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Dehydration and solid solution formation for the $LaBr_3$-$CeBr_3$ binary system

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ABSTRACT

Anhydrous cerium bromide ($CeBr_3$) and cerium doped lanthanum bromide (Ce^{+3}-$LaBr_3$) were obtained by the dehydration of hydrates synthesized by a direct acidification process. The dehydration process involves heating in vacuum through several steps and structure changes until the water is expelled leaving a pure, anhydrous form. Failing to completely remove water during dehydration leads to the formation of oxybromides and the partial reduction of these compounds at high temperatures. It was found that upon the completion of dehydration (< 200 °C) a complete solid solution can be formed between $LaBr_3$ and $CeBr_3$. These two compounds form a simple binary phase diagram. Challenges associated with the dehydration process are discussed.

Keywords: Lanthanum halides, scintillation, dehydration, phase diagram, solid solution

1. INTRODUCTION

Single crystals of cerium bromide[1] ($CeBr_3$) and cerium doped lanthanum bromide[2] (Ce^{+3}-$LaBr_3$) have shown exceptional scintillation properties at room temperature for gamma ray detection. They possess sufficient stopping power, excellent luminous efficiency, good proportionality, high spectral energy resolution at room temperature, and short decay time.[3] Since Ce^{+3} is the luminescence center for the scintillation and an intrinsic constituent of $CeBr_3$, there is a great interest in systematically studying the scintillation properties in the $LaBr_3$-$CeBr_3$ solid solution. In this paper, we investigate the dehydration of a series of lanthanum and cerium bromide hydrates synthesized by a direct acidification process

$$Ln^{o} + (xs)HBr \xrightarrow{neat} \{[Ln(\mu Br)(H_2O)_7][Br]_2\}_2 \qquad (1),$$

where Ln can be either La or Ce. In addition, all the solution synthesis routes, including the direction acidification, metathesis of lanthanum nitride[4], and ammonia metathesis of lanthanum oxide[5], involve the dehydration of intermediate heptahydrates ($LaBr_3$ $7H_2O$) to produce the final anhydrous powder. Therefore, investigation of dehydration will enhance our understanding on the conversion process, which is the main focus of this study.

The thermal dehydration of lanthanide chloride[6-7] and bromide[8] hydrates has been studied in air[6-9] and in a nitrogen[4] atmosphere by various thermal analysis techniques. Wendlandt[6], and Mayer and Zolotov,[8] reported that when these heptahydrates underwent thermal dehydration in air neither lanthanum nor cerium produced the monohydrate ($LnBr_3$ H_2O), and material directly converted to anhydrous halides. Upon heating, these anhydrous materials first changed to oxyhalides and eventually became oxides at high temperature. In addition, Zolotov[8] found that cerium bromide hydrate would directly convert into oxide without the formation of intermediate oxybromide. Thermal calorimetry measurements in a nitrogen atmosphere,[4] however, indicated that the dehydration process actually involved many thermal events (or many intermediate hydrates) as water was progressively removed from the initial heptahydrate. Above 240°C, both lanthanum and cerium hydrates will be completely converted into anhydrous compounds. These observations suggest that the dehydration process is quite complex and might be dependent on the processing conditions. To prevent the formation of oxybromides (LnBrO) or oxides, and to assist the dehydration process, we studied the dehydration process under vacuum conditions. Special attention was placed on the structural evolution during dehydration and the solid solution formation in the $LaBr_3$-$CeBr_3$ binary system. Results will be compared with dehydration processes carried out in air and nitrogen conditions. Challenges associated with the dehydration process will also be discussed.

2. EXPERIMENTAL PROCEDURE

The hydrated lanthanum and cerium bromides,$(La_{1-x}Ce_x)Br_3$, were prepared from the direct acidification process (Equation 1). Lanthanum and cerium were each cut from their stock metals and weighted according to desired composition before dissolving in excess hydrobromic acid in an argon filled, dry glove box. After the metal was completely dissolved, the clear solution was transferred into a flask for vacuum evaporation. Evaporation was performed on a hot water bath (~ 100 °C) for several hours until solution had been removed to dryness. A small amount of the as-dried powder was characterized by simultaneous thermal gravitational (TGA) and scanning thermal calorimetry (DSC) measurements (NETSCH STA449C) to determine its dehydration behavior, melting and freezing points. The rest of the powder was dried in a hot oil bath (~180 °C) under vacuum for several hours. Dry powder was transferred back to the glove box and was ground in an alumina mortar and pestle, and forced through a 125 µm nylon mesh sieve. The ground powder was dried again on the hot oil bath under vacuum for additional 4 to 6 hours. Powder was then sent for X-ray diffraction analysis to confirm the formation of anhydrous material.

The dehydration behavior was studied under vacuum in the STA to be consistent with the drying procedure used for powder preparation. Hydrated powder of ~20 mg was placed in an alumina crucible covered with a lid. An alumina crucible was used as previous results indicated that lanthanide bromide would not react with alumina up to its melting point. The powder was heated from room temperature to 200°C under vacuum at 1°C/min and held at 200°C for 20 minutes. Thermal events and weight loss were recorded during the dehydration process. After the holding period, the vacuum was turned off and the atmosphere switched to a flowing argon condition. The powder was subsequently heated to 810°C at 3°C/min. The sample was held for 5 minutes, and then cooled back to room temperature at 3°C/min. During this thermal incursion, both melting point and freezing point for the $(La_{1-x}Ce_x)Br_3$ solid solution were determined at the peak temperature of the endothermic and the exothermic events from the DSC measurements.

$(La_{1-x}Ce_x)Br_3$ powders were prepared for X-ray diffraction (XRD) analysis using a specially designed holder for air-sensitive materials. The holder employed a "Beryllium Dome" (BeD) to allow access of the X-ray beam to the specimen. For rigorous exclusion of air, the specimen was prepared inside a glove box. Powder was placed on a zero-background slide (1cm dia.), loaded into the BeD holder, and sealed via a compression o-ring so as to preserve the atmospheric conditions of the glove box. The holder was removed from the glove box and directly transported to the Siemens D500 XRD unit for analysis. The XRD unit employed a sealed-tube Cu anode X-ray source (40 kV, 30 mA), a diffracted-beam graphite monochromator, and fixed (1^o) slits. Typical scan conditions were $5\text{-}80^o$ 2θ, 0.04^o 2θ step-size, and 1 sec count-time. Scan conditions used for structural analysis were $20\text{-}120^o$ 2θ, 0.04^o 2θ step-size, and 20 sec count-time. Results of the thermal analysis and X-ray diffraction measurements were confirmed with four compositions in the $(La_{1-x}Ce_x)Br_3$ solid solution.

3. RESULTS

3.1 Dehydration under vacuum

The general behavior of thermal dehydration characterized by the thermal analysis for all compositions in the $(La_{1-x}Ce_x)Br_3$ solid solution is quite similar. Figure 1 shows the dehydration of the hydrated $La_{0.9}Ce_{0.1}Br_3$ under vacuum with a heating rate of 1°C/min. The DSC (dotted line in Figure 1) and TGA (solid line) measurements detected three major endothermic events (at 32.7°C, 70.8°C, and 111.9°C). These events indicate that several intermediate hydrates are formed during dehydration. Since all these powders were previously dried in a hot water bath before thermal analysis, it is difficult to determine the initial composition of these hydrates. Based on weight loss measurements, horizontal weight levels between the second and the third endothermic events (-4.20% compared to the theoretical value of -4.76%), and the first and the third endothermic events (-11.47%, compared to the theoretical value of -14.27%) correspond to the formation of a monohydrate and a trihydrate ($LnBr_3$ $3H_2O$), respectively. Sometimes, additional small endothermic events can be observed, and are similar to the experimental results collected under a flowing nitrogen condition.[4] These small endothermic peaks are either overlapped or isolated (especially from dihydrate to monohydrate) between these three major endothermic events. However, the weight loss during these events is almost continuous; suggesting the kinetics of dehydration is dominant since the activation energy for these dehydration steps is small (as shown by small endothermic peaks). This argument is supported by the evidence that when a fast heating rate[6,8] (> 5°C/min) is used during dehydration, only one horizontal level of weight loss is detected, which corresponds to the decomposition of $LaCl_3$ $7H_2O$ to $LaCl_3$. These observations highlight the importance of the kinetic factor in characterization of the dehydration process. In addition, results show that the weight loss during dehydration of the hydrated lanthanum bromide is similar to that of lanthanum chloride.[7]

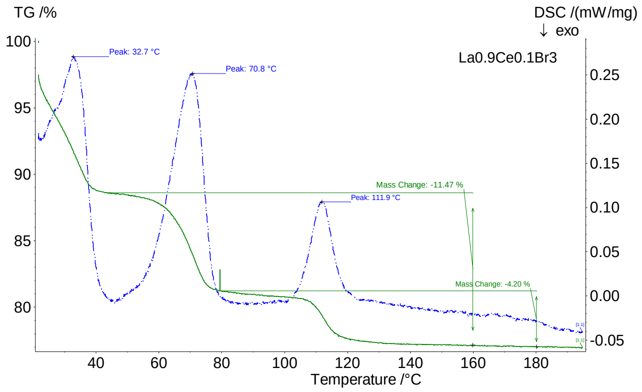


Fig. 1. The thermal dehydration behavior of hydrated lanthanum/cerium bromide in vacuum. The solid line represents the thermal gravitational analysis and the dotted line shows the thermal calorimetry measurement.

The dehydration temperatures for the decomposition of $LnBr_33H_2O$ and $LnBr_3H_2O$ in the $(La_{1-x}Ce_x)Br_3$ solid solution series are given in Figure 2, as determined by the endothermic peak temperature at which the rate of dehydration is greatest. Data indicate that the final dehydration temperature from the monohydrate to anhydrous powder in this binary system is below 145°C. Furthermore, the dehydration temperatures for $CeBr_3$ are greater than $LaBr_3$, which is consistent with dehydration behavior in a nitrogen atmosphere.[4] However, the final dehydration temperature measured under a vacuum condition (105 - 145°C) is much lower than that measured in air (210 -240 °C) and in nitrogen (180 -220°C), indicating the application of vacuum will assist the dehydration process.

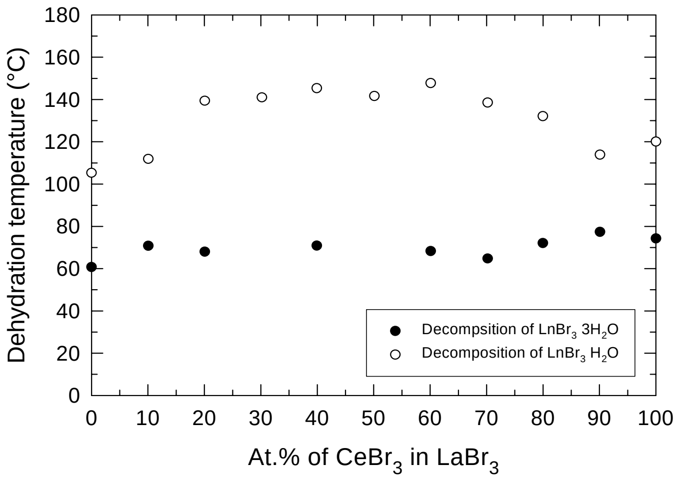


Fig. 2. The thermal dehydration temperatures for the $(La_{1-x}Ce_x)Br_3$ solid solution. The solid and the open circles represent the decomposition temperatures for $LnBr_33H_2O$ and $LnBr_3H_2O$, respectively.

3.2 Structure and morphology evolution during dehydration

Figure 3 is a scanning electron microscopy image of lanthanum bromide hydrate after the initial dehydration in a hot water bath from the direct acidification process (Equation 1). The image shows that during vacuum dehydration, the initial heptahydrate will dry and turn into agglomerated powder. This process happens at a temperature slightly below 100°C. If the powder agglomerate is crushed, partially dehydrated lanthanum heptahydrate bromide crystals can be observed inside of the powder agglomerate with well defined facets (see insert in Figure 3). Therefore, the dehydration process starts from the outside and gradually turns hydrate into powder as water is removed from the surface. At this temperature range (~ 100° C), the dehydrated powder should have less bound water than the trihydrate form, based on data presented in Figure 2.

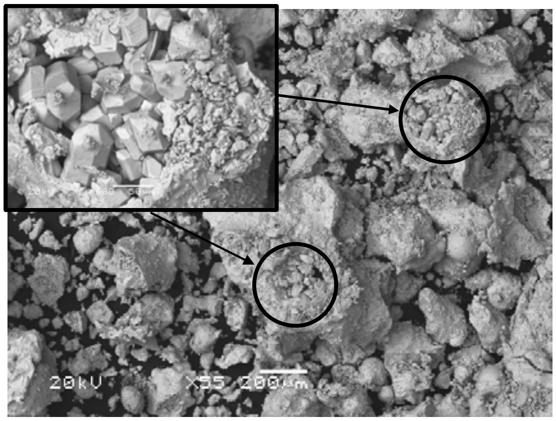


Fig. 3. SEM microphotograph of partially dehydrated lanthanum bromide heptahydrate. Insert shows a cluster of partially dehydrated $LaBr_37H_2O$ crystals.

To understand the structural evolution of the dehydration process, an *in situ* variable temperature *en vacuo* powder X-ray diffraction experiment was performed. In this process hydrated powder was placed on silicon (100) substrates and inserted into a vacuum (10^{-5} Torr) chamber for X-ray diffraction analysis. The sample was heated and diffraction pattern was collected at select temperatures. This was done for $\{[(H_2O)_7Ln(\mu\text{-}Br)]_2[Br]_4\}$ Ln = La and Ce. X-ray patterns reveal that the sample transverses through three separate phases: (A) hydrate, (B) amorphous (after the decomposition of trihydrate, based on TGA data in Figure 2), and (C) anhydrous $LnBr_3$, as temperature increases. The structure evolution during dehydration for cerium bromide hydrate is given in Figure 4. Because the transition temperatures between crystalline and amorphous phases determined by the X-ray diffraction are

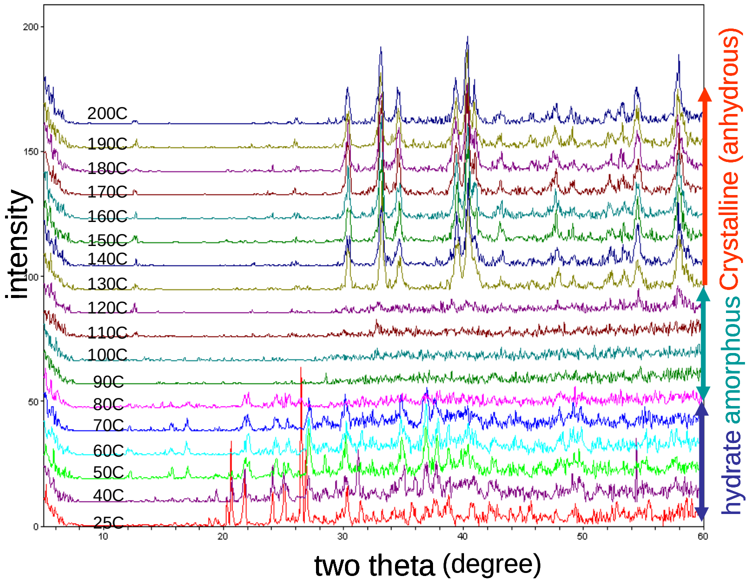
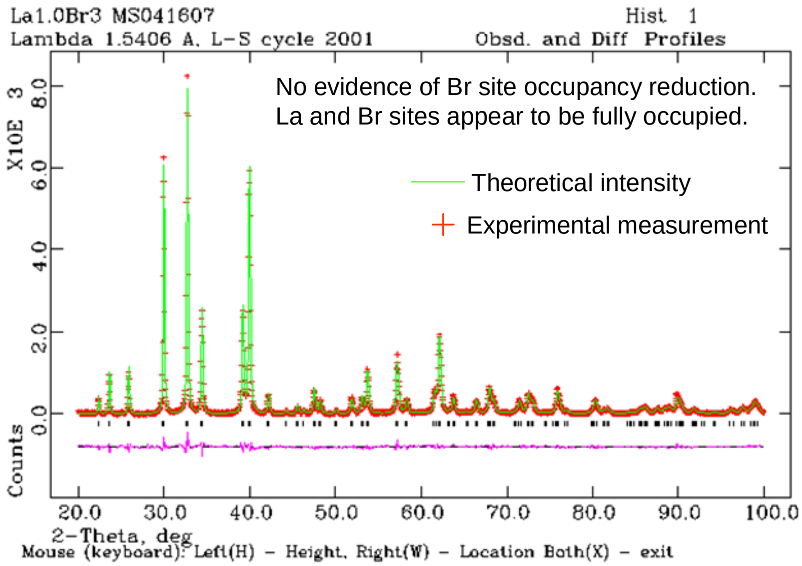


Fig. 4. *En vacuo* powder X-ray diffraction patterns illustrate the phase evolution during dehydration of cerium heptahydrate bromide.

consistent with the STA measurements (see Figure 1), one can correlate the structural evolution during the dehydration. The correlation shows that crystalline hydrates (including heptahydrates and trihydrates) become amorphous after the decomposition of trihydrates as this unique set of diffraction patterns disappears. When the temperature is continually heated above 120 °C and the last bound water expelled from the amorphous monohydrate, the sample finally transforms back to a crystalline, anhydrous cerium bromide powder, as indicated by the diffraction pattern. Therefore, the conversion from initial hydrate to final anhydrous compound involves reconstructive phase transformations (as compared to a displacive phase change such as a martensitic transformation). Furthermore, the presence of amorphous hydrates during dehydration has not been reported in the literature. X-ray diffraction results also indicate that a complete solid solution between $LaBr_3$ and $CeBr_3$ will form after vacuum dehydration at temperatures below 200°C. The formation of a complete solid solution at such a low temperature is quite extraordinary.

After the powder has been dried twice under vacuum at temperatures > 180°C for more than 6 hours, X-ray diffraction patterns were collected to examine the phase purity and to evaluate the possibility of bromine loss during dehydration. The diffraction pattern of a dehydrated lanthanum bromide and its calculated theoretical intensity are given in Figure 5. Results show that a proper dehydration can produce a phase pure lanthanum bromide. In addition, the consistency in the measured and the calculated diffraction intensities for the anhydrous powder suggest that both lanthanide (La or Ce) and bromine sites are fully occupied after dehydration. Therefore, the anhydrous $LaBr_3$ powder produced from direct acidification process is on its stoichiometry and no bromine is lost during the dehydration process.



No evidence of Br site occupancy reduction.
La and Br sites appear to be fully occupied.

Fig. 5. The measured (red cross) and calculated (line) X-ray intensities for anhydrous lanthanum bromide powder.

3.3 $LaBr_3$-$CeBr_3$ binary phase diagram

The melting and freezing points for each composition in the $(La_{1-x}Ce_x)Br_3$ solid solution series were determined by the DSC measurement under a flowing argon condition after dehydration. Results are illustrated in Figure 6. The melting points, as determined at the peak temperature from the DSC curve, for $LaBr_3$ and $CeBr_3$ are 773 °C and 722 °C, respectively. A small anomaly on the melting and freezing curves for $La_{0.9}Ce_{0.1}Br_3$ in Figure 6 was confirmed by a repeated experiment. Data indicate that both the melting and freezing points progressively decrease as the amount of Ce increased in the $(La_{1-x}Ce_x)Br_3$ solid solution.

X-ray analysis indicates that cerium bromide has an identical crystal structure to lanthanum bromide i.e, a hexagonal structure (space group $P6_3/m$ (No. 176)) with the a/c ratio greater than 1.77. The lattice parameters and unit cell volume in the $(La_{1-x}Ce_x)Br_3$ solid solution series were measured. Figure 7 depicts the change of unit cell volume as a function of increasing $CeBr_3$ in the solid solution. A good linear correlation between unit cell volume (or c axis) and $CeBr_3$ composition can be established. From the melting behavior and structural change, it can be concluded that $LaBr_3$ and $CeBr_3$ can form a simple binary system. This is not a surprise since both compounds have the same crystal structure and the ionic size difference between these trivalent cations is small; therefore, a complete solid solution can be readily formed.

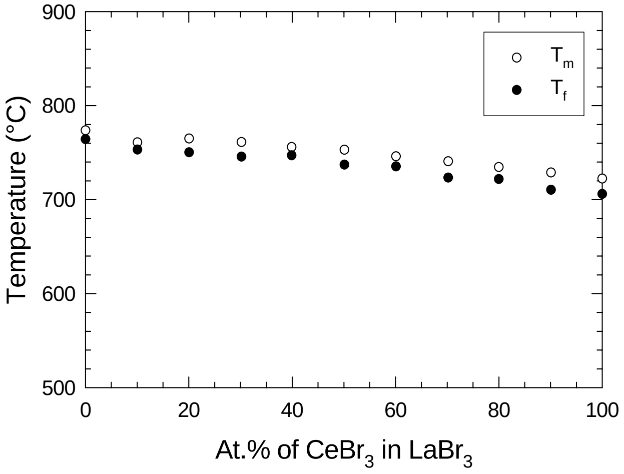


Fig. 6. The phase diagram for the $LaBr_3$-$CeBr_3$ binary system. The open circle and close circle are representing the melting and freezing points, respectively.

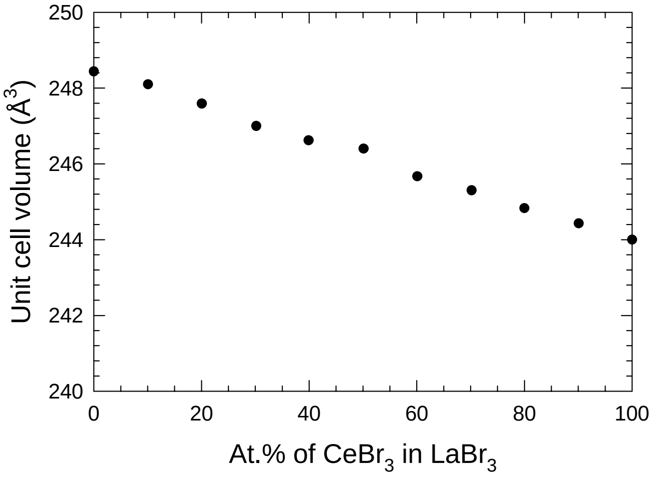


Fig. 7. The change of unit cell volume as a function of Ce in the $(La_{1-x}Ce_x)Br_3$ solid solution.

4. DISCUSSION

This work has demonstrated that small batches of lanthanide bromide hydrates prepared by chemical synthesis can be properly dehydrated under vacuum conditions. However, difficulties have been experienced with the dehydration of large quantities of hydrates. This is particularly true when the powder batch is greater than 10 grams. Part of the challenge comes from the effectiveness of heat transfer in a vacuum reactor. Another part can be attributed to a large enthalpy requirement associated with the dehydration process (see Figure 1 for tri- and monohydrates). Due to the lack of convection heat-flow in the vacuum reactor, heat has to transfer through loosely packed powder from a hot surface, which can significantly reduce its effectiveness for the thermal dehydration of a large quantity of powder. This can lead to a partial dehydration, as the powder near the hot surface has reached its dehydration temperature and decomposes, while away from the hot surface dehydration is impeded since there is insufficient energy. A good example is illustrated in Figure 3 where hydrate near the surface of agglomerates has turned into powder and partially dehydrated crystal clusters are preserved inside. Literature[10] has shown that a non-static vacuum approach seems to be effective in addressing this issue. Another part of the challenge is the amorphous nature of the dihydrate and monohydrate which is difficult to detect by the X-ray diffraction. If a trace amount of dihydrate or monohydrate is not completely removed, even an X-ray determined phase pure lanthanide bromide can turn into oxybromide (white color) when powder is heated above 400°C in a flowing argon condition, according to the following reaction

$$LnBr_3H_2O \text{ (monohydrate)} \rightarrow LnBr_3 + H_2O \text{ (vap.)} \rightarrow LnBrO + 2\ HBr \qquad (2).$$

If a large quantity of these hydrates exist in the powder, X-ray analysis shows that a significant amount of LnBrO phase and possibly a trace phase of Ce_2Br_5 (black particles with copper colored metallic luster) will be produced, and powder will turn gray or black after thermal treatment. Note that the formation of oxybromide does not come from a direct oxidation as material fired in air,[6-9] but from the reaction of anhydrous lanthanide bromide with water vapor at higher temperatures in an inert atmosphere. Thermal analysis shows that such a reaction takes place above 400°C. Since all the lanthanide bromides are extremely hygroscopic, a brief exposure to the ambient atmosphere can absorb a significant amount of moisture from the air on the powder surface. This will cause the formation of oxybromide or the partial reduction[11] of these compounds in a subsequent high temperature operation for single crystal growth or densification. The formation of these phases has been known to mar their scintillation properties. Therefore, a carefully controlled dehydration process is paramount in synthesizing high performance scintillation materials.

5. SUMMARY

The dehydration process for chemically prepared lanthanum and cerium bromide hydrates was studied under vacuum. Results show that thermal dehydration occurs at lower temperatures than those processed in air or in nitrogen atmosphere and the solid solution for $LaBr_3$ and $CeBr_3$ can be readily formed at temperature below 200°C. The dehydration involves a reconstructive crystalline-amorphous-crystalline phase change as bound water is progressively removed from its hydrate. Results show that these anhydrous compounds form a simple $LaBr_3$- $CeBr_3$ binary phase diagram, as determined by the thermal analysis. When the last monohydrate is not completely removed during dehydration processes, it can lead to the formation of oxybromide and Ln_2Br_5 which has a significant impact on its scintillation performance.

6. ACKNOWLEDGEMENT

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REFERENCES

1. K. S. Shah, J. Glodo, W. Higgins, E. V. D. van Loef, W. W. Moses, "$CeBr_3$ scintillators for Gamma-ray spectroscopy," *IEEE Trans. Nucl. Sci.* 52(2), 3157-3159 (2005).
2. E. V. D. van Loef, P. Dorenbos, C. W. E. van Eijk, K. Krämer and H. U. Güdel, "High-energy-resolution scintillator: Ce^{+3} activated $LaBr_3$," *Appl. Phys. Lett.* 79(10), 1573-1575 (2001).
3. W. W. Moses, "Current trends in scintillator detectors and materials," *Nucl. Instr. and Meth.* A487, 123-128 (2002).
4. S. J. Ashcroft and C. T. Mortimer, "The thermal decomposition of lanthanide (III) chloride hydrates," *J. Less-Common Metals* 14, 403-406 (1968).
5. G. Meyer, S. Dötsch, and T. Staffel, "The ammonium-bromide route to anhydrous rare earth bromides MBr_3," *J. Less Common Metals* 127, 155-160 (1987).
6. W. W. Wendlandt, "Thermal decomposition of yttrium, scandium, and some rare-earth chloride hydrates," *J. Inorg. Nucl. Chem.* 5, 118-122 (1957).

7. J. E. Powell and H. R. Burkholder, “The solubilities of lanthanum chloride 7-hydrate and lanthanum chloride 6-hydrate in water, and a study of the thermal decomposition of hydrated lanthanum chloride,” *J. inorg. Nucl. Chem.* 14, 65-70 (1960).
8. I. Mayer and S. Zolotov, “The thermal decomposition of rare earth and yttrium bromide hydrates,” *J. Inorg. Nucl. Chem.*, 27, 1905-1909 (1965).
9. G. Haeseler and F. MatthesA. Eisenberg, “ Über den thermischen abbau der chloridhydrate der elemente der seltenen erden,“ *J. Less-Common Metals* 9(2), 133-252 (1965).
10. D. Brown, S. Fletcher, and D. G. Holah, “The preparation and crystallographic properties of certain lanthanide and actinide tribromides and tribromide hexahydrates,” *J. Chem. Soc.* (A), 1889-1894 (1968).
11. K. Krämer, T. Schleid, M. Schulze, W. Urland, and G. Mayer, „Three bromides of lanthanum: $LaBr_2$, La_2Br_5, and $LaBr_3$,” *Z. Anorg. Allg. Chem.* 575, 61-70 (1989).