant over a length of approximately 15 mm and began to decrease. To avoid the diameter decrease we changed the temperature rate to -1°C/h , and after 10 hours to -2°C/h , which kept the diameter constant for more 10 hours. At this point we finished the growth process with a positive temperature rate of 1°C/h to avoid LiF segregation.

We also tried to begin the growth with a lower temperature rate, (-0.4°C/h). For these conditions a better diameter control was obtained, with the decrease of the steady-state diameter to 24 - 26 mm, considered as a convenient value. The temperature program was approximately the same except during the period of each rate: 31 to 33 hours with -0.4°C/h , 16 to 18 hours with -1°C/h and 5 to 8 hours with -2°C/h .

The complete empirical temperature program was determined with 5 runs. The steps of a typical growth experiment are shown in figure 2a. We have grown several crystals with the same temperature program. A photograph of some grown BaLiF_3 crystals is given in figure 3.

Based on the thermal conditions and dimensions of our Czochralski growth system, we calculated the theoretical curve from equation (1) (figure 2b). We have assumed an ideal crystal radius of $r_c = r_0/2 = 12.5$ mm, where r_0 is the radius of the crucible. Comparing the theoretical non-linear program proposed by Leckebush and Neuhaus and our step temperature program we observed that: at the beginning of the growth process the calculated change in freezing temperature caused by the change in the melt composition is overestimated because of the hypothesis of linear growth rate with a steady-state diameter. This means that, the effect of the initial crystal radius broadening was not considered. When the crystal growth process develops an equilibrium condition (steady diameter), the fast lowering of the melt level results in an additional increase of the melt temperature. At the end of the crystal growth, a higher temperature rate is necessary to set a constant diameter.

b) Interface shape and orientation

The interferograms of the first crystals showed a poor optical quality with large stressed areas. The optical homogeneity and optical transmission can be influenced by the

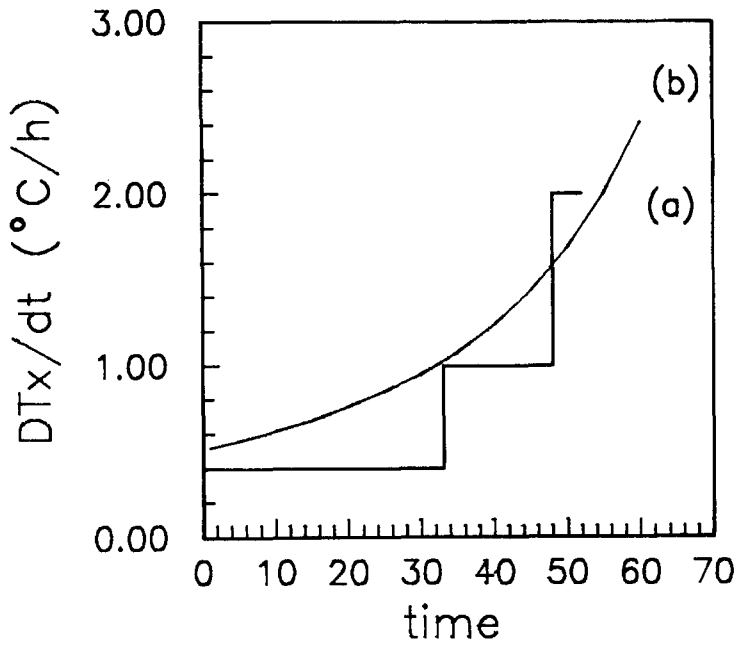


FIG. 2
Temperature program: (a) experimental ; (b) theoretical.

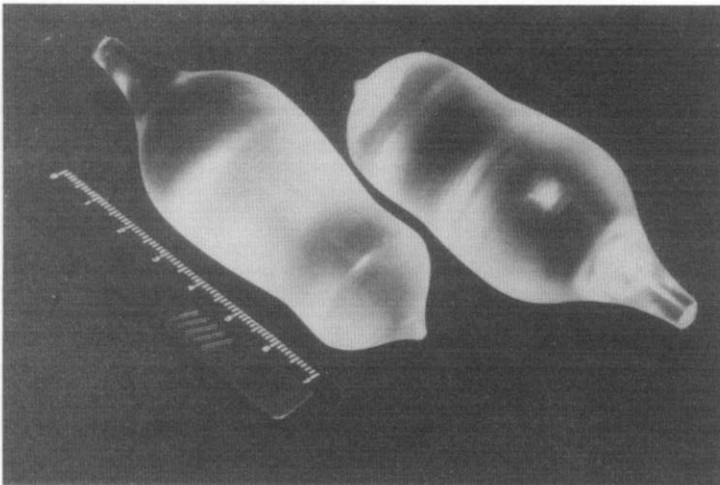


FIG. 3
Pure BaLiF₃ crystal.

solid-liquid interface shape and growth direction. To observe the macroscopic shape of the growing solid-liquid interface, growth was terminated by quickly raising the crystal from the melt, thereby preserving the interfacial growth features. To study the interface shape of BaLiF_3 crystals different rotation rates were attempted.

The rotation speed is a function of crystal and crucible diameter and the temperature gradient of the melt. For the growth system used here, the results can be summarized as follows: a) the solid-liquid interface became concave, toward the melt, up to 50 rpm, flat at 30-40 rpm and convex at low rotation rate as 10 rpm; b) the interface shape changed very slightly along the crystal growth (figure 4).

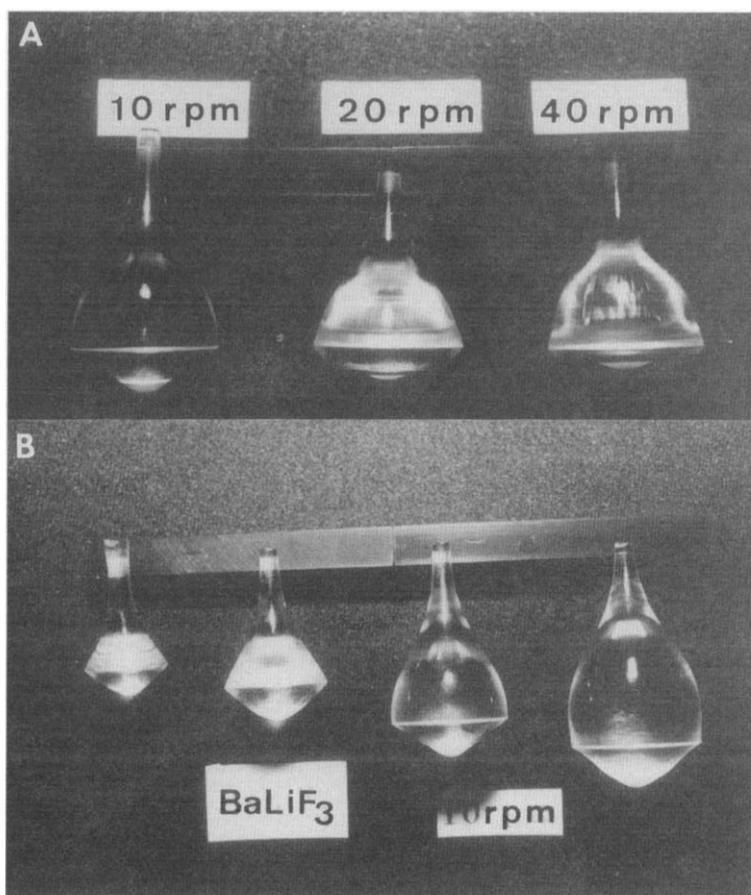


FIG. 4

Interface shape of the grown crystals: (a) with different rotation rates; (b) with the same rotation rate and increasing hours of pulling.

Considering also seed crystal direction: for every rotation rate, the $\langle 011 \rangle$ boule showed poor crystal quality, the boules along this direction always cracked during cooling or crystal growth. We supposed that high stress densities tend to be produced in this direction, however this observation could not be confirmed by interferometry due to the cracking of the crystals. For 30 - 40 rpm we obtained good optical quality $\langle 111 \rangle$ boules. However, the $\langle 001 \rangle$ boules, at the same rotation rate showed usually higher impurity segregation and cracked very easily. For lower rotation rate we observed an increase in the micro segregation for both directions - $\langle 001 \rangle$ and $\langle 111 \rangle$.

We concluded that a flat interface allowed the growth of relatively stress-free crystals with a good degree of optical quality. This effect is demonstrated in figure 5 which shows the interference pattern for a $\langle 111 \rangle$ crystal grown with 30 rpm.

It's interesting to note that we have not observed facets formation for any of the directions of growth used in this study. The velocity of growth seems to be isotropic, which is not common in the perovskite type crystals (9).

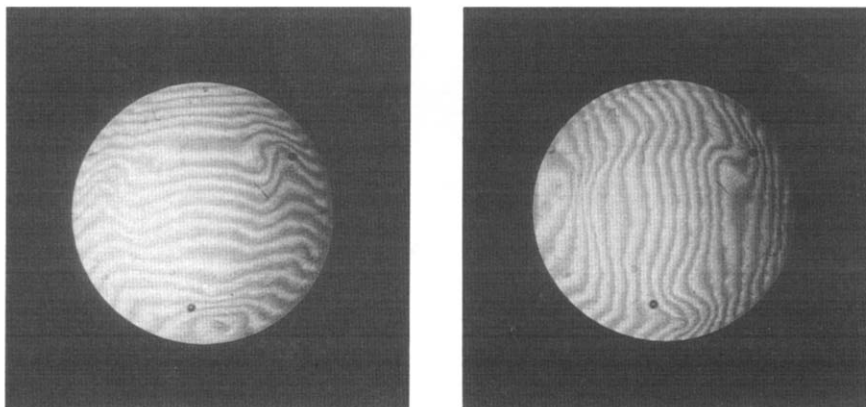


FIG. 5

Interferograms of pure BaLiF₃ crystals grown with 30 rpm in $\langle 111 \rangle$ direction.

c) BaLiF₃: Pb²⁺

The addition of PbF₂ in the melt has already been used as a purification process for the crystal growth of fluorides like CaF₂ and BaF₂ (8) to avoid hydrolysis contamination. The PbF₂ reacts with oxygen impurities in the melt and also shows high vapor pressure at fusion which results in poor incorporation of this impurity in the crystal. To ensure concentration range of 0.1 to 1.0 mole % we used melts with the following compositions: Ba_(1-x)Pb_(x)LiF₃ where $x = 0.05, 0.1$ and 0.2 . We had problems with segregation only for $x = 0.2$. In all growth processes we observed metallic lead formation on the crucible and a thin film deposition on the crystal surface, that disappeared after annealing.

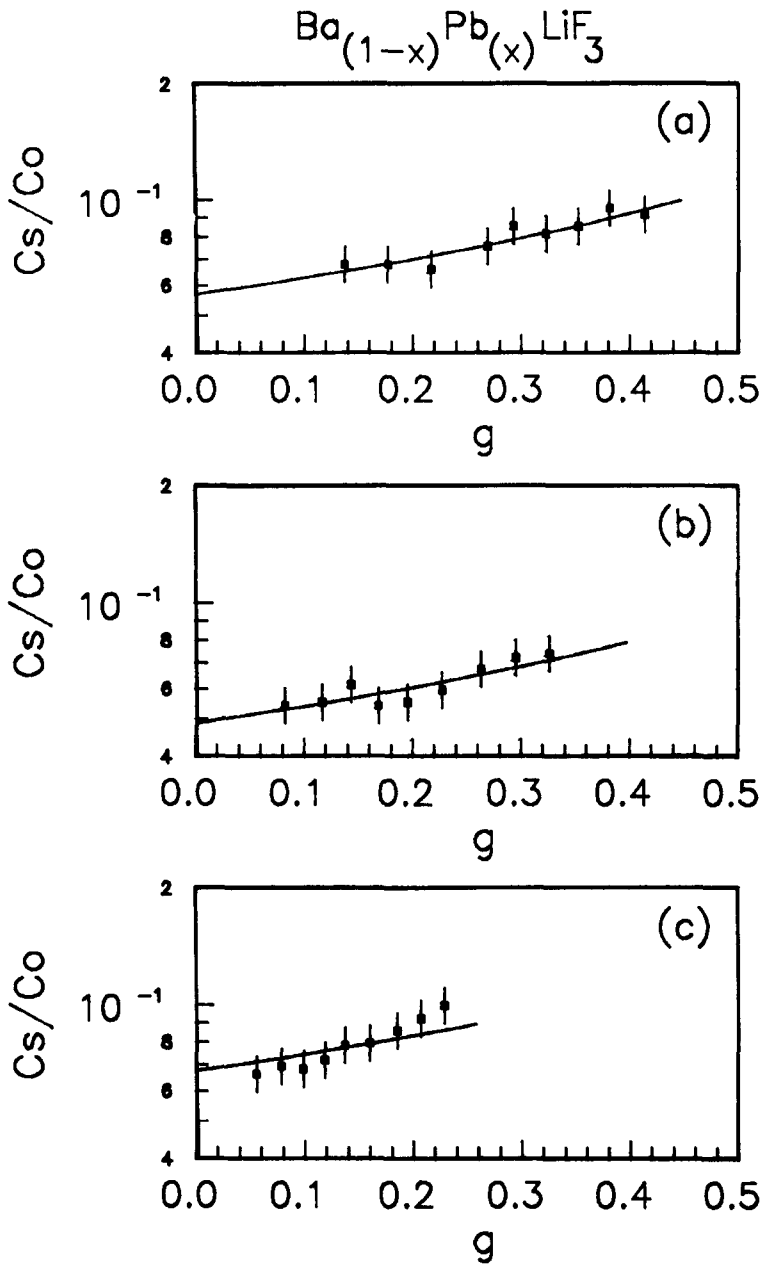


FIG.6

Relative concentration dependence with fraction of solidified mass where: (a) $x = 0.05$; (b) $x = 0.1$; (c) $x = 0.2$. The full curves are the best fits with equation [5].

The distribution coefficient of Pb in BaLiF₃ was determined by X-ray fluorescence analysis. We measured the Pb concentration along the length of 3 crystals grown from different doped melts. The measured concentrations were fitted by normal freezing formula:

$$C_s = k C_0 (1 - g)^k - 1 \quad [5]$$

where C_s and C_0 are the concentrations of impurity in the solid and liquid, k the impurity distribution coefficient (the adjustable parameter), and g the fraction of solidified mass. The results are shown in figure 6. The agreement between experimental and calculated values is rather good for melts with $x = 0.05$ and 0.1 , but the same is not observed for $x = 0.2$. This difference is probably because of the too high concentration of Pb in the melt. For initial melt concentration of 5 mole % the distribution coefficient was estimated as 0.057 ± 0.001 , and for 10 mole % as 0.049 ± 0.001 .

Conclusion

The investigation reported here shows that it's possible to grow pure and Pb doped BaLiF₃ crystals with good optical quality using a pre-purified material and suitable growth conditions to assure almost flat interface which allows relatively stress-free crystals. These properties play an important role concerning BaLiF₃ as a potential laser active host.

The distribution coefficient of Pb in BaLiF₃ was estimated as 0.05, which means that dopant diffusion have a tendency to be away from the growing crystal ($k < 1$) resulting in a small incorporation of Pb in the crystal.

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