

Structural transitions under high-pressure in a langasite-type multiferroic Ba₃TaFe₃Si₂O₁₄



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ABSTRACT

The iron containing langasite family compound Ba₃Ta⁵⁷Fe₃Si₂O₁₄ was studied at high pressure up to 30 GPa at room temperature by means of *in situ* X-ray diffraction, Raman and Mössbauer spectroscopies in diamond anvil cell. Two structural transitions at pressures ~5 and ~20 GPa are observed. At ~5 GPa, the low-pressure trigonal *P321* phase undergoes phase transition to the most likely *P3* structure as manifested by slight increase in the *c/a* ratio and by anomalies of the Mössbauer and Raman spectra parameters. At ~20 GPa, the first order phase transition to monoclinic structure occurred with a drop of unit cell volume by 9%. The appearance of the ferroelectric state at such transitions is discussed in connection with the multiferroic properties.

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1. Introduction

Recently, a great interest was attracted to the langasite family compounds containing 3*d* ions as potential new type of multiferroics [1,2]. The langasite La₃Ga₅SiO₁₄ crystal giving the name to the whole family is famous by its unique piezoelectric properties outmatching quartz [3,4]. Among such compounds, materials with iron, cobalt and manganese ions A₃BM₃X₂O₁₄ (A = Ba, Sr, Ca, Pb; B = Sb, Nb, Ta, Te; M = Fe, Co, Mn, X = Si, Ge, P, V, As) were synthesized in order to study their magnetic properties [1,3,5].

The langasite type crystal structure belongs to the trigonal non-centrosymmetrical space group *P321* and it is similar to the Ca₃Ga₂Ge₄O₁₄ crystal [6]. In A₃BM₃X₂O₁₄ compounds, the A and B cations occupy the sites in the dodecahedra and octahedra formed by oxygen atoms, respectively. M and X cations are positioned in two kinds of tetrahedra sites which share vertices (Fig. 1) [3,6]. The

tetrahedral layers are in the *ab* plane, and are separated along the *c* axis with the layers consisting of oxygen octahedra and large dodecahedra.

The magnetic [7–9] and Mössbauer spectroscopy [2,10] measurements revealed an antiferromagnetic ordering in a number of these compounds at temperatures between 7 and 38 K. By assuming a coexistence of electric and magnetic order parameters in these materials one might expect a creation of a new class of multiferroics [11–13], theoretically discussed in Refs. [14,15]. The long-range magnetic ordering with a complex helicoidal magnetic structure was found by the neutron diffraction studies in the similar crystal of Ba₃NbFe₃Si₂O₁₄. [7,9].

Below the Neel temperature T_N, the moments of Fe³⁺ cations in 3*f*-sites form a triangular magnetic lattice in the *a-b* plane with iron magnetic moments oriented at an angle of 120° relative to each other (Fig. 2). This antiferromagnetic phase in langasite Ba₃NbFe₃Si₂O₁₄ gained a helicoidal twist of the iron moments in triangles at their translation along the *c* axis [9]. In this case, the electric polarization *P* directed along the *c* axis also appears [11,14,15], and an occurrence of its component in the *a-b* plane is also not excluded [10,14,15]. Above T_N, the langasite structure becomes paramagnetic

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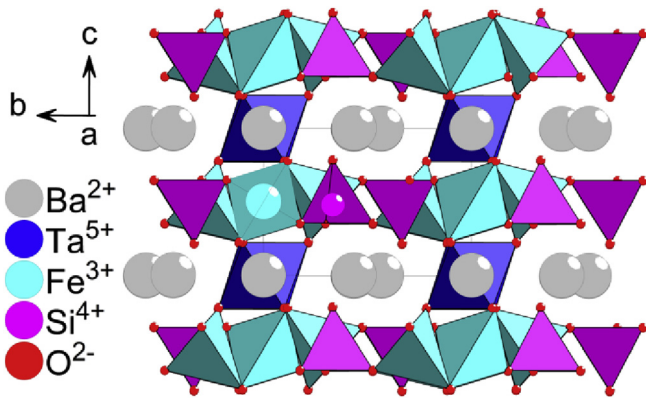


Fig. 1. The trigonal structure of $\text{Ba}_3\text{Ta}^{57}\text{Fe}_3\text{Si}_2\text{O}_{14}$ (shown on the basis of the $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ – type structure) projected along the a axes (in the b – c plane). The Fe^{3+} and Si^{4+} ions are in the tetrahedral oxygen sites, Ta^{5+} ions are inside oxygen octahedral, and Ba^{2+} ions are in the dodecahedral sites (distorted Thompson cube).

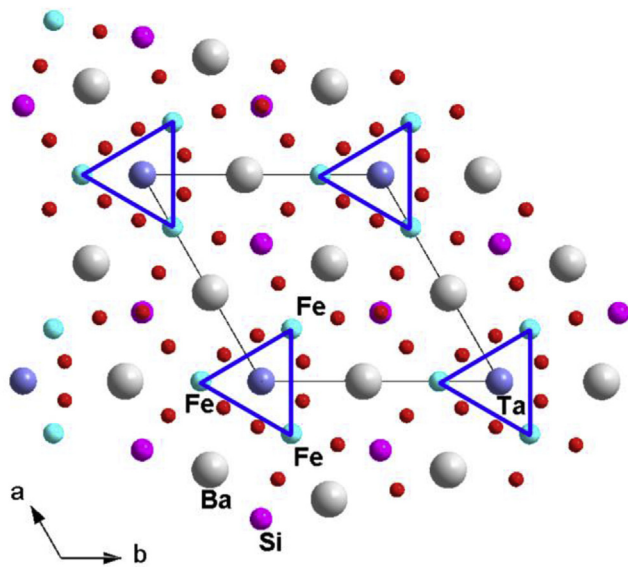


Fig. 2. The a – b projection of the trigonal $\text{Ba}_3\text{Ta}^{57}\text{Fe}_3\text{Si}_2\text{O}_{14}$ structure. The triangle plain net of magnetic Fe^{3+} ions is shown by solid blue lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and paraelectric.

Appearance of two magnetic sublattices was found by the Mössbauer spectroscopy in $\text{Ba}_3\text{TaFe}_3\text{Si}_2\text{O}_{14}$ and $\text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14}$ [2,10], which can be associated with the structural phase transition induced by the magnetic ordering below Neel temperature $T_N = 27.2$ K. Below T_N the magnetic moments of two iron sublattices rotate in the opposite directions with the temperature variation [2,10].

The possible structural phase transitions induced by temperature and pressure variation in the langasite-family compounds were discussed in Ref. [16]. The change of the trigonal symmetry (sp. gr. $P321$) to monoclinic (sp. gr. $A2-C2$) was found in $\text{La}_3\text{SbZn}_3\text{Ge}_2\text{O}_{14}$ with lowering temperature and in $\text{La}_3\text{Nb}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$ and $\text{La}_3\text{Ta}_{0.5}\text{Ga}_{5.5}\text{O}_{14}$ under high pressure [16].

Recently structural and magnetic properties of $\text{Ba}_3\text{TaFe}_3\text{Si}_2\text{O}_{14}$ langasite under high hydrostatic pressure up to 38 GPa were investigated by Raman spectroscopy and nuclear forward

scattering (NFS) of synchrotron radiation. Results reported in Ref. [17] revealed two successive transformation at ~ 6.8 and 19.5 GPa. The later transformation accompanied by a drastic increase in the T_N value was assigned to the first order structural transition.

In this paper we present the results of high-pressure X-ray diffraction, Raman spectroscopy and Mössbauer spectroscopy studies of structural properties of the $\text{Ba}_3\text{TaFe}_3\text{Si}_2\text{O}_{14}$ compound.

2. Experimental methods

The polycrystalline $\text{Ba}_3\text{Ta}^{57}\text{Fe}_3\text{Si}_2\text{O}_{14}$ compound was synthesized by the solid–state reaction of compacted mixtures of Ta_2O_5 , Fe_2O_3 , SiO_2 oxides and BaCO_3 carbonate placed in platinum crucible and annealed in air at 1225 °C. The synthesis is described in details in Ref. [3]. For the Mössbauer spectroscopy studies, iron in the sample was enriched with the ^{57}Fe isotope up to 50 wt%. The iron isotope content and single phase state were controlled by Mössbauer spectroscopy and by X-ray powder diffraction [10]. Pure phase of the $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ – type was detected at room temperature with the crystal lattice parameters $a = 8.539(2)$ and $c = 5.234(2)$ Å [8]. From the low-temperature Mössbauer measurements, the Neel temperature of this compound was found to be $T_N = 27.2^\circ(\pm 0.1)$ K [10].

The room-temperature high-pressure X-ray diffraction, Raman spectroscopy and Mössbauer spectroscopy experiments were performed using the powder $\text{Ba}_3\text{Ta}^{57}\text{Fe}_3\text{Si}_2\text{O}_{14}$ sample placed in diamond anvil cell (DAC). The culet size of the diamond anvils was 500 μm . The sample was placed in the hole of 200 μm diameter drilled in the preindented rhenium or stainless steel gaskets. The hole was filled with silicone oil served as the quasi-hydrostatic pressure transmitting medium. A standard ruby fluorescence technique was used to measure pressure.

High-pressure structural study was performed by X-ray diffraction using synchrotron radiation at Beamline 01C2 of National Synchrotron Radiation Research Center (NSRRC, Hsinchu, Taiwan) with photon energy 22 keV LaB6 was used as an external standard to determine the beam center, sample-to-detector distance, exact wavelength ($\lambda = 0.5763$ Å) and tilting angle of the image plate. Collected full-circle powder patterns were processed with FIT2D software. The analysis of the integrated diffraction patterns was performed using the Rex 0.7.4 software package [18].

A Melles Griot 25-HP-928-230 HeNe laser with a nominal power of 35 mW was used for the excitation of Raman spectra. Raman spectra were recorded in back-scattering geometry using a custom designed Raman optical microscope system for diamond anvil cells (similar to that described in [19]) with single imaging spectrograph Princeton Instruments Acton SP 2500 (focal length 500 mm) equipped with a 1200 grooves mm^{-1} diffraction grating and a liquid nitrogen cooled charge-coupled device detector. The spectral resolution in the studied spectral range was of ~ 1 cm^{-1} . Raman spectrometer was calibrated using Ne spectral lines with an uncertainty of ± 1 cm^{-1} .

The ^{57}Fe -Mössbauer spectra at pressures up to 35 GPa created in DAC were recorded in the transmission geometry with a standard spectrometer operating in the constant accelerations regime. The point Mössbauer source $^{57}\text{Co}(\text{Rh})$ was at room temperature, and the isomer shifts were measured relative to metal α -Fe at room temperature. The details of the Mössbauer spectroscopy setup are described elsewhere [20]. The Recoil 1.02 Mössbauer Analysis Software was used to fit the experimental spectra [21].

3. Results and discussion

The pressure evolution of X-ray diffraction patterns of $\text{Ba}_3\text{Ta}^{57}\text{Fe}_3\text{Si}_2\text{O}_{14}$ up to 27 GPa is shown in Fig. 3. At the lowest pressures,

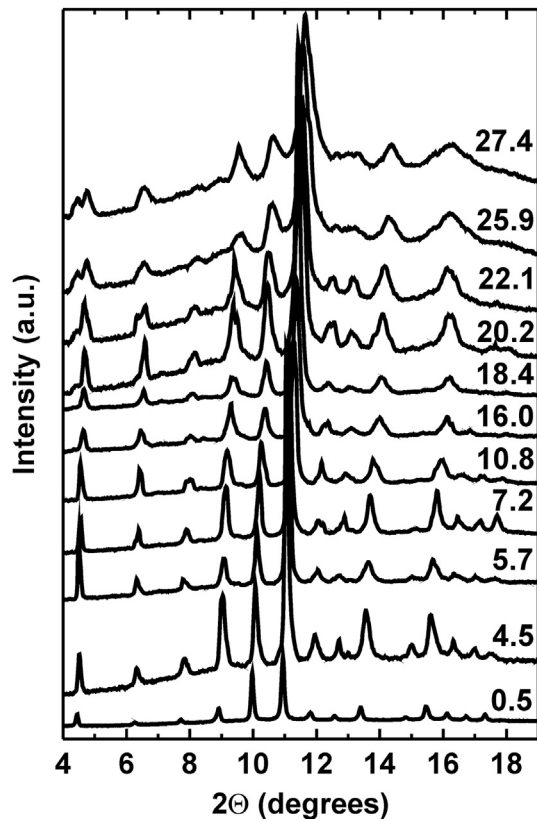


Fig. 3. Selected X-ray diffraction patterns of $\text{Ba}_3\text{Ta}^{57}\text{Fe}_3\text{Si}_2\text{O}_{14}$ monitored in the course of increasing pressure up to 27 GPa. The pressure values (in GPa) are given on the right side of the plot.

the diffraction patterns can be unambiguously indexed with trigonal lattice (see Fig. 4) with lattice parameters in full agreement with the known structural data at the ambient pressure [3]. At all pressures $P < 20$ GPa, the diffraction patterns can be indexed with

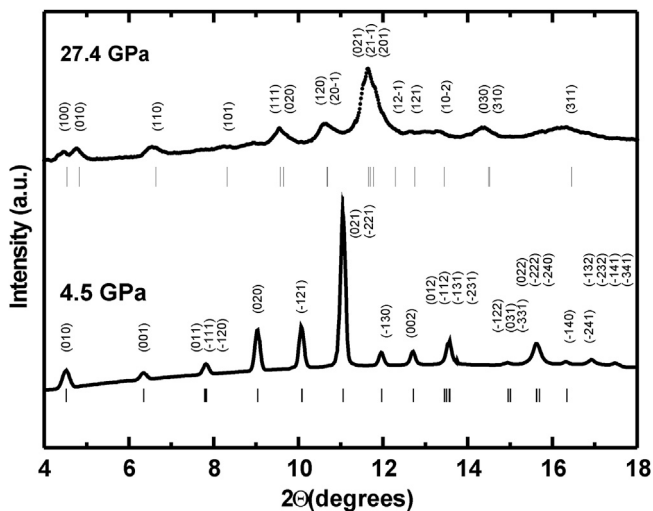


Fig. 4. X-ray diffraction patterns of “low-pressure” $\text{Ba}_3\text{TaFe}_3\text{Si}_2\text{O}_{14}$ trigonal phase at 4.5 GPa and the “high-pressure” monoclinic phase at 27.4 GPa. The observed diffraction intensities are represented by dots. Thick solid line represents the pattern for the trigonal phase calculated by Rietveld refinement procedure. Short vertical bars with the corresponding Miller indices indicate the positions of the allowed Bragg reflections for both phases.

the trigonal lattice whereas refined lattice parameters values and unit cell volume are gradually decreasing without remarkable discontinuities as pressure increases up to ~ 20 GPa (Fig. 5a, Fig. 5d). At the same time the value of the c/a -ratio exhibits a noticeable change at pressure near 5 GPa (Fig. 5b) indicating a possible isostructural phase transition.

Our Raman spectra collected at the low pressures (Fig. 6, Fig. 7) are rather complicated. To the best of author’s knowledge, the detailed Raman studies with the assignment of the vibrational modes in the langasite family were not reported so far. However, our spectra are in good qualitative agreement with the recently published high pressure studies [17]. The room temperature ^{57}Fe Mössbauer spectra of $\text{Ba}_3\text{Ta}^{57}\text{Fe}_3\text{Si}_2\text{O}_{14}$ collected at low pressure (Fig. 8) are split by the electric quadrupole interaction into a doublet with narrow symmetrical lines. The calculated value of the quadrupole splitting parameter is $\Delta E = 1.255 \pm 0.005$ mm/s. This value is in good agreement with the published data [17]. The value is very high for Fe^{3+} ions [22]. This indicates that the oxygen tetrahedrons with iron ions are essentially distorted. The value of isomer shift is $\delta = 0.23 \pm 0.1$ mm/s (relative to metallic $\alpha\text{-Fe}$). This finding supports the high spin state of ferric irons in the tetrahedral oxygen coordination with essential covalent character of the Fe–O bonds.

The structural phase transition at pressure near 5 GPa is clearly indicated by the evolution of the Raman spectra at pressure increase (Figs. 6 and 7). At pressures below 5 GPa, majority of the detected vibrational modes demonstrate moderate shift towards higher frequencies (Fig. 7). Remarkably, the mode located at ~ 250 cm^{-1} appears to be nearly insensitive to pressure whereas mode at ~ 100 cm^{-1} demonstrate considerable softening with pressure increase (Fig. 7). Such a behavior indicates instability of the $P321$ lattice to the corresponding atomic motions. At pressure near 5 GPa, onset of phase transition is indicated by the several changes in the Raman spectra: (i) splitting of the mode at the ~ 250 cm^{-1} ; (ii) splitting of the mode at ~ 550 cm^{-1} with shift towards lower frequencies; (iii) intensity of the vibrational mode at ~ 800 cm^{-1} increases drastically (Fig. 6).

The quadrupole splitting ΔE calculated from the Mössbauer spectra reveals changes at pressures above 5 GPa correlating with the transition observed in Raman spectra. As pressure increases between ambient and 5 GPa, the ΔE value remains nearly constant (Fig. 9), and then it drastically decreases to about 0.85 mm/s when pressure reaches the value of 7 GPa in good agreement with data obtained from NFS studies [17].

Thus, spectroscopic observations unambiguously indicate the structural phase transition occurring at 5 GPa whereas X-ray diffraction patterns imply that the high pressure phase has trigonal lattice. The possible structural phase transitions induced by pressure and temperature in the langasite-family compounds were discussed in Ref. [16]. It was shown that the $P321 \rightarrow P3$ transition with lowering of the symmetry is one of the most probable transitions in the langasite family crystals. A possible structural transition from $P321$ to $P3$ phase associated with the magnetic transition was recently suggested for the iron containing langasite $\text{Ba}_3\text{SbFe}_3\text{Si}_2\text{O}_{14}$ [1]. At such a transition, the two-fold axes are lost while the three-fold axis is preserved, and the Si (2d) and all O (2d and 6g) sites split into two positions, while the Fe sites remain in the equivalent positions. Since such a transition involves only the low-scattering light-elements atoms (Si and O) whereas the Fe-sublattice remains essentially unchanged we cannot distinguish between $P321$ and $P3$ symmetry groups in the refinement of the high-pressure diffraction patterns. However, the increasing of the number of observed Raman-modes in the spectra of the high-pressure phase favors the lowering of the symmetry of the crystal lattice at the phase transition. Therefore, the structural transition

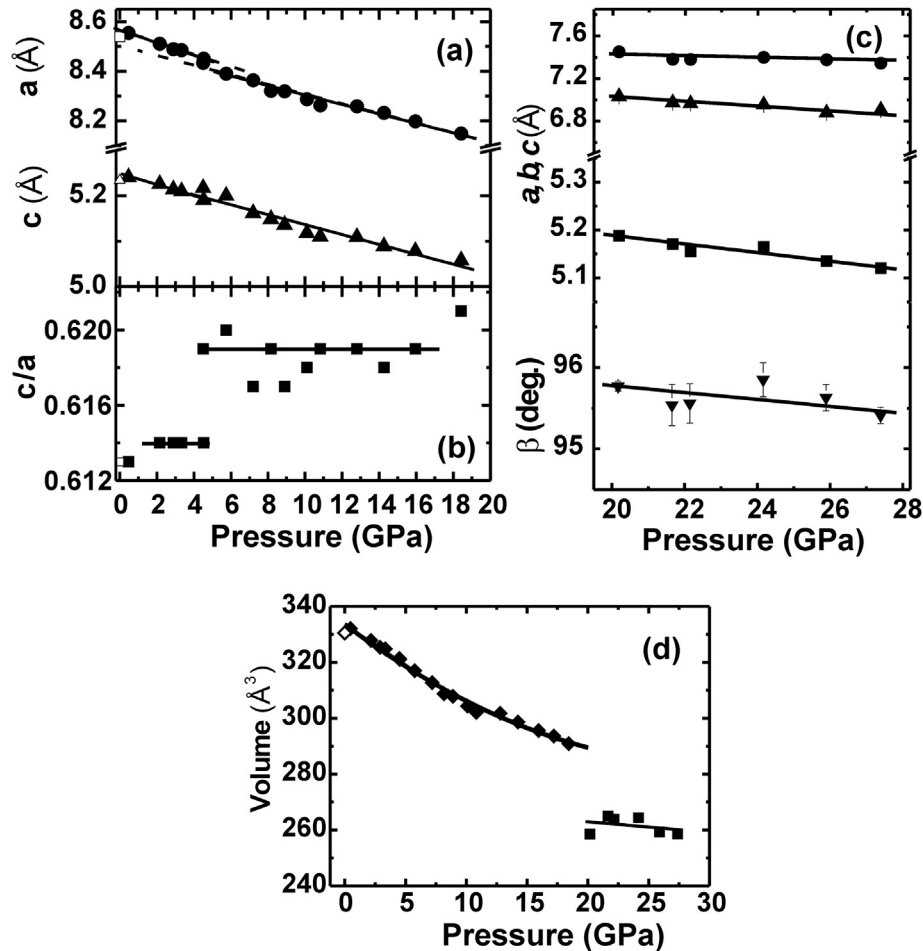


Fig. 5. Pressure dependences of the unit cell parameters *c* and *a* for the “low-pressure” trigonal phase of Ba₃Ta⁵⁷Fe₃Si₂O₁₄ (a), the *c/a* ratio (b). Unit cell parameters *a* (circle), *b* (triangle), *c* (square) and β for the “high-pressure” monoclinic phase (c). Unit cell volume per formula unit (d) measured at increasing pressure. On the panel (d) diamonds represent trigonal phase and squares stand for high-pressure monoclinic phase. Open symbols are the data for ambient pressure calculated from [3]. Lines drawn through the data points are the guides for eye.

observed at the ~5 GPa is most likely the *P321* → *P3* transition.

At further pressure increase up to ~20 GPa, lattice parameters decrease gradually with *c/a* ratio remaining nearly constant indicating the uniform compression of the *P3* lattice. The frequencies of all observed Raman modes increase with pressure as well as the value of the quadrupole splitting calculated from the Mössbauer spectra. Experimentally observed pressure dependence of the isomer shift (Fig. 9) might be explained if one presumes the similar pressure variation of the Fe–O distances.

At ~20 GPa substantial changes in the X-ray diffraction pattern indicate onset of the structural phase transition (Fig. 3). The diffraction pattern of the new phase can be indexed with monoclinic unit cell (Fig. 4). This trigonal-to-monoclinic phase transition is associated with the unit cell volume drop ~9% (Fig. 5d). The similar effects of pressure on the crystal structure of Ba₃TaFe₃Si₂O₁₄ were reported recently in Ref. [23]. Two first order phase transitions were observed at about 5 and 20 GPa accompanied by the unit cell volume decrease by 1.6% and 8.6%, respectively. This is in a good agreement with the results of the present paper. However, the transformation from trigonal to the monoclinic phase was not detected in Ref. [23]. It seems the reason is that the interval of diffraction angles $2\theta \approx 5.5^\circ$ was not analyzed in Ref. [23], whereas this is the very range where a distinct peak splitting occurred above ~20 GPa. As demonstrated in Figs. 3 and 4 (corresponding interval of diffraction angles is $2\theta \approx 11^\circ$), this is one of the important

changes of the XRD pattern signaling the transformation from the trigonal structure to monoclinic one.

Drastic changes of Raman spectra at pressure near 20 GPa also indicate a major phase transition (Figs. 6 and 7). Sharp peaks observed in low pressure phases are smeared out and only several very broad maxima can be identified in Raman spectra of the high-pressure phase (Fig. 6). Such broadening of the spectra can be related to small grain size of the sample due to large volume drop at the phase transition.

The ΔE value calculated from the Mössbauer spectra demonstrates rapid increase at pressure above 20 GPa (Fig. 9) in agreement with the data of NFS [17]. Unexpected increase in the Mössbauer isomer shift value δ at this pressure range points to the structural transformation with decrease of covalence in the Fe–O bonds obviously due to increase of the iron-oxygen distance (Fig. 9). These effects are caused by lowering of the structure symmetry at trigonal-to-monoclinic phase transition.

Small changes in the isomer shift value δ at the whole course of pressure increase lead to the value of ~0.27(1) mm/s at 34 GPa. This indicates that the spin crossover effect in Fe³⁺ ions (i.e. the high-spin to low-spin transition) at the structural transition must be ruled out. This is in agreement with theoretical considerations [17] showing that spin-crossover in the tetrahedral sites requires pressures of one order magnitude higher with respect to the octahedral sites.

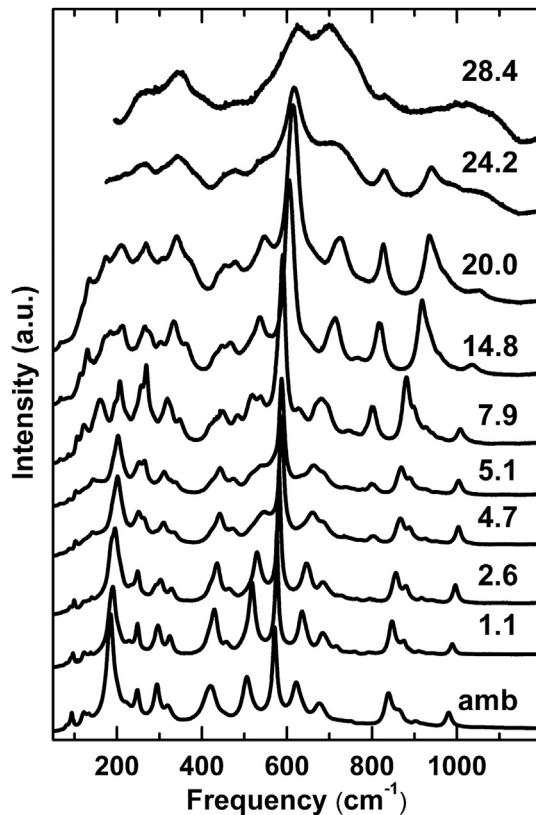


Fig. 6. Representative Raman spectra of $\text{Ba}_3\text{TaFe}_3\text{Si}_2\text{O}_{14}$ collected at pressure increasing up to 28.4 GPa. The pressure values in GPa are given on the right side of the plot («amb» is ambient pressure).

The pressure evolution of the X-ray diffraction patterns, Raman and Mössbauer spectra indicate that the observed high-pressure monoclinic phase remains stable at least up to pressure ~30 GPa.

As follows from our X-ray and Raman spectroscopy studies, the reverse transformation upon releasing pressure from 27 GPa

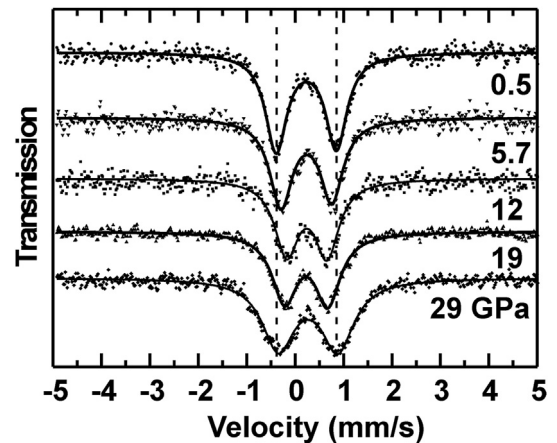


Fig. 8. The room-temperature transmission ^{57}Fe -Mössbauer spectra of $\text{Ba}_3\text{Ta}^{57}\text{Fe}_3\text{Si}_2\text{O}_{14}$ monitored in the diamond anvils cell at pressure increasing. Pressure values (in GPa) are given at the right side of the figure. Symbols represent experimental data. The spectra fitting to one quadrupole doublet is shown by thick solid lines. Dashed vertical lines indicate peaks positions at 0.5 GPa.

proceeds through rather wide hysteresis loop. Thus, monoclinic phase persists at least down to 6.2 GPa. Formation of the low-pressure trigonal phase occurred at 0.5 GPa. This is characteristic for the first-order type phase transitions accompanied by large volume changes. The similar effect was observed by Gavriluk et al. in [17] by Raman spectroscopy method.

4. Conclusion

Results of our high pressure X-rays structural studies revealed that $\text{Ba}_3\text{Ta}^{57}\text{Fe}_3\text{Si}_2\text{O}_{14}$ langasite underwent structural transitions at about 5 and 20 GPa. The first transformation behaves like an isostructural type transition with only slight increase in the lattice parameters c/a ratio of the trigonal phase. The Mössbauer data indicate that at this moment oxygen tetrahedra $3f$ containing iron became more symmetric (as follows from the ΔE behavior) and more expanded due to the increase in the Fe–O distances (because

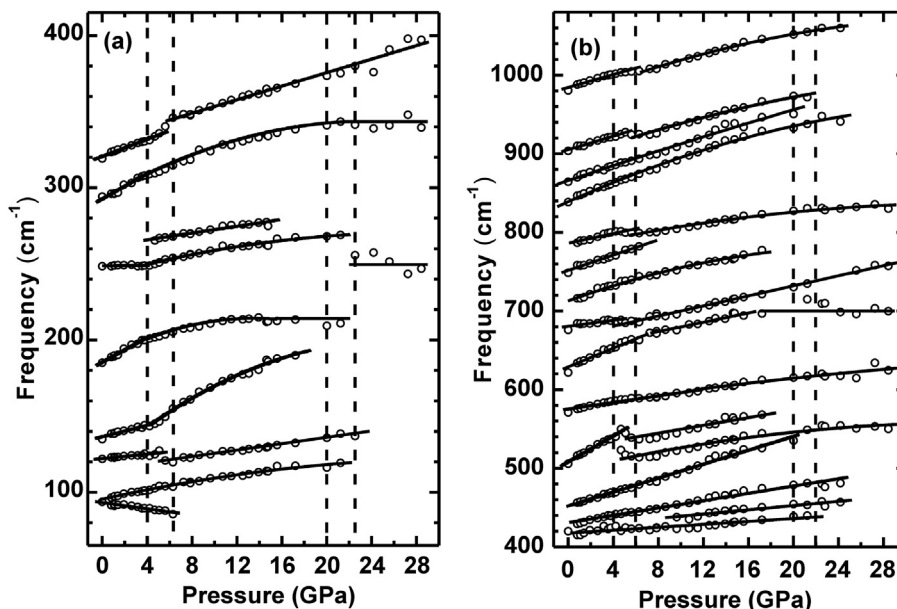


Fig. 7. Raman active modes frequencies of $\text{Ba}_3\text{TaFe}_3\text{Si}_2\text{O}_{14}$ plotted as a function of pressure. Solid black lines drawn through the data points are guides for the eye.

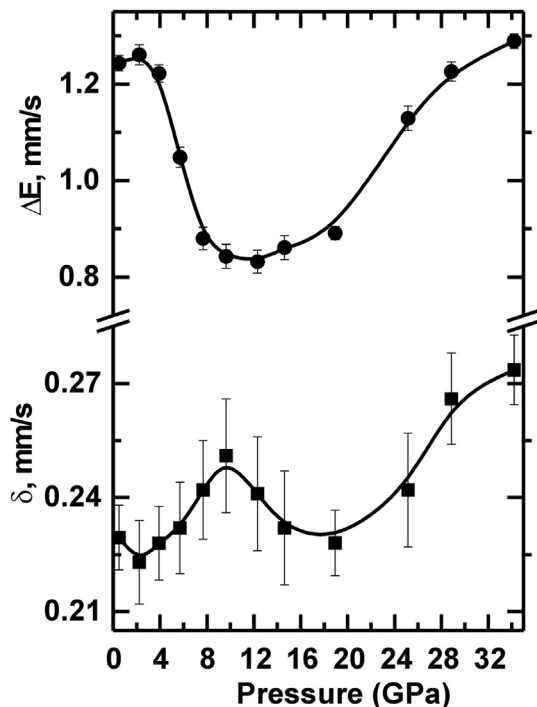


Fig. 9. Pressure dependences of the quadrupole splitting parameter ΔE and isomer shift δ obtained from the ^{57}Fe -Mössbauer spectra of $\text{Ba}_3\text{Ta}^{57}\text{Fe}_3\text{Si}_2\text{O}_{14}$ sample. Solid lines are guides for the eye.

the δ behavior indicates the decrease of covalence in the Fe–O bonds).

The second transformation is the first order phase transition from the trigonal to a monoclinic phase with the drop of the unit cell volume by about 9%.

Irregularities of the normal pressure variation of Raman active modes frequencies were detected in 4–6 GPa and 21–24 GPa pressure ranges. Within these pressures, formation of the new vibration modes, abrupt up- and downward shifts of the mode frequencies as well as mode terminations were observed. These effects are indicative of the structural transformations of the langasite lattice, which is in accordance with the XRD and Mössbauer data.

The observed anomalies in the pressure dependences of the quadrupole splitting and isomer shift in the Mössbauer spectra correspond to the similar pressure ranges where the structural transitions were detected by XRD and Raman spectroscopy. Thus, it can be concluded that these effects reflect the same structural transformations in the $\text{Ba}_3\text{TaFe}_3\text{Si}_2\text{O}_{14}$ compound induced by application of high pressure.

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