IOCC 2026 Conference
The 5th International Online Conference on Crystals
15–17 June 2026 | Online
MDPI

Tunable low thermal expansion in calcite-type $FeBO_3$ and $CrBO_3$ borates

Biryukov Y.P.[1], Zinnatullin A.L.[2], Kuznetcov M.D.[1,2], Gokhfeld Yu.S.[3], Kazak N.V.[3], Krzhizhanovskaya M.G.[4], Vagizov F.G.[2], Bubnova R.S.[1]

[1]Institute of Silicate Chemistry, 2 Makarova Emb., Saint Petersburg, 199034, Russian Federation
[2]Institute of Physics, Kazan Federal University, 18 Kremlyovskaya street, Kazan, 420008, Russian Federation
[3]Kirensky Institute of Physics, FRC KSC SB RAS, 50/38 Akademgorodok, Krasnoyarsk, 660036, Russian Federation
[4]Institute of Earth Science, St. Petersburg State University, 7/9 Universitetskaya Emb., St. Petersburg, 199034, Russian Federation

INTRODUCTION & AIM

Background. Precise thermal expansion control is critical for preventing device failure in precision optics and electronics. Materials with low thermal expansion (LTE, $\langle\alpha\rangle \leq 8 \times 10^{-6}\ K^{-1}$) are highly sought after. Magnetostriction near magnetic phase transitions can modulate TE behavior offering a route to tailor properties *via* composition.

Borates. Calcite-type borates tend to exhibit LTE, but systematic comparative studies of end-members with contrasting magnetic properties remain scarce.

$FeBO_3$ and $CrBO_3$.

- **$FeBO_3$** is a weak ferromagnet (T_c = 348 K) and commercial monochromator for synchrotron Mössbauer spectroscopy. Shows LTE ($\langle\alpha\rangle = 8 \times 10^{-6}\ K^{-1}$, 93–1173 K) with anomalous behavior near T_c [1]
- **$CrBO_3$** is an antiferromagnet (T_c = 6–15 K) paramagnetic at room temperature. DFT predicts LTE ($\alpha = 15 \times 10^{-6}\ K^{-1}$ at 300 K) [2]

Aim. This work presents the first direct experimental comparison of thermal expansion in $FeBO_3$ and $CrBO_3$ using a comprehensive suite of *in situ* techniques: HTPXRD and HTSCXRD, Mössbauer spectroscopy, magnetometry and thermal analysis (DSC + TG). We quantify LTE anisotropy, correlate structural evolution with magnetic transitions and establish composition–property trends across the calcite-type borate family providing a foundation for rational design of thermally stable functional materials.

METHOD

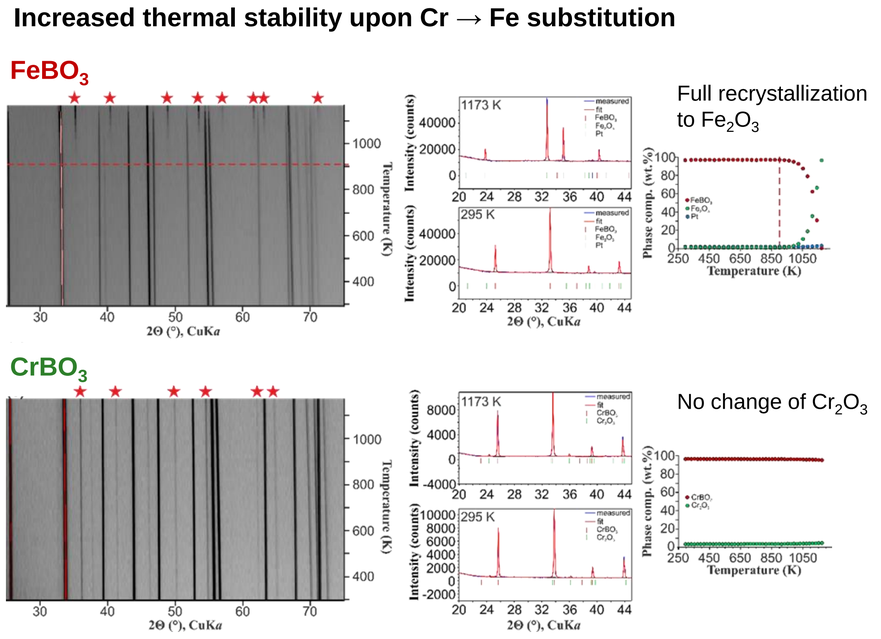
- Single crystals and polycrystalline samples growth
- *In situ* high-temperature single-crystal X-ray diffraction (295–473 K)
- *In situ* high-temperature X-ray powder diffraction (295–1173 K)
- *In situ* variable-temperature Mössbauer spectroscopy (80–478 K)
- Magnetic measurements (5–400 K)
- Thermal analysis (DSC + TG) (295–1673 K)

➢ **Original Approach.** We developed an original methodology based on the complementary independent techniques to accurately determine thermal expansion coefficients (CTE) of magnetic materials. This multi-method strategy eliminates artifacts and ensures reliable correlation between structural and magnetic properties.

➢ **Key Advantage.** Magnetic phase transitions are detected independently by two routes:
Mössbauer spectroscopy and magnetometry → direct probe of magnetic hyperfine parameters, magnetic substructures and T_c determination
X-ray diffraction → anomalies in unit-cell parameters and volume near T_c
✓ This cross-validation enables correct CTE calculation for magnetics accounting for magnetostrictive contributions near phase transitions

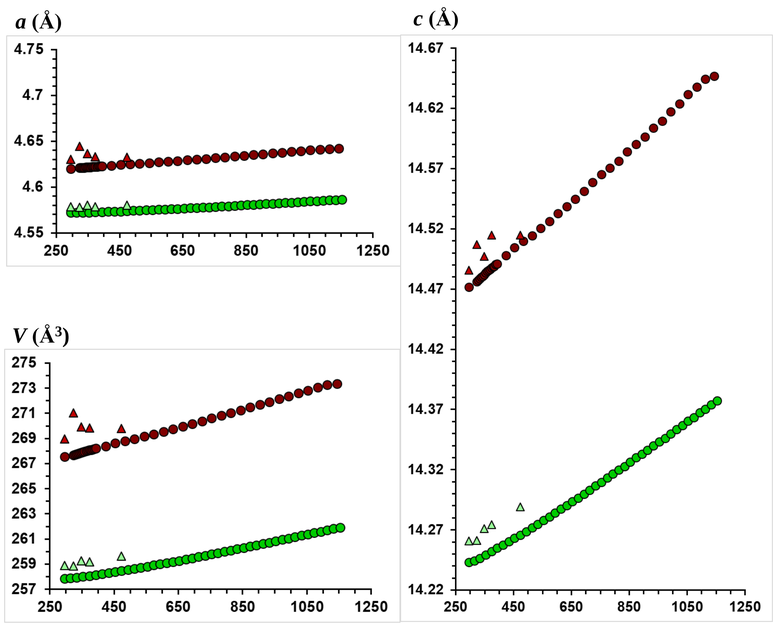
RESULTS & DISCUSSION

Increased thermal stability upon Cr → Fe substitution



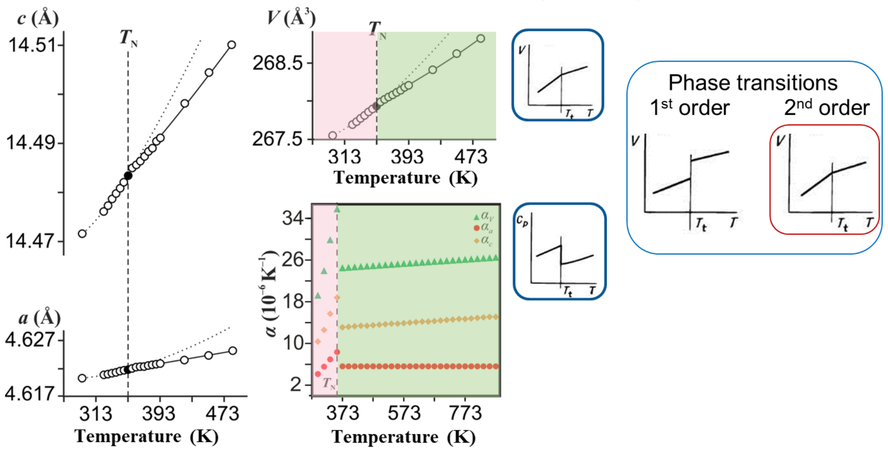
HT-PXRD data

DSC + TG

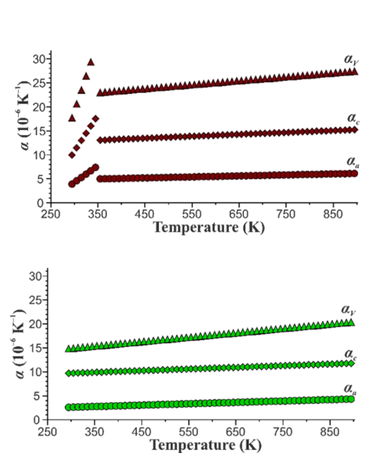


HT-PXRD (●) and SCXRD (▲) data for $FeBO_3$ and $CrBO_3$

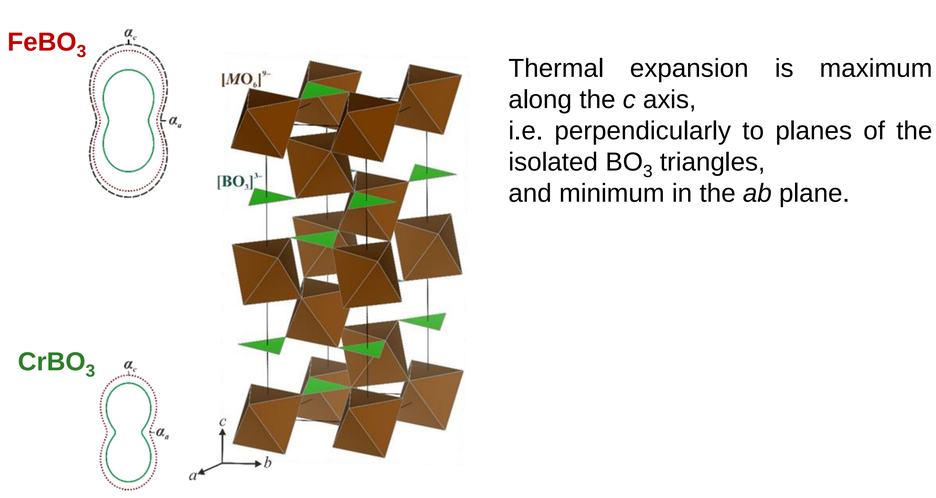
Anomalies in unit cell parameters in $FeBO_3$ near T_c



Low thermal expansion



Crystal structure *vs* CTE



Thermal expansion is maximum along the *c* axis,
i.e. perpendicularly to planes of the isolated BO_3 triangles,
and minimum in the *ab* plane.

CONCLUSIONS

➢ Both $FeBO_3$ and $CrBO_3$ exhibit low thermal expansion ($\langle\alpha\rangle$ = 8 and 6 × $10^{-6}\ K^{-1}$, respectively) meeting the LTE criterion for precision applications
➢ Anisotropic expansion is governed by rigid BO_3 triangles: minimal in the *ab* plane, maximal along the *c* axis – consistent with calcite-type compounds crystal chemistry
➢ Magnetostructural coupling in $FeBO_3$: anomalous change in lattice parameters near T_c reflects magnetostrictive contribution correctly accounted for *via* multi-method approach
➢ Enhanced thermal stability with Cr: decomposition temperature increases from ~903 K ($FeBO_3$) to >1173 K ($CrBO_3$), while maintaining LTE behavior
➢ The comparative study establishes structure–property trends across the calcite-type borate family providing a foundation for rational development of thermally stable functional materials for optics and spintronics

FUTURE WORK/ REFERENCES/ACKNOWLEDGMENT

Future work. Extension to $Fe_{1-x}Cr_xBO_3$ will enable fine-tuning of magnetic and thermal properties for applications in precision optics and spintronics

References. 1. Y.P. Biryukov, S.K. Filatov, F.G. Vagizov, A.L. Zinnatullin & R.S. Bubnova, Thermal Expansion of $FeBO_3$ and Fe_3BO_6 Antiferromagnets Near the Neel Temperature, J. Struct. Chem. 59(8) (2018) 1980–1988.
2. D. Yang & Y. Li, Unraveling low thermal expansion of $CrBO_3$ via atomic scale analysis: Flexible CrO_6 octahedron vs rigid BO_3 triangle group, Journal of Applied Physics. 138(9) (2025) 095104.

Acknowledgment. The work is funded by the Russian Science Foundation [25-73-00080]