Thin Films and Coatings

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A study of structural evolution of alkaline earth fluorides from amorphous to polycrystalline phase by in-situ TEM

X. Mu[1], A. Bach[2], W. Sigle[1], D. Fischer[2], M. Jansen[2], P.A. van Aken[1]

[1]Max Planck Institute for Intelligent Systems, Stuttgart Center for Electron Microscopy (StEM), Stuttgart, Germany
[2]Max Planck Institute for Solid State Research, Inorganic Solid State Chemistry, Stuttgart, Germany

xiaoke.mu@is.mpg.de
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New metastable modifications, their existence and the development of new ways for their synthesis have been an important subject of solid state science in both theoretical and experimental studies. One such synthesis method is the so-called low-temperature atom beam deposition (LT-ABD) [1] that has been successfully applied to the synthesis of new halides [2], alloys [3], and nitrides [4]. Deposition onto a cooled substrate leads to amorphous thin films. During annealing the formation of metastable and stable crystalline phases can be studied. The study of these processes enhances the understanding of the kinetic processes of the phase evolution as well as of the energy landscape [5]. One recent success of the LT-ABD method is the discovery of a new polymorph of magnesium difluoride (MgF_2) [6]. In addition to MgF_2, the behavior of the structure evolution of other alkaline earth fluoride compounds and their mixtures are of interest, in particular because of the role of the cationic radius.

The pair distribution function (PDF) as an effective means to characterize amorphous and nanocrystalline materials is already routinely used in neutron and X-ray diffraction. It represents the atomic density distribution oscillating around the average atomic density in the material investigated. Similarly, methods to obtain the PDF by electron diffraction, especially in combination with electron energy filtering to eliminate inelastic scattering contributions, have been widely studied [7].

In this work we applied the LT-ABD technique combined with in-situ transmission electron microscopy to investigate the phase evolution of mixtures of CaF_2/BaF_2, and of MgF_2/BaF_2 from the low-temperature amorphous phase to crystalline phases. The results are compared with pure alkaline earth fluorides. The PDF analyses are the key method to characterize the initial amorphous phase and the structural distortions in the crystalline phases. Each material was directly deposited on a carbon support cooled to -150 °C, and afterwards transferred under vacuum and cooling to the TEM. Subsequently measurements were performed during the heating process up to 1000 °C.

Differing from the pure binary fluorides (CaF_2, SrF_2, BaF_2), we observed diverse structure evolutions in the quasi-binary mixtures due to addition of a second cation. The electron diffraction results show that the crystallization of an amorphous $(Mg_{0.3}Ba_{0.7})F_2$ sample starts at 320 °C and forms first crystalline BaF_2. Further at 450 °C, the ternary compound $MgBaF_4$ crystallizes, which correlates with the thermodynamic stable phases of the phase diagram. [8]. The situation is completely different for $(Ca_{0.5}Ba_{0.5})F_2$, where the amorphous sample firstly crystallized into a solid solution phase at 370 °C (fluorite-type), which decomposes at 480 °C into the pure phase CaF_2/BaF_2. Thus, compared to earlier studies [9] we are also able to stabilizes the metastable solid solution of $(Ca_{0.5}Ba_{0.5})F_2$ by our experiments. Corresponding PDFs were calculated from the diffraction data. This study reveals the phase evolutions of the investigated materials, by which the parameter field was experimentally explored.

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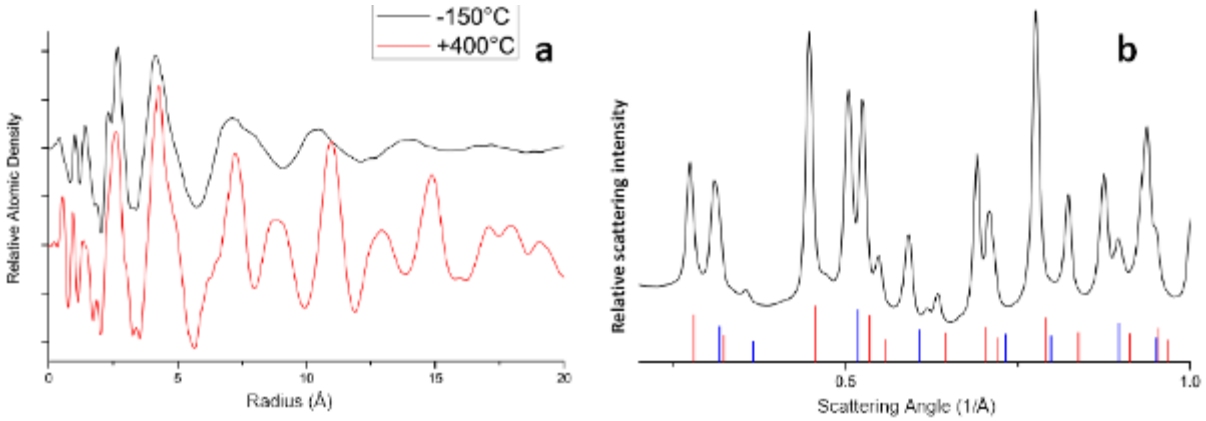

Figure. 1. Structure evolution of $(Ca_{0.5}Ba_{0.5})F_2$, (a) PDFs for the amorphous phase at -150°C (top, black) and the cubic-structure solid solution phase at +400°C (bottom, red). (b) Normalised structure factor of the phase-separated phase at +600°C (black); the sticks at the bottom represent calculated diffraction peaks (BaF_2: red, CaF_2: blue).

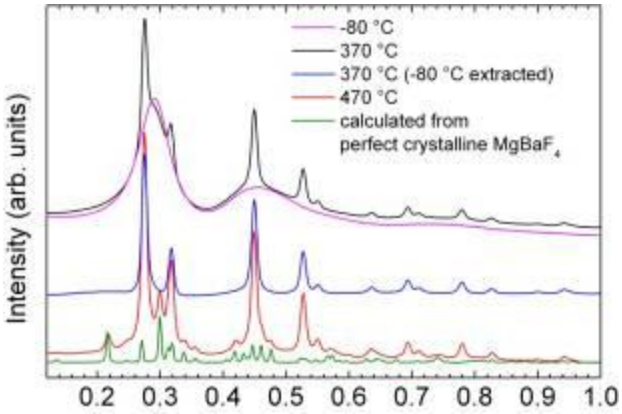

Figure 2. Experimentally measured electron diffraction patterns of the $(Mg_{0.3}Ba_{0.7})F_2$ film recorded at -80 °C (pink), 370 °C (black), and 470 °C (red) as well as the profile (blue) obtained by subtracting the -80 °C profile from the 370 °C profile and the diffraction profile calculated from database of the crystalline $MgBaF_4$ [10] (green).

	Amorphous phase	**Intermediate phase (metastable)**	**Stable phase**
$(Mg_{0.3}Ba_{0.7})F_2$	< 320 °C	320 – 450 °C amorphous + BaF_2 (fluorite-type)	> 450 °C $MgBaF_4$ + BaF_2 (fluorite-type)
$(Ca_{0.5}Ba_{0.5})F_2$	< 370 °C	370 – 480 °C solid solution $Ca_{0.5}Ba_{0.5}F_2$ (fluorite-type)	> 480 °C phase separated BaF_2 + CaF_2 (fluorite-type)
CaF_2	< 0 °C	None	> 0 °C Fluorite-type
SrF_2	< 0 °C	None	> 0 °C Fluorite-type
BaF_2	< 0 °C	None	> 0 °C Fluorite-type
MgF_2 [11]	< 185 °C	185 – 380 °C $CaCl_2$-type	> 380 °C rutile-type

Table 1. Summary of the structure evolution of the investigated alkaline earth fluorides (TEM results)