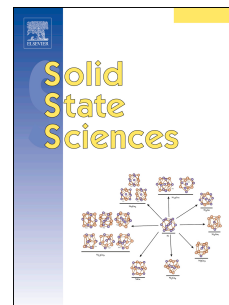


# Accepted Manuscript

Thermal stability of  $Ba_{1-x}Ca_xF_2$  solid solutions

Andre Düvel, Paul Heitjans, Pavel P. Fedorov, Valerii V. Voronov, Aleksandr A. Pynenkov, Konstantin N. Nishchev



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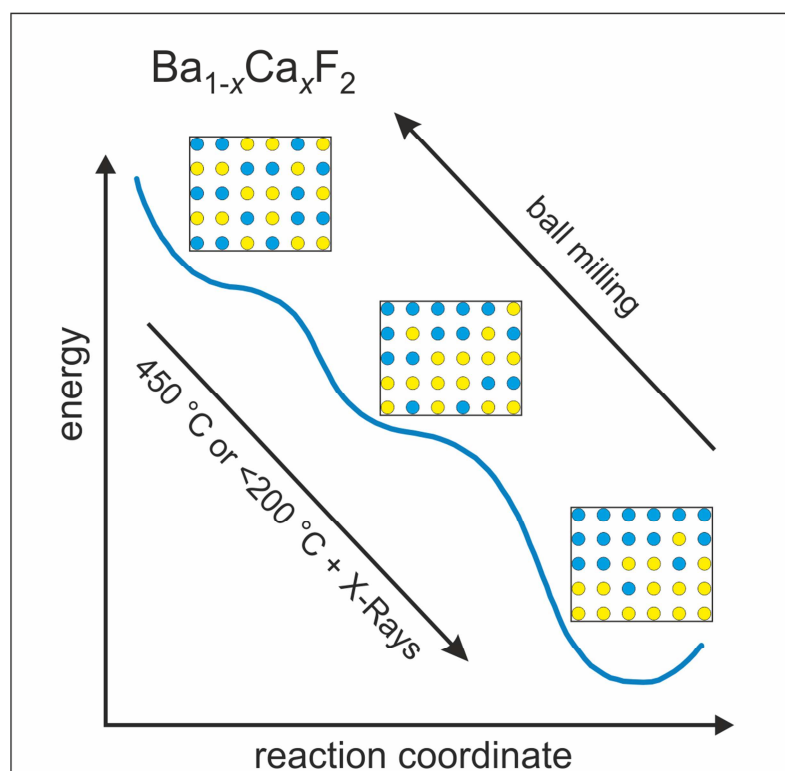
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Andre Düvel<sup>1,2</sup>, Paul Heitjans<sup>2</sup>, Pavel P. Fedorov<sup>3,4</sup>, Valerii V. Voronov<sup>3</sup>,

Aleksandr A. Pynenkov<sup>4</sup>, Konstantin N. Nishchev<sup>4</sup>

<sup>1</sup>*School of Physical Sciences, University of Kent, Canterbury, Kent CT2 7NH, UK, a.duvel@kent.ac.uk*

<sup>2</sup>*Institute of Physical Chemistry and Electrochemistry, Leibniz Universität Hannover, Callinstr. 3-3a, 30167 Hannover, Germany, heitjans@pci.uni-hannover.de*

<sup>3</sup>*General Physics Institut RAS, Moscow, Vavilov str.38, 119991 Russia, ppfedorov@yandex.ru, voronov@lst.gpi.ru*

<sup>4</sup>*Mordovia State University, Saransk, 430005 Russia, alekspyn@yandex.ru, nishchev@inbox.ru*

*Corresponding authors e-mail: ppfedorov@yandex.ru, a.duvel@kent.ac.uk*

*Ba<sub>1-x</sub>Ca<sub>x</sub>F<sub>2</sub> samples with fluorite-type structure were prepared by high-energy ball milling. DSC measurements revealed exothermic decomposition at temperatures of about 450 °C. Decomposition was also observed by high temperature X-ray experiments. As a product, two phases with compositions close to pure BaF<sub>2</sub> and CaF<sub>2</sub> were obtained. The decomposition temperature observed by X-ray measurements is lower than in the DSC experiments. This might indicate that X-ray irradiation could foster the decomposition.*

**Keywords:** High-energy ball milling, DSC, thermal phase stability, fluoride, solid solution

## **Introduction**

Fluorine-containing inorganic materials are important in many fields [1-4]. Difluorides with fluorite structure MF<sub>2</sub>, M = Ca, Sr, Ba, Pb, Cd are of particular importance [5-10]. Solid solutions of rare earth elements in fluorite matrices, as well as MF<sub>2</sub>-M'F<sub>2</sub> systems, are promising materials for photonics and electrochemical devices [1, 11-17].

Fluorides of calcium and barium crystallize into the cubic fluorite-type structure with lattice parameters  $a = 5.463$  and  $6.200 \text{ \AA}$ , respectively. They have relatively high melting points of  $1418 \text{ }^\circ\text{C}$  ( $\text{CaF}_2$ ) and  $1365 \text{ }^\circ\text{C}$  ( $\text{BaF}_2$ ) [11]. The phase diagram of the system  $\text{CaF}_2\text{--BaF}_2$  was studied in ref. [18]. Solid solutions are formed over a wide range near the melting temperature, but at room temperature the equilibrium solubility of the components in each other is very small. The solid solutions react with each other at  $870 \pm 5 \text{ }^\circ\text{C}$  according to the eutectoid scheme with the formation of intermediate composition phase. Coprecipitation from aqueous solutions [18] lead to solid solutions with compositions close to the pure binary fluorides. However, the application of mechanochemical synthesis allowed us to obtain crystalline  $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$  solid solutions in the whole concentration range of the  $\text{CaF}_2\text{--BaF}_2$  system [15, 20-22]. These samples are nanomaterials. It should be mentioned that amorphous  $\text{Ba}_{0.50}\text{Ca}_{0.50}\text{F}_2$  was prepared by low-temperature atomic beam deposition [23] which became crystalline  $\text{Ba}_{0.50}\text{Ca}_{0.50}\text{F}_2$  after heating the sample slightly above  $370 \text{ }^\circ\text{C}$ . This indicates a non-diffusive crystallisation mechanism, e.g., a rearrangement of the  $\text{Ba}_{4-y}\text{Ca}_y\text{F}$  ( $0 \leq y \leq 4$ ,  $y \in \mathbb{Z}$ ) tetrahedrons already present in the amorphous phase. At temperatures above ca.  $480 \text{ }^\circ\text{C}$  decomposition towards the pure binary fluorides was reported [23].

The materials in the  $\text{CaF}_2\text{--BaF}_2$  system are of interest from the point of view of design of new fluoride ion conductors. Nano-size effect enhanced ionic conductivities were found for the pure binary fluorides [24-26]. Nanometer scale  $\text{CaF}_2/\text{BaF}_2/\text{CaF}_2$  heterolayers prepared by molecular beam epitaxy [27-29] and heterostructures formed by eutectoid decomposition of the high temperature phase [30] showed an enhanced ionic conductivity parallel to the heterolayers. An even higher ionic conductivity was found in nanosized solid solutions  $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$  [20, 21] which was explained by decreased migration energies due to geometric frustration [21] creating a quasi super-ionic state of the fluorite lattice at low temperature.

In order to determinate the ionic conduction mechanism, the microstructure and ion dynamics of nanocrystalline  $Ba_{1-x}Ca_xF_2$  solid solutions were studied by  $^{19}F$  magic angle spinning (MAS) nuclear magnetic resonance (NMR), impedance spectroscopy [20-22], static NMR spectroscopy, extended X-ray absorption fine structure (EXAFS) and molecular dynamic (MD) simulation [22]. A small deviation from Vegard's rule towards larger lattice parameter was revealed by X-ray powder diffraction (XRPD).

Thermal stability of a material is of paramount interest from the standpoint of application. In addition, an example of the practical stability of a system in a thermodynamically unstable state is of theoretical interest.

The purpose of the present work is the study of decomposition of  $Ba_{1-x}Ca_xF_2$  solid solutions by high-temperature X-ray powder diffraction (HT XRPD) and differential scanning calorimetry (DSC).

### Experimental

We used  $CaF_2$  (99.99%, Alfa Aesar) and  $BaF_2$  (99.99%, Alfa Aesar) reagents without further reprocessing. High-energy mechanochemical synthesis of the sample  $Ba_{1-x}Ca_xF_2$  was carried out from  $CaF_2$  and  $BaF_2$  powders. These were dried for at least 12 h at 120 °C in vacuum and then handled in an argon filled glovebox. Mixtures of  $BaF_2$  and  $CaF_2$  to give  $Ba_{0.25}Ca_{0.75}F_2$ ,  $Ba_{0.50}Ca_{0.50}F_2$ , and  $Ba_{0.75}Ca_{0.25}F_2$ , assuming a complete conversion, were weighted into milling beakers made of tungsten carbide filled with 100 milling balls made of the same material (5 mm diameter, beaker and milling balls purchased from Fritsch, Germany). The overall mass of the mixtures were in all cases 2.000(5) g. Milling was done for 33 h at 600 rpm in intervals of 15 min followed by 15 min pause employing a Pulverisette 7 *premium line* planetary ball mill (Fritsch, Germany).

The thermal stability was determined by DSC, using a NETZSCH DSC 404 F1 Pegasus differential scanning calorimeter. The measurements were carried out in platinum crucibles under argon flow (20 ml/min), the heating rate was 10

degree/min, the specimen weight was  $23 \pm 1$  mg.

High temperature X-ray diffraction was performed with a Bruker D8 Discover A25 diffractometer equipped with a high temperature camera HTK 1200N employing  $\text{CuK}\alpha$  radiation using Bragg-Brentano geometry while keeping the samples under a vacuum of  $1.3 \times 10^{-3}$  to 0.13 Pa. Temperature range of measurements was from ambient temperature to 750 °C. The heating rate was 20 degree/min. When the preset temperature was reached an X-ray pattern was recorded in the range of 20-75 °2 $\theta$ . The accuracy of temperature maintenance was  $\pm 3$ °C. X-ray patterns were processed with the DIFFRAC.EVALUATION PACKAGE (DIFFRAC.EVA 4; Bruker, Karlsruhe, Germany) and TOPAS 4.2 software package (Rwp < 10) (Bruker, Karlsruhe, Germany).

### Results and Discussion.

According to the X-ray data, initial samples, prepared by mechanochemical protocol, had a *fcc* cubic structure, i.e. they are fluorite-type solid solution. The broadening of X-ray lines corresponds to the small size *D* of coherent scattering regions (Fig. 1). An average crystallite size of ca.  $18 \pm 3$  nm was obtained for the samples by Rietveld refinement. The deviation from Vegard's rule is small – in particular, for the sample  $\text{Ba}_{0.50}\text{Ca}_{0.50}\text{F}_2$  exceeding the lattice parameter compared to the arithmetic mean of  $\text{CaF}_2$  and  $\text{BaF}_2$  by 0.021 Å.

On the thermograms of all three samples an exothermal process was observed at a temperature of about 420 - 450 °C (Fig. 2), and during subsequent heating an endothermal process took place at ~870 °C. The first process corresponds to the decomposition of the non-equilibrium solid solution under heating. The second effect, in accordance with the  $\text{CaF}_2$ - $\text{BaF}_2$  phase diagram [1], reflects an eutectoid reaction of two solid phases with the formation of a high-temperature phase of intermediate composition.

The data of high temperature X-ray diffraction analysis of the  $\text{Ba}_{0.50}\text{Ca}_{0.50}\text{F}_2$  sample are shown in Fig. 1. Already at 200 °C the decomposition of the solid

solution into two fluorite-type phases is observed (Fig. 1b). In this case, the X-ray data indicate a small amount of the initial non-equilibrium solid solution. The lines are broadened. Upon further heating (Figs. 1c – 1f), X-ray patterns contain a superposition of the XRPD reflexes of two fluorite solid solutions, the lattice parameters being close to those of the fluorides of barium and calcium, respectively (Table 1). The lines are narrow, which corresponds to a size of coherent scattering regions of above 200 nm. An additional peak of low intensity at  $\sim 30^\circ 2\theta$  appears starting from 470 °C, the interpretation of which is difficult.

Taking the applicability of Vegard's rule for the system  $\text{CaF}_2\text{--BaF}_2$  at high temperature, and based on the data of Schumann et al. [31], and Neumann et al. [32] for the temperature dependence of the lattice parameters of the pure fluorides of calcium and barium, we evaluated maximal concentrations of the solid solutions on the basis of  $\text{CaF}_2$  and  $\text{BaF}_2$ . The solubility of both  $\text{CaF}_2$  in  $\text{BaF}_2$ , and  $\text{BaF}_2$  in  $\text{CaF}_2$  is negligible and amounts to 1.5-2 mol % in the range 370-750 °C. These values agree with the  $\text{CaF}_2$  -  $\text{BaF}_2$  phase diagram [18].

The appearance of exothermic effects on the thermograms clearly shows that the initial samples of solid solution were not in equilibrium state. It is worth noting that, according to the third law of thermodynamics, all solid solutions should decompose at low temperatures [33]. The transition to an equilibrium state, namely, the decomposition of a solid solution is accompanied by heat release. Interestingly, the  $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$  samples can seemingly stay in a non-equilibrium state indefinitely long at room temperature. Storage for 6 months did not lead to a change in their X-ray patterns.

It is interesting to note that the temperature of decomposition recorded thermographically is significantly higher than the one obtained with high temperature X-ray diffraction. The difference may be due to the action of X-ray radiation accelerating the process of decomposition. It is also possible that vacuum might play a role in this process. This is also in agreement with *ex situ* measurements which show no decomposition after 3 h at 340 °C [21]. It should be

mentioned that static  $^{19}\text{F}$  NMR measurements conducted on a  $\text{Ba}_{0.50}\text{Ca}_{0.50}\text{F}_2$  sample kept under vacuum in a glass ampulla showed no signs of decompositions at  $200\text{ }^\circ\text{C}$  [21,22].

Fig. 3 shows the general scheme of stable, metastable and labile state, and the proposed state diagram for the system  $\text{CaF}_2\text{-BaF}_2$  (based on the data in ref. [23], too). There are two well-known different mechanisms of solid solutions decomposition: formation of nuclei of new phases and spinodal decomposition. The first mechanism is realized for metastable states. It requires the formation of nuclei of critical size, overcoming the energy barrier, which depends on the temperature. This process is similar to the crystallization of a liquid. The second mechanism, spinodal decomposition, is quite different. It starts with small fluctuations of the concentration of the two species forming the solid solution. It is a cooperative process, which is solely controlled by diffusion. It has to go simultaneously, and once started, this process is accelerating. The behavior of the system resembles a “fall”. This mechanism is characteristic for the decay of the labile state. There are several classical papers on this problem [34-37].

Apparently, the crystalline solid solution  $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$  is in labile state at room temperature, i.e. its transition to the equilibrium state is not associated with overcoming the potential barrier. Indication of this is the lack of abrupt beginning of the exothermic effect (smooth onset). In the absence of a potential well, even a small external impact, such as X-ray irradiation, can cause a significant acceleration of the process.

Apparently, the relative stability of the crystalline samples of the solid solution  $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$  is due to the extremely low values of the diffusion coefficients of the cations. The system is “falling”, but very slowly. A similar effect was observed for the system  $\text{CaF}_2\text{-SrF}_2$  [38].

## **Conclusion.**



$Ba_{1-x}Ca_xF_2$  samples with fluorite-type structure, prepared by high-energy ball milling, are indefinitely stable at room temperature. However, they decompose under heating. As a product two phases with compositions close to pure  $BaF_2$  and  $CaF_2$  were obtained. The decomposition temperature observed by high-temperature X-ray measurements is lower than in the DSC experiments. Such behavior may be explained by a labile state of the initial samples and very low diffusivity of cations.

### **Acknowledgements**

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## REFERENCES

1. Photonic & Electronic Properties of Fluoride Materials, A.Tressaud, K.Poepelmeier (Eds.), Elsevier, Amsterdam, The Netherlands, 2016.
2. Ch. Chen, T. Sasaki, R. Li, et al. Nonlinear Optical Borate Crystals, Wiley-VCH, Weinheim, 2012.
3. 13<sup>th</sup> Laser Ceramics Symposium: Intern. Symp. on Transparent Ceramics for Photonic Applications, Fryazino, Russia, 04.12.17-08.12.17. Abstract Book, 44 p.
4. 2<sup>nd</sup> Conference and Spring School on Properties, Design and Applications of Upconversion Nanomaterials (UPCON 2018), Valencia, Spain, 2-6 April 2018 Abstract Book.
5. Crystals with the Fluorite Structure. Electronic, Vibrational, and Defect Properties, W. Hayes (Ed.), Clarendon Press, Oxford, 1974.
6. I.I. Buchinskaya, P.P. Fedorov, Lead difluoride and related systems, Rus. Chem. Rev. 73(4) (2004) 371-400.
7. A.S. Sheulin, A.E. Angervaks, A.V. Veniaminov, V.V. Zakharov, P.P. Fedorov, S.V. Kuznetsov, A.I. Ryskin, Formation of dissipative structures at hologram recording in CaF<sub>2</sub> crystals with color centers, Holography: Advances and Modern Trends IV. Proc. SPIE. 9508 (2015) 95080D-9.
8. Z. Li, Y. Zhang, L. Huang, Y. Yang, Y. Zhao, G. El-Banna, G. Han, Nanoscale “fluorescent stone”: calcium fluoride nanoparticles as theranostic platforms, Theranostics, 6(13) (2016) 2380-2393.
9. P.A. Popov, A.A. Sidorov, E.A. Kul’chenkov, A.M. Anishchenko, I.Ch. Avetissov, N.I. Sorokin, P.P. Fedorov, Thermal conductivity and expansion of PbF<sub>2</sub> single crystals, Ionics, 23(1) (2017) 233-239.
10. I. Ryskin, P.P. Fedorov, N.T. Bagraev, A. Lushchik, E. Vasil’chenko, A.E. Angervaks, I. Kudryavtseva, Stabilization of high-temperature disorder of fluorine sublattice by quenching in calcium fluoride crystals, J. Fluor. Chem. 200 (2017) 109–114.

11. B.P. Sobolev, The Rare Earth Trifluorides, Part 2. Introduction to Materials Science of Multicomponent Metal Fluoride Crystals, Inst. Estud. Catal., Barcelona, 2001.
12. I.I. Buchinskaya, P.P. Fedorov, A new optical medium -  $\text{Cd}_{0.75}\text{Sr}_{0.25}\text{F}_2$  single crystals, *Crystallogr. Rep.* 49(2) (2004) 279-281.
13. P.P. Fedorov, I.I. Buchinskaya, E.V. Chernova, Morphological stability of the solid–liquid Interface during melt crystallization of  $\text{Pb}_{1-x}\text{Cd}_x\text{F}_2$  solid solution, *Crystallogr. Rep.* 61(3) (2016) 512–516.
14. G. Scholz, S. Breitsfeld, T. Krahl, A. Düvel, P. Heitjans, E. Kemnitz, Mechanochemical synthesis of  $\text{MgF}_2\text{-MF}_2$  composite systems ( $M = \text{Ca, Sr, Ba}$ ), *Solid State Sci.* 50 (2015) 32-41.
15. M. Heise, G. Scholz, A. Düvel, P. Heitjans, E. Kemnitz, Mechanochemical synthesis, structure, and properties of solid solutions of alkaline earth metal fluorides:  $M^a_{1-x}M^b_x\text{F}_2$  ( $M: \text{Ca, Sr, Ba}$ ), *Solid State Sci.* 60 (2016) 65-74.
16. M. Heise, G. Scholz, A. Düvel P. Heitjans, E. Kemnitz, Mechanochemical Synthesis, Structure and Properties of Lead Containing Alkaline Earth Metal fluoride Solid Solutions  $M_x\text{Pb}_{1-x}\text{F}_2$  ( $M = \text{Ca, Sr, Ba}$ ), *Solid State Sci.* 77 (2018) 45-53.
17. M. Wilkening, A. Düvel, F. Preishuber-Pflügl, K. da Silva, S. Breuer, V. Šepelák, P. Heitjans, Structure and ion dynamics of mechanosynthesized oxides and fluorides; Access to nanocrystalline ceramics via high-energy ball-milling – a short review. *Zeitschrift für Kristallographie - Crystalline Materials* 232 (2017) 107-127.
18. P.P. Fedorov, I.I. Buchinskaya, N.A. Ivanovskaya, V.V. Konovalova, S.V. Lavrishchev, B.P. Sobolev,  $\text{CaF}_2\text{-BaF}_2$  phase diagram, *Doklady Phys. Chem.* 401(2) (2005) 53-55.
19. P.P. Fedorov, S.V. Kuznetsov, M.N. Mayakova, V.V. Voronov, R.P. Ermakov, A.E. Baranchikov, V.V. Osiko, Coprecipitation from aqueous solutions to prepare binary fluorides, *Rus. J. Inorg. Chem.* 56(10) (2011) 1525-1531.

20. A. Düvel, B. Ruprecht, P. Heitjans, M. Wilkening, Mixed Alkaline-Earth Effect in the Metastable Anion Conductor  $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$  ( $0 \leq x \leq 1$ ): Correlating Long-Range Ion Transport with Local Structures Revealed by Ultrafast  $^{19}\text{F}$  MAS NMR, *J. Phys. Chem. C*. 155 (2011) 23784-23789.
21. A. Düvel, NMR- und impedanzspektroskopische Untersuchungen zur Dynamik und lokalen Struktur in mechanochemisch dargestellten Nichtgleichgewichtsphasen, Doctoral Dissertation, Leibniz Universität, Hannover, 2014.
22. A. Düvel, P. Heitjans, P. Fedorov, R. Ueker, G. Scholz, G. Cibin, A.V. Chadwick, D.M. Pickup, S. Ramos, L.W.L. Sayle, T.X.T. Sayle, D.C. Sayle, Is geometric frustration-induced disorder a recipe for high ionic conductivity? *J. Am. Chem. Soc.* 139 (2017) 5842-5848.
23. X. Mu, W. Sigle, A. Bach, D. Fisher, M. Jansen, P.A. van Aken, Influence of a Second Cation ( $M = \text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) on the Phase Evolution of  $(\text{Ba}_x\text{M}_{1-x})\text{F}_2$  Starting from Amorphous Deposits, *Z. anorg. allg. Chem.* 640(10) (2014) 1868-1875.
24. W. Puin, S. Rodewald, R. Ramblau, P. Heitjans, J. Maier, Local and overall ionic conductivity in nanocrystalline  $\text{CaF}_2$ , *Solid State Ionics*, 131 (2000) 159-164.
25. B. Ruprecht, M. Wilkening, A. Feldhoff, S. Steuernagel and P. Heitjans, High anion conductivity in a ternary non-equilibrium phase of  $\text{BaF}_2$  and  $\text{CaF}_2$  with mixed cations, *Phys. Chem. Chem. Phys.* 11 (2009) 3071–3081.
26. G. Scholz, K. Meyer, A. Düvel, P. Heitjans, E. Kemnitz, Fast Ion Conducting Nanocrystalline Alkaline Earth Fluorides Simply Prepared by Mixing or Manual Shaking, *Z. anorg. allg. Chem.* 639 (2013) 960-966.
27. N. Sata, K. Eberman, K. Eberl, J. Maier, Mesoscopic fast ion conduction in nanometer-scale planar heterostructures, *Nature*, 408 (2000) 946-949.
28. N. Sata, N.Y. Jin-Philipp, K. Eberl, J. Maier, Enhanced ionic conductivity and mesoscopic size effects in heterostructures of  $\text{BaF}_2$  and  $\text{CaF}_2$ , *Solid State Ionics*, 154-155 (2002) 497-502.

29. N.Y. Jin-Philipp, N. Sata, J. Maier, C. Scheu, K. Hahn, M. Keisch, M. Ruhle, Structures of BaF<sub>2</sub>-CaF<sub>2</sub> heterolayers and their influences on ionic conductivity, *J. Chem. Phys.* 120(5) (2004) 2375-2381.
30. N.I. Sorokin, I.I. Buchinskaya, B.P. Sobolev, P.P. Fedorov, Electrical conductivity of a CaF<sub>2</sub>-BaF<sub>2</sub> nanocomposite, *Inorg. Mater.* 44(2) (2008) 189-192.
31. B. Schumann, H. Neumann, Thermal expansion of CaF<sub>2</sub> from 298 to 1173 K, *Cryst. Res. Technol.* 19 (1984) K13-K14.
32. H. Neumann, G. Kommichau, W. Schmitz, B. Schumann, Thermal expansion of BaF<sub>2</sub> from 296 to 1173 K, *J. Mat. Sci. Lett.* 5 (1986) 1131-1132.
33. P.P. Fedorov, Third law of thermodynamics as applied to phase diagrams, *Rus. J. Inorg. Chem.* 55(11) (2010) 1722-1739.
34. R. Kikuchi, Irreversible cooperative phenomena, *Ann. Phys.* 10 (1960) 127-151.
35. M. Hillert, A solid solution model for inhomogeneous systems, *Acta Met.* 9 (1961) 525-535.
36. J.W. Cahn, On spinodal decomposition, *Acta Met.* 9 (1961) 795-801.
37. J.W. Cahn, The later stages of spinodal decomposition and the beginning of particle coarsening, *Acta Met.* 14 (1966) 1685-1692.
38. P.P. Fedorov, S.N. Ushakov, M.A. Uslamina, E.V. Chernova, S.V. Kuznetsov, V.V. Voronov, A. Düvel, P. Heitjans, A.A. Pynenkov, K.N. Nishchev, V.V. Osiko, Morphological stability of solid-liquid interface during melt crystallization of Ca<sub>1-x</sub>Sr<sub>x</sub>F<sub>2</sub> solid solution, *Cryst. Rep.* 63 (2018) (in press).

Fig. 1. X-ray pattern on  $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{F}_2$ . a – room temperature, b- 200 °C, c - 370°C, d- 470 °C, e-570 °C, f - 750 °C. Circle –  $\text{BaF}_2$ -based phase, asterisk- initial solid solution

Fig. 2. DSC curve: a –  $\text{Ca}_{0.75}\text{Ba}_{0.25}\text{F}_2$  (23 mg); b-  $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{F}_2$  (22 mg); c-  $\text{Ca}_{0.25}\text{Ba}_{0.75}\text{F}_2$  (24 mg).

Fig. 3. Scheme of energetic stability of different states. a -  $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$ : 1- amorphous  $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$  solid solution, 2 - crystalline  $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$  solid solution, 3 – mixture of  $\text{BaF}_2:\text{Ca}^{2+}$  and  $\text{CaF}_2:\text{Ba}^{2+}$  solid solutions; b - generale case: 1- labile state, 2 – metastable state, 3 - stable state.

Table 1. Temperature of X-ray measurements and lattice parameters of observed cubic phases in the  $\text{Ba}_{0.50}\text{Ca}_{0.50}\text{F}_2$  system (i.e. the solid solution at 23 °C and the Ca [left] and the Ba rich [right] products of the decomposition for  $T \geq 200$  °C).

$T, ^\circ\text{C}$	Lattice parameter, Å	
23	5.853	
	Ca rich phase	Ba rich phase
200		6.182
370	5.512	6.223
470	5.515	6.235
570	5.527	6.247
750	5.55	6.265

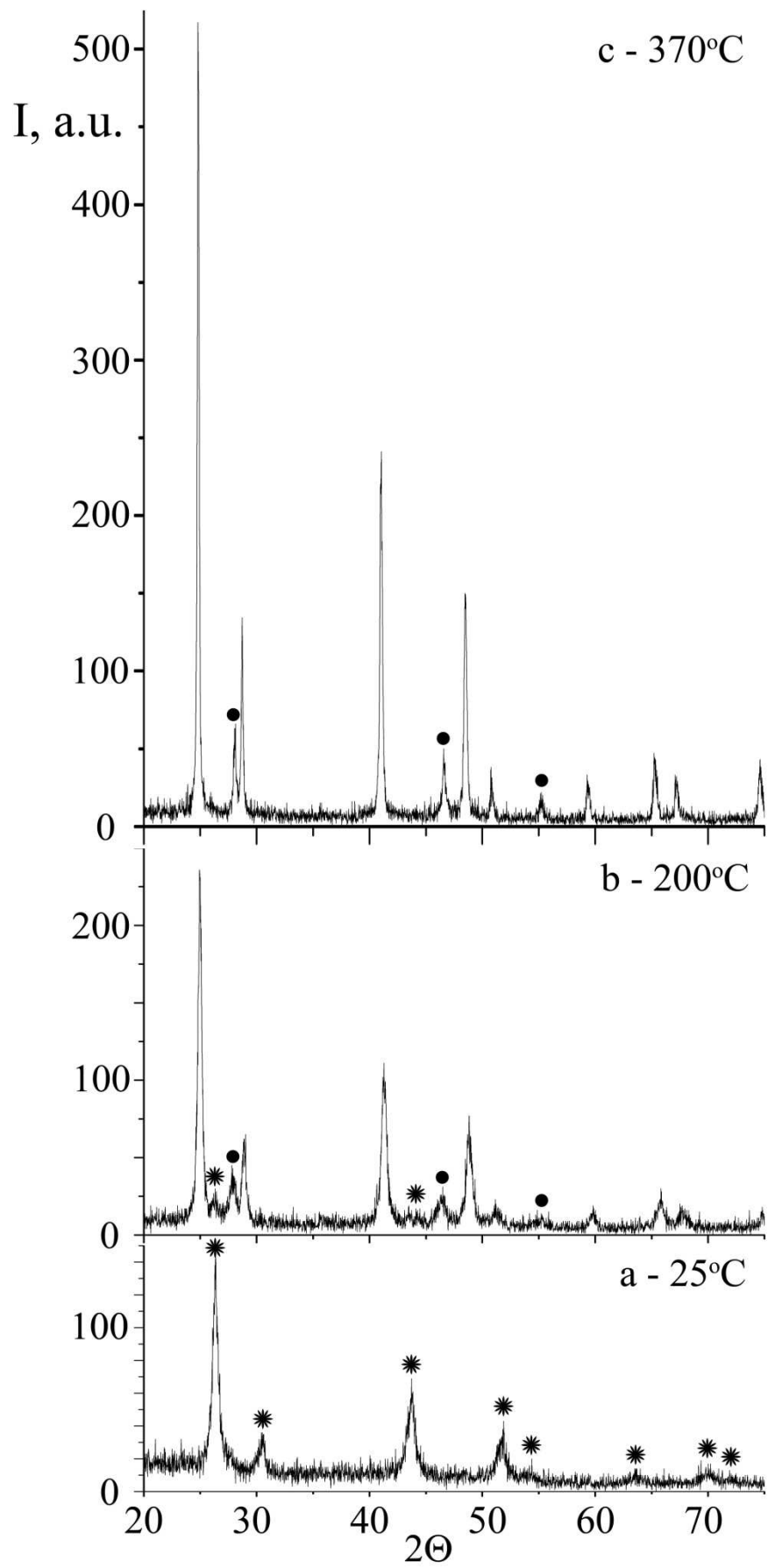


Fig.1, a-c

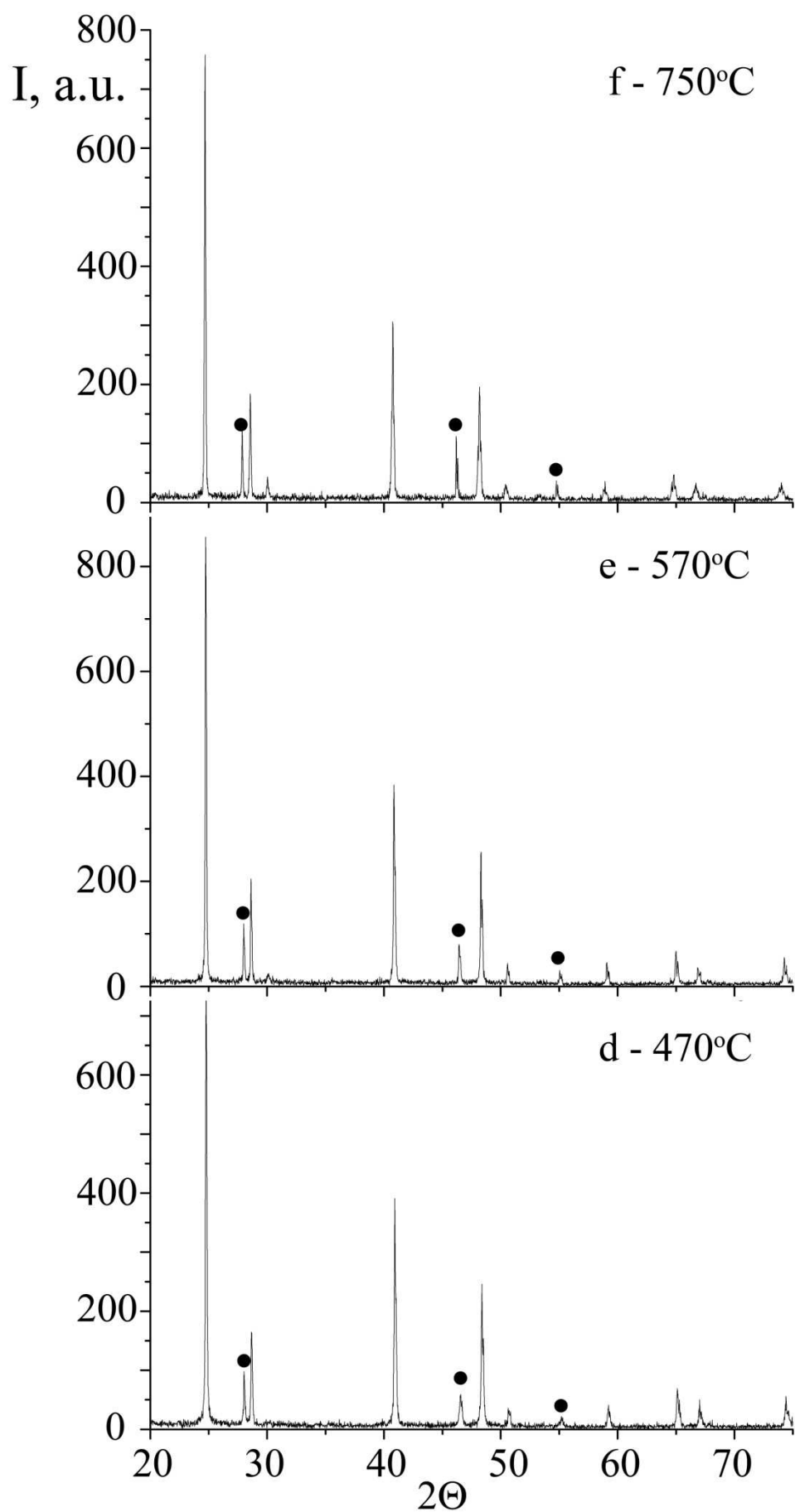


Fig.1, d-e.



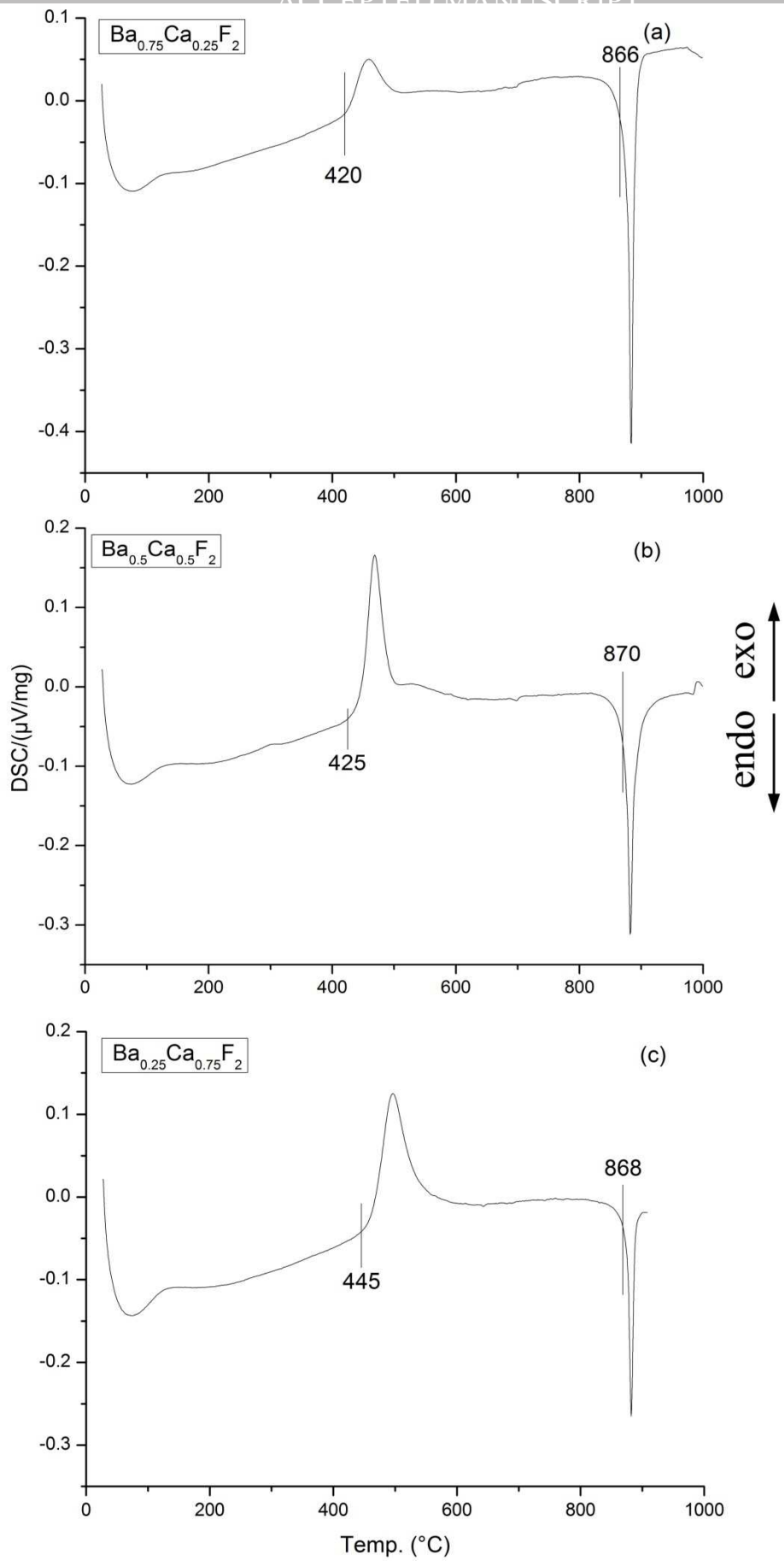


Fig.2.

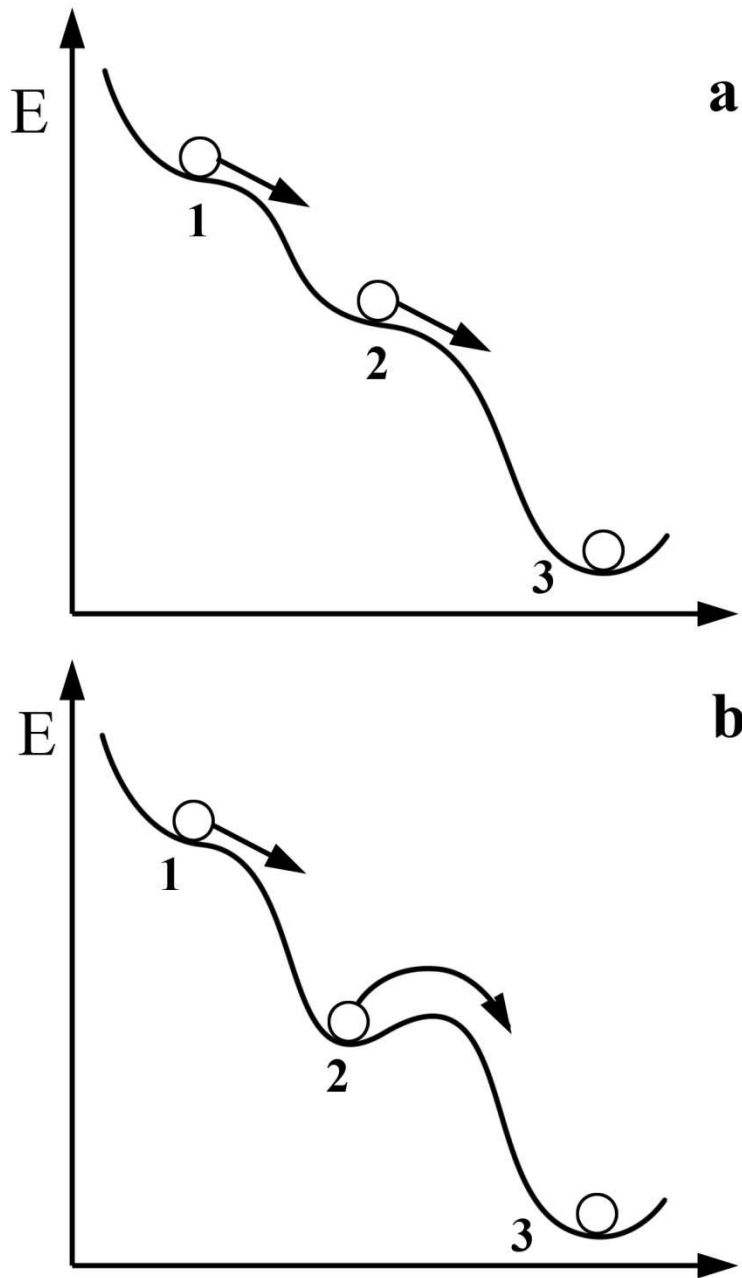


Fig. 3.

Thermal decomposition of  $\text{Ba}_{0.25}\text{Ca}_{0.75}\text{F}_2$ ,  $\text{Ba}_{0.50}\text{Ca}_{0.50}\text{F}_2$  and  $\text{Ba}_{0.75}\text{Ca}_{0.25}\text{F}_2$  seems to be fostered by X-ray radiation, leading to decomposition at temperatures 200 K lower than observed by DSC.

The three  $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$  solid solutions investigated, here (and probably all others in the thermal miscibility gap) seem to be in a labile state.

Despite being in labile state the solid solutions seem to be stable indefinitely at room temperature due to very low cation diffusivity.