Materials Science and Engineering B 129 (2006) 256–260

MATERIALS SCIENCE & ENGINEERING B

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Synthesis, powder XRD studies on LiF-BaF$_2$/EuF$_3$ systems and thermo-stimulated luminescence (TSL) of Eu^{3+} doped LiBaF$_3$

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Received 21 November 2005; accepted 8 February 2006

Abstract

In this paper, the phase equilibria of LiF-BaF$_2$ and LiF-EuF$_3$ systems under short-annealed and slow-cooled conditions have been explained. In these two systems, LiBaF$_3$ and LiEuF$_4$ exist as the line compounds in the respective systems under the present experimental conditions. The thermally stimulated luminescence (TSL) properties of EuF$_3$ doped LiBaF$_3$ compositions are investigated after irradiation with γ-ray. A typical glow peak at 390 K is observed in these samples, intensity of which increases up to 0.5 mol% of Eu^{3+} doping and then decreases due to concentration quenching. An intense glow peak at 540 K observed only in 1.0 mol% doped sample. Spectral studies of the TSL glows confirm Eu^{3+} ions as the luminescent centers.

Keywords: Fluorides; Phase equilibria; Thermally stimulated luminescence

1. Introduction

Crystalline fluorides are considered as technologically important materials owing to their interesting electrical and optical properties. Because of high electronegativity, small size and low polarizability of fluoride ion, crystalline fluorides are highly electronic insulating materials but at the same time, they exhibit enhanced ionic conductivity. Due to the higher electronegativity and low polarizability of the fluoride ions, most of the fluorides are highly ionic and have very large band gap, weak phonon loss and hence, they find application in various optical devices, viz., windows, clad to wave guides, laser crystals, up- and down-conversion materials, scintillators, phosphors, etc. Hence, the quest of new crystalline materials in the mixed fluoride systems is a strong motivation for the researchers. Thus, the study of phase relations of the starting fluorides under different heating and cooling protocols are being carried out. There are several reports [1–3] on the study of phase equilibria among metal fluorides, which led to the discovery of many new compounds. Greis [4] had studied the crystal chemistry of mixed fluorides systems, either with MF$_2$-M$'$F$_3$ system, where M is either alkaline-earth metal or divalent rare-earth metal cation and M$'$ is trivalent rare-earth ion, under the long-annealed condition. Initially the defect aggregation leading to short range ordering is formed in these mixed systems, which finally leads to the formation of various distinctly ordered phases in mixed fluorides. The defect ordering has been shown [5] to depend strongly on the temperature and annealing conditions. Greis and Haschke [2] had summarized the experimental results available in the mixed fluoride systems, and concluded that the preparation and annealing conditions significantly govern the structure of mixed fluoride systems. In this review, the authors emphasized the growing need for generating more data on the phase equilibria at lower temperature regime. It is known that the fluorides have lower melting points than the corresponding oxides, which render their physical homogenization very fast compared to that in oxides. In order to investigate the crystal chemistry of the mixed fluorides under short-annealed and slow-cooled conditions, we have investigated phase equilibria in several mixed fluoride systems [6,7] with alkaline-earth fluoride or PbF$_2$. In the present report we have explained the phase relation with alkali-metal fluoride as one component.

The alkali fluorides (MF, where M is alkali metal) crystallize in the rock salt (NaCl) structure, in which the metal ions as well as the fluoride ions exist in the octahedral coordination with fluoride and metal ions, respectively. The alkali-metal halides and

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doi:10.1016/j.mseb.2006.02.042

alkaline-earth metal halides form double salts, namely ABF_3 (perovskite or distorted perovskite). Several double fluorides of alkali-halide and rare-earth fluorides are synthesized and characterized [1,8,9]. Literature survey on LiF-BaF_2 system revealed the existence of only one mixed fluoride, i.e., $LiBaF_3$, which has been explained as an example of ideal perovskite [10]. The rare-earth fluoride and the alkali-metal fluoride systems can have several binary compounds, namely scheelite, gagarinite, fluorite or fluorite derived structure type compounds [11–13].

Later $LiBaF_3$ crystal drew a significant interest for its application for γ-ray or X-ray registration [14]. Recently the oxygen and Mg^{2+} doped crystals of $LiBaF_3$ have also been shown to have possibility for the application in TSL dosimetry [15]. Moreover, Ce^{3+} and Eu^{2+} doped $LiBaF_3$ have been investigated in detail [16,17] in view of their potential applications as scintillators. In fact, Eu^{2+} doped $LiBaF_3$ has been reported to be a promising X-ray storage phosphor on the basis of ESR, TSL and PSL studies [18]. Such prospects of this material created interest to reinvestigate the LiF-BaF_2 phase relations. In this paper the phase relation studies on LiF-BaF_2 and LiF-EuF_3 systems are being reported. The phase analyses of the two binary systems have been explained in the following sections. In addition thermally stimulated luminescence (TSL) of $LiBaF_3$ doped with EuF_3 has been studied, which may have potential as radiation dosimeter.

2. Experimental

The LiF sample (Riedel de Haen) was dried at 400 °C in flowing argon atmosphere before use. Some typical compositions with different mol% of LiF and BaF_2 or EuF_3 were prepared in each system. Pellets of homogeneous mixture of the reactants were prepared in air and then they were heated to 250 °C at a rate of 5 °C/min and held for 3 h for degassing. Further the temperature was raised at the same rate to 750 °C and held for another 3 h for reaction and then cooled back to room temperature at a rate of 5 °C/min. All the heat treatments were carried out in platinum boat under flowing argon atmosphere. In LiF-EuF_3 system, the samples were prepared by heating the appropriate amounts of LiF and EuF_3 at 650 °C for 4 h. The products obtained were characterized by powder XRD for the phase analysis. A series of EuF_3 doped compositions, namely with 0.1, 0.5, 1.0 and 2.0 mol% of EuF_3 in $LiBaF_3$, were prepared by heating LiF, BaF_2 and EuF_3 in an argon filled sealed tube.

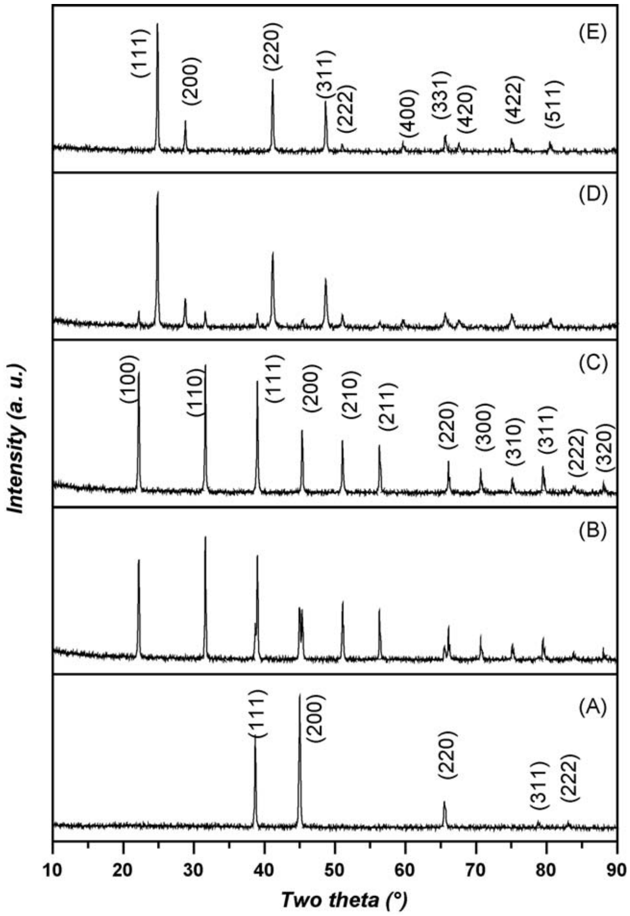

Fig. 1. Typical powder XRD pattern of the nominal compositions $Li_{1.00}Ba_{0.00}F_{1.00}$ (A), $Li_{0.80}Ba_{0.20}F_{1.40}$ (B), $Li_{0.50}Ba_{0.50}F_{1.50}$ (C), $Li_{0.20}Ba_{0.80}F_{1.80}$ (D) and $Li_{0.00}Ba_{1.00}F_{2.00}$ (E).

3. Results and discussion

3.1. Phase relations LiF-BaF_2 and LiF-EuF_3 systems

The powder XRD pattern of the selected compositions in LiF-BaF_2 and LiF-EuF_3 systems are shown in Figs. 1 and 2, respectively. The details of the compositions and their phase analyses are given in Table 1. It was found that only $Li_{0.5}Ba_{0.5}F_{1.50}$ composition exists as a single-phase compound in this system in LiF-BaF_2 system. A comparison of the XRD patterns of these phases (Fig. 1) indicates that all other compositions exist as mixture of LiF and $LiBaF_3$ or $LiBaF_3$ and BaF_2. The single phasic composition was prepared from stoichiometric

Table 1
Typical starting nominal compositions and their product analysis by XRD

Nominal compositions in LiF-BaF_2 system	Phases present	Nominal compositions in LiF-EuF_3 system	Phases present
100% LiF + 0% BaF_2	LiF	100% LiF + 0% EuF_3	LiF
80% LiF + 20% BaF_2	LiF + $LiBaF_3$	75% LiF + 25% EuF_3	LiF + $LiEuF_4$
60% LiF + 40% BaF_2	LiF + $LiBaF_3$		
50% LiF + 50% BaF_2	$LiBaF_3$	50% LiF + 50% EuF_3	$LiEuF_4$
20% LiF + 80% BaF_2	$LiBaF_3$ + BaF_2	25% LiF + 75% EuF_3	$LiEuF_4$ + EuF_3
0% LiF + 100% BaF_2	BaF_2	0% LiF + 100% EuF_3	EuF_3